Inorg. Chem. **2003**, *42*, 3772–3778

Inorganic Chemistry
Article

Synthesis and Characterization of Platinum Diimine Bis(acetylide) Complexes Containing Easily Derivatizable Aryl Acetylide Ligands

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Received December 27, 2002

New Pt(II) diimine bis(acetylide) complexes where the diimine is a substituted bipyridine or phenanthroline and the arylacetylide is 4-ethynylbenzaldehyde have been prepared in good to excellent yields. Spectroscopic characterization supports a square planar coordination geometry with *cis*-alkynyl ligands, and the crystal structure of one of the complexes, Pt(phen)($C{\equiv}CC_6H_4CHO)_2$ (**1**), confirms the assignment. The new diimine bis(acetylide) complexes exhibit an absorption band ca. 400 nm that corresponds to a Pt(d) → π^* diimine charge transfer transition and are brightly emissive in fluid solution, with excited state lifetimes in the range 100–800 ns. Correlation of diimine substituent with λ_{max} for the 400 nm absorption band gives strong support to the MLCT assignment. Complex **1** undergoes electron transfer quenching, showing good Stern–Volmer behavior with a variety of oxidative and reductive quenchers. Quenching studies conducted with DNA nucleosides (A, T, C, G) were also investigated. Silyl-protected adenosine and guanosine were found to quench the luminescence of **1** better than similarly protected cytidine or thymidine. Since the former are the more easily oxidized bases, the results suggest that the Pt(II) diimine bis(acetylide) complexes are more powerful photooxidants than photoreductants with regard to electron transfer to DNA bases.

Introduction

The development of a molecularly based system for artificial photosynthesis remains a challenge for scientists interested in light-to-chemical energy conversion. Two of the key steps in artificial photosynthesis are electron−hole creation and electron−hole separation. The former occurs at the charge transfer chromophore that functions at the center of such an artificial photosynthesis system, while the latter results from electron transfer to and from appropriately placed acceptors and donors.[1−17] In pursuit of this goal, a number of two- and three-component systems (dyads and triads) have been constructed and examined with regard to electron transfer quenching of the chromophore's excited state and the formation of charge-separated species.[10,15,18−21]

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(1) Balzani, V.; Moggi, L.; Scandola, F. In *Towards a Supramolecular Photochemistry: Assembly of Molecular Components to Obtain Photochemical Molecular Devices*; Balzani, V., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1987; pp 1−28.
(2) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.
(3) Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786−4795.
(4) Kroon, J.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Angew*. Chem., Int. Ed. Engl. **1991**, *30*, 1358−1360.
(5) Cusack, L.; Marguerettaz, X.; Rao, S. N.; Wenger, J.; Fitzmaurice, D. *Chem. Mater.* **1997**, *9*, 1765−1772.
(6) Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 92−95.
(7) Moore, A. L.; Moore, T. A.; Gust, D.; Silber, J. J.; Sereno, L.; Fungo, F.; Otero, L.; SteinbergYfrach, G.; Liddell, P. A.; Hung, S. C.; Imahori, H.; Cardoso, S.; Tatman, D.; Macpherson, A. N. *Pure Appl. Chem.* **1997**, *69*, 2111−2116.
(8) Gust, D.; Moore, T. A.; Makings, L. R.; Liddell, P. A.; Nemeth, G. A.; Moore, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 8028−8031.
(9) Imahori, H.; Cardoso, S.; Tatman, D.; Lin, S.; Noss, L.; Seely, G. R.; Sereno, L.; deSilber, J. C.; Moore, T. A.; Moore, A. L.; Gust, D. *Photochem. Photobiol.* **1995**, *62*, 1009−1014.
(10) Ziessel, R.; Juris, A.; Venturi, M. *Inorg. Chem.* **1998**, *37*, 5061−5069.
(11) Dixon, I. M.; Collin, J. P.; Sauvage, J. P.; Barigelletti, F.; Flamigni, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1292.
(12) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.
(13) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.
(14) Chan, C.-W.; Lai, T. F.; Che, C.-M.; Peng, S.-M. *J. Am. Chem. Soc.* **1993**, *115*, 11245−11253.
(15) Treadway, J. A.; Chen, P. Y.; Rutherford, T. J.; Keene, F. R.; Meyer, T. J. *J. Phys. Chem. A* **1997**, *101*, 6824−6826.
(16) Slate, C. A.; Striplin, D. R.; Moss, J. A.; Chen, P. Y.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4885−4886.
(17) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C. P.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607−2617.
(18) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519−2520.

10.1021/ic0263084 CCC: $25.00

One possible set of chromophores that has shown itself to be attractive is that of diimine-containing square planar Pt(II) complexes where the diimine corresponds to 2,2′-bipyridine, 1,10-phenanthroline or derivatives and analogues thereof. These systems possess charge transfer excited states that, depending on the anionic ligands, may be luminescent in fluid solution.[22−27] For these chromophores, the LUMO is a π^* orbital of the diimine ligand. Over the past decade, we have focused on the synthesis, characterization, and photophysical study of Pt(diimine)X_2 complexes in which X_2 is either a dithiolate or bis(acetylide) ligands. For the dithiolate systems, the HOMO has mixed metal and dithiolate character,[28−30] whereas for the bis(acetylide) complexes, the LUMO is mainly localized on Pt. The latter complexes are brightly emissive in fluid solution with emission quantum yields as high as 14%, and at 77 K in butyronitrile glass, they display resolved vibronic components.[31] A study of the effects of ligand variation on excited state energy has confirmed that the emissive state is ^{3}MLCT in origin, as originally proposed by Che.[31−33,34] The MLCT assignment is also supported by transient absorption and time-resolved infrared spectroscopies where the shift of the ν(C≡C) band to higher frequency is consistent with charge transfer away from Pt in the excited state.[33] The Pt(diimine)(C≡CAr)$_2$ complexes undergo both oxidative and reductive quenching, but the systems only exhibit long-term stability on continuous irradiation under reductive quenching conditions.[31,34]

In order to incorporate the Pt(diimine)(C≡CAr)$_2$ chromophore into multicomponent systems that have been referred to as molecular photochemical devices (MPD's), it is necessary to have functional groups present on the ligands for coupling reactions to create bridges and connections between components. To date, only one triad having a Pt(diimine)(C≡CAr)$_2$ chromophore has been reported, and its preparation was dependent on a number of Pd^{2+}-catalyzed Sonogashira−Hagihara coupling reactions[35−38] with their attendant problems of purification and catalyst metal ion removal.[21] Through the presence of an aldehyde substituent on the arylacetylide ligand, we envisioned more facile and better yielding coupling reactions between the chromophore and the potential reductive quencher. In this paper, the first step toward this goal is realized with the synthesis, characterization, and study of Pt diimine complexes having the aldehyde-containing acetylide *p*-C≡CC$_6$H$_4$CHO$^-$.

