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Article

Synthesis, Characterization and Photophysics of a New Series of Anionic C,N,C Cyclometalated Platinum Complexes[†]

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A novel series of anionic mononuclear terdentate dicyclometalated complexes (NBu$_4$)[Pt(C^N^C)X] (HC^N^CH = 2,6-diphenylpyridine) containing acetylide (X = C≡CR, R = ^{t}Bu, **1**; Ph, **2**; Tol, **3**; (4-OMe)C$_6$H$_4$, **4**) or another anionic ligand (X = CN, **5**; S-2Py, **6**; CH$_2$COCH$_3$, **7**) have been synthesized and fully characterized. The solid-state structures of complexes **1** and **4**–**6** have also been determined by X-ray diffraction studies, showing, in all the cases, the presence of several types of weak hydrogen interactions, leading to the generation of supramolecular 2D (**1**) or 3D (**4**–**6**) architectures. All the complexes (**1**–**7**) are intensely luminescent at low temperature (solid and glassy CH$_2$Cl$_2$), exhibiting concentration dependence in the emissions of the glassy CH$_2$Cl$_2$ matrix.

Introduction

There is a considerable interest in the study of transition-metal alkynyl σ complexes due to their widespread application in material science.[1−11] Since the first report on soluble [Pt(P^{n}Bu$_3$)$_2$] containing oligomeric polymers in the 1970s,[12,13] many new types of materials exhibiting very interesting prospects for the design of new molecular-site electronic devices have been studied and investigated.[1−11,14,15] In platinum chemistry, much research has been devoted to homo- and polynuclear species incorporating phosphines as auxiliary ligands (L). A wide range of rigid rod polymers,[16−22] architectures featuring a central aromatic core,[23−27] dendrimers,[28,29] macrocycles,[22,30−37] or molecular wires[38−42] bearing PtL$_2$ entities have been reported. Furthermore, polypyridyl[43−63] and related cyclometalated[55,64−73] alkynyl platinum complexes

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(1) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79.
(2) Whittal, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *43*, 349.
(3) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586.
(4) Yam, V. W.-W. *J. Organomet. Chem.* **2004**, *689*, 1393 and references therein.
(5) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555 and references therein.
(6) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K.-Y.; Haskins-Glusac, K.; Schanze, K. S. *Coord. Chem. Rev.* **2005**, *249*, 1491.
(7) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178−180*, 1251.
(8) Wong, W. Y. *Comments Inorg. Chem.* **2005**, *26*, 39.
(9) Wong, W. Y. *J. Inorg. Organomet. Polym.* **2005**, *15*, 197.
(10) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179.
(11) Lang, H.; Packheiser, R.; Walfort, B. *Organometallics* **2006**, *25*, 1836.
(12) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* **1977**, *10*, 879.
(13) Sonogashira, K.; Yatake, T.; Tahoda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291.
(14) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.
(15) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, Germany, 2004.
(16) Guo, F.; Kim, Y. G.; Reynolds, J. R.; Schanze, K. S. *Chem. Commun.* **2006**, 1887.
(17) Poon, S. Y.; Wong, W. Y.; Cheah, K. W.; Shi, J. X. *Chem.—Eur. J.* **2006**, *12*, 2550.
(18) Zhao, X.; Cardolaccia, T.; Farley, R. T.; Abboud, K. A.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 2619.
(19) Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Al-Battashi, F. R.; Al-Saadi, S.; Ahrens, B.; Bjernemose, J. K.; Mahon, M. F.; Raithby, P. R.; Younus, M.; Chawdhury, N.; Köhler, A.; Marseglia, E. A.; Tedesco, E.; Feeder, N.; Teat, S. J. *Dalton Trans.* **2004**, 2377 and references therein.
(20) Haskins-Glusac, K.; Pinto, M. R.; Tan, C.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 14964.
(21) D'Amato, R.; Fratoddi, I.; Cappoto, A.; Altamura, P.; Delfini, M.; Bianchini, C.; Bolasco, A.; Polzometti, G.; Russo, M. V. *Organometallics* **2004**, *23*, 2860.
(22) Long, N. J.; Wong, C. K.; White, A. J. P. *Organometallics* **2006**, *25*, 2525.
(23) Johnson, C. A.; Haley, M. M.; Rather, E.; Han, F.; Weakley, T. J. R. *Organometallics* **2005**, *24*, 1161.
(24) Tao, C.-H.; Zhu, N.; Yam, V. W.-W. *Chem.—Eur. J.* **2005**, *11*, 1647 and references therein.
(25) Chong, S. H.-F.; Lam, S. C.-F.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K.; Fathallah, S.; Costuas, K.; Halet, J.-F. *Organometallics* **2004**, *23*, 4924.
(26) Bruce, M. I.; Davy, J.; Hall, B. C.; Van, G.; Yvonne, J.; Skelton, B. W.; White, A. H. *Appl. Organomet. Chem.* **2002**, *16*, 559.
(27) Onitsuka, K.; Shimizu, A.; Takahashi, S. *Chem. Commun.* **2003**, 280.
(28) Onitsuka, K.; Fujimoto, M.; Kitajima, H.; Ohshiro, N.; Takei, F.; Takahashi, S. *Chem. Rev.* **2004**, *10*, 6433 and references therein.
(29) Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S. *J. Organomet. Chem.* **1998**, *569*, 195.

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have also received significant attention over the past decade, starting with the pioneering description of [Pt(phen)(C≡CPh)$_2$] carried out by Che and co-workers.[74] This class of complexes possesses interesting photophysical and photochemical properties with potential applications as tunable materials for optical power limiting,[59] photoinduced charge separation,[43−45,51,52,62] electroluminescence (OLEDs),[72,73] sensitization of singlet oxygen,[75] photocatalytic hydrogen production,[76,77] vapochromism,[46] as well as luminescent labels for metallo sensors and biomolecules.[48,49,55,60,61,71] In these systems, spectroscopic investigations have shown that the natures of the emissive states (metal-to-ligand charge transfer (^{3}MLCT), $^3\pi\pi^*$, ligand-to-ligand charge transfer (^{3}LLCT), or ligand−field (^{3}LF)) are strongly influenced by the properties of the ligands coordinated to the platinum center. In addition, some of these structures have been shown to exhibit low-lying metal-metal-to-ligand charge transfer (^{3}MMLCT) and/or excimeric $^3\pi\pi^*$ emissions associated with the occurrence of Pt···Pt and/or $\pi\cdots\pi$ ligand interactions.[47,53−55,61] Within this area, cyclometalated derivatives are of particular interest because of the very strong ligand field induced by both the acetylide group and the cyclometalated ligand. This fact usually raises the energy of metal-centered (d−d) excited states, preventing access to the deactivation of the lowest emitting excited state by radiationless transition or photoreactions.

However, research within this area has focused primarily on neutral and cationic platinum(II) complexes. To the best of our knowledge, the bis(alkynyl)(benzoquinolinate)platinate(II) complexes (NBu$_4$)[Pt(bzq)(C≡CR)$_2$], reported recently by our research group, are the first alkynyl anionic systems examined.[66] These results, together with our recent efforts using homo- and heteroleptic anionic alkynyl platinates to serve as versatile building blocks for the assembly of luminescent supramolecular hetero (Pt−M) polynuclear systems,[78−85] have prompted us to investigate the properties of a new series containing only one alkynyl fragment attached to a neutral [Pt(CNC)] core (HCNCH = 2,6-diphenylpyridine). It should be noted that although cyclometalated

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(30) Bruce, M. I.; Costuas, K.; Halet, J. F.; Hall, B. C.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; White, A. J. *J. Chem. Soc., Dalton Trans.* **2002**, 383.

(31) Jiang, H.; Lin, W. *J. Organomet. Chem.* **2005**, *690*, 5159.

(32) Jude, H.; Disteldorf, H.; Fischer, S.; Wedge, T.; Hawkridge, A. M.; Arif, A. M.; Hawthorne, M. F.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 12131.

(33) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Shardlow, E. J. *Dalton Trans.* **2005**, 234.

(34) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Jones, P. G. *Chem. Commun.* **2004**, 2658.

(35) Zhang, L.; Niu, Y. H.; Jen, A. K. Y.; Lin, W. *Chem. Commun.* **2005**, 1002.

(36) Campbell, K.; Johnson, C. A.; McDonald, R.; Ferguson, M. J.; Haley, M. M.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5967.

(37) Lee, S. J.; Luman, C. R.; Castellano, F. N.; Lin, W. *Chem. Commun.* **2003**, 2124.

(38) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W. *J. Organomet. Chem.* **2006**, *691*, 759.

(39) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem.—Eur. J.* **2003**, *9*, 3324.

(40) Zheng, Q.; Gladysz, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 10508.

(41) Zhuravlev, F.; Gladysz, J. A. *Chem.—Eur. J.* **2004**, *10*, 6510.

(42) Zheng, Q.; Hampel, F.; Gladysz, J. A. *Organometallics.* **2004**, *23*, 5896.

(43) Hua, F.; Kinayyigit, S.; Cable, J. R.; Castellano, F. N. *Inorg. Chem.* **2006**, *45*, 4304.

(44) Chakraborty, S.; Wadas, T. J.; Hester, H.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 6865.

(45) Wadas, T. J.; Chakraborty, S.; Lachicotte, R. J.; Wang, Q.-M.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 2628.

(46) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C. M.; He, Z.; Wong, K.-Y. *Chem.—Eur. J.* **2003**, *9*, 6155.

(47) Siemeling, U.; Bausch, K.; Fink, H.; Bruhn, C.; Baldus, M.; Angerstein, B.; Plessow, R.; Brockhinke, A. *Dalton Trans.* **2005**, 2365.

(48) Kang, Y.; Lee, J.; Song, D.; Wang, S. *Dalton Trans.* **2003**, 3493.

(49) Siu, P. K. M.; Lai, S. W.; Lu, W.; Zhu, N.; Che, C. M. *Eur. J. Inorg. Chem.* **2003**, 2749.

(50) Klein, A.; van Slageren, J.; Zalis, S. *Inorg. Chem.* **2002**, *41*, 5216.

(51) McGarrah, J. E.; Eisenberg, R. *Inorg. Chem.* **2003**, *42*, 4355.

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

(53) Connick, W. B.; Geiger, D.; Eisenberg, R. *Inorg. Chem.* **1999**, *38*, 3264.

(54) Field, J. S.; Haines, R. J.; McMillin, D. R.; Munro, O. Q.; Summerton, G. C. *Inorg. Chim. Acta* **2005**, *358*, 4567.

(55) Yam, V. W.-W.; Tang, R. P. L.; Wong, K. M. C.; Lu, X. X.; Cheung, K.-K.; Zhu, N. *Chem.—Eur. J.* **2002**, *8*, 4066.

(56) Yam, V. W.-W.; Hui, C. K.; Yu, S. Y.; Zhu, N. *Inorg. Chem.* **2004**, *43*, 812.

(57) Yam, V. W.-W.; Wong, K. M.-C.; Zhu, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1400.

(58) Wong, K. M. C.; Tang, W. S.; Chu, B. W.-K.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2004**, *23*, 3459.

(59) Guo, F.; Sun, W.; Lin, Y.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 4055.

(60) Wong, K. M. C.; Tang, W. S.; Lu, X. X.; Zhu, N.; Yam, V. W.-W. *Inorg. Chem.* **2005**, *44*, 1492.

