CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801842

A Luminescent Trinuclear Platinum(II) Pt_3C_2 System with a “Naked” $C\equiv C^{2-}$ Ligand That Fluctuates amongst Three Unsupported Platinum(II) Moieties

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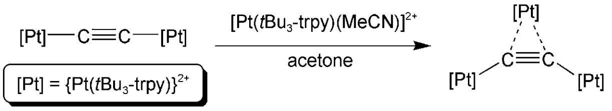
There has been growing interest in transition metal alkynyl, oligoynyl, and polyynyl systems owing to their potential applications in nanotechnology. The use of transition-metal centers to stabilize linear polyynes by the end-capping of both termini to form $[M]-(C\equiv C)_n-[M]$ has been illustrated and studied.[1–3] An interesting and unprecedented trinuclear alkynylplatinum(II) terpyridyl complex, $[\{Pt(tBu_3-trpy)\}_3(\mu_3\text{-}\eta^1,\eta^2-C\equiv C-)]^{4+}$ (**1**) was formed in the course of our study on the π coordination of a dinuclear alkynylplatinum(II) complex to d^{10} metal ions. To the best of our knowledge, this represents the first example of a $[Pt]_3C_2$, which has been characterized by X-ray crystallography, with a “naked” $C\equiv C^{2-}$ moiety coordinated to three unsupported platinum(II) fragments. The fluxional behavior and the photophysical properties were studied, the results of which have been supported by DFT and time-dependent (TD) DFT calculations.

The trinuclear alkynylplatinum(II) terpyridyl complex, $[\{Pt(tBu_3-trpy)\}_3(\mu_3\text{-}\eta^1,\eta^2-C\equiv C-)](PF_6)_4$ (**1**·PF_6), was obtained unexpectedly as a byproduct (10% yield) from the reaction of $[Pt(tBu_3-trpy)(C\equiv C)Pt(tBu_3-trpy)](OTf)_2$ (**2**·OTf) with $[Cu(MeCN)_4]PF_6$ in acetone. The corresponding OTf^- salt of the same complex (**1**·OTf) could also be prepared in high yield (85%) by the reaction of the dinuclear precursor (**2**) with one equivalent of $[Pt(tBu_3-trpy)(MeCN)](OTf)_2$ in acetone (Scheme 1). The complexes gave satisfactory elemental analysis, and were characterized by positive-ion ESI mass spectrometry; ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy; and Raman spectroscopy. The crystal structure of **1**·PF_6 was also determined by X-ray crystallography.



Scheme 1. Synthesis of **1**.

The crystal structure of the complex cation of **1**·PF_6 (Figure 1) shows a propeller-like structure with the three square-planar platinum(II) terpyridyl moieties forming the blades. The $C\equiv C^{2-}$ unit σ coordinates to two platinum(II) atoms at the two ends and connects to the third platinum(II) atom in a η^2-bonding fashion with the primary Pt–alkynyl interaction involving the π electrons of the ethynyl unit. Although it is well known that $C\equiv C^{2-}$ can form a number of $[M]_nC_2$ systems with various bonding modes,[1f,4] and that transition metal alkynyls can serve as η^2 metalloligands,[1a,b,e,f,5,6] the present system is unusual because the three discrete platinum(II) units are not linked by any other groups or bridging auxiliary ligands except the “naked” $C\equiv C^{2-}$ rod. The three platinum(II) ions are coplanar with isosceles-triangle-like geometry (Pt(1)–Pt(2) = 4.8883(10), Pt(1)–Pt(3) = 3.8477(10), Pt(2)–Pt(3) = 3.7712(10) Å; Pt(1)-Pt(3)-Pt(2) = 79.816(10), Pt(3)-Pt(1)-Pt(2) = 49.405(7), Pt(3)-Pt(2)-Pt(1) = 50.779(8)°). The rodlike $C\equiv C^{2-}$ unit lies almost in the plane, with one carbon slightly above and the other slightly below (0.062(3) and 0.066(3) Å). To minimize the mutual repulsions arising from the coplanar arrangement, the three platinum(II) terpyridyl planes are twisted with respect to each other, with the dihedral angle between

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801842.