Platinum diimine complexes are also of interest for possible binding with DNA. Intercalation of planar platinum complexes containing terpyridyl ligands has been known since 1974, while more recently, Che and co-workers have described dppz complexes of platinum, where dppz = dipyridophenazine, as possible intercalators into duplex DNA.[39] In these studies, the platinum intercalators are cationic in order to impart both aqueous solubility and Coulombic attraction to the negatively charged DNA backbone. For the dppz complexes, the luminescence of the Pt complex appears to turn on upon intercalation.

The notion of intercalative binding coupled with electron transfer quenching known for Pt(diimine)(C≡CAr)$_2$ complexes suggested that these systems, if properly derivatized for aqueous solubility and positive charge, may be of interest for photochemical initiation of charge transfer through DNA. In most of the studies reported to date of charge transfer through DNA, the process involves hole injection into the base pair stack of the DNA duplex.[39−59] Since the platinum diimine complexes appeared to be respectable photoreduc-

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(19) Lopez, R.; Leiva, A. M. Z., F.; Loeb, B.; Norambuena, E.; Omberg, K. M.; Schoonover, J. R.; Striplin, D.; Devenney, M.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2924−2930.

(20) Bates, W. D.; Chen, P.; Dattelbaum, D. M.; Jones, W. E., Jr.; Meyer, T. J. *J. Phys. Chem. A* **1999**, *103*, 5227−5231.

(21) McGarrah, J. E.; Kim, Y.-J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001,** *40*, 4510−4511.

(22) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1989**, *28*, 1529−1533.

(23) Miskowski, V. M.; Houlding, V. H.; Che, C.-M.; Wang, Y. *Inorg. Chem.* **1993**, *32*, 2518−2524.

(24) Kunkely, H.; Vogler, A. *J. Am. Chem. Soc.* **1990**, *112*, 5625−5627.

(25) Wan, K.-T.; Che, C.-M.; Cho, K.-C. *J. Chem. Soc., Dalton Trans.* **1991**, 1077−1080.

(26) Zuleta, J. A.; Chesta, C. A.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 8916−8917.

(27) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1992**, *111*, 237−248.

(28) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396−2404.

(29) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949−1960.

(30) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007−2014.

(31) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447−457.

(32) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87−97.

(33) Whittle, C. E.; Weinstein, J. A.; Geore, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053−4062.

(34) Chan, S.-C.; Chan, M. C. W.; Wang, Y.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *Chem. Eur. J.* **2001**, *7*, 4180−4190.

(35) Sonogashira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291.

(36) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, N. *J.* Organomet. Chem. **1978**, *145*, 101−108.

(37) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

(38) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromol. Chem.* **1997**, *10*, 879.

(39) Che, C.-M.; Yang, M.; Wong, K.-H.; Chan, H.-L.; Lam, W. *Chem. Eur. J.* **1999**, *5*, 3350−3356.

(40) Bond, P. J.; Langridge, R.; Jennette, K. W.; Lippard, S. J. *Proc. Natl. Aca. Sci. U.S.A.* **1975**, *72*, 4825−4829.

(41) Howe-Grant, M.; Wu, K. C.; Bauer, W. R.; Lippard, S. J. *Biochemistry* **1976**, *15*, 4339−4346.

(42) Jeanette, K. W.; Gill, J. T.; Sadownick, J. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6159.

(43) Holmlin, R. E.; Dandliker, P. J.; Barton, J. K. *Angew. Chem., Int. Ed.* **1998**, *36*, 2715−2730.

(44) Barton, J. K.; Lippard, S. J. *Biochemistry* **1979**, *18*, 2661−2668.

(45) Diederichsen, U. *Angew. Chem., Int. Edit. Engl.* **1997**, *36*, 2317−2319.

(46) Lewis, F. D.; Letsinger, R. L.; Wasielewski, M. R. *Acc. Chem. Res.* **2001**, *34*, 159−170.

(47) Grinstaff, M. W. *Angew.* Chem., Int. Ed. **1999**, *38*, 3629−3635.

(48) Giese, B.; Wesseley, S.; Spormann, M.; Lindemann, U.; Meggers, E.; Michel-Beyerle, M. E. *Angew.* Chem., Int. Ed. **1999**, *38*, 996−998.

(49) Meggers, E.; Kusch, D.; Spichty, M.; Wille, U.; Giese, B. *Angew.* Chem., Int. Ed. **1998**, *37*, 460−462.

(50) Meggers, E.; Michel-Beyerle, M. E.; Giese, B. *J. Am. Chem. Soc.* **1998**, *120*, 12950−12955.

(51) Bixon, M.; Giese, B.; Wessely, S.; Langenbacher, T.; Michel-Beyerle, M. E.; Jortner, J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 11713−11716.

(52) Armitage, B.; Yu, C.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9847−9859.

(53) Armitage, B. *Chem. Rev.* **1998**, *98*, 1171−1200.

(54) Breslin, D. T.; Schuster, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 2311−2319.

(55) Henderson, P. T.; Jones, D.; Hampikian, G.; Kan, Y.; Schuster, G. B. *J. Biol. Inorg. Chem.* **1999**, *3*, 201−209.

tants, we became interested in whether intercalative Pt systems could be used to initiate charge transfer by *electron* injection into the base pair stack of the duplex. In order to assess the feasibility of such a process, quenching studies were conducted with the Pt(phen)(p-C≡$CC_6H_4CHO)_2$ (**1**) complex using different silyl-protected nucleosides, as well as other electron transfer quenchers. The present paper describes the results of these studies.

