J|A|C|S
COMMUNICATIONS

Remarkable Bromination and Blue Emission of 9-Anthracenyl Pt(II) Complexes

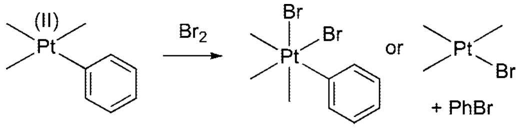
Bao-Yu Wang,[†] Alice Raphael Karikachery,[†] Yunjing Li,[‡] Anupam Singh,[†] Han Baek Lee,[†]
Wenfang Sun,*[‡] and Paul R. Sharp*[†]

125 Chemistry, University of Missouri, Columbia, Missouri 65211, and Department of Chemistry and Molecular Biology, North Dakota State University, Fargo, North Dakota 58108-6050

Received November 24, 2008; E-mail: wenfang.sun@ndsu.edu; sharpp@missouri.edu

Electrophilic aromatic substitution[1] would normally be considered incompatible with organometallic complexes containing low valent, oxidative addition[2] susceptible metal centers. For example, Br_2 addition to a Pt(II) organometallic complex with an attached aromatic ring would not be expected to undergo aromatic ring bromination. Instead, attack at the Pt(II) center would be expected resulting in Br_2 oxidative addition to the metal center and formation of a Pt(IV) complex or cleavage of the Pt−C bond (Scheme 1).[3−5]

Scheme 1

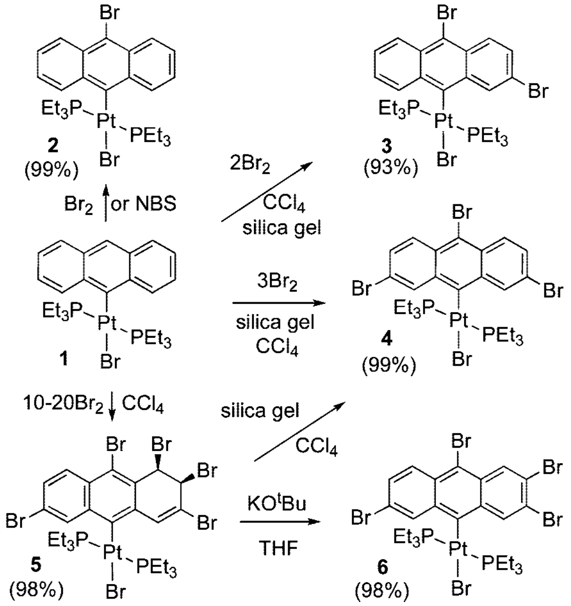


In this paper we report the opposite of this expectation, a Pt(II) anthracenyl complex that is remarkably resistant to Br_2 oxidative addition and instead undergoes selective multiple bromination of the anthracenyl ligand. In addition, the resulting complexes are highly solution photoluminescent in the blue region with high emission quantum yields ($\Phi_{em} = 0.54-0.88$) and long lifetimes.

The chemistry of the Pt 9-anthracenyl system is outlined in Scheme 2. The starting complex, *trans*-Pt(Br)(9-anthracenyl)$(PEt_3)_2$ (**1**), is readily prepared from $Pt(PEt_3)_4$ and 9-bromoanthracene. Addition of 1 equiv of Br_2 to a CCl_4 solution of **1** was expected to give a Pt(IV) complex in analogy to other Pt(II) complexes including the phenyl, 1-naphthalenyl, and 8-phenanthracenyl analogues of **1**.[6−8] Instead, a yellow complex (**2**) with ^{31}P NMR spectral characteristics consistent with a Pt(II) complex similar to **1** is isolated. Complete characterization reveals **2** to be the ring-brominated product, *trans*-Pt(Br)(10-Br-anthracen-9-yl)$(PEt_3)_2$ shown in Scheme 2.

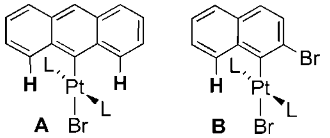
The 9- and 10-positions in anthracene are reactive,[9,10] and in **1** initial bromine attachment at the 10-position might simply be more favorable than attack at the Pt(II) center. Anticipating that a second attack would occur at the Pt center, 2 equiv of Br_2 were added to **1**. A mixture was obtained consisting of **2** and other ring brominated products described below. No Pt center oxidative addition was detected. Subsequently, it was found that, in the presence of silica gel,[11] 2 equiv of Br_2 yields exclusively *trans*-Pt(Br)(2,10-Br_2-anthracen-9-yl)$(PEt_3)_2$ (**3**). This selective second bromination is also not at the Pt center but on the ring, this time at the 2-position. Yet further selective bromination on the ring occurs with 3 equiv of Br_2 in the presence of silica gel. A high yield of *trans*-Pt(Br)(2,7,10-Br_3-anthracen-9-yl)$(PEt_3)_2$ (**4**) is obtained. Finally, excess Br_2 (10−20 equiv) gives exclusively the extensively ring-brominated complex *trans*-Pt(Br)(2,3,4,7,10-Br_5-3,4-dihydroanthracen-9-yl)$(PEt_3)_2$ (**5**). Complex **5** is readily rearomatized. Silica gel induces debromination to **4** while $KOBu^t$ dehydrobrominates **5** giving new *trans*-Pt(Br)(2,3,7,10-Br_4-anthracen-9-yl)$(PEt_3)_2$ (**6**). (Silica gel has no effect on **2**, **3**, **4**, or **6**.)

