

Influence of a Gold(I)–Acetylide Subunit on the Photophysics of Re(Phen)(CO)₃Cl

Irina E. Pomestchenko, Dmitry E. Polyansky, and Felix N. Castellano*

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received November 17, 2004

The synthesis and photophysical properties of two new Re(I) complexes are reported: *fac*-Re(phenC≡CH)(CO)₃Cl (where phenC≡CH is 5-ethynyl-1,10-phenanthroline) and its Au(I)-acetylide analogue (*fac*-Re(phenC≡CAuPPh₃)(CO)₃-Cl). Also reported are the photophysical measurements obtained for the benchmark *fac*-Re(phen)(CO)₃Cl chromophore, as well as the phenC≡CAuPPh₃ and phenC≡CH ligands. The unstable nature of the precursor gold-containing ligand illustrates the advantage of using the “chemistry on the complex” approach, which facilitated preparation of the Re–Au binuclear complex. Where possible, all compounds were studied by static and transient absorption (TA), as well as steady-state and time-resolved photoluminescence (TRPL), at room temperature (RT) and 77 K, as well as nanosecond time-resolved infrared (TRIR) spectroscopy. The spectroscopic information provided by these techniques enabled a thorough evaluation of excited-state decay in most cases. In *fac*-Re(phenC≡CH)(CO)₃Cl, the RT excited-state decay is most consistent with a metal-to-ligand charge transfer (MLCT) assignment, whereas at 77 K, the lowest excited state is dominated by the triplet intraligand (³IL) state, localized within the diimine ligand. The lowest excited state in *fac*-Re(phenC≡CAuPPh₃)(CO)₃Cl seems to result from an admixture of Re-based MLCT and ³IL states resident on the phenC≡CAuPPh₃ moiety. TA and TRIR methods indicate that these excited states are thermally equilibrated at room temperature. At 77 K, the MLCT energy of *fac*-Re(phenC≡CAuPPh₃)(CO)₃Cl is increased as a result of the glassy medium and the resulting excited state can be considered to be ligand-localized.

Introduction

Since the first report by Wrighton and Morse in 1974,¹ the photophysics and photochemistry of complexes of the general formula Re(L–L)(CO)₃Cl (where L–L is a diimine ligand) have been widely developed. Particularly noteworthy are the contributions from Meyer’s group, which outlined the systematic structure–photophysical property relationships as a function of either nonchromophoric (replacement of Cl) or chromophoric (diimine) ligand substitutions.^{2,3} Of course, many investigators have used Re(I) complexes in a variety of fundamental and applied research projects, because their photophysical properties are largely predictable prior to synthesis.^{2–24} Recently, Schanze’s group has developed a

new class of π -conjugated Re(I) chromophores where various arylethynyls are appended to the 5,5′-ends of 2,2′-bipyridine.^{25–28} These metal-organic oligomers possess photophysical properties that are not as predictable as their

* To whom correspondence should be addressed. Tel.: (419) 372-7513. Fax: (419) 372-9809. E-mail: castell@bgnet.bgsu.edu.

- (1) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998–1003.
- (2) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952–957.
- (3) Worl, L. A.; Duesing, R.; Chen, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849–858.

- (4) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790–5795.
- (5) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888–2897.
- (6) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415–7417.
- (7) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067–1069.
- (8) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K. S.; Anthon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116–1126.
- (9) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526–531.
- (10) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, 2401–2415.
- (11) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007–4011.
- (12) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335–4340.
- (13) Perkins, T. A.; Hauser, B. T.; Eyler, J. R.; Schanze, K. S. *J. Phys. Chem.* **1990**, *94*, 8745–8748.
- (14) Shaw, J. R.; Schmehl, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 389–394.

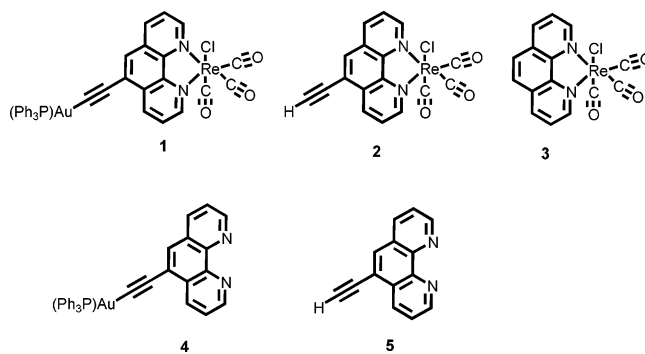
structurally simpler predecessors, yielding room-temperature (RT) excited-state decay that can best be described as a composite of metal-to-ligand charge transfer (³MLCT) and oligomer-based ³π-π* intraligand (³IL) character. Clearly, the addition of the conjugated organic ethynylene units dramatically affects the radiative decay processes in Re(I) complexes. Over the past several years, Yam's group in Hong Kong has studied the photophysical properties of a variety of Re(I)-acetylides of the general formula Re(L-L)(CO)₃-(C≡CR) (where R represents various organic-based substituents),^{29–32} The σ-donating ability of the acetylides renders the Re(I) center more electron-rich and, therefore, systematic variation of the MLCT energies is observed as a function of R. These structures have been further elaborated into various carbon-rich polynuclear luminescent materials.³²

Upon consideration of the aforementioned experimental results, we rationalized that the placement of metal-containing conjugated substituents within the diimine ligand framework should promote interesting electronic effects in Re(I) complexes. As typically observed in Re(I) compounds that contain a single chromophoric diimine unit, we expect any electronic effects to be communicated through the resultant photophysical and electrochemical properties. In addition, we were interested in the question of whether the placement of a metal–acetylide substituent possessing low-energy triplet states within the diimine ligand structure of a simple Re(I) complex would markedly influence excited-state decay. In the current offering, we selected a gold(I)–acetylide system to serve as a substituent in the 5-position of 1,10-phenanthroline, which is appended to a Re(CO)₃Cl skeleton. The newly synthesized Ph₃P–Au–C≡C-phen-containing Re(I) complex (**1**) possesses several distinguishing features that facilitated its selection for the current study. The Ph₃P–

Au–C≡C-fragment serves an electron-donating substituent, while, at the same time, the gold(I)–acetylide linkage yields a near-visible absorbing chromophore with low-lying triplet states. Therefore, the opportunity presents itself to see if the Au–acetylide states are able to sensitize the formation of, as well as interact with, the lowest Re-based MLCT excited state. Because the photophysical properties of the MLCT excited states of Re(I) complexes are well-documented, evaluating the properties of **1** and appropriate reference chromophores (**2–5**) with a battery of spectroscopic techniques will yield a detailed understanding of excited-state decay in Re(I) complexes appended with Au–acetylide conjugated substituents.

The current report provides a comprehensive photophysical study on the newly synthesized compounds Re(phen-C≡CAuPPh₃)(CO)₃Cl (**1**) and Re(phenC≡CH)(CO)₃Cl (**2**) (where phenC≡CH is 5-ethynyl-1,10-phenanthroline (**5**), in addition to the benchmark chromophore Re(phen)(CO)₃Cl (**3**). The phenC≡CAuPPh₃ ligand (**4**) was also independently synthesized to facilitate spectroscopic comparisons. The complexes were studied by static and transient absorption (TA), as well as steady-state and time-resolved photoluminescence (TRPL), at room temperature and 77 K, as well as nanosecond time-resolved infrared (TRIR) spectroscopy (**1–4** only). The spectroscopic information provided by these techniques enabled a thorough characterization of excited-state decay in compounds **1** and **2**. In **2**, the RT excited state decay is most consistent with a MLCT assignment, whereas at 77 K, the lowest excited state is clearly ³IL-based, localized within the diimine ligand. The photophysical behavior of **1** is somewhat more complex as the excited states at RT are best characterized as an admixture of Re-based MLCT and ³IL character whereas at 77 K, the ³IL state dominates excited-state decay.