(61) Yam, V. W.-W.; Chan, K. H. Y.; Wong, K. M. C.; Zhu, N. *Chem.—Eur. J.* **2005**, *11*, 4535.

(62) Chakraborty, S.; Wadas, T. J.; Hester, H.; Flaschenreim, C.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 6284.

(63) Castellano, F. N.; Pomestchenko, I. E.; Shikhova, E.; Hua, F.; Muro, M. L.; Rajapakse, N. *Coord. Chem. Rev.* **2006**, *250*, 1819.

(64) Diez, A.; Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2005**, *44*, 2443.

(65) McGale, E. M.; Murray, R. E.; McAdam, C. J.; Morgan, J. L.; Robinson, B. H.; Simpson, J. *Inorg. Chim. Acta* **2003**, *352*, 129.

(66) Fernández, S.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 822.

(67) Hoogervorst, W. J.; Elsevier, C. J.; Lutz, M.; Spek, A. L. *Organometallics* **2001**, *20*, 4437.

(68) McAdam, C. J.; Blackie, E. J.; Morgan, J. L.; Mole, S. A.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2362.

(69) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Inorg. Chem. Commun.* **2005**, *8*, 55.

(70) Back, S.; Albrecht, M.; Spek, A. L.; Rheinwald, G.; Lang, H.; van Koten, G. *Organometallics* **2001**, *20*, 1024.

(71) Yang, Q.-Z.; Wu, L.-Z.; Zhang, H.; Chen, B.; Wu, Z.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2004**, *43*, 5195.

(72) Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S.-T. *J. Am. Chem. Soc.* **2004**, *126*, 4958.

(73) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S. T.; Che, C. M. *Chem. Commun.* **2002**, 206.

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

(75) Zhang, D.; Wu, L.-Z.; Yang, Q.-Z.; Li, X. H.; Zhang, L. P.; Tung, C. H. *Org. Lett.* **2003**, *5*, 3221.

(76) Narayana-Prabhu, R.; Schmehl, R. H. *Inorg. Chem.* **2006**, *45*, 4319.

(77) Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 3440.

(78) Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V.; Lalinde, E.; Moreno, M. T. *Chem.—Eur. J.* **2006**, *12*, 8253.

(79) Gil, B.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Inorg. Chem.* **2006**, *45*, 7788 and references therein.

(80) Fornies, J.; Ibanez, S.; Martin, A.; Sanz, M.; Berenguer, J. R.; Lalinde, E.; Torroba, J. *Organometallics* **2006**, *25*, 4331.

(81) Fernández, J.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2006**, *25*, 2274.

(82) Berenguer, J. R.; Forniés, J.; Gil, B.; Lalinde, E. *Chem.—Eur. J.* **2006**, *12*, 785.

(83) Forniés, J.; Ibañez, S.; Martín, A.; Gil, B.; Lalinde, E.; Moreno, M. T. *Organometallics* **2004**, *23*, 3963.

(84) Benito, J.; Berenguer, J. R.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 4331 and references therein.

(85) Charmant, J. P. H.; Forniés, J.; Gómez, J.; Lalinde, E.; Merino, R. I.; Moreno, M. T.; Orpen, A. G. *Organometallics* **2003**, *22*, 652.

platinum(II) complexes containing terdentate ligands have been extensively investigated,[55,71−73,86−101] the most common ligands used are monoanionic six-electron donors of the "pincer" type, 2,6-$(ECH_2)_2C_6H_3$ (E = NR_2, PR_2, SR),[86−90] or conjugated donors having C−N−N$^-$,N−C−N$^-$ or C−N−S$^-$ donor sets.[91−102] Cyclometalated Pt(II) complexes featuring double deprotonated terdentate C−N−C ligands are still rare,[55,103−109] although very unusual diplatinum systems containing the highly delocalized four-fold deprotonated CNC^CNC 12-electron bridging system (L) (H_4L = 6,6′-diphenyl-2,2′-bipyridine) have been recently prepared by Zucca at al.[110]

Here we report the synthesis, characterization, electronic absorption, and emissive properties of a novel series of alkynyl dimetalated platinum complexes $(NBu_4)[Pt(CNC)(C{\equiv}CR)]$ (R = ^{t}Bu, Ph, Tol, (*p*-OMe)C_6H_4) and those of three related anionic complexes $(NBu_4)[Pt(CNC)X]$ (X = CN, S-2Py, CH_2COCH_3) synthesized for comparative purposes.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry argon, using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under dry Ar before use. NMR spectra were recorded at 293 K on Bruker ARX 300 or ARX 400 spectrometers. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$, $CFCl_3$, and 85% H_3PO_4), and all coupling constants are given in hertz (Hz). The NMR spectral assignments of the C^N^C ligand (HC^N^CH 2,6-diphenylpyridine) follow the numbering scheme shown in Figure 1. IR spectra were obtained on a Nicolet Nexus FT-IR Spectrometer, using Nujol mulls between polyethylene sheets. Elemental analyses were carried out with Perkin-Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS−O microanalyzers. Mass spectra were recorded on a HP-5989B (ES) or a Microflex MALDI-TOF Bruker (MALDI) spectrometer operating in the linear and reflector modes using dithranol as the matrix. Molar conductances were carried out on a Crison GLP31 conductimeter in acetone and CH_2Cl_2 solutions (5×10^{-4} M). The optical absorption spectra were recorded using a Hewlett-Packard 8453 (solution) spectrophotometer in the visible and near-UV ranges. Emission and excitation spectra were obtained on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter, with the lifetime measured in phosphorimeter mode. Literature methods were used to prepare the starting material [Pt(C^N^C)(dmso)] (dmso = dimethylsulfoxide).[106]

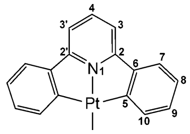

Figure 1.

Preparation of $(NBu_4)[Pt(C^\wedge N^\wedge C)(C{\equiv}C^tBu)]$ (1). [Pt(C^N^C)(dmso)] (0.25 g, 0.50 mmol) was added to a solution of LiC≡C^{t}Bu (3.00 mmol) (1:6 molar ratio) prepared from HC≡C^{t}Bu (0.36 mL, 3.00 mmol) and ^{n}BuLi (3.00 mmol) in diethyl ether (20 mL) at low temperature (−40 °C), and the mixture was allowed to warm to room temperature. After stirring for 5 h, the solvent was evaporated and the resulting orange solid was extracted with cold deoxygenated water (40 mL). The resulting orange solution was rapidly filtered under Ar through celite, and the filtrate was treated with a solution of $(NBu_4)Br$ (0.16 g, 0.50 mmol) in 5 mL of deoxygenated water. The resulting orange solid was filtered, washed with water, and air-dried (0.14 g, 37%). Found: C, 59.95; H, 7.89; N, 3.87. Anal. Calcd for $C_{39}H_{56}N_2Pt{\cdot}2H_2O$: C, 59.75; H, 7.71; N, 3.57. MS MALDI(−): *m/z* (peak anion not observed) 448.8 [Pt(C^N^C) + Na]. IR (cm^{-1}, Nujol): ν(C≡C) 2091(s). ^1H NMR (CD_3COCD_3, δ (*J*, Hz)): 8.17 (d, *J* = 7.0, ^3J(Pt−H) = 34.7, H^{10}); 7.59 (t, *J* = 7.6, H^4); 7.43 (d, *J* = 7.5, H^7); 7.33 (d, *J* = 7.8, ^4J(Pt−H) = 5.0, H^3); 7.08 (td, *J* = 7.1, 1.3, ^4J(Pt−H) = 7.0, H^9); 6.91 (td, *J* = 7.5, 1.4, H^8); 3.39 (m, NCH_2, NBu_4); 1.65 (m, $-CH_2-$, NBu_4); 1.37 (s, ^{t}Bu); 1.34 (m, $-CH_2-$, NBu_4); 0.92 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ(*J*, Hz)): 174.2 (s, ^1J(Pt−C) = 705, C^5); 167.8 (s, ^2J(Pt−C) = 63, C^2); 149.9 (s, ^2J(Pt−C) = 29, C^6); 139.0 (s, ^2J(Pt−C) = 72, C^{10}); 137.1 (s, C^4); 130.2 (s, ^3J(Pt−C) = 39, C^9); 123.1 (s, ^3J(Pt−C) = 27, C^7); 121.6 (s, C^8); 115.9 (s, tentatively assigned to ≡C_β); 113.5 (s, ^3J(Pt−C) = 44, C^3); 91.9 (s, tentatively assigned to C_α≡); 58.6 (s, N−CH_2, NBu_4); 34.3 (s, $C(CH_3)_3$); 30.1 (s, $C(CH_3)_3$); 24.3 (s, CH_2, NBu_4); 18.7 (s, CH_2, NBu_4); 14.0 (s, CH_3, NBu_4). Λ_M(acetone): 111 $mol^{-1}\ cm^2\ \Omega^{-1}$.

Preparation of $(NBu_4)[Pt(C^\wedge N^\wedge C)(C{\equiv}CPh)]$ (2). The procedure was identical to that used for **1** with 8 equiv of LiC≡CPh (4.80 mmol) and [Pt(C^N^C)(dmso)] (0.30 g, 0.60 mmol) in tetrahydrofuran (THF, 15 mL). The mixture was stirred for 30 min

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(86) van der Boom, M. E.; Kraatz, H. B.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1996**, 2167.
(87) Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *199*, 195 and references therein.
(88) Rietvel, M. P. H.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751 and references therein.
(89) Jude, H.; Bauer, J. A. K.; Connick, W. B. *Inorg. Chem.* **2004**, *43*, 725.
(90) Albrecht, M.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem.—Eur. J.* **2000**, *6*, 1431.
(91) Yip, J. H. K.; Suwarno Vittal, J. J. *Inorg. Chem.* **2000**, *39*, 3537.
(92) Williams, J. A. G.; Beeby, A.; Davies, E. S.; Weinstein, J. A.; Wilson, C. *Inorg. Chem.* **2003**, *42*, 8609.
(93) Cárdenas, D. J.; Echavarren, A. M.; Ramírez de Arellano, M. C. *Organometallics* **1999**, *18*, 3337.
(94) Chin, B. K. W.; Lam, M. H. W.; Lee, D. Y. K.; Wong, W. Y. *J. Organomet. Chem.* **2004**, *689*, 2888.
(95) Sun, W.; Zhu, H.; Barron, P. M. *Chem. Mater.* **2006**, *18*, 2602.
(96) Lu, W.; Chan, M. C. W.; Zhu, N.; Cheung, K.-K.; Li, C.; Hui, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7639.
(97) Crowley, J. D.; Steele, I. M.; Bosnich, B. *Inorg. Chem.* **2005**, *44*, 2989.
(98) Lai, S. W.; Lam, H. W.; Lu, W.; Cheung, K. K.; Che, C. M. *Organometallics* **2002**, *21*, 226 and references therein.
(99) Che, C. M.; Fu, W. F.; Lai, S. W.; Hou, Y. J.; Liu, Y. L. *Chem. Commun.* **2003**, 118.
(100) Lai, S. W.; Chan, M. C. W.; Cheung, T. C.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1999**, *38*, 4046.
(101) Pérez, S.; López, C.; Caubet, A.; Bosque, R.; Solans, X.; Bardía, M. F.; Roig, A.; Molins, E. *Organometallics* **2004**, *23*, 224 and references therein.
(102) Kui, S. C. F.; Sham, I. H. T.; Cheung, C. C. C.; Ma, C.-W.; Yan, B.; Zhu, N.; Che, C.-M.; Fu, W.-F. *Chem.—Eur. J.* **2007**, *13*, 417.
(103) Cornioley-Deuschel, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 130.
(104) Maestri, M.; Deuschel-Cornioley, C.; von Zelewsky, A. *Coord. Chem. Rev.* **1991**, *111*, 117.
(105) Cave, G. W. V.; Alcock, N. W.; Rourke, J. P. *Organometallics* **1999**, *18*, 1801.
(106) Cave, G. W. V.; Fanizzi, F. P.; Deeth, R. J.; Errington, W.; Rourke, J. P. *Organometallics* **2000**, *19*, 1355.
(107) Newman, C. P.; Cave, G. W. V.; Wong, M.; Errington, W.; Alcock, N. W.; Rourke, J. P. *J. Chem. Soc., Dalton Trans.* **2001**, 2678.
(108) Lu, W.; Chan, M. C. W.; Cheung, K. K.; Che, C. M. *Organometallics* **2001**, *20*, 2477.
(109) Kui, S. C. F.; Chui, S. S.-Y.; Che, C.-M.; Zhu, N. *J. Am. Chem. Soc.* **2006**, *128*, 8297.
(110) Zucca, A.; Petretto, G. L.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Manassero, C.; Male, L.; Albinati, A. *Organometallics* **2006**, *25*, 2253.

