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Oxidation of Organoplatinum(II) by Coordinated Dimethylsulfoxide: Metal−Metal Bonded, Dinuclear, Liquid-Crystalline Complexes of Platinum(III)

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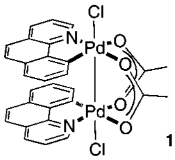
Abstract: Reaction of [$PtCl_2(dmso)_2$] with 2,5-(dialkoxyphenyl)pyridine in HOAc leads to a dinuclear, acetate-bridged, metal−metal bonded complex of platinum(III); dmso in the presence of acid is found to be responsible for the oxidation. The dimer is analogous structurally to Pd^{III} dimers implicated in catalytic acetoxylation. Platinum dimers with longer alkoxy chains are shown to be unique examples of liquid crystals of platinum(III).

Palladium-catalyzed transformations of organic substrates are ubiquitous[1] and responsible for major developments in synthetic methodology.[2] Catalyst precursors have normally been complexes of Pd^0 or Pd^{II} (or occasionally Pd^I dimers[3]), and it is these oxidation states that have been implicated predominantly in mechanistic rationalizations based mainly on classical oxidative addition/reductive elimination cycles. More recently, it has been postulated that certain palladium-catalyzed reactions involve the intermediacy of Pd^{IV} complexes, for example in oxidative functionalization of C−H bonds by the groups of Sanford[4] and of Rourke.[5] The emergence of Pd^{IV} chemistry in organic transformations has recently been reviewed comprehensively.[6] However, in 2009, Powers and Ritter,[7] and then Deprez and Sanford,[8] postulated the involvement of dinuclear complexes of Pd^{III} in catalytic cycles and complex **1** was characterized crystallographically. In both pieces of work, Pd^{III} complexes were prepared by oxidation of a Pd^{II} precursor by I^{III} reagents ($PhICl_2$ or $[R-I-R']^+$). Ritter's group then went on to provide evidence that an analogue of complex **1**, in which the *ortho*metallating group was 2-phenylpyridine and the axial chloride was replaced by acetate, was a catalyst precursor for oxidative acetoxylation of 2-phenylpyridine using $PhI(OAc)_2$.[9]



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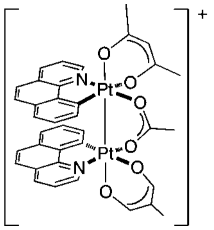
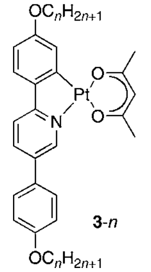


[2]$^+$

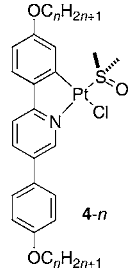
In general, third-row transition elements form more inert complexes than their second-row congeners, and so it is not uncommon for the third-row element to be used in mechanistic investigations. As such, a good deal of organoplatinum chemistry has been developed with the aim of establishing mechanistic details of palladium-catalyzed reactions. Then, both because of its inherent interest and because of the above-mentioned proposals for the involvement of Pd^{IV}, organoplatinum(IV) chemistry has enjoyed a great deal of attention recently, particularly from the groups of Sanford and of Rourke. For the most part, Pt^{IV} complexes were realized *via* the oxidation of Pt^{II} precursors using peroxide, I^{III} reagents (e.g., $PhICl_2$), or *N*-chlorosuccinimide (NCS). Sanford's group also reported two examples of organoplatinum(III) complexes. Thus, oxidation of [Pt(Bzq)(acac)] (here Bzq is *ortho*metalated benzo[*h*]quinoline) with $PhI(OAc)_2$ in acetic acid led to Pt^{III} cation [**2**]$^+$,[10] characterized crystallographically as its $[BF_4]^-$ salt, while, on other occasions, NCS oxidation of *cis*-[$Pt^{II}(2\text{-}PhPy)_2$] or I^{III} oxidation of *cis*-[$PtMe_2$(bipy)] led to unsupported, metal−metal bonded dimers (here 2-PhPy is *ortho*metalated 2-phenylpyridine).[11] Previously, oxidation of *cis*-[$Pt^{II}(2\text{-}PhPy)_2$] with elemental bromine had been found to lead to *cis*-[$Pt^{IV}Br_2(2\text{-}PhPy)_2$],[12] while NCS-oxidation of Pt^{II} has also led to Pt^{IV} species.[13]

