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# Characterization of an Unexpected Product in a Schiff Base Condensation Involving Platinum(II)

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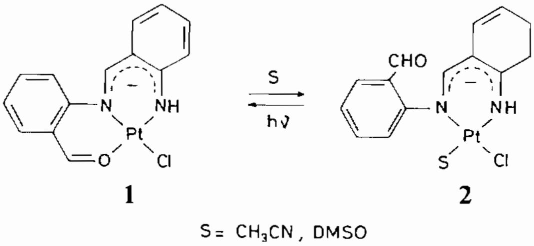
The Schiff base condensation of *o*-aminobenzaldehyde in the presence of platinum(II) ion has been shown to result in an intriguing tridentate/bidentate dimeric condensate [1, 2]. The dual nature of its denticity is the result of photochromic behavior and the lability of the terminal aldehyde [2]:



The aldehyde is quite receptive to further condensation reactions with a variety of amines [3]. The reactivity of the terminal amine of the ligand was thus also of interest, and it was thought to examine its potential for further Schiff base condensations by reacting the complex with *o*-(diphenylphosphino)benzaldehyde. It was predicted that either a Schiff base condensation would occur, or at the least, the benzaldehyde would displace the terminal aldehyde group of the coordinated ligand as observed for the reaction of triphenylphosphine with (**1**) [4]. In actuality the reaction which occurred was more complex than expected, yielding a mixture of reaction products, which were in most cases difficult to separate and characterize. One of the products, which crystallized from the reaction solution after one month, was suitable for X-ray analysis. The results of the structure showed that a somewhat unexpected side reaction had occurred.

## Experimental

### *Synthesis*

All chemicals were reagent grade. The *o*-(diphenylphosphino)benzaldehyde was synthesized by previously published methods [5], as was the starting complex, (**1**) [1]. To a solution of (**1**) (0.047 g, 0.10 mmol) in 25 ml of chloroform, *o*-(diphenylphosphino)benzaldehyde (0.31 g, 0.10 mmol) was added. The solution was stirred for several hours in the dark followed by slow evaporation over a period of ten days. The residue obtained was dissolved in 25 ml of acetonitrile, and was then placed in the dark and allowed to evaporate slowly. Orange crystals suitable for analysis by X-ray crystallographic techniques were obtained (along with a mixture of solids which were not analyzed).

### *Crystal Data*

$C_{26}H_{19}NO_2PtClPt$

M = 638.97, orthorhombic space group $Pna2_1$, $a$ = 18.88(2), $b$ = 13.10(1), $c$ = 9.66(1) Å, $D_{calc}$ = 1.775 g cm$^{-3}$ for $Z$ = 4, $D_{meas}$ = 1.75(1) g cm$^{-3}$, $\mu$(MoK$\alpha$) = 63.7 cm$^{-1}$.

A total of 3704 observed reflections were collected for $I > 3\sigma(I)$ on a Syntex P2$_1$ diffractometer as described previously [6] using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å). Neither decay nor absorption corrections were applied. The structure was solved by the heavy atom method and the positions of all non-hydrogen atoms were determined from subsequent Fourier maps**. Block-diagonal least-squares refinement in which calculated hydrogen atom positions were included as fixed contributions resulted in final $R_1$ = 0.043 and $R_2$ = 0.039. Atom parameters are listed in Table I and bond lengths and angles of interest in Tables II and III, respectively.

## Results and Discussion

Rather than yielding a Schiff base condensation product with *o*-(diphenylphosphino)benzaldehyde, the tridentate ligand associated with the original platinum complex was found to have evidently decomposed, and a new ligand, the result of Schiff base condensation of one molecule each of *o*-aminobenzaldehyde and *o*-(diphenylphosphino)benzaldehyde, was isolated as its platinum complex. Addi-

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**Programs for structure determination and refinement were written by Dr. B. K. Lee, National Institutes of Health. Programs for structure determination and refinement were local modifications of A. Zalkin's FORDAP for the Fourier summation, W. Busing, K. Martin, and H. Levy's ORFLS and ORFFE-II for least-squares and function and error calculations, and C. K. Johnson's ORTEP-II for the molecular structure drawing. Computations were performed on the Honeywell 66/60 computer at the University of Kansas. Tables of structure factors and anisotropic thermal parameters are available from author K.B.M. upon request.