- (15) Leasure, R. M.; Sacksteder, L.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722–3728.
 (16) MacQueen, D. B.; Eyler, J. R.; Schanze, K. S. *J. Am. Chem. Soc.* **1992**, *114*, 1897–1898.
 (17) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papatomas, K. I. *Chem. Mater.* **1992**, *4*, 675–683.
 (18) Sacksteder, L.; Lee, M.; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.* **1993**, *115*, 8230–8232.
 (19) Wang, Y.; Schanze, K. S. *Inorg. Chem.* **1994**, *33*, 1354–1362.
 (20) Striplin, D. R.; Crosby, G. A. *Chem. Phys. Lett.* **1994**, *221*, 426–430.
 (21) Paoletti, F.; Marcaccio, M.; Paradisi, C.; Roffia, S.; Bignozzi, C. A.; Amatore, C. *J. Phys. Chem. B* **1998**, *102*, 4759–4769.
 (22) Schanze, K. S.; Lucia, L. A.; Cooper, M.; Walters, K. A.; Ji, H.-F.; Sabina, O. *J. Phys. Chem. A* **1998**, *102*, 5577–5584.
 (23) Yam, V. W.-W.; Lau, V. C.-Y.; Wu, L.-X. *J. Chem. Soc., Dalton Trans.* **1998**, 1461–1468.
 (24) Guo, X.-Q.; Castellano, F. N.; Li, L.; Lakowicz, J. R. *Anal. Chem.* **1998**, *70*, 632–637.
 (25) Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287–307.
 (26) Ley, K. D.; Li, Y.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749–1750.
 (27) Walters, K. A.; Dattelbaum, D. M.; Ley, K. D.; Schoonover, J. R.; Meyer, T. J.; Schanze, K. S. *Chem. Commun.* **2001**, 1834–1835.
 (28) Walters, K. A.; Ley, K. D.; Cavalaheiro, C. S. P.; Miller, S. E.; Gosztola, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8329–8342.
 (29) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1995**, *14*, 2749–2753.
 (30) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740–1744.
 (31) Yam, V. W.-W.; Chong, S. H.-F.; Cheung, K.-K. *Chem. Commun.* **1998**, 2121–2122.
 (32) Yam, V. W.-W. *Chem. Commun.* **2001**, 789–796.



Experimental Section

General. All reagents not specifically listed below were obtained from commercial sources and used as received. Anhydrous dichloromethane was purchased from Aldrich Chemical Co. and distilled over CaH₂. Diisopropylamine and acetone were dried and distilled according to standard procedures, prior to use. Potassium carbonate (Aldrich Chemical Co.) was dried in an oven (140 °C) for at least 12 h before use. Copper(I) iodide, 1,10-phenanthroline (phen), and Re(CO)₃Cl were purchased from Aldrich Chemical Co. and used as received. Au(PPh₃)Cl was purchased from Alfa Aesar and used as received. 5-Bromo-1,10-phenanthroline was available from a

previous study.³³ Water was deionized by means of Barnstead E-Pure system. Silica gel used in chromatographic separations was obtained from EM Science (Silica Gel 60, 230–400 mesh). All synthetic manipulations were performed under an inert and dry argon atmosphere using standard techniques. Elemental analyses were performed by Atlantic Microlab (Norcross, GA) or QTI (Whitehouse, NJ). ¹H NMR spectra were recorded on a Varian model Gemini 300 (300 MHz) spectrometer. All chemical shifts are referenced to residual solvent signals previously referenced to tetramethylsilane (TMS) and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Static IR spectra of solid samples were measured with a Thermo Nicolet model IR 200 spectrometer. Electrospray ionization (ESI) mass spectra were measured at the University of Toledo, using an Esquire-LC spectrometer. EI mass spectra were measured in-house using a Shimadzu model QP5050A spectrometer.

Spectroscopic Measurements. UV–Vis absorption spectra were measured with a Hewlett–Packard model 8453 diode array spectrophotometer, which was accurate to ± 2 nm. Uncorrected (for spectral response) steady-state photoluminescence spectra at RT and 77 K were obtained with a single photon counting spectrofluorimeter (Edinburgh Analytical Instruments, model FL/FS 900). Radiative quantum yields (Φ_r) of each metal complex were measured, relative to Re(bpy)(CO)₃Cl, for which $\Phi_r = 0.005$ in deaerated CH₂Cl₂.² Emission intensity decays were measured and analyzed as previously described.^{33,34} TA spectra and decay kinetics were obtained using the unfocused third harmonic provided by a Continuum Surelite I Nd:YAG laser (355 nm, 5–7 ns fwhm), using the apparatus in the Ohio Laboratory for Kinetic Spectrometry, which has already been described.^{33,34} Typical excitation energies of 4–7 mJ/pulse were maintained in all experiments. All samples were thoroughly degassed prior to measurements with high-purity argon and kept under an argon atmosphere throughout each experiment conducted at ambient temperature (22 °C). TRIR measurements were performed with a step-scan instrument based on a modified Bruker model IFS55 FTIR spectrometer (step size = 20 nm, resolution = ± 8 cm⁻¹), using the third harmonic (355 nm, 1 mJ/pulse) of a Spectra Physics GCR series YAG laser as the pump source, operating at 10 Hz.³⁵ The argon-degassed solution samples were flowed at a rate of 10 mL/min between CaF₂ windows (4 mm thick) equipped with a 1 mm spacer. All other experimental details have been described in a previous report published by our colleagues at BGSU.³⁵ Cyclic voltammetry was performed in a one-compartment cell, using a three-electrode arrangement including a platinum disk working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. All electrochemistry was performed on a BAS Epsilon system, using a scan rate of 200 mV/s in 0.1 M TBAH/CH₃CN.

Preparations. 5-Ethynyl-1,10-phenanthroline (**5**) was synthesized from 5-bromo-1,10-phenanthroline, according to a literature procedure, and yielded satisfactory mass and ¹H NMR spectra.³⁶ Re(phen)(CO)₃Cl (**3**) was prepared as described in the literature.^{1–3,37}

Re(phenC≡CH)(CO)₃Cl (2). 5-Ethynyl-1,10-phenanthroline (0.232 g, 1.13 mmol) and Re(CO)₅Cl (0.399 g, 1.10 mmol) were

dissolved in isooctane and the reaction mixture was brought to reflux for 3 h. When the mixture was heated, a yellow precipitate started to appear. The solution was cooled to room temperature and the precipitate was collected by filtration and washed with cold isooctane. The solid product was purified by column chromatography (SiO₂, 5 vol % of acetone in dichloromethane as an eluent) (0.489 g, 87% yield). $R_f = 0.44$ (5 vol % acetone in CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): 9.44 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.2$ Hz, 1H); 9.40 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.5$ Hz, 1H); 9.0 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H); 8.51 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.5$ Hz, 1H); 8.25 (s, 1H); 7.96 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.1$ Hz, 1H); 7.89 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.1$ Hz, 1H); 3.70 (s, 1H). Anal. Calcd. for C₁₇H₈ClN₂O₃Re: C, 40.04; N, 5.49; H, 1.58. Found: C, 40.23; N, 5.32; H, 1.66. EI-MS (70 eV) m/z 510. FTIR (ATR): 2020, 1927, and 1888 cm⁻¹ ($\nu_{C=O}$).

