Inorganica Chimica Acta, *87* (1984) L19–L21

Chemistry of Metal–Diene Complexes; A Direct, Convenient Route to Acyloxy-Bridged Dinuclear Platinum Complexes and X-Ray Crystal Structure of $[Pt_2(\mu\text{-}OAc)_2(C_8H_{12}OAc)_2]$

ANIL B. GOEL*

Ashland Chemical Company, Ventures Research & Development, P.O. Box 2219, Columbus, Ohio 43216, U.S.A.

and DON VANDERVEER

School of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332, U.S.A.

Received February 17, 1984

Dichloro(1,5-cyclooctadiene) platinum(II) has been used frequently for the synthesis of various complexes by ligand substitution [1–4] and nucleophilic addition reactions [5–7]. We have also been engaged in the reactions of $(COD)MCl_2$ (M = Pt or Pd; COD = 1,5-cyclooctadiene) with sterically bulky phosphine ligands [8] and various nucleophiles, and have recently reported the convenient synthesis of dinuclear complexes of the type $[(C_8H_{12}OCH_3)MX]_2$ (M = Pt or Pd and X = Cl or OCH_3). We also demonstrated these to be useful starting materials for one step synthesis of bis-tertiary phosphine metal(II) hydrides [9] and coordinatively unsaturated metal(0) complexes [10]. In continuation to our investigations in this area, now we have developed a convenient and general synthesis for the rapid preparation of acyloxy-bridged dinuclear platinum complexes, $[Pt_2(\mu\text{-}OCOR)_2(C_8H_{12}Y)_2]$ (*1*) (Y = OCH_3 or OCOR). Here we wish to present the general synthesis of complexes (*1*), their reactions with sterically bulky phosphines yielding the corresponding hydrido-platinum carboxylate complexes and the X-ray crystal structure of (*1*) (R = CH_3 and Y = $OCOCH_3$).

Although the nucleophilic attack of an acetate anion on $(COD)PtCl_2$ results in the formation of $[Pt_2(\mu\text{-}Cl)_2(C_8H_{12}OAc)_2]$ and the further interaction of acetate nucleophile provides the acetoxy-bridged diplatinum complex according to eqns. 1 and 2, these reactions require the use of silver acetate salt [11]. Furthermore, for the synthesis of each different carboxylate complex, one has to use the corresponding less readily accessible silver carboxylate salt. It has been found that the carboxylic acids, RCOOH (R = alkyl or perfluoroalkyl or aryl groups) react rapidly with the methoxy-bridged diplatinum complex, $[Pt_2(\mu\text{-}OCH_3)_2(C_8H_{12}OCH_3)_2]$ [9] (*2*), yielding the corresponding acyloxy-bridged diplatinum complex in near quantitative yields. Thus, when a benzene solution of (*2*) is allowed to react with one mole equivalent of carboxylic acid (*e.g.* acetic acid) per platinum for about 5 minutes at room temperature, exchange of methoxy- and acetate-groups takes place at the platinum center (eqn. 3). This exchange can be monitored by ^{1}HNMR where the methoxy-group protons signal at δ 3.55 ppm associated with platinum satellites (J_{PtH} = 14 and 39 Hz) disappears as the reaction proceeds. The reaction is found to be exceedingly fast in most of the cases and usually reaches completion within a minute. The solution affords white crystals of the complex, $[Pt(\mu\text{-}OAc)_2(C_8H_{12}OCH_3)_2]$, [IR: 1575 cm^{-1} (bridging acetate carbon-oxygen stretching frequency); ^{1}HNMR: Singlets at δ 1.90 ppm (due to acetate group protons) and δ 3.22 ppm (due to methoxy-group protons) in 1:1 ratio], upon concentration and addition of hexane in almost quantitative yield. When the above reaction is carried out in the presence of excess acetic acid (5 fold excess), complete exchange of methoxy-groups takes place yielding the complex $[Pt_2(\mu\text{-}OAc)_2(C_8H_{12}OAc)_2]$, [IR: 1725 and 1575 cm^{-1} (ester and ionic acetate carbon-oxygen stretching frequencies); ^{1}HNMR: Singlets at δ 1.72 and 1.92 ppm (due to ester and ionic acetate group protons) in 1:1 ratio]. The complex can be recrystallized from a mixture of benzene and hexane providing colorless crystals suitable for single-crystal X-ray diffraction.

