

## Preliminary communication

## First $\alpha$ -ketoacyl complex with planar *s-cis* oxalyl configuration. Crystal structure of *trans*-[Pt(COCOOME)(OH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (CF<sub>3</sub>SO<sub>3</sub>)

Jwu-Ting Chen <sup>\*</sup>, Yu-Sung Yeh, Gene-Hsiang Lee and Yu Wang

Department of Chemistry, National Taiwan University, Taipei 10764 (Taiwan)

(Received May 6th, 1991)

**Abstract**

The abstraction of chloride from *trans*-Pt(COCOOME)(Cl)(PPh<sub>3</sub>)<sub>2</sub> (**1**) by Ag(CF<sub>3</sub>SO<sub>3</sub>) yields methoxyoxalyl triflate complex *trans*-Pt(COCOOME)(OTf)(PPh<sub>3</sub>)<sub>2</sub> (**2**). Attempts to crystallize the triflate product in CH<sub>2</sub>Cl<sub>2</sub>/n-hexane under ambient conditions result in a cationic aquo complex, *trans*-[Pt(COCOOME)(OH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>) (**3**). Its oxalyl carbonyls are disposed in an unprecedented nearly planar *s-cis* configuration in the solid-state structure.

$\alpha$ -Ketoacyl complexes have been proposed as intermediates in double carbonylation reactions [1]. Mechanistic investigation indicates that the C–C bond formation in the Pd-catalyzed double carbonylation reactions is likely established by reductive elimination of two “acyl” ligands in the species of the type RC(O)–Pd–C(O)Y (R = hydrocarbyl, Y = OR' or NR'<sub>2</sub>) [2–5]. On the other hand, consecutive CO insertion in the acyl complexes, yielding  $\alpha$ -ketoacyl intermediates, is considered to be an energetically disfavored process [5,6]. However, the formation of  $\alpha$ -ketoacyl complexes by a rare insertion of CO into a metal–acyl bond was indeed observed in several early transition metal complexes through the promotion of an oxidation/NO addition reaction sequence [7,8,9]. A relatively feasible method to prepare  $\alpha$ -ketoacyl complexes is by the oxidative addition reactions of electron-rich metal complexes (or anions) with  $\alpha$ -ketoacyl halides [2,5,6,10]. Using the ( $\alpha$ -ketoacyl)chloroplatinum(II) complexes in the form of *trans*-Pt(COCOR)(Cl)(PPh<sub>3</sub>)<sub>2</sub> as the starting material, we have further prepared several novel  $\alpha$ -ketoacyl derivatives of platinum(II) [11,12]. The X-ray single crystal structures of several stable  $\alpha$ -ketoacyl complexes have been determined [9–12]. A common feature of the known  $\alpha$ -ketoacyl ligands is the *s-trans* configuration of their oxalyl carbonyls, whose torsional angle, however, randomly ranges from a nearly perpendicular 102° to the planar 177°. We herein report a cationic aquo  $\alpha$ -ketoacyl complex which contains the unprecedented *s-cis* planar oxalyl moiety.

The abstraction of Cl<sup>−</sup> from *trans*-Pt(COCOOME)(Cl)(PPh<sub>3</sub>)<sub>2</sub> (**1**) by an equimolar amount of AgOTf (OTf = CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>) in CH<sub>2</sub>Cl<sub>2</sub> under dried N<sub>2</sub> at 20 °C