Re(phenC≡CAuPPh₃)(CO)₃Cl (1). Compound **2** (0.1 g, 0.196 mmol) was dissolved in dry CH₂Cl₂ (75 mL) in a sealable reaction vessel and the solution was degassed with argon for 15 min. Au(PPh₃)Cl (0.097 g, 0.196 mmol) and freshly distilled (ⁱPr)₂NH (1 mL) were added to the reaction mixture under an argon atmosphere. The reaction vessel was sealed with a Teflon screw cap that had been fitted with an O-ring and was stirred at 40 °C for 1 week. The reaction mixture was filtered, and the solvent was removed. The remaining orange–yellow residue was dissolved in CH₂Cl₂ and precipitated by the addition of isooctane. The solid was collected on a frit, washed with isooctane, and purified by column chromatography on silica (5 vol % of acetone in dichloromethane as an eluent). $R_f = 0.53$ (5 vol % acetone in CH₂Cl₂). Experimental yield = 85% (0.160 g). ¹H NMR (300 MHz; CDCl₃): 9.37 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.5$ Hz, 1H); 9.25–9.30 (m, 2H); 8.41 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H); 8.11 (s, 1H); 7.88 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.1$ Hz, 1H); 7.79 (dd, $J_1 = 8.1$ Hz, $J_2 = 5.1$ Hz, 1H); 7.48–7.63 (m, 15H). Anal. Calcd. for C₃₅H₂₂AuClN₂O₃PRE•C₃H₆O: C, 44.47; N, 2.73; H, 2.75. Found: C, 44.77; N, 3.02; H, 2.93. ESI-MS: m/z 966 [M–H]⁺. FTIR (ATR): 2015, 1902, and 1880 cm⁻¹ ($\nu_{C=O}$).

phenC≡CAuPPh₃ (4). 5-Ethynyl-1,10-phenanthroline (0.1 g, 0.489 mmol) was dissolved in dry CH₂Cl₂ (100 mL) in a sealable reaction vessel and the solution was degassed with argon for 15 min. Au(PPh₃)Cl (0.242 g, 0.489 mmol) and freshly distilled (ⁱPr)₂NH (2 mL) were added to the reaction mixture under an argon atmosphere. The reaction vessel was sealed with a Teflon screw cap that had been fitted with an O-ring and was stirred at 40 °C for 6 days. Volatiles were removed under reduced pressure, yielding a pale yellow solid. Crude product was purified by preparative thin-layer chromatography (TLC) on silica (1 vol % of MeOH and 2 vol % of Et₃N in dichloromethane as an eluent). $R_f = 0.12$ –0.30 (broad band). MALDI-MS: Calculated for C₃₂H₂₂AuN₂P 662.47; found 663.21. ¹H NMR (300 MHz; CDCl₃): 9.18 (dd, $J_1 = 4.5$ Hz, $J_2 = 1.8$ Hz, 1H); 9.12 (dd, $J_1 = 4.5$ Hz, $J_2 = 1.8$ Hz, 1H); 9.07 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.8$ Hz, 1H); 8.16 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 1H); 8.02 (s, 1H); 7.67–7.70 (m, 2H), 7.497–7.631 (m, 15H).

Results and Discussion

Structures. Compounds **2** and **3** were prepared by displacement of CO from Re(CO)₅Cl, using the appropriate phenanthroline ligand in refluxing isooctane.³⁷ The synthesis of **1** features a “chemistry on the complex” approach, where the acetylene-terminated diimine ligand chelated to the Re(I) center couples to Ph₃PAuCl under mild reaction conditions.^{38–41} Complexes **1**–**3** were purified by column chromatography on silica gel, and final isolated yields were

(33) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154–8161.

(34) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.

(35) Fedorov, A. V.; Daniolov, E. O.; Merzlikine, A. G.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem. A* **2003**, *107*, 3208–3214.

(36) Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535–6546.

(37) Lin, R.; Fu, Y.; Brock, C. P.; Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 4346–4353.

Table 1. ¹H NMR Chemical Shifts of the Phenanthroline Ring Protons in Compounds **1**, **2**, **4**, and **5**

compound	Chemical Shift ^a (ppm)						
	H(2)	H(9)	H(4)	H(7)	H(6)	H(8)	H(3)
5	9.23	9.21	8.76	8.22	8.09	7.73	7.66
4	9.17	9.12	9.06 ^b	8.16	8.02	7.69	<i>c</i>
2	9.44	9.40	9.00	8.51	8.25	7.96	7.89
1	9.37	9.29	9.27 ^b	8.41	8.11	7.88	7.79

^a The protons are numbered according to their corresponding positions on the phenanthroline ring. ^b Downfield shift of H(4) is due to higher through-space deshielding by acetylide. ^c The signal from H(3) is overlapped with aromatic protons of the -Au(PPh₃) group.

Table 2. Cyclic Voltammetry Data in in 0.1 M TBAH/CH₃CN

compound	<i>E</i> _{ox} (V)	<i>E</i> _{red} (V)	Δ <i>E</i> ^a (V)
1	1.45	-1.28	2.73
2	1.45	-1.19	2.64
3 ^b	1.41	-1.36	2.77
5 ^c		-1.13	

^a Δ*E* = *E*_{ox} - *E*_{red}. ^b Data taken from ref 21. ^c Measured in CH₂Cl₂.

quite significant (≥85%). All compounds have been structurally characterized with ¹H NMR, mass spectrometry, elemental analysis, and FTIR, where appropriate. The three-band IR pattern observed in the CO stretching region is consistent with the *facial* arrangement of the three COs in the coordination sphere, as typically observed in related Re(I) organometallic structures.¹⁻³ In the ¹H NMR spectra, all the proton signals residing within the phenanthroline ligand are shifted upfield in **1**, relative to the acetylene precursor **2** (Table 1). This upfield shift is consistent with back-donation from the gold(I) center to the σ-ethynyl bond in the substituted phenanthroline ligand. A similar upfield shifting effect has been observed in the phenanthroline protons in Ru(II)-systems-containing Au-acetylide molecular wires.⁴² Elemental analysis and mass spectrometry data are also consistent with the proposed structures.

The newly synthesized complexes **1** and **2**, as well as the benchmark chromophore **3**, are air-stable solids, in addition to being thermally and photochemically stable in solution. Compound **4** is photochemically unstable in solution; therefore, multiple precautions were taken during all measurements and fresh samples were used for all experiments. The UV-Vis spectra of **4** were measured before and after each photochemical exposure, to ensure data quality.

Electrochemistry. The redox behavior of the new complexes measured in CH₃CN by cyclic voltammetry are consistent with data typically obtained in Re(L-L)(CO)₃Cl complexes (see Table 2).^{3,8,11,21} The first oxidation in **1** and **2** is rhenium-based, occurring at peak potentials of 1.45 and 1.46 V, respectively, versus Ag/AgCl. These oxidations are not reversible on the electrochemical time scale and likely

(38) Pabst, G. R.; Pfuller, O. C.; Sauer, J. *Tetrahedron* **1999**, *55*, 8045-8064.

(39) Aspley, C. J.; Williams, J. A. G. *New. J. Chem.* **2001**, *25*, 1136-1147.

(40) Goze, C.; Kozlov, D. V.; Castellano, F. N.; Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **2003**, *44*, 8713-8716.

(41) Goze, C.; Kozlov, D. V.; Tyson, D. S.; Ziessel, R.; Castellano, F. N. *New. J. Chem.* **2003**, *27*, 1679-1683.

(42) Shiotsuka, M.; Yamamoto, Y.; Okuno, S.; Kitou, M.; Nozaki, K.; Onaka, S. *Chem. Commun.* **2002**, 590-591.