at −40 °C and then allowed to reach room temperature. The volatile materials were removed in vacuo, and the resulting residue was extracted with cold deoxygenated water (25 mL), filtered, and treated with $(NBu_4)Br$ (0.194 g, 0.60 mmol), affording **2** as an orange solid (0.21 g, 45%). Found: C, 63.99; H, 6.98; N, 3.27. Anal. Calcd. for $C_{41}H_{52}N_2Pt$: C, 64.12; H, 6.83; N, 3.27. MS MALDI(−): *m/z* (peak anion not observed) 448.8 [Pt(C^N^C) + Na]. IR (cm^{-1}, Nujol): ν(C≡C) 2105(sh), 2073(s). ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 8.14 (d, J = 6.3, ^{3}J(Pt−H) = 36.0, H^{10}); 7.58 (t, J = 8.1, H^4); 7.42 (d, J = 7.3, H^7); 7.33 (m, H^3 and *o*-H, Ph); 7.15 (t, J = 7.5, *m*-H, Ph); 7.05 (td, J = 7.0, 0.9, ^{4}J(Pt−H) ≈ 7.1, H^9); 6.97 (t, J = 6.7, *p*-H, Ph); 6.88 (td, J = 7.2, 1.6, H^8); 3.46 (m, NCH_2, NBu_4); 1.71 (m, $-CH_2-$, NBu_4); 1.37 (m, $-CH_2-$, NBu_4); 0.88 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): 173.5 (s, ^{1}J(Pt−C) = 705, C^5); 167.8 (s, ^{2}J(Pt−C) = 63, C^2); 150.1 (s, ^{2}J(Pt−C) = 31, C^6); 139.0 (s, ^{2}J(Pt−C) = 70, C^{10}); 137.8 (s, C^4); 131.4 (s, *o*-C, Ph); 130.3 (s, ^{3}J(Pt−C) = 40, C^9); 127.9 (s, *m*-C, Ph); 123.5 (s, *p*-C, Ph); 123.3 (s, ^{3}J(Pt−C) = 26, C^7); 122.1 (s, C^8); 119.0 (s, *i*-C, Ph); 114.2 (s, C_α≡); 113.7 (s, ^{3}J(Pt−C) = 25, C^3); 108.9 (s, ^{2}J(Pt−C) = 403, ≡C_β); 58.7 (s, N−CH_2, NBu_4); 24.3 (s, CH_2, NBu_4); 19.7 (s, CH_2, NBu_4); 13.9 (s, CH_3, NBu_4). Λ_M(acetone): 113 mol^{-1} cm^2 Ω^{-1}.

Preparation of (NBu_4)[Pt(C^N^C)(C≡CTol)] (3). [Pt(C^N^C)(dmso)] (0.30 g, 0.60 mmol) was added to a solution of LiC≡CTol (4.80 mmol) in THF (15 mL) at −45 °C. The mixture was stirred at this temperature for 2 min. The reaction mixture was then allowed to warm to room temperature. The remaining steps were identical to the procedure described for **1** (0.18 g, 39%). Found: C, 64.38; H, 6.82; N, 3.99. Anal Calcd for $C_{42}H_{54}N_2Pt$: C, 64.51; H, 6.96; N, 3.58. MS MALDI(−): peak anion not observed. IR (cm^{-1}, Nujol): ν(C≡C) 2103(sh), 2083(s). ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 8.14 (d, J = 6.7, ^{3}J(Pt−H) = 35.2, H^{10}); 7.59 (t, J = 8.0, H^4); 7.44 (d, J = 7.4, H^7); 7.35 (d, J = 7.9, H^3); 7.25 (t, J = 7.8, Tol); 7.07 (t, J = 7.7, H^9); 6.99 (d, J = 7.8, Tol); 6.90 (td, J = 8.0, 0.9, H^8); 3.39 (m, N−CH_2, NBu_4); 2.26 (s, CH_3, Tol); 1.65 (m, $-CH_2-$, NBu_4); 1.32 (m, $-CH_2-$, NBu_4); 0.85 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): 173.6 (s, ^{1}J(Pt−C) = 704, C^5); 167.8 (s, ^{2}J(Pt−C) = 64, C^2); 150.1 (s, ^{2}J(Pt−C) = 29, C^6); 139.0 (s, ^{2}J(Pt−C) = 69, C^{10}); 137.7 (s, C^4); 131.8 (s, C^4, Tol); 131.3 (s, CH, Tol); 130.3 (s, ^{3}J(Pt−C) = 41, C^9); 128.7 (s, CH, Tol); 128.4 (s, C^1, Tol); 123.3 (s, ^{3}J(Pt−C) = 26, C^7); 122.0 (s, C^8); 115.9 (s, tentatively assigned to C_α≡); 113.7 (s, ^{3}J(Pt−C) = 25, C^3); 108.6 (s, ^{2}J(Pt−C) = 405, ≡C_β); 58.8 (s, N−CH_2, NBu_4); 24.3 (s, CH_2, NBu_4); 21.6 (s, CH_3, Tol); 19.8 (s, CH_2, NBu_4); 14.0 (s, CH_3, NBu_4). Λ_M(acetone): 120 mol^{-1} cm^2 Ω^{-1}.

Preparation of (NBu_4)[Pt(C^N^C){C≡C(4-OCH_3)C_6H_4}] (4). To a fresh (−50 °C) solution containing 8 equiv of LiC≡C(4-OCH_3)C_6H_4 (4.8 mmol) in THF (15 mL) [Pt(C^N^C)(dmso)] (0.30 g, 0.6 mmol) was added, and the mixture was stirred at this temperature for 2 min. The mixture was then allowed to reach room temperature. The solvent was evaporated to dryness, and the red solid residue was extracted with cold deoxygenated water (50 mL). The resulting orange aqueous solution was rapidly filtered under Ar through celite, and the filtrate was treated with vigorous stirring with a solution of $(NBu_4)Br$ (0.29 g, 0.9 mmol) in 5 mL of H_2O. The resulting red solid was filtered, washed with water and ^{i}PrOH, and air-dried (0.22 g, 48%). Found: C, 63.62; H, 6.52; N, 3.10. Anal Calcd. for $C_{42}H_{54}N_2PtO$: C, 63.22; H, 6.82; N, 3.51. MS ES(−): *m/z* 556 M$^-$, 100%. IR (cm^{-1}, Nujol): ν(C≡C) 2081(s). ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 8.15 (d, J = 6.8, ^{3}J(Pt−H) = 35.7, H^{10}); 7.59 (t, J = 7.9, H^4); 7.44 (d, J = 7.5, H^7); 7.34 (d, J = 7.9, ^{4}J(Pt−H) ≈ 5.6, H^3); 7.29 (d, J = 7.5, CH, $C_6H_4-OCH_3$); 7.07 (t, H^9); 6.90 (td, J = 7.4, 1.2, H^8); 6.78 (d, J = 7.5, CH, $C_6H_4-OCH_3$); 3.77 (s, OCH_3); 3.39 (m, NCH_2, NBu_4); 1.63 (m, $-CH_2-$, NBu_4); 1.37 (m, $-CH_2-$, NBu_4); 0.85 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): 173.4 (s, C^5); 167.7 (s, C^2); 156.5 (s, C^4, $C_6H_4-OCH_3$); 150.1 (s, C^6); 138.8 (s, C^{10}); 137.8 (s, C^4); 132.4 (s, CH, $C_6H_4-OCH_3$); 130.3 (s, C^9); 124.5 (s, C^1, $C_6H_4-OCH_3$); 123.3 (s, C^7); 122.1 (s, C^8); 114.4 (s, tentatively assigned to C^{α}≡); 113.6 (s, C^3); 113.4 (s, CH, $C_6H_4-OCH_3$); 103.0 (s, tentatively assigned to ≡C_β); 59.0 (s, N−CH_2, NBu_4); 55.5 (s, OCH_3); 24.5 (s, CH_2, NBu_4); 19.8 (s, CH_2, NBu_4); 14.0 (s, CH_3, NBu_4). Λ_M(acetone): 98 mol^{-1} cm^2 Ω^{-1}.

Preparation of (NBu_4)[Pt(C^N^C)(CN)] (5). A mixture of [Pt(C^N^C)(dmso)] (0.30 g, 0.60 mmol) and $(NBu_4)CN$ (0.24 g, 0.90 mmol) in acetone (15 mL) was stirred at room temperature for 48 h. The resulting suspension was evaporated to dryness. The crude solid was washed twice with water (5 mL) and recrystallized from acetone/water to give a yellow microcrystalline solid (0.27 g, 65%). Found: C, 58.65; H, 6.64; N, 5.99. Anal. Calcd for $C_{34}H_{47}N_3Pt$: C, 58.94; H, 6.84; N, 6.06. MS ES(−): *m/z* 450 M$^-$, 100%. IR (cm^{-1}, Nujol): ν(CN) 2095(m). ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 7.99 (dd, J = 7.1, ∼1.0, ^{3}J(Pt−H) = 34.7, H^{10}); 7.61 (t, J = 7.9, H^4); 7.41 (d, J = 7.6, H^7); 7.34 (d, J = 7.9, ^{4}J(Pt−H) = 6.5, H^3); 7.05 (td, J = 7.2, 1.3, ^{4}J(Pt−H) = 6.1, H^9); 6.91 (td, J = 7.5, 1.5, H^8); 3.41 (m, NCH_2, NBu_4); 1.75 (m, $-CH_2-$, NBu_4); 1.38 (m, $-CH_2-$, NBu_4); 0.93 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): 171.3 (s, ^{1}J(Pt−C) ≈ 703, C^5); 168.3 (s, C^2); 149.9 (s, C^6); 139.8 (s, ^{3}J(Pt−H) = 73, C^{10}); 139.2 (s, C^4); 131.2 (s, CN); 131.0 (s, ^{3}J(Pt−H) ≈ 40, C^9); 123.7 (s, ^{3}J(Pt−H) = 25, C^7); 122.9 (s, C^8); 114.1 (s, ^{3}J(Pt−H) ≈ 30, C^3); 58.8 (s, N−CH_2, NBu_4), 24.3 (s, CH_2, NBu_4); 19.7 (s, CH_2, NBu_4); 13.9 (s, CH_3, NBu_4). Λ_M(acetone): 145 mol^{-1} cm^2 Ω^{-1}.

