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Unusual Transformation of Trialkylamines Mediated by Platinum

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*Summary: An interesting chemical transformation of trialkylamines has taken place during the reaction of 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**1**) with $K_2[PtCl_4]$ in refluxing methanol in the presence of trialkylamines, leading to the formation of organoplatinum complexes (**2** and **3**), where ligand **1** is coordinated as a bidentate N,O donor and the transformed trialkylamines are coordinated as bidentate C,N donors.*

There has been considerable current interest in metal-mediated chemical transformations of organic molecules.[1] Such reactions often proceed via a C−H bond activation step, leading to the formation of an organometallic complex as the reactive intermediate,[2] which then undergoes further reactions to yield the final product. Metal-mediated C−H bond activation of suitable organic molecules is therefore of significant importance, and the present work has originated from our interest in this area.[3] Recently we have observed very interesting C−H as well as C−C bond activation of 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**1**) mediated by ruthenium,[3c,e] osmium,[3c] and iridium,[3b] which has encouraged us to explore the reactivity of ligand **1** with other platinum metals. During this exploration we have observed an unusual chemical transformation of simple trialkylamines, viz. triethylamine and *N*-ethyldiisopropylamine, mediated by platinum and herein we wish to report our preliminary findings on this particular reaction.

Reaction of ligand **1** with $K_2[PtCl_4]$ has been first carried out in refluxing methanol in the presence of triethylamine, which has afforded a pinkish red complex (**2**).[4] The structure determination of complex **2** by X-ray crystallography[5] has revealed that, apart from coordination of ligand **1** to platinum, an unexpected interesting reaction has also taken place during the formation of this complex (Scheme 1). The structure (Figure

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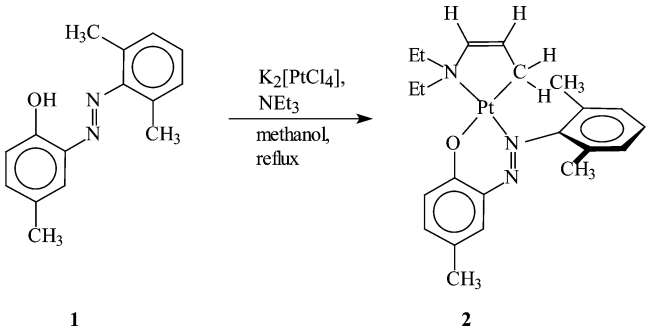
Scheme 1. Formation of Complex 2



1 **2**

1) shows that 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**1**) is coordinated to platinum, via dissociation of the phenolic proton, as a bidentate N,O donor, forming a six-membered chelate ring. The other two coordination sites of platinum are occupied by another bidentate C,N donor ligand, which has originated from triethylamine. The structure determination thus demonstrates that triethylamine, which was used to serve as a base, has undergone an unusual chemical transformation during the synthetic reaction and the transformed triethylamine remains coordinated to the metal center, forming a five-membered chelate ring. A closer look at the triethylamine-derived ligand shows that while two ethyl groups of the parent triethylamine have remained intact, one ethyl group has undergone several chemical changes, whereby it has been converted into a C(H)═C(H)CH_2 fragment. The observed bond distances within this fragment are consistent with its bond description. In complex **2** platinum is sitting in a CN_2O coordination sphere, which is distorted from ideal square-planar geometry, as reflected in the bond parameters around the metal center. However, the pendant 2′,6′-dimethylphenyl fragment of the coordinated ligand **1** as well as the two ethyl groups of the triethylamine-derived ligand are almost orthogonal to this square plane.