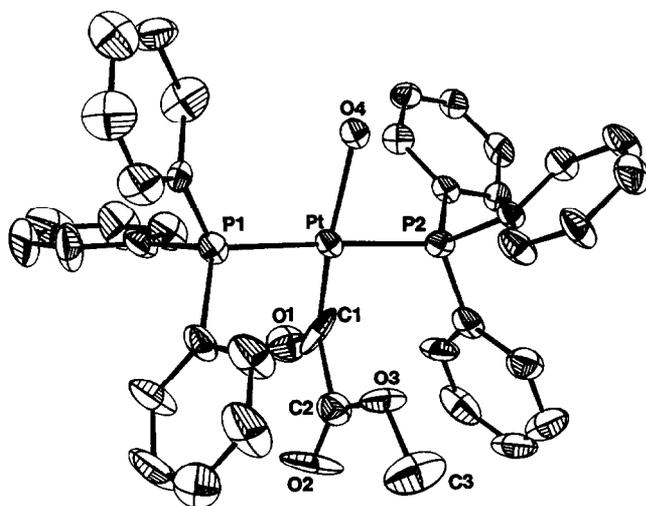


Fig. 1. The ORTEP drawing of complex **3** (all hydrogen atoms are omitted). Some bond distances and angles: Pt–P1 2.312(6), Pt–P2 2.307(7), Pt–C1 1.83(2), Pt–O4 2.17(1), C1–C2 1.58(3), C1–O1 1.26(3), C2–O2 1.16(3), C2–O3 1.31(3), C3–O3 1.46(3) Å; P1–Pt–P2 177.3(2), P1–Pt–C1 92.0(7), P1–Pt–O4 94.6(4), P2–Pt–C1 86.9(7), P2–Pt–O4 86.6(4), C1–Pt–O4 173.4(8), Pt–C1–C2 127(1), Pt–C1–O1 128(2), C2–C1–O1 104(2), C1–C2–O2 128(2), C1–C2–O3 106(2), O2–C2–O3 126(2)°.

leads to a meta-stable species which presumably is the triflate complex [13], *trans*-Pt(COOCOMe)(OTf)(PPh<sub>3</sub>)<sub>2</sub> (**2**). Attempts at crystallization of **2** in CH<sub>2</sub>Cl<sub>2</sub>/n-hexane in ambient atmosphere result in a cationic yellow crystalline aquo derivative, *trans*-[Pt(COOCOMe)(OH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>) (**3**), in a 93% yield [14\*]. Complex **2** showed a <sup>31</sup>P NMR resonance at δ 22.78 (*J*(P–Pt) = 3308 Hz) in CDCl<sub>3</sub>; in the <sup>1</sup>H NMR spectrum its methyl protons were observed as a singlet at δ 3.03. Complex **3** exhibited ν(CO) infrared stretching bands at 1735 (sh), 1721, 1670 and 1637 cm<sup>-1</sup>; ν(OH) at 3200 cm<sup>-1</sup>; and a strong sulfonyl absorption for the triflate counteranion at 1285 cm<sup>-1</sup>. In its <sup>31</sup>P NMR spectrum in CDCl<sub>3</sub>, broadened resonances were found at δ 22.21 (*J*(P–Pt) = 3306 Hz) and δ 22.67 (*J*(P–Pt) = 3234 Hz). The methoxyoxalyl signal in the <sup>1</sup>H NMR spectrum of **3** is at δ 3.02, essentially same as that of **2**. A broad peak observed at δ 1.8 is ascribed to the aquo protons. The addition of H<sub>2</sub>O to the solution of **2** provided identical spectroscopic results with those of **3**.

The structure of complex **3** has been confirmed by X-ray crystallography [14]. To our knowledge, only one organoquo complex of Pt<sup>II</sup> has even been structurally characterized [15]. The ORTEP plot of **3** is illustrated in Fig. 1, in which all hydrogen atoms are omitted. The molecular structure was a normal *trans* square-planar geometry. The most intriguing feature is that the vicinal carbonyls of the methoxyoxalyl ligand, unlike all known α-ketoacyl ligands, are disposed in an unprecedented nearly planar *s-cis* configuration with the torsional angle O1–C1–C2–O2 being 10(1)°. The reason for holding such an unique structure is not immediately clear. It could simply originate from the requirement of packing of the

\* Reference number with asterisk indicates a note in the list of references.

complex in the crystal. Considering the rather long C1–C2 bond, one may assume that the rotation energy along this bond is not necessarily large, particularly in solutions. It is therefore not surprising that no unusual chemical behavior of **3** has been observed yet. Water has been considered to be a weak donor ligand in the complexes of Pt<sup>II</sup> [16,17]. This is supported by the relatively long distance of the Pt–O(4) bond in **3**, being 2.17(1) Å. The weak Pt–OH<sub>2</sub> interaction probably makes the metal center gain compensation by strengthening its *trans* Pt–C1 bond to cause the unusually short length of 1.83(2) Å, although it could be somewhat exaggerated by the decay of crystal quality during irradiation [14\*]. The weak coordination of water in **3**, resulting in its ready replacement by CO, CH<sub>3</sub>CN, or PPh<sub>3</sub> and the facile decarbonylation of the methoxyoxalyl ligand, is consistent with its structural character, and is similar to its analogous complexes containing other weak-donor ligands [11].