$$\begin{tikzcd} (C_8H_{12})PtCl_2 + AgOAc \arrow[r] & \tfrac{1}{2}[(C_8H_{12}OAc)_2Pt_2Cl_2] \arrow[d, "AgOAc"'] & (1) \\ (C_8H_{12})PtCl_2 + 2AgOAc \arrow[r] & \tfrac{1}{2}[(C_8H_{12}OAc)_2Pt_2(OAc)_2] & (2) \end{tikzcd}$$

$$[(C_8H_{12}OCH_3)_2Pt_2(OCH_3)_2] + 2HOAc \longrightarrow [(C_8H_{12}OCH_3)_2Pt_2(OAc)_2] + CH_3OH \qquad (3)$$

$$[Pt_2(OCH_3)_2(C_8H_{12}OCH_3)_2] + AcOH(excess) \longrightarrow [Pt_2(OAc)_2(C_8H_{12}OAc)_2] + 4CH_3OH \qquad (4)$$

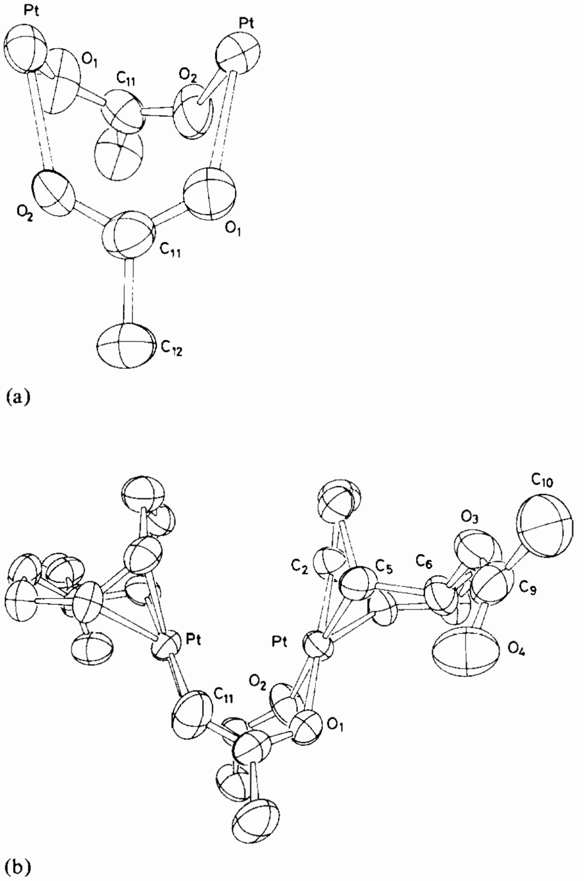
Unit-cell parameters and intensity data were obtained using a Syntex $P2_1$ four-circle diffractometer. The complex crystallized in the monoclinic space group C_2/C with a = 18.443(3), b = 9.276(3), c = 15.502(4) Å, β = 99.00(2)°, Z = 4 (MoKα radiation) with d_{exp} = 2.11 g cm^{-3} (d_{cal} = 2.13 g cm^{-3}). A semi empirical absorption correction using $\psi°$ scans was applied to the measured intensities. 1915 unique reflections having $F \geq 3\sigma_F$ were collected.

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

The structure was solved [12] using conventional heavy-atom techniques. For a three-dimensional Patterson map, the position of the platinum was determined and subsequent electron density maps provided the positions of all the oxygen and carbon atoms. Hydrogen positions were either calculated by the program or located from Fouriers. The non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least squares refinement of all the atom positions and temperature factors yielded a final R of 0.035.



(a)

(b)

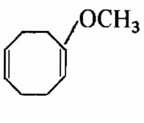
Fig. 1. ORTEP Diagram of $[(C_8H_{12}OAc)_2Pt_2(OAc)_2]$. Principal bond lengths (Å): Pt–O1 = 2.068(7), Pt–O2 = 2.166(7), Pt–C1 = 2.114(10), Pt–C2 = 2.105(10), Pt–C5 = 2.031(10), and bond angles (°): O2–Pt–O1 = 89.1(3), C1–Pt–O1 = 143.4(4), C1–Pt–O2 = 85.8(4), C2–Pt–O1 = 174.4(4), C2–Pt–O2 = 96.4(4), C2–Pt–C1 = 38.6(4), C5–Pt–O1 = 90.6(4), C5–Pt–O2 = 176.9(4), C5–Pt–C1 = 92.7(4), C5–Pt–C2 = 83.9(4).