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TABLE I. Final Positional Parameters.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt | 0.36681(2) | 0.02107(3) | 0.00000(0) |
| Cl | 0.3218(2) | 0.0896(3) | 0.2112(4) |
| P | 0.2857(2) | −0.1000(2) | 0.0105(9) |
| N | 0.4021(6) | −0.0217(9) | −0.1728(11) |
| O(1) | 0.4506(5) | 0.1281(7) | 0.0313(12) |
| O(2) | 0.5437(6) | 0.2079(9) | −0.0395(12) |
| C(1) | 0.3251(7) | −0.2175(9) | −0.0614(13) |
| C(2) | 0.3017(7) | −0.3114(10) | −0.0173(24) |
| C(3) | 0.3278(9) | −0.4034(10) | −0.0725(19) |
| C(4) | 0.3778(8) | −0.3959(11) | −0.1764(23) |
| C(5) | 0.4010(8) | −0.3003(11) | −0.2305(17) |
| C(6) | 0.3773(7) | −0.2103(10) | −0.1698(16) |
| C(7) | 0.4063(7) | −0.1149(10) | −0.2262(14) |
| C(8) | 0.4284(7) | 0.0585(10) | −0.2657(13) |
| C(9) | 0.4056(9) | 0.0582(13) | −0.4022(17) |
| C(10) | 0.4332(8) | 0.1325(12) | −0.4892(28) |
| C(11) | 0.4755(10) | 0.2104(14) | −0.4506(19) |
| C(12) | 0.4971(8) | 0.2128(12) | −0.3093(19) |
| C(13) | 0.4706(8) | 0.1351(11) | −0.2155(15) |
| C(14) | 0.4896(8) | 0.1453(11) | −0.0657(18) |
| C(15) | 0.2542(7) | −0.1386(9) | 0.1833( 4) |
| C(16) | 0.1789(11) | −0.1480(15) | 0.2102(21) |
| C(17) | 0.1632(10) | −0.1826(12) | 0.3522(22) |
| C(18) | 0.2121(12) | −0.2059(12) | 0.4467(17) |
| C(19) | 0.2861(9) | −0.1898(10) | 0.4164(17) |
| C(20) | 0.3040(8) | −0.1582(10) | 0.2847(16) |
| C(21) | 0.2067(7) | −0.0711(11) | −0.0876(14) |
| C(22) | 0.1762(10) | 0.0264(11) | −0.0720(20) |
| C(23) | 0.1139(10) | 0.0492(13) | −0.1385(21) |
| C(24) | 0.0819(8) | −0.0214(15) | −0.2276(25) |
| C(25) | 0.1105(9) | −0.1196(15) | −0.2415(20) |
| C(26) | 0.1749(15) | −0.1480(16) | −0.1650(20) |

TABLE II. Interatomic Distances (Å).

TABLE II. *(continued)*

| | |
|---|---|
| Pt–Cl | 2.386(4) |
| Pt–P | 2.206(3) |
| Pt–N | 1.88(1) |
| Pt–O(1) | 2.14(1) |
| P–C(1) | 1.84(1) |
| C(1)–C(6) | 1.44(2) |
| C(1)–C(2) | 1.37(2) |
| C(2)–C(3) | 1.40(2) |
| C(3)–C(4) | 1.38(2) |
| C(4)–C(5) | 1.43(2) |
| C(5)–C(6) | 1.39(2) |
| C(6)–C(7) | 1.47(2) |
| C(7)–N | 1.33(1) |
| N–C(8) | 1.47(2) |
| C(8)–C(13) | 1.37(2) |
| C(8)–C(9) | 1.39(2) |
| C(9)–C(10) | 1.39(2) |
| C(10)–C(11) | 1.35(2) |
| C(11)–C(12) | 1.42(2) |
| C(12)–C(13) | 1.45(2) |
| C(13)–C(14) | 1.51(2) |
| C(14)–O(1) | 1.24(2) |
| C(14)–O(2) | 1.26(2) |
| P–C(15) | 1.84(1) |
| C(15)–C(16) | 1.45(2) |
| C(16)–C(17) | 1.48(2) |
| C(17)–C(18) | 1.33(2) |
| C(18)–C(19) | 1.44(2) |
| C(19)–C(20) | 1.38(2) |
| C(20)–C(15) | 1.38(2) |
| P–C(21) | 1.81(1) |
| C(21)–C(22) | 1.41(2) |
| C(22)–C(23) | 1.37(2) |
| C(23)–C(24) | 1.40(3) |
| C(24)–C(25) | 1.40(2) |
| C(25)–C(26) | 1.47(3) |
| C(26)–C(21) | 1.39(2) |