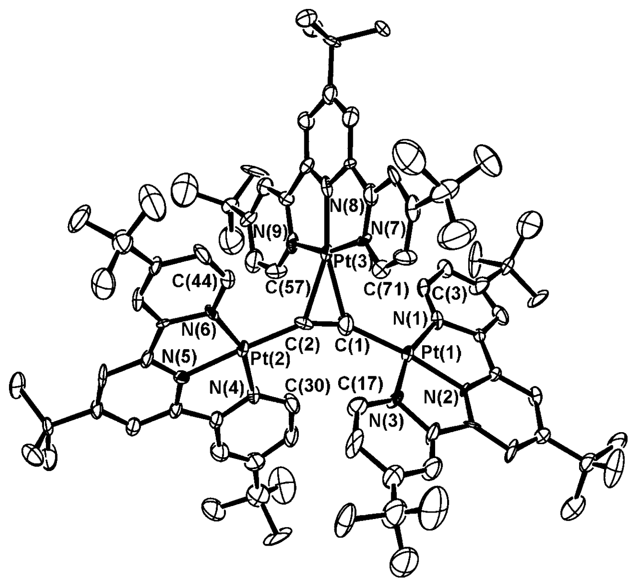
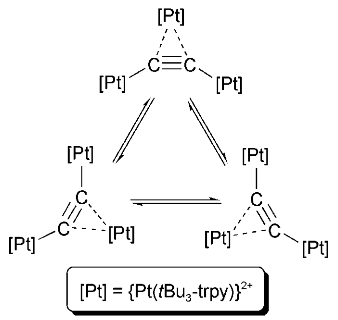


Figure 1. Perspective drawing of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Pt(1)−C(1) = 2.043(3), Pt(2)−C(2) = 1.953(19), Pt(3)−C(1) = 2.197(4), Pt(3)−C(2) = 2.198(3), C(1)−C(2) = 1.249(3); Pt(1)-C(1)-C(2) = 154.8(3), Pt(2)-C(2)-C(1) = 154.6(3), C(1)-Pt(3)-C(2) = 33.01(8), Pt(1)-C(1)-Pt(3) = 130.28(14), Pt(2)-C(2)-Pt(3) = 130.52(13).

the σ- and π-coordinated platinum(II) terpyridyl planes and that between the two σ-coordinated platinum(II) terpyridyl planes being 83.387(12)–88.683(19) and 81.023(18)°, respectively. The two σ-bound platinum(II) atoms in **1** are bent about the $C{\equiv}C^{2-}$ unit (Pt(1)-C(1)-C(2) = 154.844(212), Pt(2)-C(2)-C(1) = 154.633(209)°) with the Pt(1)-C(1)-C(2)-Pt(2) torsion angle being 34.139(984)°, which is probably due to the π back donation from the platinum(II) center to the alkynyl ligand as well as the steric strain introduced by the three platinum(II) terpyridyl units. The C≡C bond length of 1.249(3) Å is slightly longer than those found in other related platinum(II) systems,[2a,b,3b,6c] which indicates a weakening of the C≡C bond upon π coordination to platinum(II), in accordance with the observation of a lower C≡C stretching frequency of 1895 cm^{-1} in the Raman spectrum. The bond lengths of Pt(1)−C(1) and Pt(2)−C(2) of 1.953(2) and 2.043(3) Å, respectively, are normal and correlate with those found in other alkynylplatinum(II) systems.[2a,b,3b,6c] The Pt(3)−C(1) and Pt(3)−C(2) bond lengths of 2.198(3) Å are comparable with those in other Pt^{II}−(η^2-alkynyl) systems.[7a,b]

The σ- and π-coordinated [Pt(tBu$_3$−trpy)] fragments are in nonequivalent environments, so two sets of terpyridyl signals in a 2:1 ratio and two platinum resonances would be anticipated in the NMR spectroscopic study. However, only one set of ^{1}H, ^{13}C and ^{195}Pt signals were observed in all the corresponding NMR spectra of **1**·OTf, even upon cooling to −80 °C. These results suggest that a dynamic fluxional process may be occurring, which arises from an exchange of the σ- and π-coordinated platinum(II) atoms about the $C{\equiv}C^{2-}$ unit (Scheme 2). Time-averaged ^{1}H, ^{13}C and ^{195}Pt resonances were observed on the NMR timescale. The exchange process could arise from rotation of the alkynyl ligand inside the triangle of three platinum(II) atoms. The observation of time-averaged resonances, even at low temperature, suggests a small activation barrier for the σ–π alkynyl exchange, which is supported by the DFT calculation (see below).