Supported dimeric Pt^{III} complexes are reasonably well-known in the literature and normally consist of a metal−metal bonded arrangement supported by four bridging ligands, for example OAc^-,[14] SO_4^{2-},[15] pyrophosphites,[16] and formamidinates.[17] In all cases, they were obtained from Pt^{II} precursors using an external oxidant.

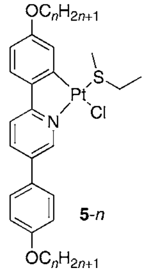
As part of our abiding interest in metallomesogens, we have recently reported series of emissive Pt^{II} complexes with liquid crystal properties[18,19] for potential applications in OLED fabrications.



3-*n*



4-*n*



5-*n*

One of these series is represented by **3-*n***, normally obtained directly from reaction of a di-μ-Cl dimer of an *ortho*metalated 2-phenylpyridine complex of platinum(II) with Na(acac). In this case, however, the elongated ligands rendered this dimer rather insoluble, and so it was found to be better to proceed through the *S*-dmso complex **4-*n***. However, preparing **4-*n*** in two steps is inefficient, and so its preparation directly from *cis*-[$PtCl_2(dmso)_2$] was investigated. Thus, in one set of conditions, *cis*-[$PtCl_2(dmso)_2$] was heated under reflux in AcOH with 2,5-*bis*(4-ethoxyphenyl)pyridine. However, the product obtained after workup was not the characteristic yellow of **4-*n***, but rather an orange material.

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Fortunately, the complex crystallized, and upon determination of the structure, it emerged that the product, **6**-*n*,*m* (here *n* refers to the number of carbons in the ligand chain, while *m* refers to the number of carbons in the chain bound to the bridging carboxylate function), was a dinuclear $\mathrm{Pt^{III}}$ complex (Charts 1 and 2). The two Pt centers were supported by two μ^2-acetato ligands at a distance of 2.5730(3) Å, consistent with a Pt−Pt single bond (*cf.* 2.5647(2) Å in **2**); the diamagnetic nature was also evidenced by obtaining a high-resolution ^{1}H NMR spectrum. Each platinum was also bound to a diphenylpyridine ligand, which lay in the opposite orientation with respect to that bound to the other Pt center. The structure is unsymmetric in that there are two $d_{\mathrm{Pt-Cl}}$ at 2.465(1) and 2.442(1) Å and the two square planes are offset by ~18.8°. The two ligands are not coparallel, and planes defined by the two five-membered Pt-ligand rings are at an angle of 17.03°.

Chart 1. Preparation and Structure of the New Dinuclear $\mathrm{Pt^{III}}$ Complex, **6**-*n*,*m*

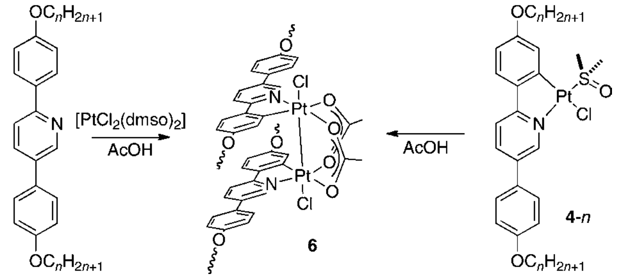
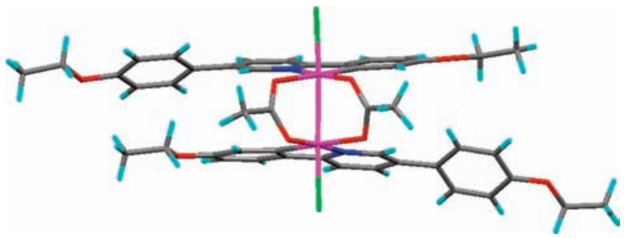