Experimental Section

Reagents. 1,10-Phenanthroline, 5-Cl-phenanthroline (Clphen), 5-Me-phenanthroline (Mephen), bipyridine (bpy), 4,4′-dimethylbipyridine (dmbpy), 4,4′-diphenylbipyridine (dphbpy), and 4-trimethylsilylethynylbenzaldehyde (all from Aldrich) and potassium tetrachloroplatinate (Johnson Matthey) were used without further purification. The diimine complexes Pt(Rphen)Cl_2 and Pt(4,4′-R_2′-bpy)Cl_2, where R is Me, H, Cl and R′ is Me, H, Ph, respectively, were prepared according to a literature method.[60] The acetylide precursor 4-ethynylbenzaldehyde was obtained by TMS removal following a literature method using K_2CO_3 in anhydrous methanol.[61] The syntheses of the different Pt(diimine)(p-C≡$CC_6H_4CHO)_2$ complexes were performed under nitrogen with degassed solvents following a procedure similar to that previously reported.[31,36] The DNA nucleosides adenosine, guanosine, cytidine, and thymidine were protected by a standard silylation procedure,[62] while all other quenchers were purified prior to use.

Pt(phen)(C≡$CC_6H_4CHO)_2$ (1). A Schlenk tube was charged with Pt(phen)Cl_2 (0.100 g; 0.22 mmol), CuI (10 mg), 4-ethynylbenzaldehyde (0.33 g, 2.5 mmol), and 10 mL of DMSO:DMF:NEt_3 (5:3:2 v/v/v). The resulting solution was stirred at 65 °C for 20 h. The solvent was removed, water was added, and the organic material was isolated by vacuum filtration. The solids were then dissolved in CH_2Cl_2, reprecipitated by the addition of hexanes, and isolated by vacuum filtration. An analytically pure sample was obtained by preparative TLC on neutral alumina using CH_2Cl_2/MeOH (99.5:0.5 v/v) and recrystallized from CH_2Cl_2/hexanes. Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 9.97 (2H, s), 9.76 (2H, d, $J = 4$ Hz), 9.06 (2H, d, $J = 8$ Hz), 8.31 (2H, s), 8.25 (dd, 2H, $J = 5.2$ Hz, $J = 5.2$ Hz), 7.86 (4H, d, $J = 8$ Hz), 7.63 (4H, d, $J = 8$ Hz). MS (FD): m/z (%) 634.0 ([M]$^+$, 100). Anal. Calcd for $C_{30}H_{18}N_2O_2Pt$ ($M_r = 634$): C, 56.87; H, 2.86; N, 4.42. Found: C, 56.68; H, 2.84; N, 4.47.

Pt(Mephen)(C≡$CC_6H_4CHO)_2$ (2). The procedure followed for **1** was used except that Pt(Mephen)Cl_2 (0.100 g; 0.21 mmol) was used. Yield: 60%. ^{1}H NMR (DMSO-d_6): δ 9.97 (2H, s), 9.79 (1H, d, $J = 5$ Hz), 9.68 (1H, d, $J = 9$ Hz), 9.11 (1H, d, $J = 2$ Hz), 8.94 (1H, d, $J = 8$ Hz), 8.29 (1H, dd, $J = 5.2$ Hz, $J = 5.2$ Hz), 8.21 (1H, dd, $J = 8.0$ Hz, $J = 4.0$ Hz), 8.11 (1H, s), 7.86 (4H, d, $J = 8$ Hz), 7.63 (4H, d, $J = 6$ Hz). MS (FD): m/z (%) 647.0 ([M]$^+$, 100). Anal. Calcd for $C_{31}H_{20}N_2O_2Pt$ ($M_r = 647$): C, 57.50; H, 3.11; N, 4.33. Found: C, 57.53; H, 2.89; N, 4.11.

Pt(Clphen)(C≡$CC_6H_4CHO)_2$ (3). The procedure followed for **1** was used except that Pt(Clphen)Cl_2 (0.100 g; 0.21 mmol) was used. Yield: 50%. ^{1}H NMR (DMSO-d_6): δ 9.97 (2H, s), 9.86 (1H, d, $J = 8$ Hz), 9.76 (1H, d, $J = 3$ Hz), 9.18 (1H, d, $J = 3$ Hz), 9.01 (1H, d, $J = 9.0$ Hz), 8.66 (1H, s), 8.38 (1H, dd, $J = 4.0$ Hz, $J = 4.0$ Hz), 8.28 (1H, dd, $J = 5.2$ Hz, $J = 8.00$ Hz), 7.86 (4H, d, $J = 8$ Hz), 7.64 (4H, m, $J = 4$ Hz). MS (FD): m/z (%) 668.0 ([M]$^+$, 100). Anal. Calcd for $C_{30}H_{17}ClN_2O_2Pt$ ($M_r = 668$): C, 53.94; H, 2.57; N, 4.19. Found: C, 54.22; H, 2.23; N, 4.04.

Pt(bpy)(C≡$CC_6H_4CHO)_2$ (4). A Schlenk tube was charged with Pt(bpy)Cl_2 (0.100 g; 0.24 mmol), CuI (10 mg), 4-ethynylbenzaldehyde (0.3079 g; 2.3 mmol), and a solution of DMSO:triethylamine (5:1 v/v). The resulting solution was stirred at 65 °C for 20 h, the solvent was removed, water was added, and the resulting precipitate was isolated by vacuum filtration. It was then dissolved in a minimum amount of CH_2Cl_2 and recrystallized from hexanes. An analytically pure sample was obtained by preparative TLC (neutral alumina; 99.5% CH_2Cl_2/ 0.5% MeOH). Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 9.95 (2H, s), 9.51 (2H, d, $J = 8$ Hz), 8.70 (2H, d, $J = 8$ Hz), 8.45 (2H, t, $J = 7$ Hz), 7.93 (2H, t, $J = 8.0$ Hz), 7.83 (4H, d, $J = 8$ Hz), 7.57 (4H, d, $J = 12$ Hz). MS (FD): m/z (%) 609.0 ([M]$^+$, 100). Anal. Calcd for $C_{28}H_{18}N_2O_2Pt$ ($M_r = 609$): C, 55.17; H, 2.97; N, 4.59. Found: C, 54.93; H, 2.74; N, 4.25.