Scheme 2. Proposed dynamic fluxional process of **1**.

Reports on isolated species of alkynes that are π coordinated to platinum(II) remain relatively scarce,[5f,7,8] probably due to their lability and instability arising from the weak Pt^{II}−(η^2-alkynyl) interaction, in which the presence of a four-electron destabilization interaction between the occupied out-of-plane π orbital of the alkynyl ligand and the symmetry-adapted filled metal d_π orbital significantly weakens the overall metal–ligand bonding interaction.[9] Moreover, such π-coordinated alkynylplatinum(II) species have been suggested as reactive intermediates in the reactions of platinum(II) complexes with simple alkynes because the π-coordinated alkynyl group would usually readily undergo oligo- or polymerization or further rearrangements resulting from nucleophilic attack of the solvent, insertion reactions, or alkynyl formation.[7,8] The fluxionality arising from the σ–π exchange process, analogous to the exchange of the three platinum(II) fragments, might play an important role in stabilizing the trinuclear complex, which has relatively labile π coordination between the platinum(II) atom and the C≡C alkynyl ligand, particularly in solution.

The electronic absorption spectrum of **1** in dichloromethane at room temperature shows intense high-energy intraligand absorptions and low-energy absorption bands at about 400–450 nm (Figure 2a), which can be assigned to a [d_π(Pt)→π*(tBu$_3$−trpy)] metal-to-ligand charge-transfer (MLCT) transition, mixed with [π(C≡C)→π*(tBu$_3$−trpy)] alkynyl-to-terpyridine ligand-to-ligand charge-transfer (LLCT) character.[3b] Such an assignment is supported further by the TDDFT calculation (see below). The observation of the low-energy absorption band in **1** (400–450 nm) at higher energy than that found in the dinuclear precursor complex **2**, which absorbs at about 496–532 nm, is in accordance with the assignment of a MLCT/LLCT transition. Coordination of the third cationic platinum(II) metal center to the C≡C unit renders the Pt−C≡C−Pt moiety more elec-

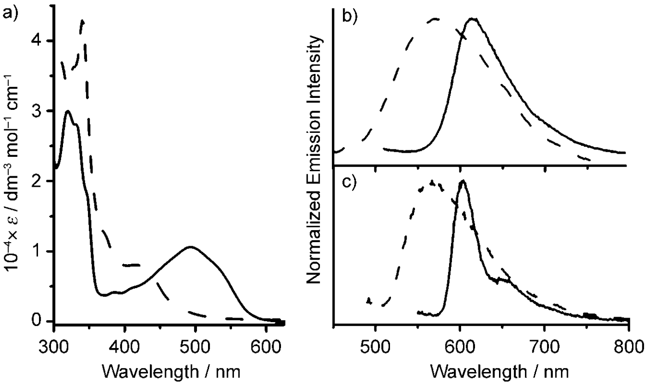


Figure 2. a) Electronic absorption spectra of **1** (——) and **2** (– – –) in dichloromethane at 298 K. Solid-state emission spectra of **1** (——) and **2** (– – –) at b) 298 and c) 77 K .

tron deficient and hence lowers the d_{π}(Pt) and $\pi(C\equiv C)$ orbital energies, giving rise to a higher-energy MLCT/LLCT transition.