Preparation of (NBu_4)[Pt(C^N^C)(S-2Py)] (6). A solution of [Pt(C^N^C)(dmso)] (0.25 g, 0.50 mmol) in acetone was treated, at 0 °C, with NBu_4OH (1.5 mL of a 0.7 M solution in MeOH) and 2-mercaptopyridine (0.067 g, 0.60 mmol). After stirring the mixture for 5 min, the resulting red solution was evaporated to dryness and treated with cold ^{i}PrOH to yield **6** as a red solid (0.31 g, 80%). Found: C, 58.35; H, 6.83; N, 5.36; S, 4.26. Anal Calcd for $C_{38}H_{51}N_3PtS$: C, 58.74; H, 6.62; N, 5.41; S, 4.12. MS MALDI(−): peak anion not observed. ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 8.03 (d, J = 3.8, H^2, SPy); 7.83 (d, J ≈ 8, H^5, Spy); 7.80 (d, J = 8.0, ^{3}J(Pt−H) = 31, H^{10}) (both signals overlap); 7.64 (t, J = 7.9, H^4); 7.44 (d, J = 7.4, H^7); 7.37 (d, J = 8.0, ^{4}J(Pt−H) ≈ 6, H^3): 6.90 (m, $H^{8,9}$ dppy, CH, SPy); 6.52 (t, J = 7.0, H^3, SPy); 3.43 (m, NCH_2, NBu_4); 1.75 (m, $-CH_2-$, NBu_4); 1.37 (m, $-CH_2-$, NBu_4); 0.93 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): the complex **6** is not stable enough in solution to record the spectrum. Λ_M(acetone): 90 mol^{-1} cm^2 Ω^{-1}.

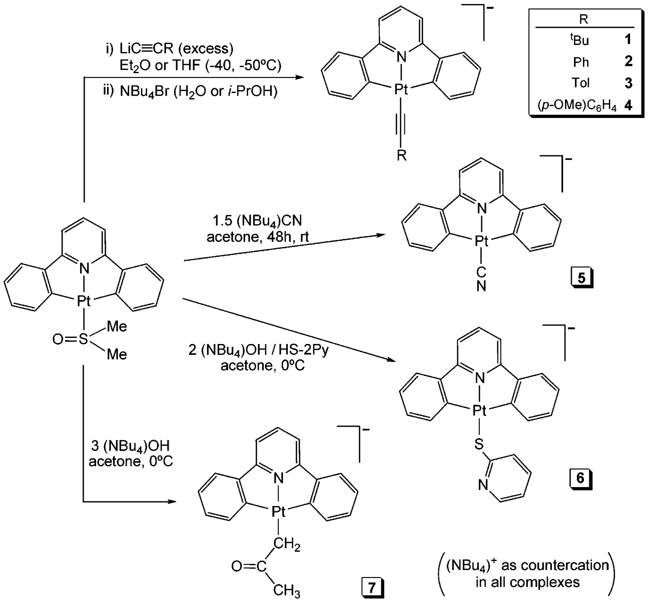
Preparation of (NBu_4)[Pt(C^N^C)(CH_2COCH_3)] (7). A measure of 3 equiv of NBu_4OH (1.1 mL of a 0.7 M solution in MeOH) was added to a yellow solution of [Pt(C^N^C)(dmso)] (0.18 g, 0.37 mmol) in acetone (20 mL) at 0 °C. The resulting orange solution was evaporated to ∼1 mL of volume, and the addition of H_2O (25 mL) gave **7** as an orange solid, which was dried with anhydrous $MgSO_4$ in CH_2Cl_2 and recrystallized from $CHCl_3/Et_2O$ (0.12 g, 45%). Found: C, 59.82; H, 7.32; N, 3.75. Anal. Calcd for $C_{36}H_{52}ON_2Pt$: C, 59.73; H, 7.24; N, 3.87. MS ES(−): *m/z* 481 M$^-$, 100%. IR (cm^{-1}, Nujol): ν(C=O) 1630(m). ^{1}H NMR (CD_3COCD_3, δ (J, Hz)): 7.96 (d, J = 7.9, ^{3}J(Pt−H) = 23.4, H^{10}); 7.57 (t, J = 7.7, H^4); 7.39 (d, J = 7.5, H^7); 7.39 (d, J = 7.6, ^{4}J(Pt−H) = 13, H^3); 7.15 (t, J = 6.6, H^9); 6.89 (t, J = 6.8, H^8); 3.47, 3.40 (s, ^{2}J(Pt−H) = 114, 115, CH_2, $-CH_2COCH_3$); 3.32 (m, NCH_2, NBu_4); 1.67 (m, $-CH_2-$, NBu_4); 1.34 (m, $-CH_2-$, NBu_4); 1.03 (s, CH_3, $-CH_2COCH_3$); 0.91 (t, $-CH_3$, NBu_4). ^{13}C NMR ($CDCl_3$, δ (J, Hz)): the complex **7** is not stable and soluble enough to record the spectrum. Λ_M(acetone): 102 mol^{-1} cm^2 Ω^{-1}.

X-ray Crystallography. Table 4 reports details of the structural analyses for all complexes studied. Red (**1** and **4**) or orange (**6**) crystals were obtained by the slow diffusion of *n*-hexane into dichloromethane (**1** and **4**) or fluorobenzene (**6**) solutions of each compound at −30 °C. Orange crystals of complex **5** were prepared by the slow evaporation of a solution of the complex in chloroform at room temperature. For complex **4** one molecule of CH_2Cl_2 and for complex **6** one-half a molecule of C_6H_5F were found in the asymmetric unit, respectively. X-ray intensity data were collected with a NONIUS κCCD area-detector diffractometer, using graphite-monochromated Mo Kα radiation. Images were processed using the *DENZO* and *SCALEPACK* suite of programs.[111] The structures were solved by Patterson and Fourier methods using the *DIRDIF92* program,[112] and the absorption correction was performed using *SORTAV*.[113] All structures were refined by full-matrix least squares on F^2 with *SHELXL-97*,[114] and all non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic and CH_2 hydrogens and that of 1.5 for the methyl groups. For complex **5**, which crystallizes in the noncentrosymmetric space group $P2_1$, the crystal chosen for this structural analysis was found to be a meroedric twin, as confirmed by the absolute structure parameter (0.493(6)). Notwithstanding, inspection of the symmetry (using *PLATON*[115]) reveals the possibility of the existence of an inversion center. Thus, the structure has also been solved and refined in the centrosymmetric group $P2_1/c$, but with worse results. For **6**$\cdot$0.5C_6H_5F, to establish the position of the N atom in the 2-pyridyl-thiolate ligand, the structure was refined in three different ways (with the identities of the *p*-C and N in one position, with the element types reversed, and with a 50/50 hybrid scattering factor at each of the affected atomic sites). Examination of the ΔMSDA values for bonds involving these atoms revealed the correct assignment, with the nitrogen atom endo to the platinum center.[115,116] Furthermore, for complex **6**$\cdot$0.5C_6H_5F, one aliphatic chain (C35−C38) of the NBu_4^+ cation presents positional disorder, which could be refined over three positions with partial occupancy factors of 0.56/0.22/0.22. In this structure, the C_6H_5F molecule was also disordered and modeled adequately. Finally, the structures present one (**5** and **6**$\cdot$0.5C_6H_5F) or two (**1** and **4**$\cdot CH_2Cl_2$) residual peaks greater than 1 e Å^{-3} in the vicinity of the platinum atoms or the solvent (**4**$\cdot CH_2Cl_2$), but with no chemical significance.

Results and Discussion

The synthetic routes to complexes **1**−**7** are summarized in Scheme 1. Starting from [Pt(C^N^C)(dmso)] (HC^N^CH = 2,6-diphenylpyridine, dppy) we have synthesized new anionic platinate(II) compounds by substitution of the dmso molecule with anionic alkynyl (C≡CR$^-$), CN$^-$, S-2Py$^-$, and acetonyl ligands. Treatment of [Pt(C^N^C)(dmso)] with an excess of LiC≡CR in diethyl ether (R = ^{t}Bu, **1**) or THF (R = Ph, **2**; Tol, **3**; (*p*-OMe)C_6H_4, **4**), followed by reaction with NBu_4Br in deoxygenated water (see Experimental Section for details), afforded the corresponding products as orange (**1**−**3**) or red (**4**) solids in moderate yield (37−48%). However, it is to be noted that all attempts to obtain the analogous dinuclear derivative {[Pt(C^N^C)]$_2$(1,4-C≡CC_6H_4C≡C)}$^{2-}$ under similar conditions, but starting from [Pt(C^N^C)(dmso)] and Li_2(C≡CC_6H_4C≡C) in a different molar ratio, were unsuccessful. The reaction of [Pt(C^N^C)-(dmso)] with a slight excess (1.5 equiv) of (NBu_4)CN in acetone gave **5** as a yellow microcrystalline product, while complex **6** was isolated as a red microcrystalline solid by reaction with HS-2Py in the presence of 2 equiv of (NBu_4)-OH at low temperature (0 °C). With the aim of preparing the related hydroxy derivative, we also reacted [Pt(C^N^C)-(dmso)] with 3 equiv of (NBu_4)OH in acetone at 0 °C. Nevertheless, the treatment of the resulting solution (see Experimental Section) yielded the acetonyl complex **7** as an orange microcrystalline solid. Metalated ketones are important reagents in organic synthesis,[117,118] those with transition metals being of particular interest.[119−123] The formation of complex **7** is remarkable because the number of ketonyl complexes of platinum(II) is rather scarce.[123−125] In addition, it is generated within minutes at room temperature. Other

Scheme 1



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(111) Otwinowski, Z.; Minor, W. In *Methods in Enzymololgy*; Carter, C. V., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276A, p 307.

(112) Beursken, P. T.; Beursken, G.; Bosman, W. P.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Smith, J. M. M.; Smykalla, C. *The DIRDIF92 Program System*; Technical Report of the Crystallography Laboratory: University of Nijmegen: Nijmegen, The Netherlands, 1992.

(113) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(114) Sheldrick, G. M. *SHELX-97, a Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(115) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C.

(116) Hirshfeld, F. L. *Acta Crystallogr., Sect. A* **1976**, *32*, 239.

(117) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624.

(118) Culkin, D. A.; Hartwing, J. F. *Acc. Chem. Res.* **2003**, *36*, 234.

(119) Ogo, S.; Uehara, K.; Abura, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 3020.

(120) Masamune, S.; Choy, W.; Sita, L. R. *Angew. Chem., Int. Ed.*. **2004**, *24*, 1.

(121) Cheng, G. S.; Kwong, F. Y.; Chan, H. O.; Yu, W. Y.; Chan, A. S. C. *Chem. Commun.* **2006**, 1413.

(122) Sodeoka, M.; Hanashima, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 941.

