

Chemistry of Metal–Diene Complexes; Isolation, X-Ray Crystal Structure and Reactions of Methoxy-Bridged Dinuclear Platinum Complex $[\text{Pt}_2(\mu\text{-OCH}_3)_2(\text{C}_8\text{H}_{12}\text{OCH}_3)_2]$ with Tertiary Phosphines

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One of the most convenient methods of preparing metal hydrides of the type $[\text{MH}(\text{X})\text{L}_2]$ is the reaction of an alkoxide anion with the corresponding metal halide complex [1]. This presumably involves incipient formation of an alkoxo-complex followed by a β -elimination. Recently some mono-nuclear methoxy-platinum complexes of the type $[\text{PtR}(\text{OMe})(\text{PPh}_3)_2]$ [2, 3], and a mixed methoxy- and chloro-bridged dinuclear platinum complex, $[\text{Pt}_2(\mu\text{-OMe})(\mu\text{-Cl})(\text{Bu}^t\text{PCMe}_2\text{CH}_2)_2]$ [4], have been prepared by the metathesis of corresponding chloro-complex with NaOMe. Bennett *et al.*, [5] reported the formation of a methoxy-platinum complex from the oxidative addition of methanol to a zero valent hexanyl-platinum complex. In the course of our investigations on diene complexes of metals [6], we have isolated a stable dinuclear platinum complex containing bridging methoxy-groups, $[\text{Pt}_2(\mu\text{-OCH}_3)_2(\text{C}_8\text{H}_{12}\text{OCH}_3)_2]$ 1. We wish to present here its X-ray crystal structure and reactions with tertiary phosphine ligands. A most convenient preparation of dihydridoplatinum complexes, *trans*- $\text{PtH}_2(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PCy}_3$ and PPr_3^1) from the reaction of complex 1 with corresponding phosphine is also presented here.

When a suspension of $(\text{COD})\text{PtCl}_2$ (COD = 1,5-cyclo-octadiene) is treated with two equivalents of sodium hydroxide in aqueous methanol, a clear solution is formed within a few minutes [7], which on further stirring (≈ 15 minutes) afforded an air and moisture stable white crystalline solid in $\approx 90\%$ yield. Analysis of the recrystallized sample from a mixture of benzene/methanol, corresponds to $[\text{Pt}(\text{OCH}_3)(\text{C}_8\text{H}_{12}\text{OCH}_3)]_2$. This appears to be the same complex reported earlier by Chatt and co-workers [1], which they did not characterize conclusively. Perhaps due to the unusual stability of this complex towards moisture, these workers suggested the presence of methoxy-groups on the carbons of the

cyclooctadienyl moiety rather than on the platinum.

The ^1H NMR spectrum of this complex 1 consists of two types of methoxy signals, one at δ 3.55 ppm associated with two sets of platinum satellites ($J \text{ PtH} = 14$ and 39 Hz) and the other at δ 3.25 ppm with no platinum satellites. The former pattern suggests that the methoxy group is probably bonded with two platinum nuclei in an unsymmetrical fashion. This has been confirmed by the X-ray structure determination.

X-Ray Crystal Data

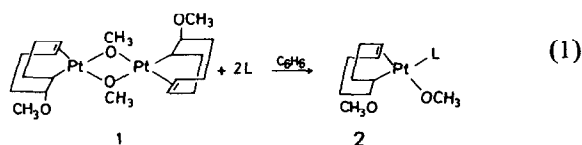
Unit cell parameters and intensity data were obtained using a Syntex P2₁ four-circle diffractometer. The complex crystallized in the monoclinic space group $\text{P2}_1/\text{c}$ with $a = 6.648(2)$, $b = 14.186(5)$, $c = 14.237(4)$ Å, $\beta = 126.30(2)^\circ$, $Z = 2$ ($\text{MoK}\alpha$ radiation). A semi-empirical absorption correction using ψ_ω scans was applied to the measured intensities.

The structure was solved* using conventional heavy-atom techniques and refined to a final R of 0.023 for 1684 observations having $F \geq 3\sigma_F$ and 131 variable parameters. The temperature factors of all non-hydrogen atoms were refined anisotropically. Hydrogen positions were either calculated by the program or located from difference Fouriers. Their temperature factors were refined isotropically.

The complex is a dimer located about a crystallographically imposed inversion center. The bridging methoxy groups are bound asymmetrically to the platinum with the two unique Pt–O distances differing by 0.119 Å.