Upon photoexcitation, complex **1** exhibits intense emission bands at about 550–565 nm in the solid state at 298 and 77 K as well as in a low-temperature glass (Figure 2b and c). On the basis of the spectroscopic study of **2**,[3b] an emission origin of a ^{3}MLCT/LLCT excited state is tentatively assigned. Complex **1** emits at higher energy than the precursor complex **2** in all cases, similar to the results of the electronic absorption study, and is attributed to the π coordination of the Pt−C≡C−Pt moiety to the [Pt(*t*Bu$_3$−trpy)] unit, which leads to a higher ^{3}MLCT/LLCT emission energy. It is interesting to note that **1** is essentially non-emissive in dichloromethane at room temperature in contrast to the precursor complex **2**, which shows intense emission under the same conditions. Topomerization of **1** in solution, arising from the dynamic σ–π exchange process of the alkynyl ligand, may account for this lack of emission.

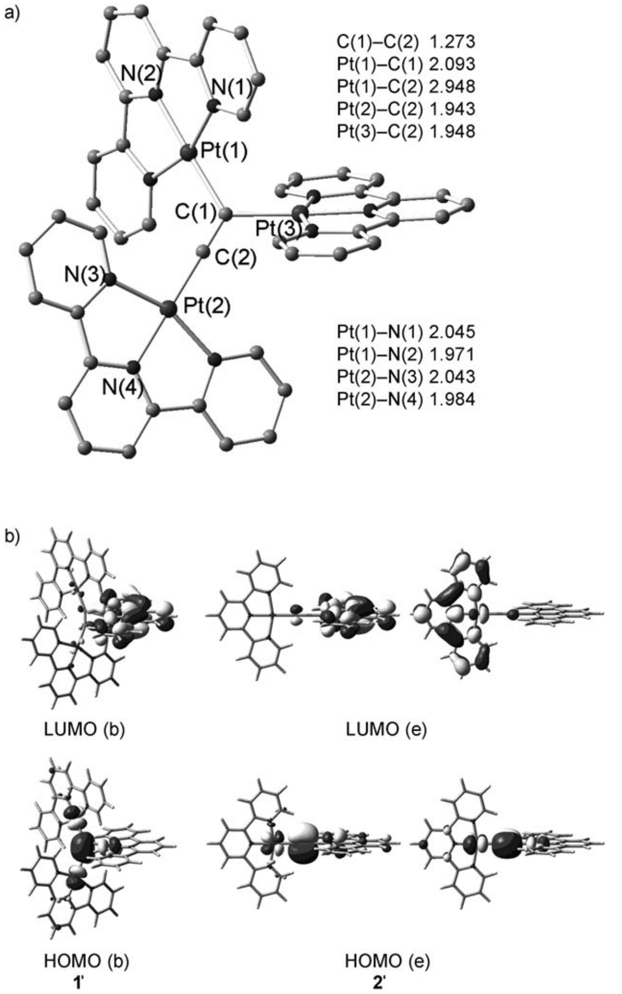


Figure 3. a) The optimized geometry of the transition state for the σ–π alkynyl exchange of **1′** with selected structural parameters (bond lengths in Å). Hydrogen atoms have been omitted for clarity. b) Spatial plots (isovalue = 0.03) of the HOMOs and LUMOs for **1′** (left) and **2′** (right) with the orbital symmetry in parentheses.

To gain insight into the activation barrier that must be overcome for the σ–π exchange of the alkynyl unit with the three Pt centers in **1** to take place, DFT calculations on a model complex $[\{Pt(trpy)\}_3(\mu_3\text{-}\eta^1,\eta^2\text{−}C\equiv C\text{−})]^{4+}$ (**1′**), in which all the *t*Bu-groups of the terpyridyl ligands were replaced by hydrogen atoms, at the PBE1PBE level of theory (for computational details, see the Supporting Information) were performed to study the topomerization (Scheme 2). In general, the optimized structural parameters are in agreement with the experimental data of **1** obtained by X-ray crystallography (see Figure S1 and Table S1 in the Supporting Information), implying that the level of theory and basis sets applied are reliable. In the transition state of the topomerization process (Figure 3a), the [(trpy)Pt(2)−C(2)] group was found to be further away from the Pt(3) metal center and closer to the Pt(1) center, with an increase in the Pt(3)−C(2) length of 0.686 Å, while the Pt(1)−C(2) distance decreased by 0.270 Å. The C(1)−C(2) distance is 1.273 Å in the transition-state, which indicates a partial C≡C bond character in the transition-state structure. The activation enthalpy ($\Delta H^{\neq}$) calculated for the topomerization of **1′** is 4.3 kcal mol^{-1}. It is anticipated that the *tert*-butyl groups on the terpyridyl ligand should not significantly affect the calculated barrier for the topomerization. The small barrier calculated for the topomerization in **1′** is consistent with the experimental observation of a facile exchange for the σ and π coordination of the alkynyl unit among the three Pt centers in **1**, even at low temperature. A similar exchange of the σ and π coordination of the alkynyl unit has also been proposed for other related M_3C_2 complexes.[5b,e]