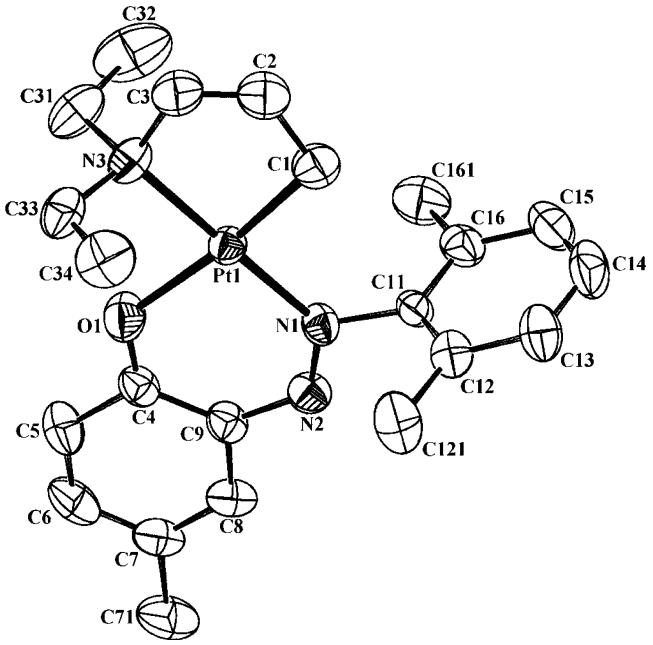


Figure 1. Molecular structure of complex **2** (50% probability ellipsoids). Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−C1 = 2.028(9), Pt1−N3 = 2.096(6), Pt1−N1 = 1.977(6), Pt1−O1 = 2.071(6), C4−O1 = 1.314(9), N1−N2 = 1.300(7), C1−C2 = 1.501(11), C2−C3 = 1.284(13), C3−N3 = 1.487(11); C1−Pt1−N3 = 84.4(3), N1−Pt1−O1 = 92.1(2), C1−Pt1−O1 = 172.8(3), N1−Pt1−N3 = 179.3(2).

The observed transformation of triethylamine, involving incorporation of a CH_2 fragment via C−C and Pt−C bond formation, and conversion of a C(H)C(H) fragment to a C═C fragment, has been very interesting. To test the generality of such a transformation, reaction of ligand **1** with $K_2[PtCl_4]$ has also been carried out in the presence of another base, viz. *N*-ethyldiisopropylamine. This particular base has been picked up as it has two different alkyl groups, viz. ethyl and isopropyl, and thus provides an opportunity to see which of these two alkyl groups actually undergoes the transformation. This new reaction has also afforded a pinkish red complex (**3**),[6] and its structure determination by X-ray crystallography[7] shows that, as before,

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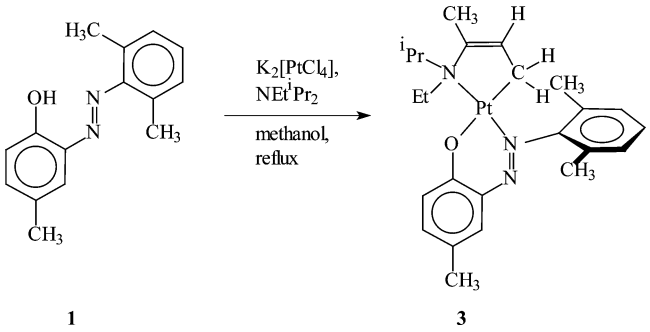
(4) Complex **2**: to a solution of 2-(2′,6′-dimethylphenylazo)-4-methylphenol (58 mg, 0.24 mmol) in hot methanol (30 mL) was added triethylamine (120 mg, 1.20 mmol) followed by $K_2[PtCl_4]$ (50 mg, 0.12 mmol). The mixture was then heated at reflux for 24 h, whereby a pinkish red solution was generated along with a black precipitate. The solution was filtered, and evaporation of the filtrate gave a dark solid, which was subjected to purification by thin-layer chromatography on a silica plate. Using 1:1 hexane−benzene as the eluant, a pinkish red band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave pinkish red crystals of **2**. Yield: 53 mg (40%). Anal. Calcd for $C_{22}H_{29}N_3OPt$: C, 48.3; H, 5.3; N, 7.7. Found: C, 47.8; H, 5.5; N, 7.6. Mass spectral data (positive ion ES): *m*/*z* 570 (M + Na), 547 (M + H). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.58 (s, C(8)H), 7.42 (d, J = 8.8 Hz, C(5)H), 7.07 (d, J = 7.5 Hz, C(13)H and C(15)H), 7.02 (t, J = 6.5 Hz, C(14)H), 6.79 (d, J = 8.7 Hz, C(6)H), 5.19 (m, C(3)H), 4.78 (m, C(2)H), 3.46 (m, 2H, C31), 2.42 (m, 2H, C33), 2.30 (s, 3H, C71), 2.22 (s, 6H, C121 and C161), 1.51 (m, 2H, C1), 1.42 (t, J = 7.12 Hz, 6H, C32 and C34). ^{13}C NMR ($CDCl_3$, 25 °C): δ 154.0 (C4), 151.8 (C9), 141.7 (C11), 138.5 (C5), 135.0 (C8), 132.4 (C6), 129.3 (C14), 127.5 (C13 and C15), 126.3 (C7), 124.4 (C12), 124.3 (C16), 57.8 (C33), 29.3 (C31), 19.6 (C71), 19.4 (C3), 16.7 (C121 and C161), 13.9 (C2), 12.6 (C32 and C34), 3.11 (C1). UV−vis spectral data (acetonitrile): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 538 (2100), 506 (2400), 434 (1500), 372 (4200), 310 (5300), 254 (14 800).