Pertinent distances angles are presented in Fig. 1.

The methoxy-bridges of the complex 1 are readily cleaved by tertiary phosphine ligands in benzene solution resulting in the formation of corresponding mono-nuclear methoxy platinum complexes $[(\text{C}_8\text{H}_{12}\text{OCH}_3)\text{Pt}(\text{OCH}_3)\text{L}]$ 2 ($\text{L} = \text{Ph}_3\text{P}$, Pr_3^1P , Cy_3P , (*p*-tolyl) $_3\text{P}$).



In the ^1H NMR spectra of 2, the protons of the methoxy group attached to platinum appear as a

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

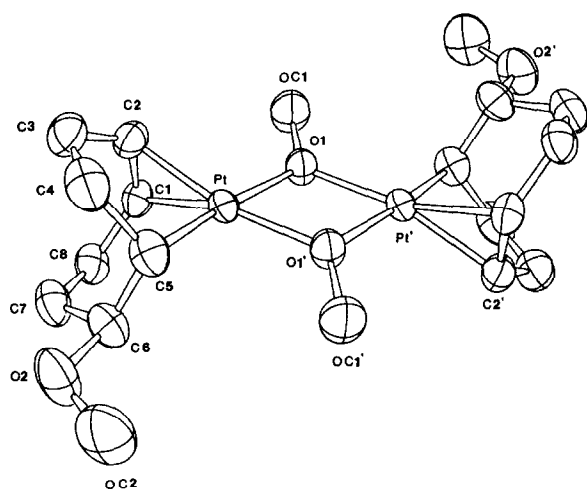
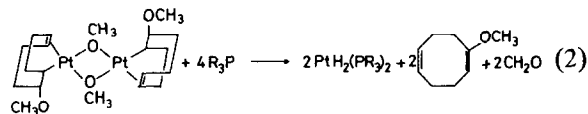


Fig. 1. ORTEP diagram of $[\text{Pt}_2(\mu\text{-OCH}_3)_2(\text{C}_8\text{H}_{12}\text{OCH}_3)_2]$. Principal bond lengths (Å): $\text{Pt}-\text{C}_1 = 2.093(5)$, $\text{Pt}-\text{C}_2 = 2.098(6)$, $\text{Pt}-\text{C}_5 = 2.028(6)$, $\text{Pt}-\text{O}_1 = 2.034(3)$, $\text{Pt}-\text{O}_1' = 2.153(3)$, and bond angles ($^\circ$): $\text{C}_1-\text{Pt}-\text{C}_2 = 39.6(2)$, $\text{C}_1-\text{Pt}-\text{O}_1 = 95.2(2)$, $\text{C}_2-\text{Pt}-\text{C}_5 = 82.5(3)$, $\text{C}_5-\text{Pt}-\text{O}_1' = 98.1(2)$, $\text{O}_1-\text{Pt}-\text{O}_1' = 76.2(3)$.

singlet associated with platinum satellites (e.g., when $\text{L} = \text{Ph}_3\text{P}$ or $(p\text{-tolyl})_3\text{P}$: $J_{\text{PtH}} \approx 54 \text{ Hz}$). ^{31}P NMR spectra contain only one main singlet associated with platinum satellites ($J_{\text{PtP}} \approx 1730 \text{ Hz}$) suggesting the presence of only one isomeric form of the complex. The smaller magnitude of the platinum–phosphorus coupling constant is in support of the structure in which the phosphine ligand is at the *trans*-position to the σ -bonded carbon of the 2-methoxy-5-cyclooctenyl group. These terminal methoxy complexes 2 are highly susceptible to moisture, readily producing hydroxo-complexes.

Preliminary results indicate that the reactions of complex 1 with sterically bulky tertiary phosphine

such as Cy_3P and Pr_3P in methanol, results in the formation of *trans*- PtH_2L_2 ($\text{L} = \text{Pr}_3\text{P}$, Cy_3P). This offers a new and convenient preparation of these dihydrido-platinum complexes. Presumably, β -H transfers from the 2-methoxy-5-cyclooctenyl group as well as methoxy-platinum group are involved in this reaction.



A detailed mechanistic study of this reaction as well as further investigations on the reactions of complexes 1 and 2 are currently in progress.

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- 7 Probably a complex $[(\text{C}_8\text{H}_{12}\text{OCH}_3)_2\text{Pt}_2(\mu\text{-Cl})_2]$ is formed at this stage of the reaction. See Ref. 1.
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