Pt(dmbpy)(C≡$CC_6H_4CHO)_2$ (5). The procedure followed for **4** was used except that Pt(4,4′-Me_2bpy)Cl_2 (0.100 g; 0.22 mmol) was employed. Yield: 55%. ^{1}H NMR (DMSO-d_6): δ 9.97 (2H, s), 9.31 (2H, d, $J = 4$ Hz), 8.59 (2H, s), 7.85 (4H, d, $J = 2$ Hz), 7.76 (2H, d, $J = 4$ Hz), 7.57 (4H, d, $J = 8$ Hz), 2.53 (6H, s). MS (FD): m/z (%) 637.0 ([M]$^+$, 100). Anal. Calcd for $C_{30}H_{22}N_2O_2Pt$ ($M_r = 637$): C, 56.51; H, 3.48; N, 4.39. Found: C, 56.14; H, 3.06; N, 4.43.

Pt(dphbpy)(C≡$CC_6H_4CHO)_2$ (6). The procedure followed for **4** was used except that Pt(Ph_2bpy)Cl_2 (0.100 g; 0.17 mmol) was employed. Yield: 45%. ^{1}H NMR (DMSO-d_6): δ 9.96 (2H, s), 9.53 (2H, d, $J = 8$ Hz), 9.19 (2H, s), 8.30 (2H, dd, $J = 4$ Hz, $J = 2$ Hz), 8.14 (2H, t, $J = 8.0$ Hz), 7.83 (4H, d, $J = 8$ Hz), 7.85 (4H, d, $J = 8$ Hz), 7.63 (4H, d, $J = 8$ Hz), 7.58 (4H, d, $J = 8$ Hz). MS (FD): m/z (%) 762.0 ([M]$^+$, 100). Anal. Calcd for $C_{40}H_{26}N_2O_2Pt$ ($M_r = 762$): C, 63.07; H, 3.44; N, 3.68. Found: C, 63.06; H, 3.11; N, 3.74

Physical Measurements. ^{1}H NMR spectra were recorded on Bruker AMX-400 or Avance 400 spectrometers. Field desorption mass spectrometry was performed by the Analytical Services Division of the Kodak Research Laboratories, Rochester, NY, and elemental analyses were provided by Quantitative Technologies, Whitehouse, NJ. Absorption spectra were recorded on a Hitachi U2000 spectrometer while luminescence spectra and Stern−Volmer experiments were measured on a SPEX Fluorolog-2 spectrophotometer corrected for instrument response. Fluid solution emission samples, as well as those used in the quenching studies, were subjected to at least 4 freeze−pump−thaw cycles.

Lifetime data were collected on an excimer pumped dye laser system (1−3 mJ/pulse) and fit to single exponential decays.[63] Quenching studies were performed by luminescence intensity measurements and fit to the modified Stern−Volmer equation:

$$I_{em}^{\circ}/I_{em} = 1 + \tau_o k_q[Q]$$

where k_q is the quenching rate constant, [Q] is the concentration of quencher, τ_o is the excited state lifetime of the chromophore, and

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(56) Hall, D. B.; Kelley, S. O.; Barton, J. K. *Biochemistry* **1998**, *37*, 15933−15940.

(57) Hall, D. B.; Barton, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 5045−5046.

(58) Rajski, S. R.; Kumar, S.; Roberts, R. J.; Barton, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 5615−5616.

(59) Lewis, F. D.; Liu, X.; Wu, Y.; Miller, S. E.; Wasielewski, M. R.; Letsinger, R. L.; Sanishvili, R.; Joachimiak, A.; Tereshko, V.; Egli, M. *J. Am. Chem. Soc.* **1999**, *121*, 9905−9906.

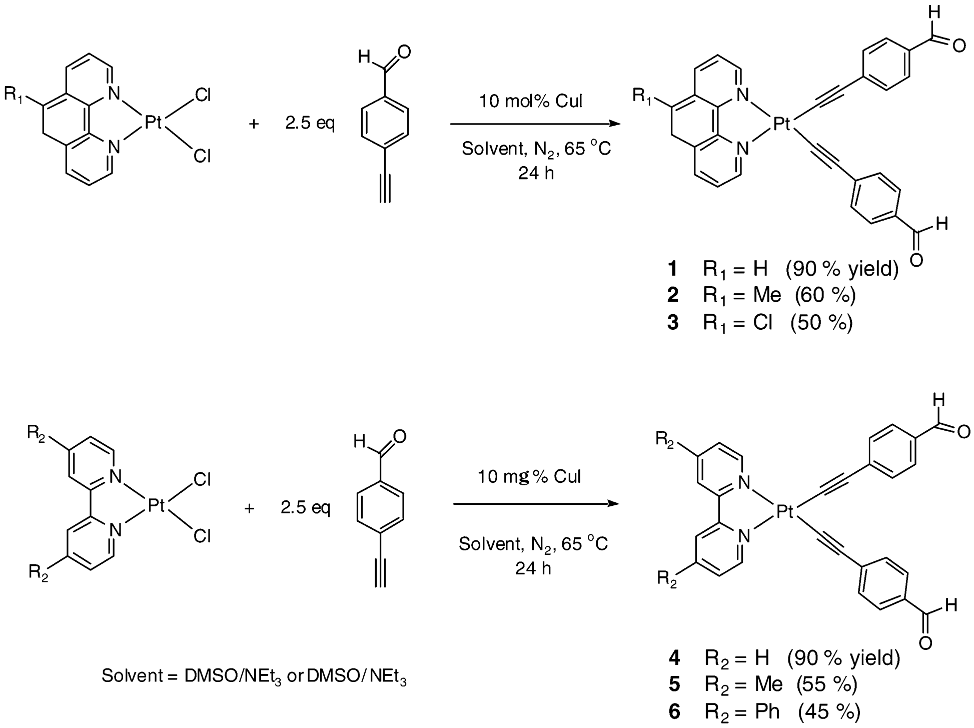
(60) Hodges, K. D.; Rund, J. V. *Inorg. Chem.* **1975**, *14*, 525−528.