TABLE III. Bond Angles (deg).

| | |
|---|---|
| P–Pt–N | 94.2(4) |
| N–Pt–O(1) | 93.3(4) |
| O(1)–Pt–Cl | 84.0(3) |
| Cl–Pt–P | 89.1(2) |
| Pt–P–C(1) | 107.5(5) |
| P–C(1)–C(6) | 120(1) |
| P–C(1)–C(2) | 120(1) |
| C(6)–C(1)–C(2) | 120(3) |
| C(1)–C(2)–C(3) | 122(2) |
| C(2)–C(3)–C(4) | 117(1) |
| C(3)–C(4)–C(5) | 122(1) |
| C(4)–C(5)–C(6) | 119(1) |
| C(5)–C(6)–C(7) | 116(1) |
| C(1)–C(6)–C(7) | 125(1) |
| C(5)–C(6)–C(1) | 118(1) |
| C(6)–C(7)–N | 128(1) |
| C(7)–N–Pt | 130(1) |
| C(7)–N–C(8) | 114(1) |
| Pt–N–C(8) | 117(1) |
| N–C(8)–C(9) | 118(1) |
| N–C(8)–C(13) | 120(1) |
| C(13)–C(8)–C(9) | 121(1) |
| C(8)–C(9)–C(10) | 117(2) |
| C(9)–C(10)–C(11) | 126(2) |
| C(10)–C(11)–C(12) | 117(2) |
| C(11)–C(12)–C(13) | 119(2) |
| C(12)–C(13)–C(14) | 114(1) |
| C(12)–C(13)–C(8) | 120(1) |
| C(8)–C(13)–C(14) | 113(1) |
| C(13)–C(14)–O(1) | 122(1) |
| C(14)–O(1)–Pt | 121(1) |
| C(13)–C(14)–O(2) | 118(1) |
| O(1)–C(14)–O(2) | 119(2) |
| Pt–P–C(15) | 117.6(3) |
| P–C(15)–C(16) | 120(1) |
| C(15)–C(16)–C(17) | 113(2) |
| C(16)–C(17)–C(18) | 124(2) |
| C(17)–C(18)–C(19) | 120(2) |

*(continued on facing page*

TABLE III. *(continued)*

| | |
|---|---|
| C(18)–C(19)–C(20) | 118(2) |
| C(19)–C(20)–C(15) | 123(1) |
| C(16)–C(15)–C(20) | 122(1) |
| C(20)–C(15)–P | 118(1) |
| C(1)–P–C(15) | 104.1(4) |
| Pt–P–C(21) | 113.5(2) |
| P–C(21)–C(22) | 118(1) |
| C(21)–C(22)–C(23) | 120(2) |
| C(22)–C(23)–C(24) | 121(2) |
| C(23)–C(24)–C(25) | 120(2) |
| C(24)–C(25)–C(26) | 120(2) |
| C(25)–C(26)–C(21) | 116(2) |
| C(26)–C(21)–C(22) | 122(1) |
| C(26)–C(21)–P | 119(1) |
| C(1)–P–C(21) | 108.1(5) |
| C(15)–P–C(21) | 105.4(2) |