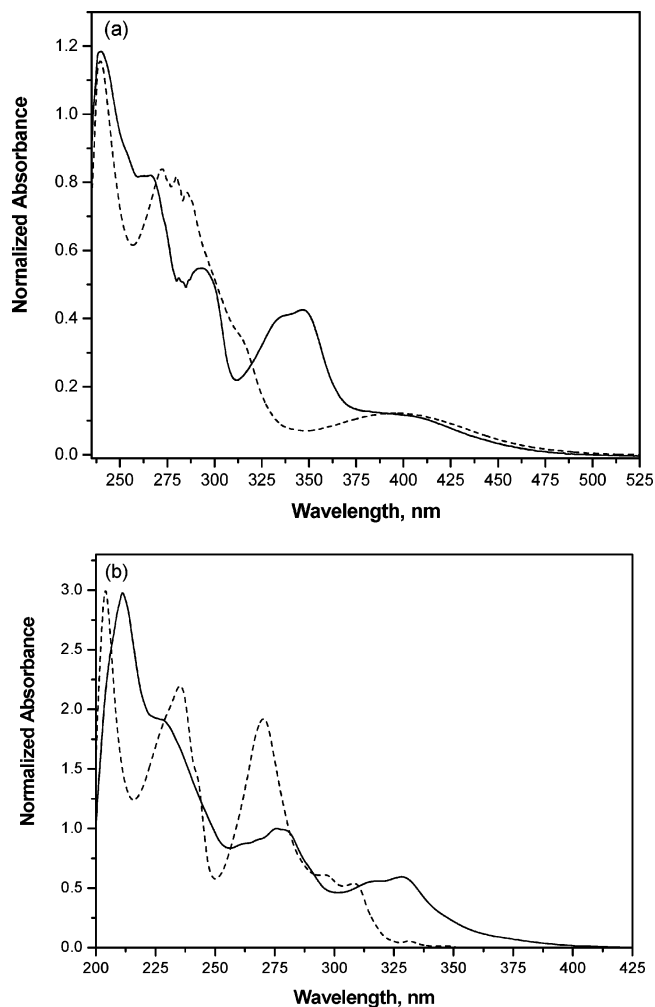


Figure 1. (a) Room-temperature (RT) absorption spectra of **1** (solid line) and **2** (dotted line) in CH₃CN. (b) RT absorption spectra of **4** (solid line) and **5** (dotted line) in an ethanol/methanol (EtOH/MeOH) mixture (4:1).

result from rereduction of Re(II) by the solvent or an impurity. Partially reversible phen-based reductions are observed in compounds **1** and **2**, with the first wave centered at -1.28 and -1.18 V, respectively. Electron back-donation from the gold(I) unit is responsible for the negative shift of the reduction potential of the phenanthroline ligand in **1** compared to **2**. Additional independent evidence for the electron-donating nature of the gold(I) unit was obtained by comparing ¹H NMR chemical shifts of compounds **1** and **2**, as well as **4** and **5** (see Table 1). No electrochemical measurements could be performed on compound **4**, because of its decomposition under cyclic voltammetry experimental conditions. The electrochemical properties of **1** and **2** are consistent with those previously measured in **3**, where the first oxidation is metal-based and the first reduction takes place on the diimine ligand (*E*_{ox} = 1.41 V and *E*_{1/2,red} = -1.36 V).²¹ The decrease in reduction potential of phenanthroline ligand in **2**, relative to **3**, is probably due to the higher conjugation of the aromatic system.

Absorption and Photoluminescence Properties. The ground-state absorption spectra of complexes **1** and **2** in CH₃CN are presented in Figure 1a, whereas the electronic spectra of the “free” ethynylated ligands **4** and **5** are provided in

Figure 1b. The broad lowest-energy absorption feature in **1** and **2** are assigned to a $d\pi(\text{Re}) \rightarrow \pi^*(\text{phen-R})$ (where R is $\text{C}\equiv\text{C}-\text{AuPPh}_3$ and $\text{C}\equiv\text{CH}$, respectively) MLCT transition with more-intense features at higher energy being of diimine-ligand $\pi-\pi^*$ origin. The gold(I)-acetylide chromophore is responsible for the relatively strong near-visible $\pi-\pi^*$ absorption band centered at 347 nm in **1**.^{42–44} This assignment is consistent with observations made in Ru(II) complexes that contain gold(I)-acetylides linked in the 3- and 3,8-positions of 1,10-phenanthroline.⁴² We note that the lowest-energy transition in **4** is somewhat blue-shifted, relative to the position of the corresponding band in the binuclear complex **1**. Upon coordination to the Re(I) center, the energy of this transition is reduced, relative to the free ligand **4**. This observation is consistent with the electrochemical data presented previously but represents only a minor effect, because the Re-based MLCT transitions are approximately the same energy in both **1** and **2** (see Figure 1a).

Complex **1** displays an emission band centered at 598 nm in deaerated 2-methyltetrahydrofuran (MTHF) at RT, which is completely invariant to the excitation wavelength over the range of 300–480 nm (see Figure 2a). The corrected excitation spectrum of **1** measured over a range of 300–500 nm can be largely superimposed with its absorption spectrum, suggesting that the gold(I)-acetylide chromophore harvests near-visible light and efficiently converts it into a broad luminescence in the visible range. The emission spectrum in **1** is largely characteristic of ³MLCT-based luminescence typically observed in Re(I) diimine complexes, with the exception of a minor high-energy shoulder between 525 and 550 nm. The position of this shoulder coincides with the most significant feature observed in the phosphorescence of the free ligand **4** when excited at 337 nm (see Figure 2b). Because the ligand-localized phosphorescence spectrum in **4** is dependent on excitation wavelength (see below), it is difficult to interpret whether the high-energy emission shoulder in **1** results from a ligand-localized contribution or not. This point will be discussed further during the presentations of the time-resolved absorption and IR data.

It is well-established that **3** possesses a lowest-energy $d-\pi^*$ MLCT excited-state configuration, even at cryogenic temperatures as low as 4 K.²⁰ Similarly, photoluminescence centered at 615 nm was observed for the model complex **2** upon excitation into the low-energy charge-transfer band (see Figure 2a). The blue shift in the emission observed in **1**, relative to **2**, is consistent with a higher reduction potential of **1**, compared to **2**, and the electron-donating effect of the gold(I)-acetylide unit, as demonstrated by the ¹H NMR chemical shifts (see Table 1). The electron-rich Ph_3PAu substituent is clearly responsible for this effect by rendering the phen-ligand harder to reduce in **1**. We note that there is no evidence of a high-energy shoulder in **2** and the broad,