(5) (a) Crystallographic data for **2**: $C_{22}H_{29}N_3OPt$, M_r = 546.57, triclinic, space group $P1$, a = 7.941(9) Å, b = 9.115(12) Å, c = 16.865(17) Å, α = 81.037(10)°, β = 88.203(10)°, γ = 69.624(10)°, V = 1130(2) Å^3, Z = 2, μ = 6.223 mm^{-1}, T = 293 K, λ = 0.710 73 Å, R1 = 0.0367 wR2 = 0.0784, GOF = 1.07.

(6) Complex **3**: complex **3** was prepared similarly to complex **2**, using *N*-ethyldiisopropylamine instead of triethylamine. Yield: 42 mg (30%). Anal. Calcd for $C_{24}H_{33}N_3OPt$: C, 50.1; H, 5.7; N, 7.3;. Found: C, 50.5; H, 5.6; N, 7.5. Mass spectral data (positive ion ES): *m*/*z* 598 (M + Na), 575 (M). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.55 (s, C(8)H), 7.42 (d, J = 8.95 Hz, C(5)H), 7.06 (d, J = 7.4 Hz, 2H, C13 and C15), 7.01 (t, J = 7.4 Hz, C(13)H), 6.76 (d, J = 8.8, C(6)H), 4.98 (s, C(2)H), 3.79 (m, 1H, C31), 3.01 (m, 2H, C342), 2.29 (s, 3H, C121), 2.27 (s, 3H, C161), 2.19 (s, 3H, C71), 1.50 (d, J = 6.2, 3H, C32), 1.48 (m, 2H, C1), 1.30 (d, J = 7.93 Hz, 3H, C352), 1.29 (d, J = 7.93, 2H, C33), 1.26 (s, 3H, C37), 0.88 (m, 3H, C352). ^{13}C NMR ($CDCl_3$, 25 °C): δ 154.0 (C4), 151.8 (C9), 142.8 (C11), 141.0 (C5), 135.5 (C8), 132.8 (C6), 129.9 (C14), 128.2 (C13), 128.0 (C15), 126.8 (C7), 125.0 (C12), 124.8 (C16), 61.6 (C31), 49.4 (C342), 30.1 (C37), 21.6 (C71), 20.2 (C121 and C161), 19.8 (C2), 17.4 (C32), 17.3 (C33), 13.5 (C3), 10.5 (C352), 2.7 (C1). UV−vis spectral data (acetonitrile): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 544 (2000), 510 (2400), 434 (2100), 374 (5700), 312 (7600), 252 (18 500).

(7) (a) Crystallographic data for **3**: $C_{24}H_{33}N_3OPt$, M_r = 574.62, orthorhombic, space group $P2_12_12_1$, a = 7.965(9) Å, b = 16.941(17) Å, c = 17.97(2) Å, V = 2425 (5) Å^3, Z = 4, μ = 5.804 mm^{-1}, T = 293 K, λ = 0.710 73 Å, R1 = 0.1037, wR2 = 0.1529, GOF = 1.17.

Scheme 2. Formation of Complex 3



1 **3**

a similar interesting transformation of the *N*-ethyldiisopropylamine has taken place during the formation of this complex (Scheme 2). The structure (Figure 2) shows that 2-(2′,6′-dimethylphenylazo)-4-methylphenol (**1**) is coordinated to platinum as in complex **2** and another ligand, originating from *N*-ethyldiisopropylamine, is also coordinated to the metal center as a bidentate C,N donor. An inspection of the *N*-ethyldiisopropylamine-derived ligand shows that one isopropyl group has undergone a similar chemical transformation as before, whereby it has been converted into a $C(CH_3)=C(H)CH_2$ fragment, while the other isopropyl and ethyl groups have remained intact. The observed bond distances in this fragment are in good agreement with its bond description.