Scheme 2



There are two outstanding features of the above reactions: (1) The resistance of the Pt(II) center to oxidative addition and (2) the selectivity of the ring brominations. The selectivity contrasts sharply with that of anthracene itself where multiple (>2) bromination yields mixtures of products.[12] The oxidative addition resistance is explained by the blocking effect of the *peri*-hydrogen atoms of the anthracenyl ligand. As shown in **A** (Chart 1), these hydrogen atoms shield the fifth and sixth coordination sites that would be occupied in the incipient octahedral Pt(IV) complex. Consistent with this concept we have also observed oxidative addition resistance in the Pt(II) complexes of type **B** where the larger vicinal Br atom of **B** realizes the same role as a *peri* hydrogen atom (Chart 1).[8] Resistance to oxidative addition has also been reported for $PtL_2(Mes)_2$ (L_2 =

Chart 1



[†] University of Missouri.
[‡] North Dakota State University.

10.1021/ja809046p CCC: $40.75

a bidentate ligand, Mes = 2,4,6-trimethylphenyl) and $[Pt(C_6Cl_5)_4]^{2-}$ where the 2- and 4-methyl groups or Cl atoms similarly block the Pt axial positions.[13,14]

These brominated 9-anthracenyl Pt(II) complexes exhibit interesting photophysical properties, especially strong photoluminescence in the blue region. As shown in Figure 1, the UV−vis absorption spectra and the emission spectra of **1**, **2**, and **4** red-shift as the degree of bromination increases. This could be due to the electron-donating ability of the bromine atom(s) through a resonance effect, which increases the electron density of the anthracene and subsequently decreases the HOMO−LUMO gap. Both the UV−vis and the emission spectra resemble those of anthracene, indicating that the electronic absorption and the emission originate from the π,π^* transition of anthracene. This is consistent with other platinum−anthracenyl complexes reported in the literature.[15] In line with the trend observed in the UV−vis and emission spectra, the triplet transient difference absorption spectra of **1**, **2**, and **4** also resemble that of anthracene and red-shift with a higher degree of bromination (see Supporting Information). The photophysical data for **1**, **2**, and **4** are listed in Table 1.

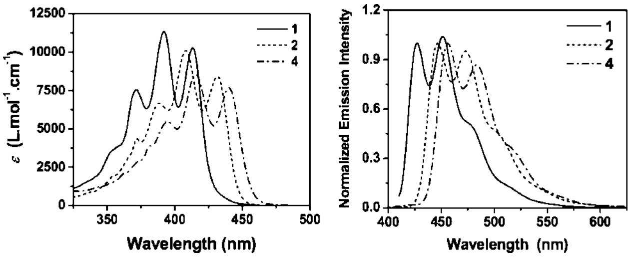


Figure 1. UV−vis absorption and normalized emission spectra of **1**, **2**, and **4** in toluene at room temperature.

Table 1. Photophysical Parameters of **1**, **2**, and **4** in Toluene

	τ_{em} /μs	Φ_{em}	$\lambda_{T1\text{-}Tn}$/nm (τ_T/μs)
1	3.24	0.54	450 (3.92)
2	2.85	0.88	455 (2.78)
4	4.09	0.63	460 (5.36)

The emission lifetimes of **1**, **2**, and **4** are much longer than the lifetime of the prompt-fluorescence from anthracene. With reference to the reported work on the delayed fluorescence of anthracene,[16] the emission from **1**, **2**, and **4** can be ascribed to *P*-type delayed fluorescence of the anthracene ligand. This notion is supported not only by the similar emission energy to the delayed fluorescence of anthracene[16] but also by the significant oxygen quenching of the emission (Supporting Information). The emission quantum yields of **1**, **2**, and **4** are much higher compared to other recently reported blue-emitting Pt and Ir complexes.[15,17−19] This could be explained by the heavy-atom effect of the Pt and Br atoms, which enhances spin−orbit coupling and thus increase the quantum yield of the anthracene triplet excited state. The increased triplet population would enhance triplet−triplet annihilation, resulting in high delayed fluorescence quantum yields. Further evidence supporting *P*-type delayed fluorescence include the quadratic dependence of the emission quantum yield on excitation light intensity (Supporting Information) and the similarity of the emission lifetime to the triplet excited-state lifetime obtained from the decay of the triplet transient difference absorption of these complexes (Table 1). In addition, the emission measured at 77 K is quite similar to that at room temperature, with more distinct vibronic structures (Supporting Information). This confirms that the observed emission of **1**, **2**, and **4** does not emanate from *E*-type delayed fluorescence.