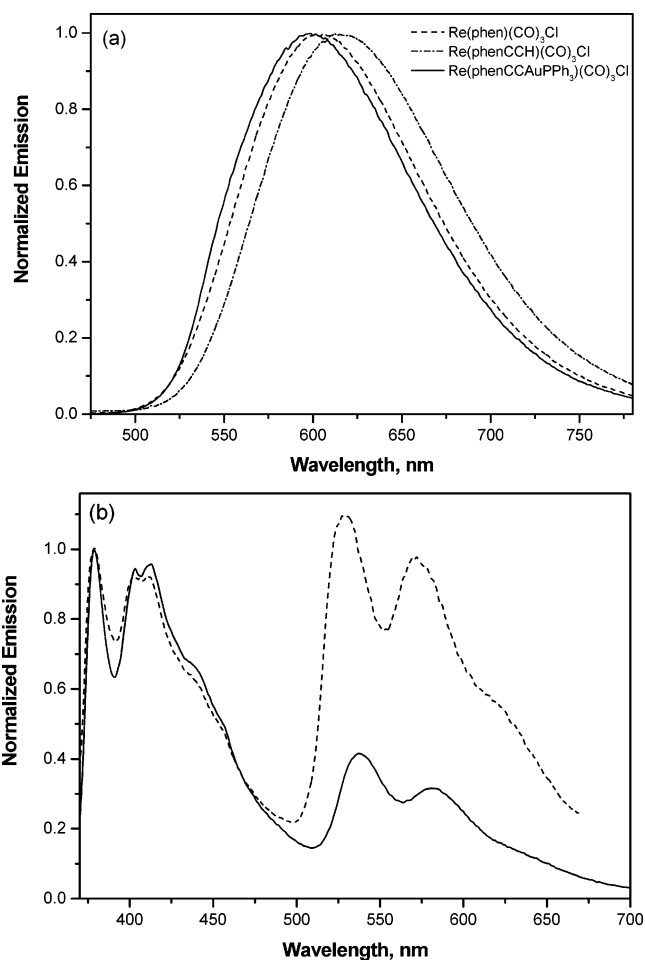


Figure 2. (a) RT emission spectra of (a) **1–3** in MTHF using 400-nm excitation. (b) RT emission spectra of **4** in CH_2Cl_2 using 360-nm (solid line) and 337-nm (dashed line) excitation.

structureless nature of its emission band at RT is consistent with a “pure” $d-\pi^*$ MLCT assignment.

The terminal acetylene-containing ligand **5** does not display any phosphorescence at RT, whereas the gold-containing diimine ligand **4** is phosphorescent and displays excitation-wavelength-dependent phosphorescence emission spectra (see Figure 2b), which are almost quantitatively quenched by dissolved oxygen (only those features between 500 and 700 nm). Although **4** is photochemically unstable, the absorption spectra acquired before and after the static luminescence spectra indicated no significant sample decomposition. The following discussion, in regard to free ligand **4**, assumes that the photoluminescence (PL) emanates from only one species; however, we cannot exclude contributions from minor impurities or decomposition products. Although the PL data of **4** provide some insight into the photophysical behavior of dinuclear **1**, we believe that the TA and TRIR data discussed later in this work provides more-definitive experimental evidence for its proposed “mixed” excited-state behavior. The excitation wavelength-dependent phosphorescence in **4** is illustrated in Figure 2b, where excitation at 337 nm in deaerated CH_2Cl_2 generates a spectrum that consists of fluorescence and phosphorescence bands with essentially equal intensity; the phosphorescence maxima are positioned at 529 and 571 nm. Please note that

(43) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541–3547.

(44) Che, C.-M.; Chao, H.-Y.; Miskowski, V. M.; Li, Y.; Cheung, K.-K. *J. Am. Chem. Soc.* **2001**, *123*, 4985–4991.

Table 3. Measured and Calculated Photophysical Parameters in MTHF

compound	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{em,max}}$ (nm)		τ (ns)		Φ^a	k_r (s ⁻¹) ^b	k_{nr} (s ⁻¹) ^b
		at RT	at 77 K	at RT	at 77 K			
1	347, 400	598	527, 570, 620	960, 930 (TA) ^c	456	0.018	1.9×10^4	1.02×10^6
2	400	615	504, 543, 585	163, 156 (TA) ^c	30 (0.53), ^d 410 (0.47) ^d	0.008	4.9×10^4	6.08×10^6
3	386	606	535	227, 214 (TA) ^c	7.6	0.013	5.77×10^4	4.35×10^6
4^e	328	(379, 403, 413), ^f (529, 571), ^g (538, 581) ^h	(518, 528, 564, 577), ⁱ (532, 580) ^j	41 μs (TA), ^c 192 μs (TA) ^c	450 ^g	0.005		
5^e	296, 308	(365, 375, 386, 408), ^f no phos.	(363, 376, 381, 398), ^f (495, 505, 516, 537, 581) ^k		(7 ms, 80 ms) ^k			

^a Photoluminescence quantum yield, measured relative to Re(bpy)(CO)₃Cl, $\Phi_{\text{DCM}} = 0.005$;² values are $\pm 10\%$. ^b Radiative (k_r) and nonradiative (k_{nr}) rate constants calculated by $k_r = \Phi/\tau$ and $k_{\text{nr}} = (1 - \Phi)/\tau$. ^c Excited-state lifetime determined by transient absorption spectroscopy, using 355-nm excitation. ^d Relative amplitudes of each intensity decay component, determined from a biexponential fit. ^e RT data measured in CH₂Cl₂ and 77 K data obtained in EtOH/MeOH (4:1). ^f Fluorescence peaks. ^g Phosphorescence peak, 337-nm excitation. ^h Phosphorescence peaks, 360-nm excitation. ⁱ Phosphorescence peaks, 330-nm excitation. ^j Phosphorescence peaks, 365-nm excitation. ^k Phosphorescence peaks.

dichloromethane was used as a consequence to solubility limitations in MTHF. On the other hand, 360-nm excitation generates emission spectra with significantly more intense singlet fluorescence at the same relative band positions. However, the phosphorescence bands are red-shifted (~ 10 nm), relative to that measured using 337-nm excitation, perhaps suggesting the presence of another energetically proximate triplet state. We believe the fluorescence bands are derived mostly from a phen-like singlet state that is not heavily influenced by the spin-orbit coupling provided by the Au unit. The two distinct RT phosphorescence spectra observed in **4** possess the same vibronic spacing within experimental error (~ 1380 cm⁻¹), indicating a similar excited-state structure. Because the C \equiv C stretching frequency occurs at higher energy (~ 2100 cm⁻¹), the two phosphorescence spectra are more consistent with triplet excited states intimately coupled to the C=C and/or C=N ring stretching vibrations of the phenanthroline structure. Therefore, the Au-acetylide unit serves to facilitate spin-orbit coupling but does not seem to be the source of the RT phosphorescence. These data imply that there are multiple, close-lying intraligand triplet states based within the phenanthroline structure in **4**. Assuming that the integrity of **4** was not compromised in the aforementioned static experiments, it is reasonable to assume that binuclear complex **1** has at least two closely lying triplet ligand manifolds with which the Re-based MLCT excited state can potentially interact.

The RT single-exponential PL lifetimes for **1–3** measured in deaerated MTHF are 960, 163, and 227 ns, respectively (Table 3). These lifetimes were completely invariant to monitoring wavelength. The longer lifetime observed in **1** reflects a larger energy gap between ground and excited states, decreasing the nonradiative rate constant by a factor of ~ 6 in **1**, relative to **2**. However, there is likely a contribution associated with electron delocalization into the Au-acetylide fragment in **1** that enhances the excited-state lifetime in the charge-transfer excited state.^{45,46} Alternatively, the participation of a ligand-localized triplet state in the

excited-state manifold may be responsible for the lifetime extension in **1**, relative to **2** and **3**. No phosphorescence transients could be measured in optically dilute (OD < 0.2) degassed solutions of **4** in CH₂Cl₂. All measured and derived photophysical parameters are collected in Table 3 for compounds **1–4**. The photoluminescence data obtained for **2** and **3** at room temperature are most consistent with a lowest-energy MLCT excited state, whereas an assignment for **1** cannot be made by sole reliance on luminescence data.