The observed chemical transformation of the trialkylamines, viz. triethylamine and *N*-ethyldiisopropylamine, has been very unusual and, to our knowledge, unprecedented. Incorporation of the CH_2 fragment in the trialkylamines has been the most interesting aspect of the observed transformations, and it may be relevant to mention in this context that such incorporation of a CH_2 fragment in organic molecules is rare.[8] Two sources

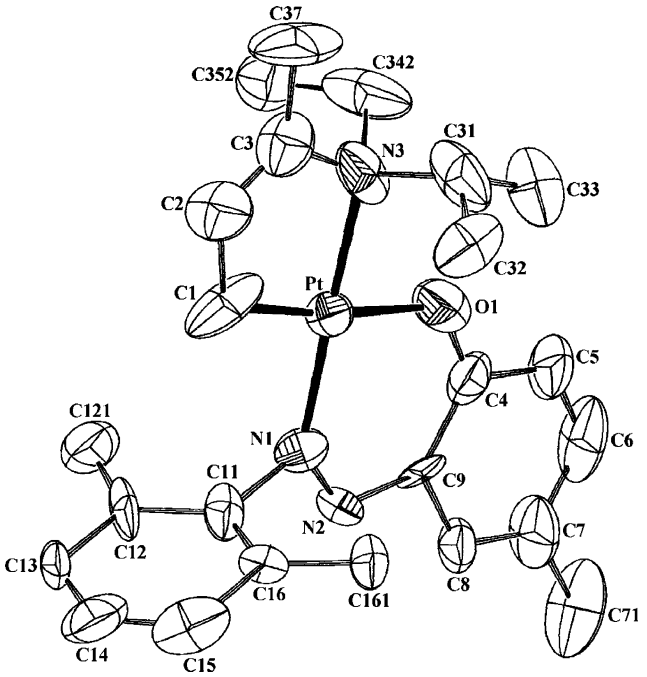
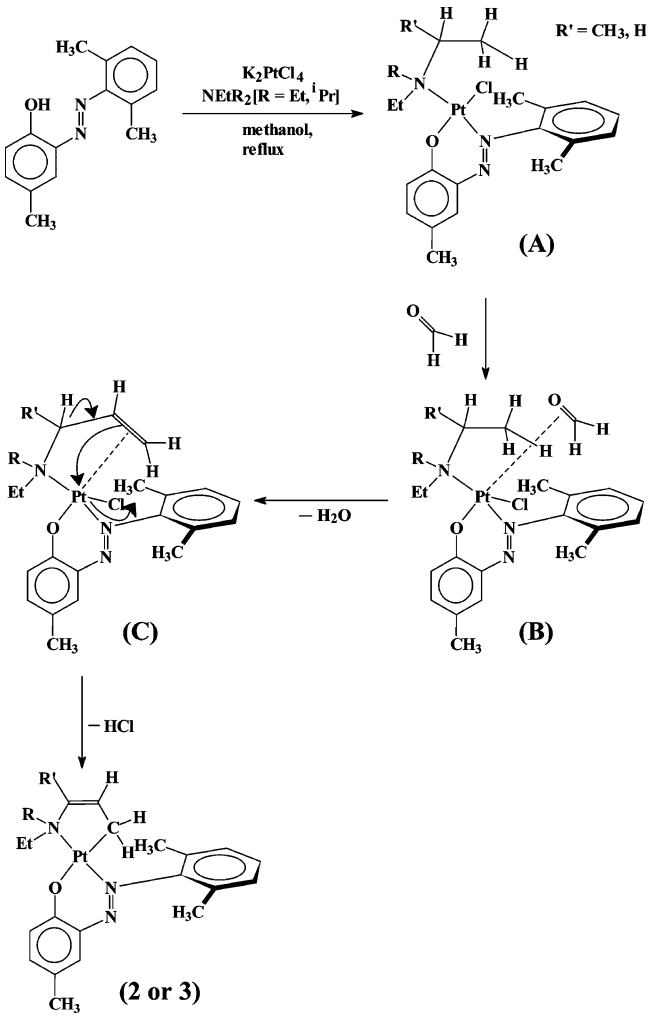


Figure 2. Molecular structure of complex **3** (50% probability ellipsoids). Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt-C1 = 1.95(2), Pt−N3 = 2.11(2), Pt−N1 = 1.976(15), Pt−O1 = 2.067(15), C4−O1 = 1.33(3), N1−N2 = 1.28(2), C1−C2 = 1.47(3), C2−C3 = 1.29(4), C3−N3 = 1.51(4); C1−Pt−N3 = 80.9(9), N1−Pt−O1 = 88.9(6), C1−Pt−O1 = 173.4(8), N1−Pt−N3 = 175.9(6).