(61) Halbes, U.; Pale, P. *Tetrahedron Lett.* **2002**, *43*, 2039−2042.

(62) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190−6191.

(63) Chen, L.; Farahat, M. S.; Gaillard, E. R.; Farid, S.; Whitten, D. G. *J. Photochem. Photobiol. A: Chem.* **1996**, *95*, 21−25.

Scheme 1



$I_{em}°/I_{em}$ is the ratio of emission intensities of the chromophore in the absence and presence of quencher. The concentration of the Pt chromophore was held constant at 3×10^{-5} M while the quencher concentration varied from 1×10^{-4} to 8×10^{-3} M. All samples were maintained in the absence of light until measurements were taken.

Crystal Structure Determination of Pt(phen)(C≡CC$_6$H$_4$CHO)$_2$ (1). Crystals were grown by slow liquid diffusion of hexanes into a concentrated solution of **1** in CH$_2$Cl$_2$. A yellow colored fragment of approximate dimension $0.18 \times 0.08 \times 0.04$ mm^3 was cut from a larger plate and mounted under Paratone-8277 on a glass fiber, and it was immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus Mo-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.5°). The total data collection time was approximately 13 h. Frames were integrated to a maximum 2θ angle of 46.5° with the Siemens SAINT program to yield a total of 5988 reflections, of which 3746 were independent. Unit cell, space group, data collection,[64] and refinement parameters are summarized in Table 1. The structure was solved using direct methods and refined by full matrix least squares on F^2. All non-hydrogen atoms of the metal complex were refined with anisotropic thermal parameters, while the non-hydrogen atoms of the solvent were refined isotropically. The hydrogen atoms were included in idealized positions.

Results and Discussion

Synthesis and Characterization. The synthetic strategy for making the Pt(diimine)(C≡CC$_6$H$_4$CHO)$_2$ complexes **1**−**6** (Scheme 1) is based on the CuI-catalyzed chloride-to-acetylide metathesis that has been used for synthesizing other Pt alkynyl derivatives.[21,31,36]

Table 1. Crystallographic Data for Pt(phen)(C≡CC$_6$H$_4$CHO)$_2$·CH$_2$Cl$_2$

emp formula	C$_{31}$H$_{20}$Cl$_2$N$_2$O$_2$Pt	abs correction	SADABS^b
fw	718.48	transm range	0.489−0.928
T, K	193(2)	F(000)	696
λ, Å	0.71073	2θ range, deg	1.73−23.25
cryst syst	triclinic	limiting indices	$-21 \le h \le 19$ $-11 \le k \le 10$ $-12 \le l \le 13$
space group	$P\bar{1}$ (No. 2)	no. of reflns collected	5988
Z	2		
a, Å^a	10.4736(10)	no. of data/restraints/ params	3746/0/328
b, Å^a	10.8580(10)		
c, Å^a	11.8959(11)	GOF^c	1.017
β, deg^a	96.221(2)	R1, wR2 ($I > 2\sigma$)^d	0.0369, 0.0976
V, Å^3	1334.3(2)	R1, wR2 (all data)^d	0.0382, 0.0987
ρ_{calcd}, g cm^{-3}	1.788		
μ, mm^{-1}	5.490		

[a] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10 × the listed value. [b] The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, *51*, 33. [c] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$×e2 where n and p denote the number of data and parameters. [d] R1 = $(||F_o| - |F_c||)\Sigma|F_o|$; wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2 + aP)^2 + bP]$ and $P = [(\text{Max}; 0, F_o^2) + 2F_c^2]/3$.

Due to the relative insolubility of the Pt(diimine)Cl$_2$ starting material, the reactions were run in solvent mixtures of DMF, DMSO, and NEt$_3$ that upon heating to 65 °C easily solubilized all starting materials (Scheme 1). All of the complexes were characterized by NMR, electronic absorption, and emission spectroscopies, mass spectrometry, and elemental analyses. The spectroscopic data support the expected structural assignment of a square planar Pt(II) complex with a coordinated diimine and two cis acetylide ligands. For example, in the case of Pt(bpy)(C≡CC$_6$H$_4$CHO)$_2$

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(64) Wavefunction, Inc., 18401 Von Karman, Suite 370, Irvine, CA 92612.

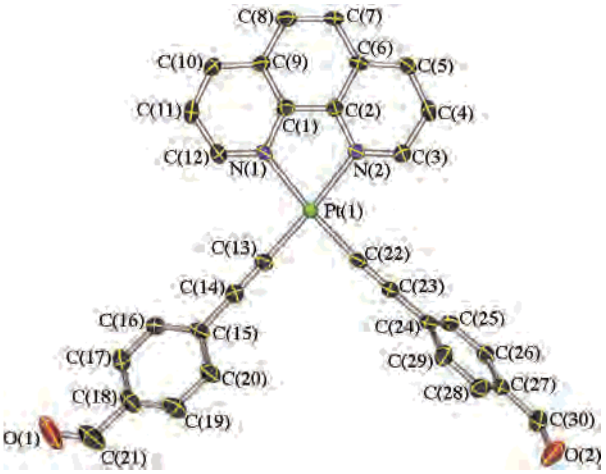

Figure 1. Molecular structure and atom-numbering scheme for $Pt(phen)(C\equiv CC_6H_4CHO)_2$ (**1**) (30% probability ellipsoids). Hydrogens and molecule of CH_2Cl_2 omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pt(1)−C(22)	1.943(7)	N(2)−C(2)	1.346(9)
Pt(1)−C(13)	1.950(7)	C(13)−C(14)	1.208(11)
Pt(1)−N(1)	2.072(6)	C(14)−C(15)	1.425(10)
Pt(1)−N(2)	2.076(6)	C(18)−C(21)	1.477(12)
N(1)−C(12)	1.331(9)	C(22)−C(23)	1.212(10)
N(2)−C(3)	1.335(9)	C(23)−C(24)	1.429(10)
C(3)−C(4)	1.402(10)	C(27)−C(30)	1.482(11)
C(4)−C(5)	1.369(11)	C(21)−O(1)	1.212(13)
C(5)−C(6)	1.408(10)	C(30)−O(2)	1.200(11)
C(6)−C(2)	1.418(9)		
C(22)−Pt(1)−C(13)	89.8(3)	N(1)−Pt(1)−N(2)	80.0(2)
C(22)−Pt(1)−N(1)	174.1(2)	Pt(1)−N(1)−C(12)	129.3(5)
C(13)−Pt(1)−N(1)	95.8(3)	C(12)−N(1)−C(1)	118.0(6)
C(22)−Pt(1)−N(2)	94.69(2)	Pt(1)−C(13)−C(14)	177.3(6)
C(13)−Pt(1)−N(2)	174.3(2)	C(13)−C(14)−C(15)	176.1(8)
		O(1)−C(21)−C(18)	125.3(10)