A nonequilibrium TDDFT calculation at the PBE1PBE level was employed to investigate the nature of the low-lying excited states in **1′** and the model complex $[Pt(trpy)(C\equiv C)Pt(trpy)]^{2+}$ (**2′**) to provide a better understanding of the lowest-energy absorption and emission origins. The lowest-energy dipole-allowed singlet–singlet transitions and the first singlet–triplet transitions calculated for **1′** and **2′** are listed in the Supporting Information (Table S2). For **1′**, the $S_0\rightarrow S_1$ and $S_0\rightarrow T_1$ transitions calculated at 470 and 490 nm, respectively, correspond to the excitation from the HOMO to the LUMO. The HOMO mainly receives contributions from the antibonding combination of the interaction between the π orbital of the alkynyl unit and the d_π orbitals of the three platinum(II) centers, whereas the LUMO is a π^* orbital localized on the terpyridyl ligand of the π-coordinated [Pt(trpy)] fragment (Figure 3b). This is understandable because the terpyridyl ligand of the π-coordinated [Pt(trpy)] fragment should be the one that is most electron deficient and hence the strongest π-acceptor ligand. Therefore, the lowest-energy absorption and emission of **1′** can be assigned as the transitions derived from an admixture of the $[d_\pi(\mathrm{Pt})\rightarrow\pi^*(\mathrm{trpy})]$ MLCT and $[\pi(\mathrm{C{\equiv}C})\rightarrow\pi^*(\mathrm{trpy})]$ LLCT excited states, which involve a charge transfer from the Pt_3C_2 core to the terpyridyl unit of the π-coordinated [Pt(trpy)] fragment. Similarly, the $S_0\rightarrow S_3$ and the $S_0\rightarrow T_1$ transitions for **2′** calculated at 520 and 616 nm, respectively, are also attributed to an admixture of the $[d_\pi(\mathrm{Pt})\rightarrow\pi^*(\mathrm{trpy})]$ MLCT and $[\pi(\mathrm{C{\equiv}C})\rightarrow\pi^*(\mathrm{trpy})]$ LLCT transitions. The larger HOMO–LUMO energy difference found in **1′** (3.5 eV) compared with **2′** (3.1 eV) is in agreement with the observed experimental findings, in which the lowest-energy absorption and emission of **1** is higher that those of **2**.

In summary, an interesting trinuclear platinum(II) terpyridyl complex, in which three discrete unsupported [Pt(trpy)] fragments are linked by a "naked" $C{\equiv}C^{2-}$ alkynyl rod in both σ- and π-coordination modes, has been isolated and structurally characterized. The photophysical and fluxional behavior have been described and correlate with theoretical calculations.

Acknowledgements

V.W-W.Y. acknowledges receipt of the Distinguished Research Achievement Award, and the support of the University Development Fund, the Faculty Development Fund, and the URC Strategic Research Theme on Molecular Materials from The University of Hong Kong. The work described in this paper has been supported by the RGC Central Allocation Vote (HKU 2/05C) and a CERG Grant from the Research Grants Council of Hong Kong Special Administrative Region, China (Project No. HKU 7057/07P). W.H.L. acknowledges the receipt of a University Postdoctoral Fellowship from The University of Hong Kong. We also thank the Computer Center at The University of Hong Kong for providing computational resources.

Keywords: alkynes • fluxionality • luminescence • platinum

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Received: September 6, 2008