The emission properties of **1–3** were studied in MTHF low-temperature glasses at 77 K, whereas **4** was measured in a 4:1 ethanol/methanol (EtOH/MeOH) mixture, as a function of excitation wavelength (Figure 3). The emission manifold in **3** is broad and structureless at 77 K (see Figure 3a), which is consistent with radiative decay from a MLCT manifold whose vibronic components are broadened as a result of large solvent reorganizational energies and greater distortions in the low-frequency modes coupling the ground and excited states.³ The large reorganization energy in **3** is apparent from the large energetic difference between the RT and 77 K spectra (2190 cm⁻¹), also called the thermally induced Stokes shift (ΔE_s), which can be roughly approximated as $2\lambda_s$, where λ_s is the outer-sphere reorganization energy for the MLCT excited state.^{47,48} The emission lifetime of **3** at 77 K is 7.6 μs , thus benchmarking the lifetime expected for a ³MLCT excited state in a Re(I)-phen complex at this temperature. The static 77 K spectra of compounds **1** and **2** contain well-defined structured vibronic components (Figure 3), indicating that the emission is not of MLCT origin. (Static emission spectra of **1**, **2**, **4**, and **5** are given in the Supporting Information.) Although the low-temperature spectra of **1** and **2** are shifted in energy, the major vibronic spacing of the two highest-energy bands are identical (~ 1450 cm⁻¹), implying that these emissions are both diimine-ligand-based. The 77 K emission maximum of **1**, relative to that of **2**, is 23 nm red-shifted compared to a 17-nm blue shift measured in the RT spectra. We believe these observations reflect the distinct natures of the emitting states as a function

(45) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395–7396.

(46) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473–487.

(47) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053–4062.

(48) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439–1477.

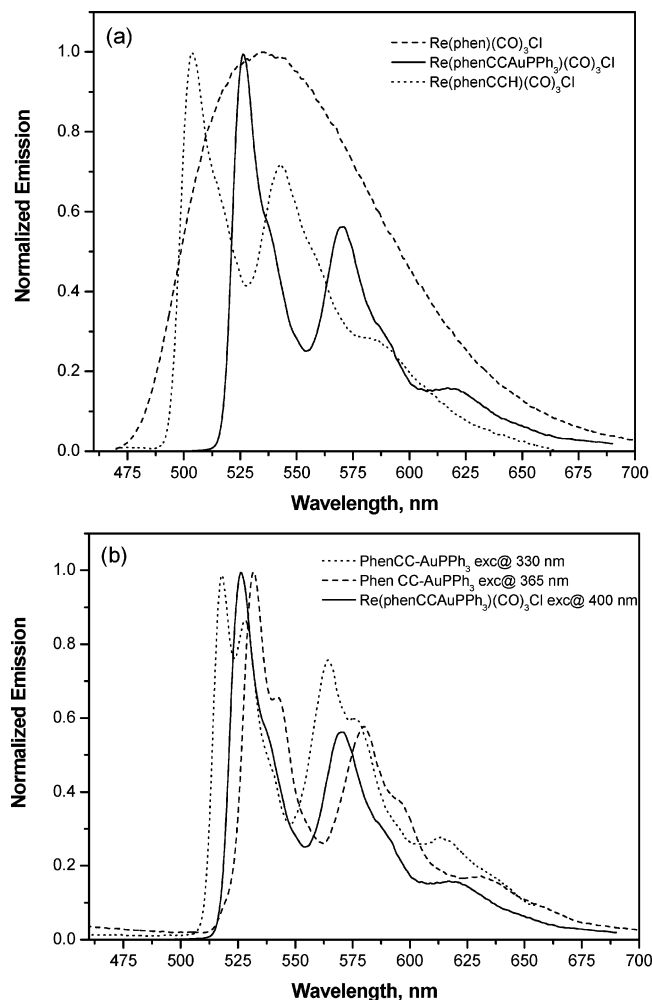


Figure 3. Emission spectra (at 77 K) of (a) **1–3** measured in MTHF glasses using 400-nm excitation and (b) **4** measured in an EtOH/ MeOH (4:1) glass using 330- and 365-nm excitation; the spectrum of **1** (in MTHF) is superimposed in each panel, for comparative purposes.

of temperature, i.e., diimine-centered $\pi-\pi^*$ at 77 K and $d-\pi^*$ charge transfer at RT.

Although measured in a different matrix (due to solubility limitations), the 77 K phosphorescence of **4** displays excitation-wavelength-dependent emission profiles (see Figure 3b). Sandwiched between these two distinct profiles is the 77 K spectrum of **1** measured in MTHF. Although the differences are hard to interpret, the energetic proximity and structure of these three spectra are approximately similar, suggesting at least that the emissions are emanating from states composed of similar electronic structures. The recovered lifetime of **1** at 77 K is 456 μs , whereas the decay in **2** is biexponential with two long-lifetime components: 30 and 410 μs . We note that the complex nature of the emission intensity decay has been observed in other Re(I)-phen complexes.¹² However, the measured lifetimes are well beyond that expected for Re(I)-diimine-based MLCT excited states at 77 K. The excited-state lifetime of **4** measured at 77 K ($\lambda_{\text{ex}} = 337 \text{ nm}$) in a 4:1 EtOH/MeOH glass is 450 μs , which is in quantitative agreement with that observed for **1** at 77 K. Taken together, the 77 K results are consistent with an intraligand-based $\pi-\pi^*$ phosphorescence emanating from

each respective phenanthroline ligand. This phenomenon is not unprecedented and, because it is well-established that the $^3\text{MLCT}$ level in Re(I) complexes increases as temperature decreases, whereas the ^3IL states are largely unaffected by environment,^{1,12,15,18} it is not surprising that the ^3IL and $^3\text{MLCT}$ states invert at low temperature in **1** and **2**. This state inversion leads to emission from the lowest excited state, which can be largely attributed to the ^3IL state localized on the diimine ligand structure in **1** and **2**.

Transient Absorption. Nanosecond laser flash photolysis experiments were performed on compounds **1–3** in MTHF solutions and **4** in CH_2Cl_2 (due to solubility restrictions) at RT using 355-nm excitation (see Figure 4). In complexes **1–3**, the absorption transients decay with the same single exponential kinetics observed in the respective luminescence intensity decays, within a few percent (see Table 3). These data illustrate that each luminescent species is mostly likely of the same origin as that which produces the absorption transients. The data obtained for **3** represent the absorption spectral features associated with the MLCT excited state in MTHF, which display TAs throughout the entire spectrum, except at wavelengths of $>520 \text{ nm}$, where the PL dominates the signal (see Figure 4a). The ground-state bleaching of the MLCT band appears as a depression between 375 and 450 nm, whereas broad features are observed in the range of 450–520 nm while a large transient is obtained near 300 nm. This difference spectrum is in complete agreement with that reported for the same complex in CH_3CN , where the absorptions near 305 and $\sim 480 \text{ nm}$ were assigned to reduced phen in the MLCT excited state.¹⁰ The absorption spectrum of phen $^{\cdot-}$ possesses strong features in the 520–650 nm region, as well in the ultraviolet (UV) region.^{49,50} Although we cannot evaluate the long wavelength segment and the MLCT bleach interferes with the 375–450 nm range, the absorptions at $<375 \text{ nm}$ and in the range of 450–520 nm are assigned to the reduced phen ligand in **3**. Similar excited-state spectroscopic features are observed in reference chromophore **2**, except the MLCT bleach is largely obscured by the absorption transients assigned to the reduced phen $\equiv\text{CH}$ species (see Figure 4b).