(**4**), the ^{1}H NMR spectrum displays a strong singlet at 9.95 ppm indicating the presence of the aldehyde protons which are located on the arylacetylide ligand. Four resonances associated with a symmetrically substituted bipyridine ring system (two doublets and two triplets) are located at 9.51, 8.70, 8.45, and 7.93 ppm, respectively. These resonances are also shifted approximately 1 ppm downfield when compared to the ^{1}H NMR spectrum of uncoordinated bipyridine. Two strong doublets at 7.83 and 7.57 ppm are also observed and have been assigned to the ring protons associated with the para-substituted arylacetylide. Finally, the integration pattern of the entire spectrum is consistent with the 2:1 ratio of acetylide:diimine ligands and is confirmed by mass spectral data.

Molecular Structure of $Pt(phen)C\equiv CC_6H_4CHO)_2$ (1). The molecular structure of **1** which has approximate C_2 symmetry is shown in Figure 1 along with the numbering scheme used. Important bond lengths and angles are given in Table 2, while a complete tabulation of distances and angles is found in the CIF deposited as Supporting Information. The Pt−N distance of 2.076(6) Å compares well with corresponding values found in other Pt phenanthroline complexes such as 2.063(3), 2.033(6), and 2.040(5) Å in $Pt(phen)_2Cl_2$,[65] $Pt(phen)(C\equiv CC_6H_4CH_3)_2$,[31] and $Pt(dbbpy)(C\equiv CC_6H_4CH_3)_2$,[66] respectively. The Pt−C(acetylide) bond distances average 1.946(7) Å and agree well with the values of 1.948(3),[31] 1.947(17),[66] 2.01(3),[67] 2.026(9),[68] 2.013(1),[69] and 1.998(4) Å,[70] for $Pt(phen)(C\equiv CC_6H_4CH_3)_2$, $Pt(dbbpy)(C\equiv CC_6H_4CH_3)_2$, $[cis\text{-}\{Pt(C_6F_6)_2(C\equiv CSiMe_3)_2\}Pd(\eta^3\text{-}C_3H_5)]]^-$, $[(PPh_3)_2Pt(\mu\text{-}\eta^1\text{-}\eta^2\text{-}C\equiv C^tBu)_2Pd(\eta^3\text{-}C_3H_5)]^+$, $[\{cis\text{-}Pt(C_6F_5)_2(-C\equiv CPh)_2\}Ag_2]^{2-}$, and *trans*-Pt(2,2′:6′,2″-terpyridine-4′-ylethynyl)$(PBu_3)^{2+}$, respectively. Only the Pt−C distance of 2.17(2) Å found in $[Pt_2(\mu\text{-}C{=}CHPh)(C\equiv CPh)(PEt_3)_4]$[71] is significantly longer than that found in the present structure. Deviations from a square planar geometry are relatively minor with a C−Pt−C angle of 89.8(3)° and a N−Pt−N bond angle of 80.0(2)°, the latter resulting from the constraint of the phenanthroline ligand. Finally, an examination of the crystal packing (not shown) reveals that the closest intermolecular Pt···Pt contact is greater than 7 Å, indicating the absence of any interactions between neighboring metal centers. This observation is in accord with other recently published Pt(diimine) bis(acetylide) complexes.[31]

Absorption and Emission Spectra. The absorption spectra of all of the complexes were taken in acetonitrile and are presented in Figure 2. All of the complexes exhibit a band around 400 nm, which has been previously assigned as the charge transfer transition corresponding to excitation from a filled Pt(d) orbital to an unoccupied π^* diimine orbital (MLCT).[32,33] Also seen are the high-energy bands ($\lambda < 370$ nm) that are assigned to diimine and acetylide-based intraligand transitions. The transition comprising the 400 nm band shifts to lower energy as the electron-withdrawing ability of the diimine substituent increases (phen, Me < H < Cl; bpy, Me < H < Ph), consistent with a lowering of the LUMO energy and the resultant charge transfer to diimine transition.[31]

Figure 3 presents the normalized emission spectra of the complexes in acetonitrile. All of the complexes are brightly emissive in fluid solution and, with the exception of $Pt(dmbpy)(C\equiv CC_6H_4CHO)_2$ (**5**), show a broad structureless emission. The relative quantum yield for emission of **1** was measured using $Ru(bpy)_3^{2+}$ as a standard ($\phi_{rel} = 0.062$[72]) and found to have a value (ca. 0.03) similar to what we reported previously for other Pt diimine bis(acetylide) systems.[31] The influence of substituent variation on the emission energies for the $Pt(Rphen)(C\equiv CC_6H_4CHO)_2$ and $Pt(R_2bpy)(C\equiv CC_6H_4CHO)_2$ is tabulated in Table 3, with the magnitude of the observed shifts greater than that seen for the ∼400 nm band in the absorption spectra. As the electron-

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(65) Hazell, A.; Mukhopadhyay, A. *Acta* Crystallogr. **1980**, *B36*, 1647−1649.

(66) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J.* Organomet. Chem. **1997**, *543*, 233−235.

(67) Berenguer, J. R.; Fornies, J.; Lalinde, E.; Martinez, F. *J. Organomet. Chem.* **1994**, *470*, C15−C18.

(68) Berenguer, J. R.; Fornies, J.; Lalinde, E.; Martinez, F. *Organometallics* **1996**, *15*, 4537−4546.

(69) Espinet, P.; Fornies, J.; Martinez, F.; Sotes, M.; Lalinde, E.; Moreno, M. T.; Ruiz, A.; Welch, A. J. *J. Organomet. Chem.* 1991, *403*, 253−267.