In conclusion, we have found that in certain Pt(II) σ-bonded polycyclic aromatic complexes two hydrogen atoms or a hydrogen atom and a bromine atom of the polycyclic aromatic block the axial positions of the Pt(II) centers suppressing oxidative addition. At least in the case of the anthracene ligand, this permits the Pt(II) substituent to activate and direct electrophilic substitution on the anthracene ligand yielding novel polybrominated anthracene ligands. In principle, this concept can be extended to other polycyclic aromatic ligands, metal centers, and electrophilic reagents for the synthesis of novel polycyclic aromatic compounds. In addition, the introduction of the *trans*-$Pt(Br)(Et_3P)_2$ center to the anthracene ring greatly increases the delayed fluorescence of anthracene in the blue region due to a significantly enhanced quantum yield of the anthracene triplet excited state.

Acknowledgment. We thank the National Science Foundation for supporting this work (CHE-0406353 for P. Sharp and CHE-0449598 for W. Sun). We also thank Dr. Charles Barns for X-ray data collection and processing.

Supporting Information Available: Synthetic procedures and characterization data for all compounds; CIF files for **2**, **3**, **4**, and **6**; the excitation spectra for **1**, **2**, and **4** at rt; the quenching of the emission by oxygen; the quadratic dependence of the emission quantum yield on the excitation light intensity; the excitation and emission spectra for **1**, **2**, and **4** at 77 K; and the triplet transient difference absorption spectra for **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: Chichester, 1990.
(2) Crabtree, R. H. *The organometallic chemistry of the transition metals*, 3rd ed.; Wiley: New York, 2001.
(3) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735–1754.
(4) Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2006**, *128*, 8710–8711.
(5) Chanda, N.; Sharp, P. R. *Organometallics* **2007**, *26*, 3368–3373.
(6) Abicht, H. P.; Issleib, K. *Z. Anorg. Allg. Chem.* **1983**, *500*, 31–39.
(7) Uson, R.; Royo, P.; Gimeno, J. *Revista de la Academia de Ciencias Exactas, Fisicas, Quimicas y Naturales de Zaragoza* **1973**, *28*, 355–371.
(8) Lee, H. B. PhD, University of Missouri, Columbia, 2007.
(9) de Barry-Barnett, E. *Anthracene and anthraquinone*; Baillière, Tindall, and Cox: London, 1921.
(10) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.
(11) (a) Ghiaci, M.; Asghari, J. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1151–1152. (b) Seetula, J. A. *J. Mol. Catal., A* **2005**, *231*, 153–159.
(12) Cakmak, O.; Erenler, R.; Tutar, A.; Celik, N. *J. Org. Chem.* **2006**, *71*, 1795–1801.
(13) (a) Klein, A.; Hausen, H.-D.; Kaim, W. *J. Organomet. Chem.* **1992**, *440*, 207–217. (b) Klein, A.; Kaim, W. *Organometallics* **1995**, *14*, 1176–1186.
(14) Uson, R.; Fornies, J.; Tomas, M.; Menjon, B.; Bau, R.; Suenkel, K.; Kuwabara, E. *Organometallics* **1986**, *5*, 1576–1581.
(15) Hu, J.; Lin, R.; Yip, J. H. K.; Wong, K.-Y.; Ma, D.-L.; Vittal, J. J. *Organometallics* **2007**, *26*, 6533–6543.
(16) Parker, C. A.; Joyce, T. A. *Chem. Commun.* **1967**, 744–745.
(17) Orselli, E.; Albuquerque, R. Q.; Fransen, P. M.; Fröhlich, R.; Janssen, H. M.; De Cola, L. *J. Mater. Chem.* **2008**, *18*, 4579–4590.
(18) Batema, G. D. L., M.; Spek, A. L.; van Walree, C. A.; de Mello Donegá, C.; Meijerink, A.; Havenith, R. W. A.; Pérez-Moreno, J.; Clays, K.; Büchel, M.; van Dijken, A.; Bryce, D. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2008**, *27*, 1690–1701.
(19) Sarova, G. H.; Bokach, N. A.; Fedorov, A. A.; Berberan-Santos, M. N.; Kukushkin, V. Y.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Dalton Trans.* **2006**, *379*, 8–3805.

JA809046P