Compound **1**, on the other hand, displays a noticeably different spectrum than **2** and **3**. There is a detectable ground-state bleaching near 350 nm in the region where the gold(I)-acetylide chromophore is the predominate absorber and there are transients observed at $>370 \text{ nm}$ with peaks at $\sim 450 \text{ nm}$ and $<330 \text{ nm}$ with a maximum at $\sim 320 \text{ nm}$ (see Figure 4c). When the formation of the charge-transfer excited state occurs, several spectroscopic features should be observed. One is the ground-state bleaching of the MLCT transition, which, in the case of **1**, is completely obscured by other transient absorptions, precluding its use as a diagnostic tool. Another is the formation of the diimine ligand radical anion that generally possesses strong, highly allowed absorption features in the UV and visible regions. These would be associated with the $\text{Ph}_3\text{PAuC}\equiv\text{Cphen}$ ligand in **1**, and should

(49) Kato, T.; Shida, T. *J. Am. Chem. Soc.* **1979**, *101*, 6869–6876.

(50) Turro, C.; Chung, Y. C.; Leventis, N.; Kuchenmeister, M. E.; Wagner, P. J.; Leroi, G. E. *Inorg. Chem.* **1996**, *35*, 5104–5106.

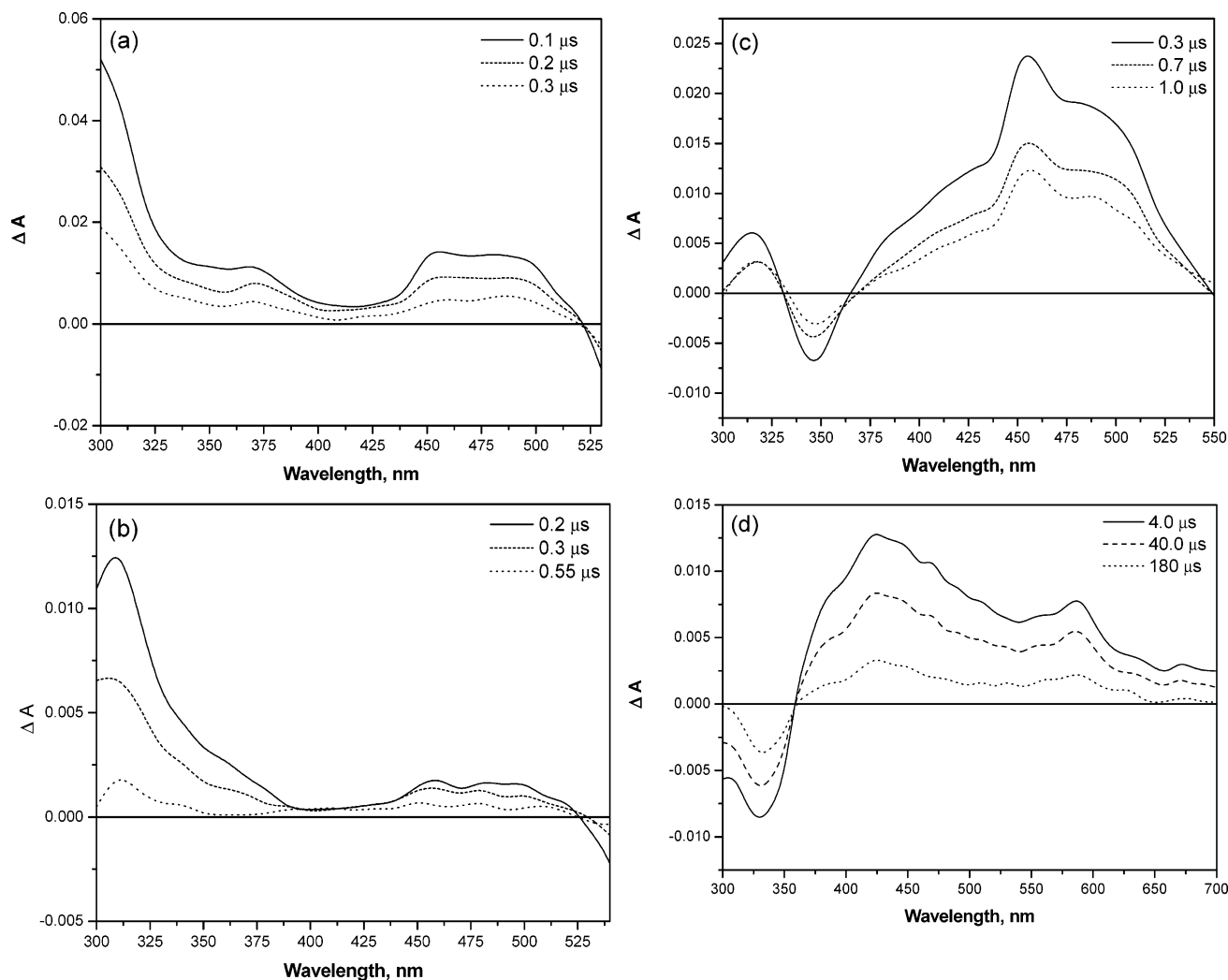


Figure 4. Excited-state absorption difference spectra of (a) **3** in MTHF, (b) **2** in MTHF, (c) **1** in MTHF, and (d) **4** in CH_2Cl_2 , generated by 355-nm excitation at 4, 7, 4, and 2 mJ/pulse, respectively. All delay times are specified in each graph.

be distinct from phen (**3**) or phenC \equiv CH (**2**), which may be the case. Compound **1** happens to possess low-energy $\pi-\pi^*$ transitions centered near 350 nm, because of the Au-acetylide linkage in strong electronic contact with the phenanthroline ligand.⁴² It stands to reason that, when the formation of the Re-based MLCT excited state occurs, the spectral features associated with the $\text{Ph}_3\text{PAuC}\equiv\text{Cphen}$ ligand would bleach and simultaneously yield strong diimine ligand radical anion transients. If the ligand radical anion transients are responsible for the large absorption features in the visible, then the TA data are consistent with a lowest MLCT excited state in **1**. However, it is somewhat surprising that the transient features, as well as the relative intensities, are so markedly different when comparing compound **1** to compounds **2** and **3**, suggesting that the excited-state picture in **1** is more complex. Figure 4d displays the excited-state absorption difference spectrum of the free ligand **4** in CH_2Cl_2 , following 355-nm excitation. As a result of sample decomposition, the solution was changed every 50 nm during the excited-state difference spectrum measurements, which were collected in 10-nm segments. Because transient luminescence measurements performed on **4** at RT were unsuccessful, the TA kinetics provides an independent measure-

ment of the excited-state lifetime. At all wavelengths, the kinetics was best modeled by a sum of two single exponentials, with a short component of $\sim 41 \mu\text{s}$ and a longer component of $\sim 192 \mu\text{s}$. Given the unstable nature of free ligand **4**, we performed these experiments under the most controlled conditions possible and believe that the data are representative of a pure sample. The long-lived transients are tentatively assigned to the lowest ^3IL state of **4**, because no other low-lying long-lived species are expected to be present. It stands to reason that the absorption transients produced as a result of 355-nm excitation correspond to the lowest-energy ^3IL state, which seems to decay to the ground state in a biexponential fashion, although we cannot completely exclude components arising from decomposition products generated during the experiment. A comparison of Figure 4c and 4d indicates that the difference spectra cannot be completely superimposed, which may suggest that the nature of the excited states of the two complexes is somewhat different. However, there are also similarities in the transient spectra of **1** and **4**, which may indicate that there is some degree of ^3IL character in the excited state of **1**. Up to this point, the combined photophysical properties of **1** are most consistent with an excited state of largely Re-based MLCT

character yet apparently influenced by the ^3IL state(s) resident on the $\text{phenC}\equiv\text{CAuPPh}_3$ ligand. The nature of the proposed interaction is uncertain but may have its origin in excited-state equilibrium or configuration mixing between the MLCT and ^3IL states.