(70) Harriman, A.; Hissler, M.; Ziessel, R.; DeCian, A.; Fisher, J. *J. Chem. Soc., Dalton Trans.* **1995**, 4067−4080.

(71) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 3050−3052.

(72) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991−1024.

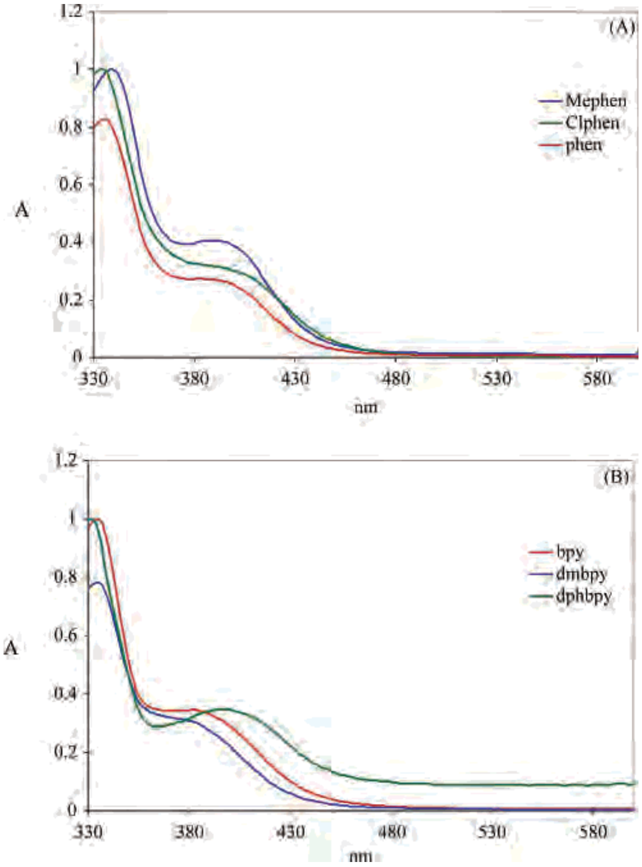

Figure 2. Normalized absorption spectra of Pt(Rphen)(C≡$CC_6H_4CHO)_2$ series (A) and Pt(R_2bpy)(C≡$CC_6H_4CHO)_2$ series (B) in acetonitrile at room temperature. Units are arbitrary.

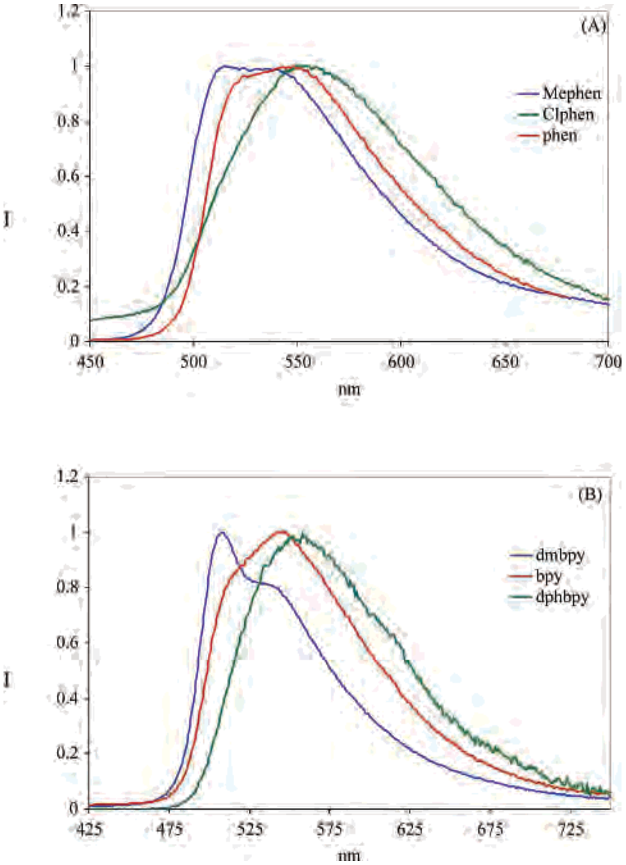

Figure 3. Normalized room temperature emission spectra of Pt(Rphen)-(C≡$CC_6H_4CHO)_2$ series (A) and Pt(R_2bpy)(C≡$CC_6H_4CHO)_2$ series (B) in acetonitrile. Units are arbitrary.

Table 3. Absorbance Maxima, Emission Maxima, and Excited State Lifetimes[a]

compound	λ abs (nm)	λ em (nm)	τ_o (ns)
Pt(Mephen)(C≡$CC_6H_4CHO)_2$ (**2**)	390 (22500)	515	360
Pt(phen)(C≡$CC_6H_4CHO)_2$ (**1**)	392 (8950)	548	340
Pt(Clphen)(C≡$CC_6H_4CHO)_2$ (**3**)	400 (12900)	554	54
Pt(dmbpy)(C≡$CC_6H_4CHO)_2$ (**5**)	375 (10500)	508	790
Pt(bpy)(C≡$CC_6H_4CHO)_2$ (**4**)	383 (13000)	546	124
Pt(dphbpy)(C≡$CC_6H_4CHO)_2$ (**6**)	395 (11500)	558	98

[a] Measured in acetonitrile at room temperature.

Table 4. Quenching Constants and Electrochemical Data for Oxidative Quenchers, Reductive Quenchers, and Nucleosides

quencher	$E_{1/2(red)}$ (V)[f]	k_q $(Ms)^{-1}$ [e]
phenothiazine[a]	0.83	1.3×10^{10}
10-Me-phenothiazine[b]	0.97	1.2×10^{10}
N,*N*′-dimethylaniline[b]	1.05	1.2×10^{10}
nitrobenzene[b]	−0.91	5.2×10^{8}
4-nitrobenzaldehyde[b]	−0.62	9.9×10^{9}
dinitrobenzene[b]	−0.45	1.2×10^{10}
thymidine[c,d]	−2.18	0
cytidine[c,d]	−2.35	9.5×10^{7}
adenosine[c,d]	−2.52	6.4×10^{8}
guanosine[c,d]	<−2.76	5.9×10^{8}

[a] Kowert, B. A.; et al. *J. Am. Chem. Soc.* **1972**, *94* (16), 5538−5550. [b] Bock, C. R.; et al. *J. Am. Chem. Soc.* **1979**, *101* (17), 4815−4824. [c] TBDMS-protected. [d] Seidel, C. A. M.; et al. *J. Phys. Chem.* **1996**, *100*, 5541−5553. [e] Measured in acetonitrile. [f] As reduction potentials (V vs NHE).

withdrawing ability of the diimine substituent increases, the emission band shifts to lower energy, consistent with a mainly metal based HOMO that is affected little by substituent and a π^* diimine LUMO that is highly substituent dependent.