(123) Vicente, J.; Abad, J. A.; Chicote, M. T.; Abrisqueta, M. A.; Lorca, J. A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564.

(124) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2006**, *24*, 4404.

(125) Lai, S.-W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **1999**, *38*, 4262 and references therein.

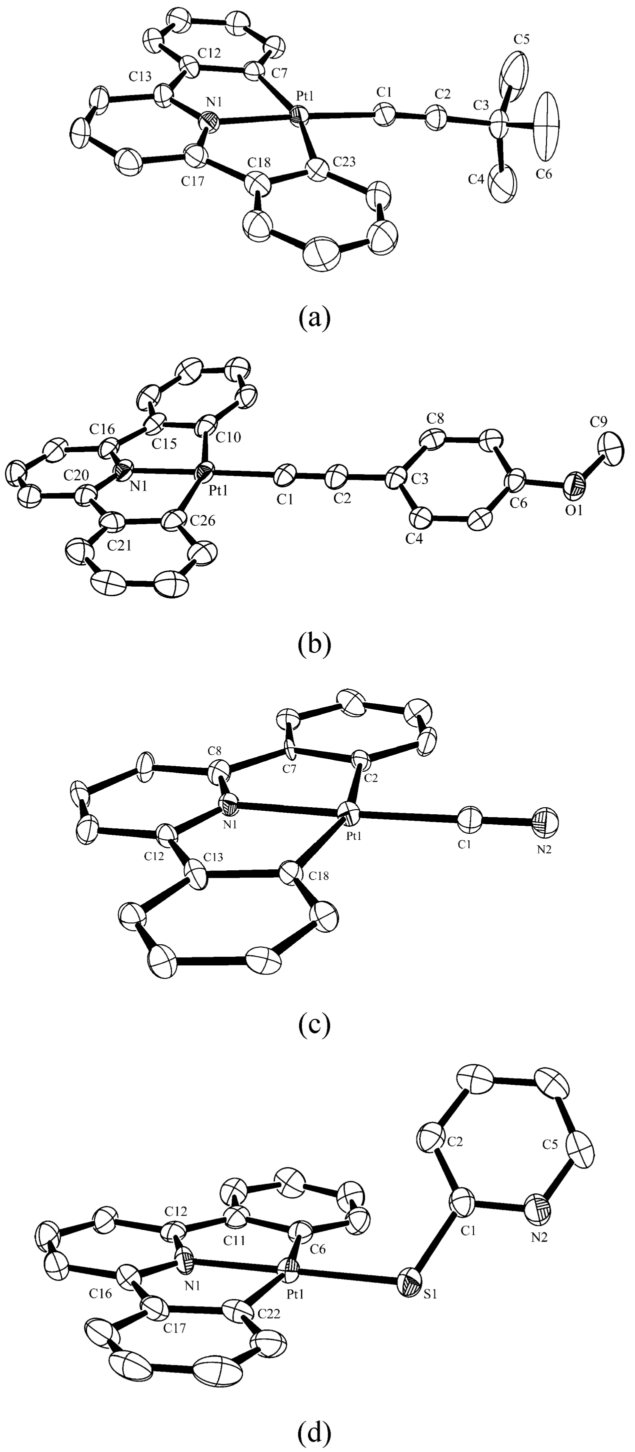

Figure 2. ORTEP view of the molecular anions in complexes **1** (a), **4** (b), **5** (c), and **6** (d). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent have been omitted for clarity.

ketonyl derivatives have been prepared by reacting ketones with hydroxo complexes[126−130] or with chloro complexes in the presence of a base,[123,131−133] but on the whole, they need longer reaction times[127,132,133] or harsh thermal conditions.[123,126,128−131] Despite their anionic nature, all complexes are stable in solution (CH_2Cl_2, $CHCl_3$, and acetone, except **6** and **7**) and in the solid state, and their identities have been fully established by ^{1}H NMR, ^{13}C{^{1}H} NMR, and IR spectroscopies, and satisfactory elemental analyses. The crystal structures of **1**, **4**, **5**, and **6** have also been determined. Different red crystals of **7**, obtained from evaporation of acetone solutions of the complex, were subjected to several X-ray diffraction studies. Unfortunately, the crystals were not of sufficient quality to give high accuracy analyses, although the connectivity shown in Scheme 1, with the presence of the acetonyl ligand, can be unequivocally established since it has also been confirmed by the ES(−) mass spectrum (481 [Pt(C^N^C)(CH_2COCH_3)]$^-$ 100%).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**, **4b**·CH_2Cl_2, **5**, and **6**·$0.5C_6H_5F$

	1	**4**·CH_2Cl_2	**5**	**6**·$0.5C_6H_5F$
Pt(1)−N(1)	2.012(3)	2.012(4)	2.031(5)	1.996(3)
Pt(1)−$C_{(aryl)}$	2.038(4)	2.053(5)	2.058(7)	2.060(5)
	2.045(4)	2.064(6)	2.062(7)	2.064(5)
Pt(1)−C(1) (or S(1))	1.969(4)	1.957(5)	1.950(7)	2.277(1)
C(1)−C(2) (or N(2))	1.206(5)	1.226(7)	1.163(8)	1.762(5) S(1)−C(1)
C(2)−C(3)	1.483(5)	1.435(7)		
$C_{(aryl)}$−Pt(1)−$C_{(aryl)}$	161.1(2)	160.9(2)	161.0(2)	161.6(2)
N(1)−Pt(1)−$C_{(aryl)}$	80.4(2)	80.0(2)	80.2(2)	80.7(2)
	80.7(2)	80.9(2)	80.8(2)	80.9(2)
$C_{(aryl)}$−Pt(1)−C(1)	97.3(2)	97.9(2)	98.3(2)	95.3(1)
(or S(1))	101.6(2)	101.2(2)	100.8(2)	103.1(1)
Pt(1)−C(1)−C(2) (or N(2))	175.2(4)	178.7(5)	178.4(6)	112.3(2) Pt(1)−S(1)−C(1)
C(1)−C(2)−C(3)	175.5(4)	174.5(5)		

The alkynyl derivatives **1**−**4** show one ν(C≡C) intense absorption in the expected region (2081−2091 cm^{-1}), with a shoulder in complexes **2** and **3** (2105 cm^{-1}, **2**; 2103 cm^{-1}, **3**) probably due to effects in the solid state, while complex **5** shows one ν(C≡N) absorption at 2095 cm^{-1}, corresponding to the terminal cyanide ligand, and in the IR spectrum of compound **7** the absorption due to the ν(C=O) of the acetonyl group can be observed at 1630 cm^{-1}. Also, the conductivity measurements of all of them (**1**−**7**) confirm their behavior as 1:1 electrolytes. Well-resolved ^{1}H and ^{13}C{^{1}H} NMR spectra were observed for all derivatives (except for complexes **6** and **7**, whose ^{13}C{^{1}H} NMR spectra could not be recorded, as they decompose in solution). The assignments of the signals (see Experimental Section), consistent with the presence of symmetric dicyclometalated (C^N^C) ligand, were made on the basis of coupling constants and ^{1}H−^{1}H COSY and g-HSQC experiments carried out on complexes **1** and **5**.

Crystal structure determination: Perspective drawings of the complex anions of **1** and **4**−**6** are given in Figure 2. Selected bond lengths and angles are shown in Table 1. Complex **5** crystallizes in the noncentrosymmetric space group $P2_1$, showing, in the asymmetric unit, two different

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(126) Ruiz, J.; Martínez, M. T.; Rodríguez, V.; López, G.; Pérez, J.; Chaloner, P. A.; Hitchcock, P. B. *Dalton Trans.* **2004**, 3521.

(127) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

(128) Appleton, T. G.; Bennet, M. A. *Inorg. Chem.* **1978**, *17*, 738.

(129) Bennet, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(130) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(131) Lai, S.-W.; Chan, M. C. W.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **1999**, *38*, 4262.

(132) Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *209*, 415.

(133) Cairus, M. A.; Dixon, K. R.; Smith, M. A. R. *J. Organomet. Chem.* **1977**, *135*, C33.

Table 2. Absorption Data (5 × 10^{-5} M CH$_2$Cl$_2$ Solutions) for Complexes **1**−**7**

compound	absorption/nm (10^{-3} ϵ/M^{-1} cm^{-1})
(NBu$_4$)[Pt(C∧N∧C)(C≡CBu^t)], **1**	231(32.8), 249(36,4), 258(29.3), 277sh(32.0); 287(36.8), 330(9.7), 364(8.5), 423(5.6), 532(0.2)
(NBu$_4$)[Pt(C∧N∧C)(C≡CPh)], **2**	231 (25.6), 242sh(24.6), 277sh(27.4), 287(29.9), 328sh(14.5), 355sh(9.1), 371sh(6.2), 421(3.6), 527 (0.1)
(NBu$_4$)[Pt(C∧N∧C)(C≡CTol), **3**	231(26.0), 242(25.1), 258 (25.0), 276(26.1), 287(25.7), 330sh(12.1), 363sh(6.4), 422(3.1), 529 (0.2)
(NBu$_4$)[Pt(C∧N∧C){C≡C(4-OCH$_3$)C$_6$H$_4$}], **4**	232(33.3), 243(35.1), 256sh(35.3), 277sh(41.4), 287(42.3), 328(16.8), 368(11.4), 423(8.3), 529(0.6)[a]
(NBu$_4$)[Pt(C∧N∧C)(CN)], **5**	230(13.9), 244sh(19.4), 259(29.4), 275(31.6), 283(32.5), 316(6.7), 348(8.7), 365sh(7.8), 427(0.6), 452(0.5),[a] 516(0.1)[a]
(NBu$_4$)[Pt(C∧N∧C)(S-2Py)], **6**	231(25.9), 246(27.6), 278sh(23.4), 286(24.1), 328sh(12.0), 369(6.7), 396(5.0), 462(1.9), 529(1.1)[a]
(NBu$_4$)[Pt(C∧N∧C)(CH$_2$COCH$_3$)], **7**	232(34.8), 243sh(33.3), 265sh(29.3), 271(28.3), 303sh(17.4), 327sh(11.2), 364(5.4), 412(2.0), 472(0.4),[a] 529(0.1)[a]

[a] These absorptions follow the Lambert−Beer Law in the range of 5 × 10^{-5} to 10^{-3} M.