Time-Resolved Infrared Spectroscopy. The three strongly IR-absorbing $\text{C}\equiv\text{O}$ groups present in the coordination shell of molecules **1**–**3** provide a diagnostic probe that is valuable in elucidating their excited-state behavior.^{27,51–53} Compound **3** has been well-studied in this regard, and the formation of the MLCT excited state produces ground-state bleaching signals, as well as characteristic $\nu(\text{C}\equiv\text{O})$ shifts to higher frequency in all three bands.⁵¹ This shifting to higher frequency is a direct result of the charge transfer: i.e., oxidation of the Re(I) metal center to Re(II) is accompanied by the transient shortening of all three $\text{C}\equiv\text{O}$ bonds. Therefore, in cases where TA spectra are ambiguous and somewhat speculative, TRIR spectra can substantiate or even diagnose the composition of the lowest excited state. This notion has been convincingly argued by several investigators over the past decade, and TRIR has been used to identify the lowest excited-state configuration in several instances.^{27,52,53} Figure 5 presents the FTIR and TRIR spectra of compounds **1** and **2** measured in the $\text{C}\equiv\text{O}$ stretching region in CHCl_3 . The TRIR spectrum of **4** was also measured but yielded no observable transients in the window of the experiment. The $\nu(\text{C}\equiv\text{O})$ frequencies measured in the FTIR and TRIR experiments are indicated throughout Figure 5. In both cases, the FTIR solution spectra are effectively the same within experimental error ($\pm 8\text{ cm}^{-1}$) and are very similar to that observed for $\text{Re}(\text{phen})(\text{CO})_3\text{Cl}$ in CH_3CN .⁵¹ The FTIR spectra measured 150 ns after 355-nm excitation display distinguishing features in **1** and **2**. In **2**, all three original $\nu(\text{C}\equiv\text{O})$ bands are bleached and their positions clearly shift to higher energy following excitation, which is diagnostic of the MLCT excited state (see Figure 5a). The difference spectrum measured in **1** provides the most compelling evidence for a “mixed” excited-state composition (see Figure 5b). It is clear that the origin vibrations are all bleached following the 355-nm laser pulse, and each of these bands seem to have a corresponding transient IR absorption at higher energy, which is consistent with the formation of the Re-based MLCT excited state. However, there is also a major absorption feature at 2014 cm^{-1} , whose band position is too high in energy to result from the blue shift of the 1924 cm^{-1} absorption. We believe the intense positive transient at 2014 cm^{-1} actually results from a red shift of the 2026 cm^{-1} band, which is somewhat indicative of the presence of a ^3IL state.^{52,53} At the present time, we are not certain why only a single vibration seems to display a red shift; however, note that TRIR spectra measured as a function of time demonstrate that all the transients decay to the ground state on the same time scale. In essence, all of the vibrations are coupled to the same dynamic excited-state processes, which indicate that both MLCT and ^3IL states coexist in **1** at RT and are most

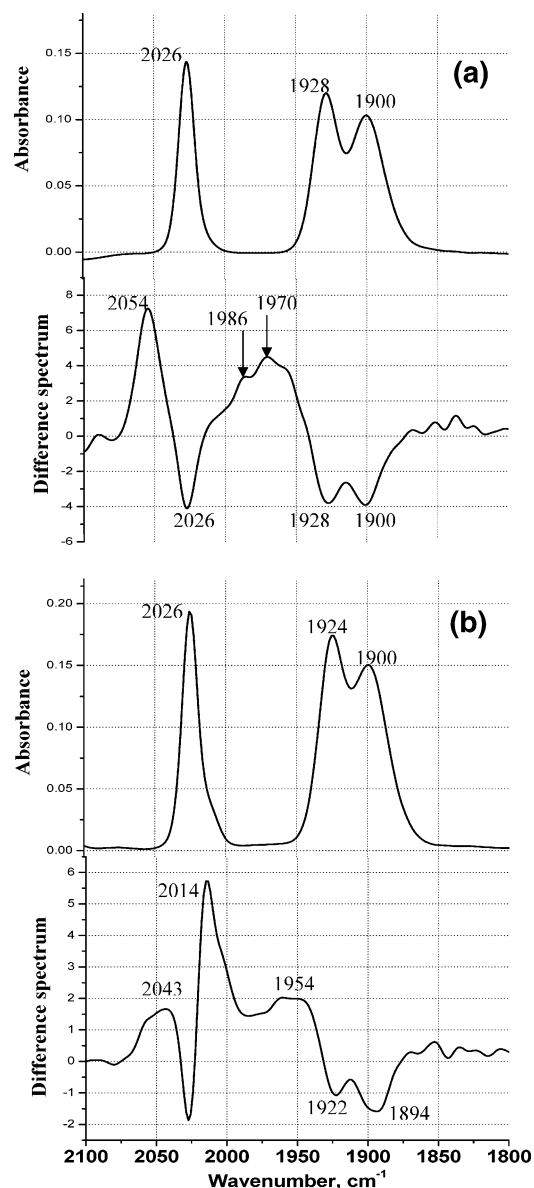


Figure 5. Fourier transform infrared (FTIR) and time-resolved infrared (TRIR) spectra of (a) **2** and (b) **1** in CHCl_3 ; the TRIR spectra are measured 150 ns following 355-nm excitation at 1 mJ/pulse.

likely thermally equilibrated.^{33,34} This picture is consistent with observations made in the TA and PL experiments presented earlier. Importantly, the diagnosis of multiple, coexisting excited states in Re(I) complexes has been previously demonstrated using TRIR spectroscopy,⁵³ and we believe that, in the present study, transient IR yields the most definitive evidence for the presence of multiple excited states. This may seem somewhat surprising, given the fact that these observations result from indirectly probing $\text{C}\equiv\text{O}$ vibrations, which respond to the oxidation changes at the metal center. In any case, the TRIR technique can be considered most valuable in understanding excited-state equilibrium processes in molecules bearing the appropriate IR-active moieties.

(51) George, M. W.; Turner, J. J. *Coord. Chem. Rev.* **1998**, *177*, 201–217.

(52) Schoonover, J. R.; Strouse, G. F. *Chem. Rev.* **1998**, *98*, 1335–1355.

(53) Schoonover, J. R.; Strouse, G. F.; Dyer, R. B.; Bates, W. D.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 273–274.

Conclusion

The present study revealed that the excited-state composition of **1** can be best described as an admixture of metal-to-ligand charge transfer (MLCT) and triplet intraligand (³IL) states most likely in thermal equilibrium. One piece of evidence for this observation comes from the fact that the room-temperature excited-state lifetime of **1** is modestly enhanced, relative to two structural model systems, possessing a lowest d- π^* MLCT excited state. Transient absorption data independently obtained for **1**, and its corresponding free diimine ligand **4**, demonstrated similarities in their difference spectra, implying that some ³IL character was present in the lowest excited state. Time-resolved infrared (TRIR) spectroscopy data were most definitive in demonstrating that the

excited state in **1** can best be described as being composed of MLCT and ³IL states in thermal equilibrium.

Acknowledgment. This project was financially supported by the National Science Foundation (CAREER Award CHE-0134782) and the ACS-PRF (36156-G6). All TRIR and TA measurements were performed in the Ohio Laboratory for Kinetic Spectrometry at Bowling Green State University. We thank Charles R. Luman for his assistance with the electrochemical measurements and Dr. Radek Pohl for the synthesis of phen-C \equiv C-TMS.

Supporting Information Available: Static emission spectra of compounds **1**, **2**, **4**, and **5** at 77 K (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC048376R