Lifetime measurements were recorded at dilute concentrations for all of the complexes and are tabulated in Table 3. All complexes have radiative lifetimes τ_o in the hundreds of nanoseconds range, with **5** having the longest lifetime of 790 ns. This is noteworthy in light of the planned strategy of using synthetically modified complexes for the preparation of multicomponent systems for photoinduced charge separation through functional group coupling and the concern that substituents used for these couplings may facilitate nonradiative decay and yield complexes having shorter-lived excited states.

Quenching Studies. As with other reported Pt diimine bis(acetylide) complexes,[31] **1** undergoes electron transfer quenching with both donors and acceptors, and bimolecular quenching of the excited state was studied quantitatively. Analysis of the results gave linear Stern−Volmer plots of I_{em}^{o}/I_{em} vs [Q] for both reductive and oxidative quenchers (I_{em}^{o} and I_{em} are the emission intensities in the absence and presence of quencher and [Q] is quencher concentration). The results are summarized in Table 4. For the electron donor quenchers phenothiazine, 10-methylphenothiazine, and *N*,*N*′-dimethylaniline and the electron acceptor quenchers 4-nitrobenzaldehyde and dinitrobenzene, the rate of quenching was diffusion controlled with k_q values of $\sim 1 \times 10^{10}$ s^{-1}.

For nitrobenzene on the other hand, k_q was determined to be 5.2×10^8 s^{-1}, consistent with the fact that it was the poorest of the oxidative quenchers examined. However, quenching by nitrobenzene was still 3 orders of magnitude faster than with $Ru(bpy)_3^{2+}$ (2.2×10^5),[73] indicative of the fact that **1** is a more powerful photoreductant. Only complex **1** was examined quantitatively in terms of a quenching study because of its analytical purity and structural characterization, but it should be representative of the other complexes reported here.

The interest in electron transfer through DNA and the fact that **1** was a strong photoreductant stimulated the notion of using Pt diimine bis(acetylide) complexes as electron donors to hybridized DNA. However, in order to assess the feasibility of such a reaction prior to derivatization of **1** for aqueous solubility and cationic charge, quenching studies were conducted using the four different nucleosides adenosine, thymidine, cytidine, and guanosine (A, T, C, G). Because of the insolubility of the nucleosides, they were first TBDMS-protected to render them more lipophilic and readily soluble in acetonitrile for the quenching measurements. The results are summarized in Table 4. Stern−Volmer behavior is observed in every case except with T, for which no quenching was observed. The fastest rates of quenching were found for the nucleosides G and A, for which the quenching rate constants were determined to be ca. 10^8 M^{-1} s^{-1}. These values are 2 orders of magnitude smaller than the nearly diffusion controlled quenching rates reported for organic dyes with DNA subunits.[74] Since G and A are the most easily oxidized bases in DNA,[75] quenching by these bases most likely occurs through a reductive quenching mechanism wherein an electron is transferred *from* the nucleoside *to* the excited platinum complex. The fact that the lowest triplet state of any nucleoside is 3.21 eV[76] whereas E_{00} for **1** is 2.55 eV rules against any energy transfer path as an alternative means of quenching.

The rate of quenching by C is approximately 1 order of magnitude slower than determined for either G or A, and 2 orders of magnitude slower than found for other oxidative quenchers like dinitrobenzene ($k_q \approx 10^{10}$). For T, no quenching is observed, even at high quencher concentrations. Given that C and T are the most easily reduced bases,[46,77] it can be concluded that quenching is not occurring through a mechanism wherein the excited Pt chromophore transfers an electron *to* the nucleoside. The results thus suggest that while the Pt diimine bis(acetylide) complexes appear to be strong photoreductants, they are not potent enough to effect electron transfer *to* DNA upon irradiation. On the other hand, the Pt diimine bis(acetylide) complexes are observed to be strong enough photooxidants to transfer a hole to the more easily oxidized bases for electron transfer through duplex DNA.

Conclusions

Several new $Pt(diimine)(C\equiv CC_6H_4CHO)_2$ complexes have been synthesized with substituted phenanthroline and bipyridine ligands. All of the complexes are brightly emissive in fluid solution and have long-lived excited states, making them potentially useful in the construction of multicomponent systems for photoinduced charge separation. $Pt(phen)(C\equiv CC_6H_4CHO)_2$ was found to obey Stern−Volmer behavior with a series of oxidative and reductive quenchers. In studies with DNA nucleosides, the A and G nucleosides were able to quench the luminescence of the Pt chromophore better than C or T nucleosides. The results indicate that the Pt diimine bis(acetylide) complexes may be more effective photooxidants than photoreductants for initiating charge transfer through the bases of duplex DNA.

Acknowledgment. This research was supported by the Department of Energy, Division of Basic Chemical Sciences, for which we are grateful. We also thank Dr. James E. McGarrah for carrying out lifetime measurements.

Supporting Information Available: Complete crystallographic information including crystal data and structure refinement parameters, atomic positional coordinates, calculated hydrogen atom coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for **1** as a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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(73) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815−4824.

(74) Seidel, C. A. M.; Schulz, A.; Sauer, M. H. M. *J. Phys. Chem.* **1996**, *100*, 5541−5553.

(75) Steenken, S.; Jovanovic, S. V. *J. Am. Chem. Soc.* **1997**, *119*, 617−618.

(76) Wood, P. D.; Redmond, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 4256−4263.

(77) Steenken, S.; Telo, J. P.; Novais, H. M.; Candeias, L. P. *J. Am. Chem. Soc.* **1992**, *114*, 4701−4709.