molecular anions, both having identical structural details within experimental error. Therefore, only one of them will be considered in the discussion. As expected, in all anions, the platinum(II) center adopts a distorted square-planar geometry with trans aryl carbon atoms C−Pt−C (range = 160.9(2)−161.6(2)°) significantly deviated from linearity due to the steric restriction caused by the dicyclometalated ligand (C^N^C). The anion [Pt(C^N^C)(CN)]$^-$ (**5**$^-$) and the central “Pt(C^N^C)(C≡CR)” core in the alkynyl anions of **1**$^-$ and **4**$^-$ are essentially planar, with the *p*-OMe−C$_6$H$_4$ ring in **4** forming a dihedral angle of 17.5(1)° with the platinum coordination plane. In **6**$^-$, the 2-pyridinthiolate ligand is not coplanar with the Pt(C^N^C) moiety (dihedral angle 51.00(7)°) and is oriented with the nitrogen atom N(2) exo to the platinum center. The Pt−C$_\alpha$ alkynyl bonds in **1**$^-$ and **4**$^-$ and the Pt−C(≡N) bond in **5**$^-$ (1.969(4) Å, **1**; 1.957(5) Å, **4**; and 1.950(7) Å, **5**) are unexceptional and compare well with those of related complexes. In **6**$^-$, the Pt−S bond (2.277(1) Å) is within the range of those observed for typical platinum(II) dithiolate derivatives[134,135] and close to the values found in [Pt(bpy)(S-2Py)$_2$] (2.300(3) Å)[136] or [Pt(terpy)(S-2Py)]$^+$ (2.299(2) Å).[136] Evidence that has gradually been accumulated over the last decades shows that weak hydrogen bonds[137−140] are almost ubiquitous, this being an important factor in controlling crystal packing and playing a vital role in various specific phenomena in chemistry and biochemistry, including molecular recognition. Further inspection of the crystal structures of four complexes reveals the presence of different types of weak intermolecular hydrogen bonds, including C−H···π[47,141−147] (aromatic, C···C = 3.38−3.84 Å, H···C = 2.66−3.23 Å, C−H···C = 176−113°; C≡C, C···C = 3.41−3.76 Å, H···C = 2.66−2.94 Å, C−H···C = 172−119°), C−H···N[148−151] (C···N = 3.26−3.84 Å, H···N = 2.54−2.96 Å, C−H···N = 165−109°), C−H···O[152−155] (C···O = 3.68−3.75 Å, H···O = 2.72−3.22 Å, C−H···O = 173−118°), C−H···S[156−159] (C···S = 3.76−3.81 Å, H···S = 2.90−3.00 Å, C−H···S = 143−141°), C−H···Cl[141,153,160−163] (C···Cl = 3.51−3.90 Å, H···Cl =

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(134) Berenguer, J. R.; Bernechea, M.; Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2004**, *43*, 8185.

(135) Paw, W.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **1998**, *37*, 4139.

(136) Tzeng, B.-C.; Fu, W.-F.; Che, C.-M.; Chao, H. Y.; Cheung, K.-K.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1999**, 1017.

(137) Nishio, M. In *Weak Hydrogen Bonds*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker, Inc.: New York, 2005; pp 1576.

(138) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

(139) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397.

(140) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960.

(141) Bernechea, M.; Lugan, N.; Gil, B.; Lalinde, E.; Lavigne, G. *Organometallics* **2006**, *25*, 684.

(142) Nishio, M. *CrystEngComm* **2004**, *6*, 130 and references therein.

(143) Benito, J.; Berenguer, J. R.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 4331.

(144) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C. M.; He, Z.; Wong, K.-Y. *Chem.*—*Eur. J.* **2003**, *9*, 6155 and references therein.

(145) Suezawa, H.; Yoshida, T.; Umezawa, Y.; Tsuboyama, S. T.; Nishio, M. *Eur. J. Inorg. Chem.* **2002**, 3148.

(146) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669.

(147) Steiner, T.; Tamm, M. *J. Organomet. Chem.* **1998**, *570*, 235.

(148) Maly, K. E.; Maris, T.; Gagnon, E.; West, J. D. *Cryst. Growth Des.* **2006**, *6*, 461.

(149) Stephenson, M. D.; Hardie, M. J. *Cryst. Growth Des.* **2006**, *6*, 423.

(150) Basavoju, S.; Aitipamula, S.; Desiraja, G. R. *CrystEngComm* **2004**, *6*, 120.

(151) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565.

(152) Gil, B.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Inorg. Chem.* **2006**, *45*, 7788.

(153) Sreerama, S. G.; Pal, S. *Inorg. Chem.* **2005**, *44*, 6299.

(154) Desiraju, G. R. *Chem. Commun.* **2005**, 2995.

(155) Potrzebowski, M. J.; Michalska, M.; Koziol, A. E.; Kazmierski, S.; Lis, T.; Pluskowski, J.; Ciesielski, W. *J. Org. Chem.* **1998**, *63*, 4209.

(156) Novakovic, S. B.; Fraisse, B.; Bogdanovic, G. A.; Spasojević-de Biré, A. *Cryst. Growth Des.* **2007**, *7*, 191.

(157) Ma, C.; Zhang, Q.; Qiu, L. *J. Organomet. Chem.* **2005**, *690*, 3033.

(158) Planas, J. G.; Viñas, C.; Teixidor, F.; Comas-Vives, A.; Ujaque, G.; Lledos, A.; Light, M. E.; Hursthouse, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 15976.

(159) Cosp, A.; Larrosa, I.; Anglada, J. M.; Bofill, J. M.; Romea, P.; Urpi, F. *Org. Lett.* **2003**, *5*, 2809.

(160) Youm, K.-T.; Ko, J.; Jun, M.-J. *Polyhedron* **2006**, *25*, 2717.

(161) Moorthy, J. N.; Natarajan, R.; Mal, P.; Venugopalan, P. *J. Am. Chem. Soc.* **2002**, *124*, 6530.

(162) Thallapally, P. K.; Nangia, A. *CrystEngComm.* **2001**, *3*, 114.

2.89−3.12 Å, C−H···Cl = 157−112°), and C−H···F[164−167] (C···F = 3.16−3.48 Å, H···F = 2.34−2.67 Å, C−H···F = 158−118°). The weakness of most of these hydrogen interactions may be due not only to the soft acidity of the C−H donor bond[142] but also to the steric requirement of the NBu_4^+ cation. Notwithstanding, these interactions seem to be strong enough to arrange the solid-state structure of complexes **1**, **4**·CH_2Cl_2, **5**, and **6**·$0.5C_6H_5F$, leading to the generation of supramolecular networks (bidimensional sheetlike organization in complex **1** or 3D architecture in complexes **4**−**6** (see Figures S1−S4 in the Supporting Information).

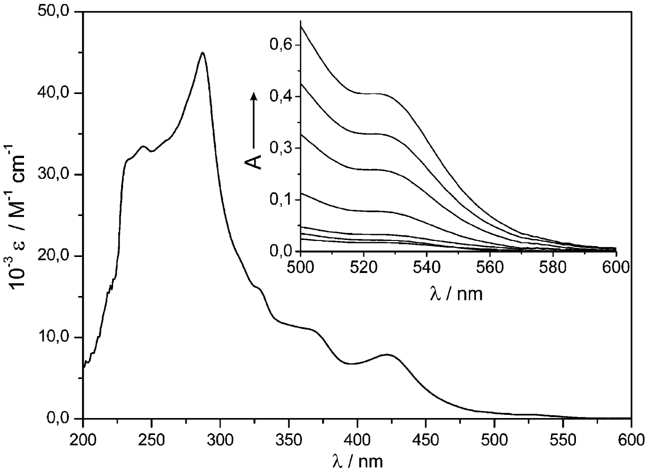

Figure 3. UV−vis absorption spectrum of **4** in CH_2Cl_2 (5×10^{-5} M). Inset: absorbance variation of the low-energy band (529 nm) in the concentration range of 5×10^{-5} to 1×10^{-3} M.

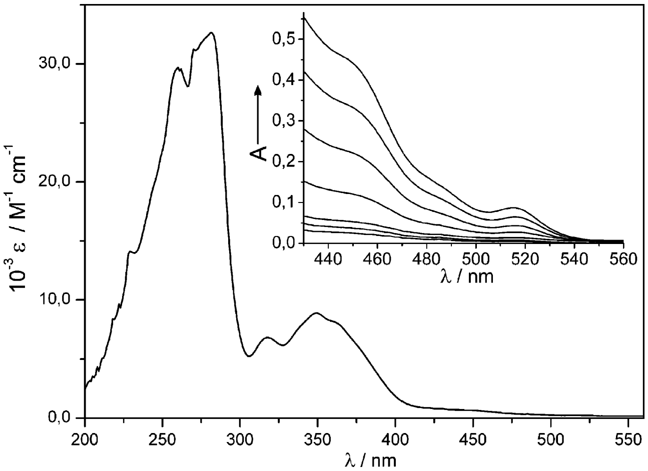

Figure 4. UV−vis absorption spectrum of **5** in CH_2Cl_2 (5×10^{-5} M). Inset: absorbance variation of the two low-energy bands (452 and 516 nm) in the concentration range of 5×10^{-5} to 1×10^{-3} M.

Electronic Absorption and Emission Spectroscopy. The UV−vis absorption data are summarized in Table 2. Complexes **1**−**4** display absorption maxima below 370−363 nm, which are attributed to ligand-centered transitions (^{1}IL $\pi \rightarrow \pi^*$) of the dicyclometalated C^N^C and alkynide groups, together with a low-energy band (ϵ = 3.1−8.3 10^3 dm^3 mol^{-1} cm^{-1}) that appears to be fairly insensitive to the alkynyl substituent (423 nm, **1** and **4**; 421 nm, **2**; 422 nm, **3**). Previous work on related neutral derivatives [Pt(C^N^C)L][108,168] has attributed this absorption to a spin-allowed dπ(Pt) → π^* ^{1}MLCT transition. A similar assignment is therefore suggested for this absorption (421−423 nm) in complexes **1**−**4**. In agreement with this assignment, the low-energy absorption in related neutral complexes [Au(C^N^C)(C≡CR)] reported by Yam et al. appears at higher energies (399−402 nm)[169] and has been assigned as a metal-perturbed intraligand (IL) $\pi-\pi^*$ transition of the CNC ligand. All four complexes of **1**−**4** also show a very weak band at 527−532 nm (ϵ = 0.1−0.6 10^3 dm^3 mol^{-1} cm^{-1}). As an illustrative example of the influence of complex concentration on this band, the absorption spectra of **4** in the concentration range of 5×10^{-5} to 10^{-3} M were recorded. As is shown in the inset of Figure 3, the intensity of the low-energy absorption at 529 nm increases with the concentration. A linear plot of absorbance versus concentration demonstrates that this band (529 nm) obeys Beer's Law, which excludes the presence of ground-state oligomerization processes. Both ligands (C^N^C and C≡CR) are strong σ donors, and hence, ligand−field d−d transitions are unlikely to occur at such low energies. The very weak bands (527−532 nm) are tentatively attributed to direct population of a $^3\pi-\pi$ (C^N^C) state, facilitated by the high spin−orbit coupling associated with the Pt(II) ion. A similar assignment has been suggested for an absorption at similar energies in related neutral [Pt(C^N^C)L] complexes.[55] In complex **7**, the low-energy band at 412 nm (ϵ = 2.0 10^3 dm^3 mol^{-1} cm^{-1}) is attributed, as in complexes **1**−**4**, to ^{1}MLCT transition. The electronic absorption spectra of **5** and **7** were examined in the 5×10^{-5} to 10^{-3} M concentration range. As shown in Figure 4 for complex **5**, the absorption spectra reveal two very weak features at 452 and 516 nm in CH_2Cl_2 (472 and 529 nm for **7**), which obey Beer's Law, being tentatively attributed to the direct population of ^{3}MLCT and $^3\pi\pi$ states, respectively. In both complexes **5** and **7**, the absorption profile of these low-energy bands is similar in MeCN. The vibronic-structured bands at 316−365 nm for complex **5** comprise at least two overlapping bands, which are assigned to an admixture of ^{1}IL ($\pi\pi^*$) and ^{1}MLCT transitions. In this complex (**5**), the large destabilization of ^{1}MLCT from the alkynyl (421−423 nm, **1**−**4**) and ketonyl (412 nm, **7**) derivatives could be attributed to the strongly electron-withdrawing character of the CN^- ligand, as has been previously noted in other polypyridyl platinum complexes containing the strong field cyanide ion.[53,170−172] The 2-py-

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(163) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222.