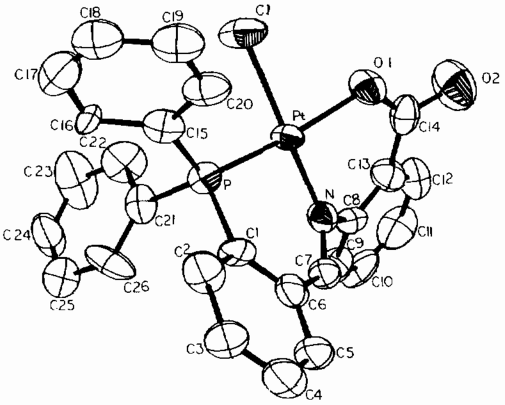
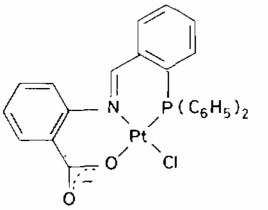


Fig. 1. Perspective view.

tionally, the anticipated terminal aldehyde of such a reaction was apparently oxidized in the process, resulting in a coordinated carboxylato group (3). A perspective view of the molecule is shown in Fig. 1.



3

The complex is, as expected for platinum(II), planar, with the platinum atom coordinated to the phosphorus, nitrogen, and oxygen atoms of the Schiff base condensate and to a chloride atom. The overall structure of the complex resembles that of its precursor (*1*) (*e.g.* a coordinated chloride ion and a tridentate ligand derived from a Schiff base condensation). There is a difference in the charge carrier in the new ligand, however. Instead of the negative charge being delocalized in the deprotonated *o*-aminobenzylidene ring as in (1) and (2), the carboxylate carries the charge for the new ligand in (3). As can be seen in the Figure, the chelating ligand is not planar, the dihedral angle between the mean planes defined by the two benzo groups is 128°.

Bond lengths within the immediate coordination sphere of the platinum ion reflect a certain degree of strain. The Pt–N bond is significantly shorter compared to the corresponding bond in its precursor (1) [1] and the triphenylphosphine analog of (2) [4] (1.88(1) Å *vs.* 1.99(1) and 2.07(1) Å, respectively). There appears to be no apparent cause for this observation. The platinum complex can be compared with two copper(I) complexes resulting from the condensation of *o*-(diphenylphosphino)benzaldehyde with ethylenediamine and containing both diphenylphosphino and imino moieties [7]. The potentially tetradentate ligand is the result of the condensation of two molecules of the aldehyde with one of the diamine, but one of the copper complexes isolated exhibits only P,N,P coordination, *i.e.* one of the imines is not coordinated. In neither of these complexes are the Cu–N bonds unusually shortened (averaging 2.07 Å). The copper complexes maintain a relatively distorted tetrahedral geometry as opposed to the square planar platinum complex, yet the P–M–N 'bite' angles for the former are apparently more strained (averaging 90.9° for the tetradentate form and 92.1° for the tridentate isomer compared to the somewhat less strained 94.2(4)° for the platinum complex.

Additionally of interest is the relatively short Pt–P bond length of 2.206(3) Å in (3), which can be compared to those in the triphenylphosphine adduct of (1) of 2.274(5) Å [4] and in dichlorobis(triphenylphosphine)platinum(II) of 2.335(3) Å [8]. The shortened Pt–P bond can be considered to be a reflection of the strong *trans* effect of phosphorus which can be exerted in the presence of the opposing more weakly coordinating carboxylato group. Similar findings have been observed in other *trans* phosphine complexes [9–11]. Correspondingly, the Pt–O bond length of 2.14(1) Å is considerably longer than that of the precursor aldehyde (1) which is 2.01(1) Å [1]. This again is obviously related to the *trans* influence of the phosphine.

The conclusion to be drawn from the mixture of products of this reaction is that the coordinated imino functionality is not necessarily as activated toward Schiff base condensations as the coordinated aldehyde, since the aldehyde reaction proceeds cleanly to the condensation product in high yield with no detectable side-products. Condensations on coordinated amines are known, as exemplified by Sargeson's work with the sepulchrates [12, 13]. Nonetheless, to this author's knowledge these invariably involve amino rather than imino functionalities. It is probable that the delocalization of the negative charge throughout the chelate ring drastically reduces any potential nucleophilicity of that terminal nitrogen.

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