**Supplementary material available.** Tables of complete crystal data, atomic coordinates of all non-hydrogen atoms, bond lengths and angles, thermal parameters, and a listing of structure factors for **3** are available from the authors.

**Acknowledgements.** We are grateful to the National Science Council, Taipei, R.O.C. for financial support.

## References and notes

- 1 F. Ozawa, T. Sugimoto, T. Yamamoto and A. Yamamoto, *Organometallics*, **3** (1984) 683.
- 2 F. Ozawa, T. Sugimoto, T. Yamamoto and A. Yamamoto, *Organometallics*, **3** (1984) 692.
- 3 L. Huang, F. Ozawa and A. Yamamoto, *Organometallics*, **9** (1990) 2603, 2612.
- 4 T.-M. Huang, J.-T. Chen, M.-C. Cheng and Y. Wang, *Organometallics*, **10** (1991) 175.
- 5 J.-T. Chen and A. Sen, *J. Am. Chem. Soc.*, **106** (1984) 1506.
- 6 C.P. Casey, C.A. Bunnell and J.C. Calabrese, *J. Am. Chem. Soc.*, **98** (1976) 1166.
- 7 J.B. Sheridan, G.L. Geoffroy and A.L. Rheingold, *J. Am. Chem. Soc.*, **109** (1987) 1584.
- 8 J.B. Sheridan, S.H. Han and G.L. Geoffroy, *J. Am. Chem. Soc.*, **109** (1987) 8097.
- 9 J.B. Sheridan, J.R. Johnson, B.M. Handwerker and G.L. Geoffroy, *Organometallics*, **7** (1988) 2404.
- 10 A. Sen, J.-T. Chen, W.M. Vetter and R.R. Whittle, *J. Am. Chem. Soc.*, **109** (1987) 148 and references therein.
- 11 T.-M. Huang, Y.-J. You, C.-S. Yang, W.-H. Tzeng, J.-T. Chen, M.-C. Cheng and Y. Wang, *Organometallics*, **10** (1991) 1020.
- 12 J.-T. Chen, T.-M. Huang, M.-C. Cheng and Y. Wang, *Organometallics*, accepted.
- 13 P.J. Stang, M.H. Kowalski, M.D. Schiavelli and D. Longford, *J. Am. Chem. Soc.*, **111** (1989) 3347.
- 14 Crystal data: C<sub>39</sub>H<sub>35</sub>O<sub>3</sub>Pt·CF<sub>3</sub>SO<sub>3</sub>·2n-hexane, FW = 1146.17 monoclinic, *P*2<sub>1</sub>/*n*, *a* = 17.981(9), *b* = 15.142(4), *c* = 18.613(9) Å, β = 115.97(4)°, *V* = 4556(3) Å<sup>3</sup>, *Z* = 4, λ(Mo-K<sub>α</sub>) = 0.7107 Å, *T* = 300 K, 2θ<sub>max</sub> = 45°. Total reflections, 5946; least-squares refinement on 4150 reflections, *I* > 2.0σ(*I*), for 487 variables led to *R* = 0.069, *R*<sub>w</sub> = 0.071. A 10% intensity drop occurred during data collection. The atomic parameters of n-hexane solvent are not refined at the final cycle of the least-squares.
- 15 A.R. Siedle, W.B. Gleason, R.A. Newmark and L.H. Pignolet, *Organometallics*, **5** (1986) 1969.
- 16 J.A. Davis and F.R. Hartley, *Chem. Rev.*, **81** (1981) 79.
- 17 F.R. Hartley and J.A. Davis, *Rev. Inorg. Chem.*, **4** (1982) 27.