Chart 2. Molecular Structure of **6**-2,1^a

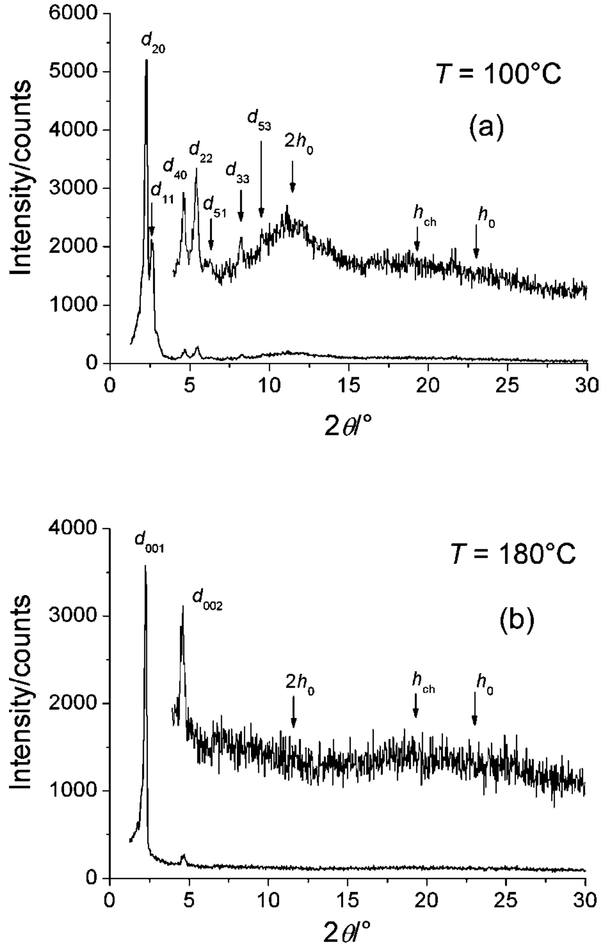


^{a} Molecules of $CHCl_3$ of crystallization are omitted for clarity (Figure S1).

This complex is a direct analogue of the $\mathrm{Pd^{III}}$ dimer reported by Powers and Ritter[7] containing an *ortho*metalated Bzq ligand, except that their complex was stable only below −30 °C in the solid state; above this temperature it eliminated 10-chlorobenzo[*h*]-quinoline leaving a mixture of undefined $\mathrm{Pd^{II}}$ complexes. Complexes **6**-*n*,*m* are shown by TGA analysis to be stable to over 200 °C. This type of complex has not been reported previously for $\mathrm{Pt^{III}}$, the closest analogue being a di-μ^2-acetato complex described by Steele and Vrieze (Figure S2).[20]

However, as indicated above, previously $\mathrm{M^{III}}$ and $\mathrm{M^{IV}}$ (M = Pd, Pt) complexes were obtained by direct oxidation of $\mathrm{M^{II}}$ precursors, but in this case the identity of the oxidizing agent was not immediately apparent as the reaction was carried out with the rigorous exclusion of atmospheric oxygen. Attention therefore turned to the coordinated dmso, and its role as the oxidizing agent was established when the reaction was repeated using *cis*-$[PtCl_2(S(Me)Et)_2]$ as starting material, which led simply to **5**-*n* with coordinated methylethylsulfide with no trace of **6**. Further evidence was provided (Chart 1) by the observation that reaction of **4**-12 with acetic acid led smoothly to **6**-12,1, consistent with the need for both dmso and acidic conditions as now described.