Scheme 3. Probable Paths for the Formation of Complexes 2 and 3



of this CH_2 fragment are in principle probable: viz. the solvent methanol or ligand **1**. To sort this out, reaction of ligand **1** with $K_2[PtCl_4]$ has also been carried out in the presence of triethylamine similarly as before, using CD_3OD as the solvent instead of methanol. The pinkish red complex **4**, similar to complex **2**, is obtained from this reaction. Characterizations (^{1}H NMR, ^{2}H NMR, ^{13}C NMR and mass spectra) of complex **4** show it to be almost identical with complex **2**, except the metal-bound CH_2 fragment in **2** is replaced by a CD_2 fragment in **4**.[9] This clearly indicates that methanol has served as the source of the CH_2 fragment. It may be recalled at this point that complexes **2** and **3** are obtained in relatively low yields along with a notable quantity of a black precipitate.[4,6] It may be also be mentioned in this context that merely heating a solution of $K_2[PtCl_4]$ in

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(9) Complex **4**: complex **4** was prepared similarly to complex **2**, using CD_3OD instead of methanol. Yield: 53 mg (40%). Mass spectral data (positive ion ES): *m*/*z* 549 (M + H). ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.58 (s, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.09−6.99 (m, 3H), 6.79 (d, J = 8.9 Hz, 1H), 5.19 (d, J = 8.4 Hz, 1H), 4.78 (d, J = 8.5 Hz, 1H), 3.46 (m, 2H), 2.45 (m, 2H), 2.30 (s, 3H), 2.22 (s, 6H), 1.42 (t, J = 7.13 Hz, 6H). ^{2}H NMR ($CHCl_3$, 25 °C): δ 1.47 (s). ^{13}C NMR ($CDCl_3$, 25 °C):[12] δ 154.2 (C4), 151.9 (C9), 141.8 (C11), 138.6 (C5), 135.1 (C8), 132.5 (C6), 129.4 (C14), 127.6 (C13 and C15), 126.4 (C7), 124.5 (C12), 124.4 (C16), 57.8 (C33), 29.6 (C31), 19.7 (C71), 19.5 (C3), 16.8 (C121 and C161), 14.0 (C2) 12.7 (C32 and C34). UV−vis spectral data (acetonitrile): λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}), 531 (2200), 504 (2400), 433 (1700), 372 (4500), 310 (6500), 252 (18 300).

methanol has been observed to produce black particles of elemental platinum along with formaldehyde.[10] The mechanism of the observed chemical transformation of the trialkylamines during the formation of complexes **2** and **3** is not completely clear to us. However, the speculative sequences illustrated in Scheme 3 seem probable. In the initial step an intermediate (**A)** is believed to be formed, which contains ligand **1**, coordinated as a bidentate N,O donor via loss of the phenolic proton, chloride, and trialkylamine coordinated to platinum through the nitrogen. In the next step formadehyde, generated in situ, binds to the metal center in a η^2 fashion (intermediate **B**), which is followed by a condensation reaction between the formaldehyde and a terminal CH_3 fragment of the trialkylamine (intermediate **C**). The new C═C fragment thus formed remains π-bonded to the metal center. In the final step elimination of a hydrogen ion and new Pt−C bond formation takes place associated with simultaneous cleavage of the Pt−Cl bond, yielding the organoplatinum complex (**2** or **3**). It may be mentioned here that though such transformation of trialkylamines has no precedence, metal-mediated transformation of triisopropylphosphine of similar nature is documented in the literature.[11]

The present study shows that, in combination with ligand **1**, platinum can mediate interesting transformations of trialkylamines in methanol medium involving incorporation of a CH_2 fragment from the solvent. This study also demonstrates that, given an option between ethyl and isopropyl groups, the latter undergoes the transformation.

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Supporting Information Available: CIF files giving crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited at the Cambridge Crystallographic Data Center (CCDC No. 256356 for **2** and 288927 for **3**).

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(10) Generation of formaldehyde was verified by preparing its 2,4-dinitrophenyl hydrazone derivative.

(11) (a) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Onate, E. *Organometallics* **2005**, *24*, 5180. (b) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Onate, E. *Organometallics* **2005**, *24*, 2030. (c) Baya, M.; Esteruelas, M. A.; Gonzalez, A. I.; Lopez, A. M.; Onate, E. *Organometallics* **2005**, *24*, 1225. (d) Esteruelas, M. A.; Gonzalez, A. I.; Lopez, A. M.; Onate, E. *Organometallics* **2004**, *23*, 4858. (e) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Onate, E. *Organometallics* **2004**, *23*, 1416.

(12) The same atom-labeling scheme, used for complex **2** (Figure 1), has been followed for complex **4**.