Pertinent bond distances and angles are presented in Fig. 1. The complex is a dimer having a crystallographic two-fold axis of rotation. The bridging acetate-groups are bound asymmetrically to the platinums with two unique Pt–O distances differing by 0.098 Å. Interestingly, both the acetoxy-cyclooctadienyl groups are located on the same side of platinum and opposite side of acetate groups which are bonded to platinums with oxygen–platinum–oxygen angles as 89.1(3)°. The distance between two platinums has been determined to be 3.03 Å. The two carbons (C2 and C5) of acetoxy-octadienyl moiety and the oxygen of acetate groups are bonded to platinum in square planar geometry (Fig. 1b). A similar type of arrangement has been observed earlier by us in the pyrazolato-bridged diplatinum complex, $[Bu_2{}^tPCMe_2CH_2)_2Pt_2(Pz)_2]$ ($Pz = C_5H_7N_2$) where both the pyrazolato-groups were located on the same side forming a boat-form [13]. The acetate groups on the cyclooctadiene are observed to have exo-geometry with respect to platinums.

Complex (*1*) ($Y = OCH_3$) has been found to react readily with two mole equivalents of sterically bulky phosphine ligands ($R_3P = Cy_3P$, $Bu_2{}^tBu^nP$, $Pr_3{}^iP$, $Bu_3{}^tP$) per platinum in methanol to give the corresponding hydrido-platinum carboxylate, *trans*-$[PtH(OCOR)(PR_3)_2]$, in fairly good yields (60–85%). The organic product formed as in eqn. 5 was isolated by GLC; its elemental analysis, proton NMR and mass-spectral data suggested it to be methoxy-cyclooctadiene, $C_9H_{14}O$ (obs. m/e = 138.1). A mechanism involving β-hydrogen elimination from the 2-methoxy-5-cyclooctenyl group can be proposed for platinum hydride formation [9].

$$[(C_8H_{12}OCH_3)_2Pt_2(OAc)_2] + 4PR_3 \longrightarrow$$

$$2\ \textit{trans}\text{-}[PtH(OCOR)(PR_3)_2] + 2$$



(5)

Preliminary results indicate that the exchange reactions of complex (*2*) with various other reagents with reactive protons (*e.g.* pyrazole, amines, secondary phosphines, etc.) also proceed in a manner similar to that outlined in eqns. 3 and 4 yielding the corresponding exchanged products. A detailed study is currently in progress.

References

1 J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).
2 F. R. Hartley, 'The Chemistry of Platinum and Palladium', Applied Science, London, 1973, Chapter 13.
3 H. C. Clark and L. E. Manzer, *J. Organomet. Chem., 59,* 411 (1973); G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem., 20,* 1636 (1981); *20,* 3607 (1981).
4 A. B. Goel and S. Goel, *Inorg. Chim. Acta, 59,* 237 (1982).
5 C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani and U. Belluco, *J. Chem. Soc. Chem. Comm., 187,* (1969); B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian and D. A. White, *J. Chem. Soc. (A),* 1793 (1969) and references therein.
6 R. N. Haszeldine, R. U. Parish and D. W. Robbins, *J. Chem. Soc. Dalton,* 2355 (1976) and references therein.

7 J. Soulie, J. C. Chottard and D. Mansucy, *J. Organometal. Chem., 171,* 113 (1979).

8 A. B. Goel and S. Goel, *J. Ind. Chem. Soc., 59,* 141 (1982).

9 A. B. Goel and S. Goel, *Inorg. Chim. Acta, 45,* L185 (1980); H. C. Clark, A. B. Goel and S. Goel, *J. Organomet. Chem., 216,* C25 (1981); A. B. Goel, S. Goel and D. VanDerVeer, *Inorg. Chim. Acta, 54,* 169 (1981).

10 A. B. Goel and S. Goel, *Inorg. Chim. Acta, 77,* L5 (1983).

11 C. B. Anderson and B. J. Burreson, *Chem. Ind.,* 620 (1967).

12 Sheldrick's SHELX-76 program was used for solution and refinement of the structure.

13 A. B. Goel, S. Goel and D. VanDerVeer, *Inorg. Chim. Acta, 82,* L9 (1984).