Chart 3. Small-Angle X-ray Diffraction Pattern for **6**-14,1 at 100 °C (a) and 180 °C (b)



Thus, oxidation of $\mathrm{Pt^{II}}$ by coordinated dmso was established first in 1968 upon treatment of *cis*-$[PtCl_2(dmso)_2]$ with concentrated aqueous HCl to give *trans*-$[PtCl_4(SMe_2)_2]$.[21] It is now a more widely recognized reaction.[22] More recent and detailed mechanistic studies have shown the necessity for acidic conditions and implied that the reaction involves dissociation of dmso and then recoordination of $[\mathrm{dmsoH}]^+$ through oxygen, followed by successive intramolecular electron transfers and elimination of the oxygen as H_2O.[23] However, in all previous cases that we can find, the Pt product was in the +4 oxidation state, and while dinuclear $\mathrm{Pt^{III}}$ intermediates have been either proposed[24] or isolated[25] for other oxidation routes, none has been reported with coordinated dmso. Clearly then, in accord with the findings of Dick et al.,[10] the presence of acetate promotes a dinuclear, bridged motif which appears to constrain the Pt centers to the +3 oxidation state.

The difference in thermal stability of **6**-*n*,*m* and **1** has been noted already and so other examples were prepared to investigate the thermal properties more thoroughly, especially given that similar complexes with this extended *bis*-2,5-diphenylpyridine ligand (**3**-*n* and **4**-*n*) were liquid crystalline. Thus, investigations of **6**-14,1 by hot-stage polarizing optical microscopy and small-angle X-ray diffraction (Chart 3) showed that, from room temperature to 170 °C, the complex existed in a liquid-crystalline mesophase that could be indexed into the centered rectangular plane group *c*2*mm*, identified clearly from indexation of the reflections shown in Chart 3a; full indexation is found in Table S1. Above 170 °C, the mesophase transformed to show a lamellar (smectic) arrangement with two orders of reflection, d_{001} and d_{002}, corresponding to a repeat distance of 37.5 Å. The lower-temperature phase is assigned as a ribbon phase with a structure analogous to the Sm$\tilde{A}$ phase (Figure S3),[26] except that this is much more ordered. This is preferred over the alternative assignment as a Col$_r$ phase both because the molecular shape is not conducive to columnar phase formation and because of the similarity in the rectangular *b* dimension (35.7 Å) and the lamellar spacing in the higher-temperature phase (37.5 Å). However, this lamellar spacing is less than the molecular length (max. *ca*. 51 Å), which suggests either a tilted phase or one that is interdigitated, or both. Interdigitation would allow efficient filling of space as the complexes cannot pack well together side by side owing to the lateral carboxylate group, although a strongly tilted arrangement could achieve the same end. In this case, the correspondence between the rectangular *b*-parameter and d_{001} spacing would suggest a tilted ribbon phase, reducing the symmetry below *c*2*mm*, which is not excluded by the indexation. Microscopy shows that the ribbon phase is extremely well organized, while the smectic phase becomes quite fluid. However, there is strong paramorphosis, and so a characteristic texture was not obtained and so the data presently do not allow unequivocal resolution of this question.

With the notable exception of various dimetal tetracarboxylates of Cu, Rh, Ru, and Mo,[27] dinuclear metallomesogens are rare and with metal−metal bonded species being rarer still. There is one previous example of a metal−metal bonded complex showing nematic or smectic phases that uses ruthenium,[28] but no previous examples with platinum. Neither are there examples of a Pt^{III} liquid crystal. The closest analogous structures are found in dinuclear acetato-bridged dipalladium(II) complexes of azines,[29] which are similar to **6**-*n*,*m* except that there is no metal−metal bond and no axial Cl ligands.[30] As such, the present complexes are novel and without precedent.

However, of equal significance is the fact that oxidation of Pt^{II} to Pt^{III} is demonstrated using coordinated dmso rather than using I^{III}-based oxidants. The resulting complex is directly analogous to that proposed in palladium chemistry as having involvement in catalytic oxidative acetyloxylation and as such suggests alternative approaches in terms of both catalytic reactivity and mechanistic study.[7,9]

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Supporting Information Available: Details of the preparation of the complexes and their spectral and analytical data; cif file for complex **6**; representation of ribbon phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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