(164) Chopra, D.; Thiruvenkatam, V.; Manjunath, S. G.; Guru Row, T. N. *Cryst. Growth Des.* **2007**, *7*, 868.

(165) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martín, A.; Serrano, B. *J. Chem. Soc., Dalton Trans.* **2001**, 2926 and references therein.

(166) Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 5352.

(167) Dunitz, J. D.; Taylor, R. *Chem.*—*Eur. J.* **1997**, *3*, 89.

(168) Lai, S. W.; Lam, H. W.; Lu, W.; Cheung, K. K.; Che, C. M. *Organometallics* **2002**, *21*, 226.

(169) Wong, K. M.-C.; Hung, L.-L.; Lam, W. H.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2007**, *129*, 4350.

(170) Wilson, M. H.; Ledwaba, L. P.; Field, J. S.; McMillin, D. R. *Dalton Trans.* **2005**, 2754.

(171) Field, J. S.; Haines, R. J.; Ledwaba, L. P.; McGuire, J. R.; Munro, O. Q.; Low, M. R.; McMillin, D. R. *Dalton Trans.* **2007**, 192.

(172) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913.

Table 3. Photophysical Data for Complexes **1**−**7**

compound	medium (T/K)	λ_{em}/nm	τ/μs
$(NBu_4)[Pt(C\hat{}N\hat{}C)(C{\equiv}C^tBu)]$, **1**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	493, 529(λ_{exc}390)	16.4
	CH_2Cl_2 1×10^{-3} M (77)	572, 675(λ_{exc}454)	19.5 at 572 nm
		675 (λ_{exc}524)	11.0 at 675 nm
	solid (298)	not emissive	
	solid (77)	675(λ_{exc}520)	10.5
$(NBu_4)[Pt(C\hat{}N\hat{}C)(C{\equiv}CPh)]$, **2**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5}M (77)	493, 526, 623sh(λ_{exc}380)	27.9
	CH_2Cl_2 1×10^{-3} M (77)	572, 635, 665sh(λ_{exc}464)	∼14.4 at 572−635 nm
		635sh, 665(λ_{exc}520)	9.9 at 665 nm
	solid (298)	606(weak, λ_{exc}500)	
	solid (77)	638(λ_{exc}515)	13.1
$(NBu_4)[Pt(C\hat{}N\hat{}C)(C{\equiv}CTol)]$, **3**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	497, 527, 665(weak)(λ_{exc}390)	9.5
	CH_2Cl_2 1×10^{-3} M (77)	560, 630, 655sh(λ_{exc}460)	∼13.2 at 560−600 nm
		630, 655(λ_{exc}520)	7.5 at 655 nm
	solid (298)	639 (weak, λ_{exc}475)	
	solid (77)	658(λ_{exc}517)	9.4
$(NBu_4)[Pt(C\hat{}N\hat{}C)\{C{\equiv}C(4\text{-}OCH_3)C_6H_4\}]$, **4**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	508, 532, 626sh, 665(λ_{exc}400)	20.1
	CH_2Cl_2 1×10^{-3} M (77)	508, 550, 660(λ_{exc}450)	7.4 at 508 nm; 9.6 at 550 nm; 7.5 at 660 nm
		660(λ_{exc}520)	
	solid (298)	618, 636(weak, λ_{exc}490)	
	solid (77)	666(λ_{exc}520)	8.6
$(NBu_4)[Pt(C\hat{}N\hat{}C)(CN)]$, **5**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	490(weak), 525(weak), 560, 623 (λ_{exc}375−450)	15.6 at 490−525 nm; 13.0 at 560 nm; 8.8 at 623 nm
	CH_2Cl_2 1×10^{-3} M (77)	628(λ_{exc}452−500)	7.2
	solid (298)	590(weak, λ_{exc}438)	
	solid (77)	631(λ_{exc}510)	12.3
$(NBu_4)[Pt(C\hat{}N\hat{}C)(S\text{-}2Py)]$, **6**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	508, 530, 570sh(λ_{exc}440)	17.2
	CH_2Cl_2 1×10^{-3} M (77)	513, 555, 620(λ_{exc}440)	8.9 at 513 nm; 8.5 at 555 nm; 5.7 at 640−660 nm
		640, 660(λ_{exc}525)	
	solid (298)	not emissive	
	solid (77)	640(λ_{exc}515)	11.3
$(NBu_4)[Pt(C\hat{}N\hat{}C)(CH_2COCH_3)]$, **7**	CH_2Cl_2 5×10^{-5} M (298)	not emissive	
	CH_2Cl_2 5×10^{-5} M (77)	485, 510, 545, 585(λ_{exc}375)	21.6 at 485 nm
		510, 545, 585, 610(λ_{exc}460)	13.5 at 585 nm
	CH_2Cl_2 1×10^{-3} M (77)	485sh, 510, 550, 585(λ_{exc}380)	
		510, 550, 585(λ_{exc}460)	
		550, 585, 675(λ_{exc}500)	
		675(λ_{exc}525)	8.8 at 675 nm
	solid (298)	not emissive	
	solid (77)	612, 660(λ_{exc}460−515)	10.7 at 612 nm 9.6 at 660 nm

ridinthiolate derivative **6** shows intense absorption bands at 246−396 nm and two broad low-energy peaks at 462 (ϵ = 1.9 10^3 dm^3 mol^{-1} cm^{-1}) and 529 (1.1 10^3 dm^3 mol^{-1} cm^{-1}), respectively. The high-energy bands are due to IL transitions, although a detailed assignment is impeded by band overlapping. According to previous studies[135,173−175] of diimine and polypyridine thiolate derivatives in which the low-energy absorptions have been systematically attributed to ligand (thiolate) or metal−thiolate-to-ligand (polyimine) charge-transfer transitions, we assign the band at 462 nm to a LL′CT.[176] In accordance with this assignment, this band exhibits a negative solvatochromic behavior, appearing at 435 nm in a polar solvent such as MeCN. This behavior is indicative of a significant difference between the ground- and excited-state dipole moments, and is typical of MLCT/LLCT transitions.[177] The weakest manifold at 529 nm seen in CH_2Cl_2 could be assigned to a single-triplet satellite, which would be of considerable oscillator strength due to the presence of a heavy Pt(II) center.[178]

Emission Properties. The emission data for all the complexes are depicted in Table 3. All complexes are intensely luminescent in low temperature (77 K) rigid matrix (glassy CH_2Cl_2 and in the solid state) while they are nonemissive in fluid solution, probably caused by efficient

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(173) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, *103*, 1559.

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

(175) Paw, W.; Cummings, R. J.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125.

(176) It should be noted that the analogous absorption CT band in related dithiolatediimineplatinum(II) systems has been designated as MMLL′CT (mixed metal ligand-to-ligand charge transfer), indicating that significant metal character exits in the HOMO (ref 175).

(177) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Amsterdam: Oxford, 1984.

(178) Weinstein, J. A.; Blake, A. J.; Davies, E. S.; Davis, A. L.; George, M. W.; Grills, D. C.; Lileev, I. V.; Maksimov, A. M.; Matousek, P.; Mel'nikov, M. Y.; Parker, A. W.; Platonov, V. E.; Towrie, M.; Wilson, C.; Zheligovskaya, N. N. *Inorg. Chem.* **2003**, *42*, 7077.

Table 4. Crystallographic Data for **1**, **4**, **5**, and **6**

	1	**4**·CH_2Cl_2	**5**	**6**·0.5C_6H_5F
empirical formula	$C_{39}H_{56}N_2Pt$	$C_{43}H_{56}Cl_2N_2OPt$	$C_{34}H_{47}N_3Pt$	$C_{41}H_{53.5}F_{0.5}N_3Pt$
fw	747.95	882.89	692.84	825.02
T (K)	173(1)	100(1)	100(1)	100(1)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$	$P2_1$	$P2_1/a$
a (Å)	9.8700(1)	9.1570(3)	9.8599(3)	18.0030(7)
b (Å)	16.3790(2)	38.6540(12)	18.5513(7)	10.0970(2)
c (Å)	22.1480(3)	11.8350(4)	16.5784(6)	20.5330(8)
α (deg)	90	90	90	90
β (deg)	96.400(1)	108.951(1)	91.567(2)	96.496(1)
γ (deg)	90	90	90	90
V (Å^3)	3558.15(7)	3962.0(2)	3031.29(18)	3708.4(2)
Z	4	4	4	4
D_{calcd} (Mg/m^3)	1.396	1.480	1.518	1.478
abs coeff (mm^{-1})	3.971	3.711	4.655	3.875
F(000)	1528	1792	1400	1676
cryst size (mm)	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.10	0.20 × 0.15 × 0.10
θ range for data collection (deg)	2.49 to 27.94	1.05 to 27.70	1.23 to 27.84	2.28 to 27.48
no. of data/restrains/params	8486/0/386	9220/0/442	14202/1/686	8501/14/403
GOF on F^2	1.041	1.209	1.023	1.036
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, $R_2 = 0.0820$	$R_1 = 0.0358$, $R_2 = 0.0903$	$R_1 = 0.0362$, $R_2 = 0.0687$	$R_1 = 0.0404$, $R_2 = 0.0830$
R indices (all data)	$R_1 = 0.0517$, $R_2 = 0.0891$	$R_1 = 0.0617$, $R_2 = 0.1341$	$R_1 = 0.0571$, $R_2 = 0.0741$	$R_1 = 0.0652$, $R_2 = 0.0899$
largest diff peak and hole (e·A^{-3})	1.242 and −1.390	1.243 and −1.946	1.022 and −1.498	1.825 and −1.552

nonradiative decay via low-lying d−d excited states or solvent interactions in the open coordination states. In the solid state at 298 K, lumophore quenching due to weak hydrogen contacts seems to be prevalent, so only very weak or negligible emission is observed. Figure 5 shows the emission spectra in CH_2Cl_2 glass and at low concentrations (5×10^{-5} mol dm^{-3}) for **1**−**4** and **6**. The structured emissions observed at 493−508 nm, with vibrational spacing of about 1300 cm^{-1}, are reminiscent of those observed in related neutral [Pt(C^N^C)L],[108] [Au(C^N^C)(C≡CR][179] (470−529 nm), and [Au(C^N^C)(SPy)][180] (488 nm) complexes. This fact and the long emission lifetimes (9.5−27.9 μs), which are suggestive of triplet parentage, indicate that the emissions presumably come from states of metal-perturbed $^3\pi-\pi^*$ (C^N^C) origin. Time-resolved emission profiles for **1**−**4** and **6** (Figures S5−S7, Supporting Information) show the presence of monoexponential decay, thus implying that at low concentrations a single emitting species is present. However, the emission profiles are sensitive to complex concentration (see Table 3 and Figure 6 for complex **4**). Thus, with increasing concentration, complexes **3**, **4**, and **6** develop two additional bands centered around 550−560 and 640−660 nm. The structured high-energy emission is visible even at a concentration of 10^{-3} M. At this concentration (10^{-3} M), complexes **1** and **2** show only the two low emission bands centered at 572 and 665−675 nm. As shown in Figure 6 for complex **4**, the excitation spectra monitored at 508 and 550 nm are similar, suggesting that the band at 550 nm is excimeric in nature. However, the excitation profile of the low-energy band at 665 nm is different, suggesting that this band originates from emissive states resulting from ground-state aggregation. For complexes **1** and **2**, the excitation spectra monitored at 572 nm and at the low-energy band (675 nm for **1** and ∼665 nm for **2**) were also found to be different, indicating that the two emissive bands are from different origins tentatively attributed to excimeric and ground-state aggregation of the complexes. The absence of monomeric emissions at 10^{-3} M for complexes **1** and **2** indicates a stronger tendency of these compounds to form excimers or aggregates. In complexes **4** and **6**, the presence of more bulky C≡C(p-OMe)C_6H_4 and S-2Py ligands makes such processes less favorable. In agreement with this hypothesis, the planar cyanide complex **5** exhibits, even at low concentration (5×10^{-5} M), in addition to the vibronic-structured emission (see Figure 7) due to the $^3\pi\pi^*$(IL) excited state with a long lifetime (∼15.6 μs), a broad emission centered at 623−628 nm, attributed to oligomerization with a shorter lifetime (∼7.2 μs). Upon increasing the concentration to 5×10^{-4} M, only the low emission is observed (see Figure 7). Interestingly, the ketonyl derivative **7** exhibits two different vibronic bands with different emissive origins (485 and 510 nm) at low concentration (10^{-5} M), clearly visible by changing the excitation wavelength. Excitation at 360−390 nm produces an emission vibronic profile with peak maxima starting at 485 nm, while excitation at longer wavelengths (460 nm) gives rise to a vibronic emission with peak maxima at 510, 545, 585, and 610 nm (Figure S8, Supporting Information). Lifetime measurements recorded at 485 (λ_{exc} 375) and 585 nm (λ_{exc} 460) give values of 21.6 and 13.5 μs, respectively, confirming long-lived spin-forbidden excited states. These emissions are tentatively attributed to $^3\pi\pi^*$(IL) and ^{3}MLCT (or a mixed ^{3}IL/^{3}MLCT manifold), respectively. As in the remaining **1**−**6** complexes, two additional low-energy emissions at ca. 585 and 675 nm, respectively, due to excimeric/ground state $^3\pi\pi$ excited states are also observed by increasing the concentration to 10^{-3} M. The appearance of low-energy bands at *77*

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(179) Yam, V. W.-W.; Wong, K. M. C.; Hung, L. L.; Zhu, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 2.

(180) Wong, K.-H.; Cheung, K.-K.; Chan, M. C.-W.; Che, C.-M. *Organometallics* **1998**, *17*, 3505.

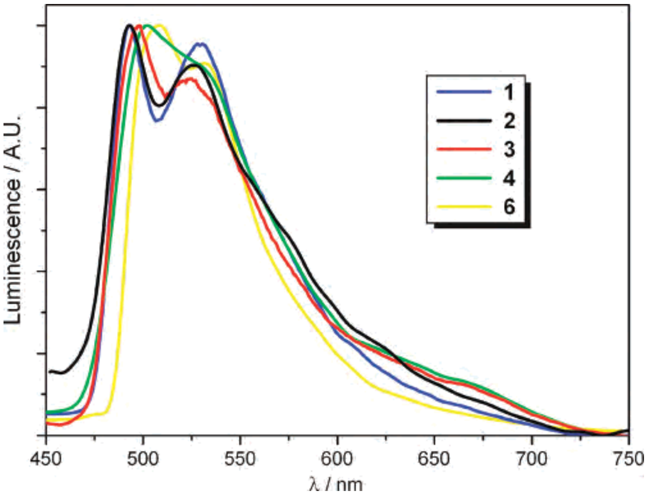

Figure 5. Emission spectra of complexes **1**−**4** and **6** in CH_2Cl_2 glasses (5×10^{-5} M, 77 K).

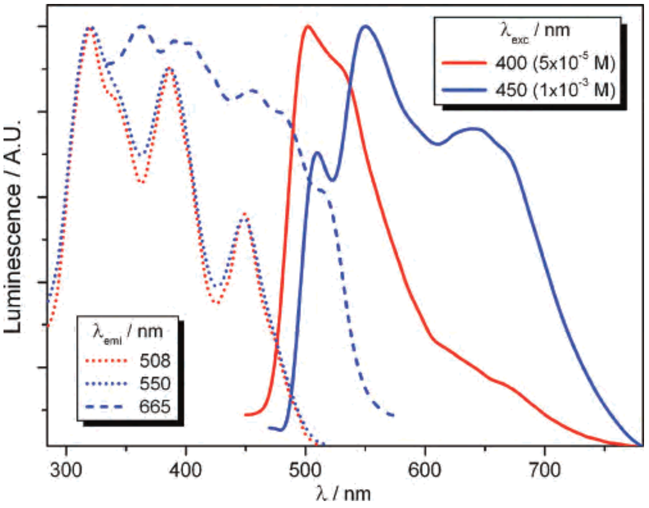

Figure 6. Steady-state spectra of CH_2Cl_2 glasses of **4** at different concentrations.

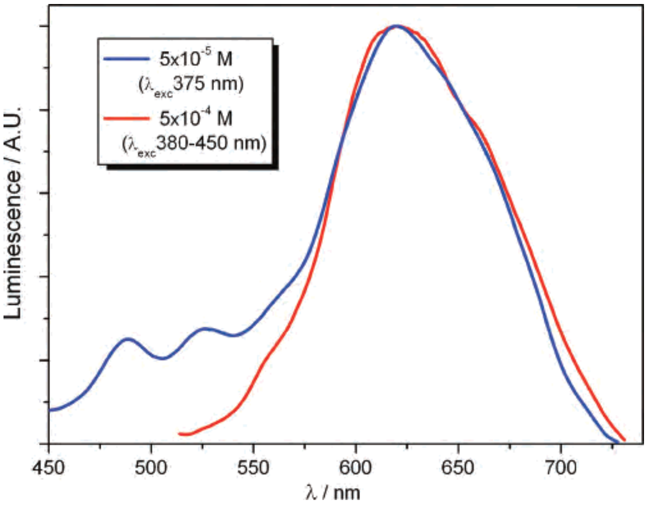

Figure 7. Emission spectra of **5** for CH_2Cl_2 glasses (77 K) at different concentrations.

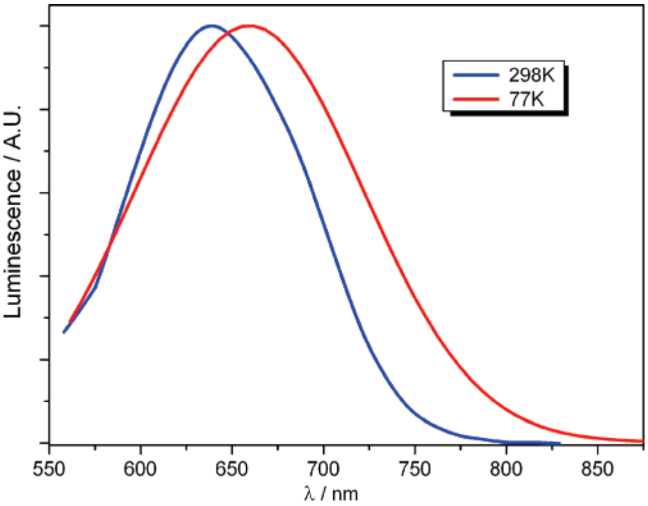

Figure 8. Solid-state emissions of **3** at 298 and 77 K.

K for glasses in all complexes, due to ground-state oligomerization, is not unprecedented,[55,181] although they appeared to obey Beer's Law in their electronic absorption at *room temperature*. In the solid state at 298 K, all complexes (except **1** and **7**) exhibit a weak emission with λ_{max} between 590 nm (**5**) and 639 nm (**3**). Upon cooling to 77 K, the emissions increase their intensity, with λ_{max} values red-shifted to 631 nm (**5**) to 666 nm (**4**). At low temperatures, complex **1** is also emissive, exhibiting a broad unstructured band centered at λ_{max} 675 nm. The emission profile of complex **7** (77 K, solid) is slightly dependent on excitation wavelength, exhibiting a band at 612 with a shoulder at 660 by excitation at 460 nm. However, the shoulder increases its intensity by excitation at 515 nm. As an illustration of this, Figure 8 shows the solid-state emission of complex **3** at 298 and 77 K. These emissions are comparable to the low-energy emissions observed in the 77 K CH_2Cl_2 glasses, and therefore, we tentatively attribute the emissions to ground state (or excimeric) $^3\pi\pi^*$ excited states. The red shift to lower energies observed at 77 K relative to room temperature can be attributed to a lattice compression of the solid sample at low temperature.

Conclusions

Mononuclear anionic cyclometalated complexes (NBu_4)-$[Pt(C^\wedge N^\wedge C)X]$ ($HC^\wedge N^\wedge CH$ = 2,6-diphenylpyridine, X = C≡CR, **1**−**4**; CN, **5**; S-2Py, **6**; CH_2COCH_3, **7**) have been prepared and fully characterized. The solid-state structures of complexes **1**, **4**, **5**, and **6** have been determined showing, in all the cases, the presence of several types of weak hydrogen interactions, which lead to the formation of supramolecular networks. The electronic absorption spectra of **1**−**5** and **7** are dominated by IL $\pi\pi^*$ and MLCT transitions. In complex **6**, the lower-energy absorption is attributed to a LL′CT transition. In all complexes, the weak absorption at 516−532 nm is thought to be due to spin-forbidden $^3\pi-\pi^*$ ($C^\wedge N^\wedge C$) (^{3}IL) transition. The emissions at 77 K are sensitive to solvent concentration. In dilute glassy solutions, complexes **1**−**4** and **6** exhibit highly structured bands, which are assigned to a metal-perturbed $^3\pi\pi^*$ excited state, while complex **5** also shows an additional low-energy

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(181) Sun, F. G.; Lin, Y.; Schanze, K. S. *Inorg. Chem.* **2005**, *44*, 4055.

emission attributed to ground-state aggregation. For the ketonyl derivative **7**, a dual emission is observed, which is tentatively attributed to the fact that $^3\pi\pi^*$(IL) and ^{3}MLCT (or mixed $^3\pi\pi^*$(IL)/^{3}MLCT) excited states are not coupled. Complexes **3**, **4**, **6**, and **7** exhibit two additional low-energy emissions (∼575 and ∼670 nm) when the concentration is increased, which are tentatively assigned to excimeric and ground-state oligomerization of the complexes, respectively. The following tendency to exhibit excimeric and ground state oligomerization is observed: $\mathbf{7} < \mathbf{3} \approx \mathbf{4} \approx \mathbf{6} < \mathbf{1} \approx \mathbf{2} < \mathbf{5}$. The broad and unstructured emissions observed in the solid state (298 and 77 K) compare well to the low-energy emissions observed in the 77 K CH_2Cl_2 glasses and, therefore, are similarly assigned.

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Supporting Information Available: Figures of bidimensional organization of complex **1** (Figure S1) and 3D arrangement of complexes **4**−**6** (Figures S2−S4); time-resolved emission profiles for complexes **1**, **3**, and **6** (Figures S5−S7) and steady-state spectra of complex **7** with different excitation wavelengths (Figure S8), both in diluted CH_2Cl_2 solutions at 77 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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