

Formation of Platinum(II) Compounds Containing Isomeric σ -Vinyllic and σ -Allylic Six-membered Chelate Rings by Deprotonation of the Co-ordinated Isopropenyl Group: X-Ray Structure of the σ -Vinyllic Complex Di- μ -acetato-bis[o -isopropenylphenyl(diphenyl)arsineplatinum(II)]

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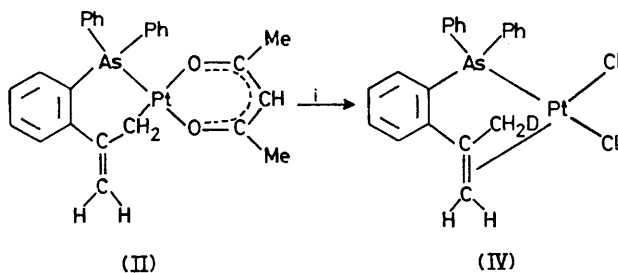
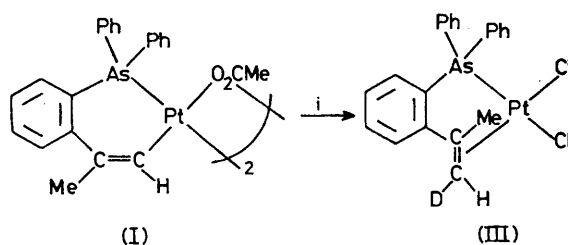
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Summary The o -isopropenylphenyl(diphenyl)arsine (ipa) compounds $\text{PtCl}_2(\text{ipa})$ and $[\text{Pt}(\text{acac})(\text{ipa})][\text{BF}_4]$ (Hacac = acetylacetonate) react with metal acetates to give, respectively, $[\text{AsPh}_2\text{C}_6\text{H}_4\text{-}o\text{-C}(\text{Me})=\text{CH}-\text{Pt}(\text{O}_2\text{CMe})_2]$ (I), shown from X-ray analysis to have the deprotonated olefin bonded to the platinum atom as a σ -vinyl group, and $[\text{AsPh}_2\text{C}_6\text{H}_4\text{-}o\text{-C}(\text{=CH}_2)\text{CH}_2-\text{Pt}(\text{acac})]$ (II) in which the ligand is bonded as a σ -allylic group.

In the past year there has been increasing interest in σ -allyl complexes of platinum.¹ We report the first X-ray structure of a bidentate σ -vinyl ligand complex and also the isolation and characterisation of a complex containing the isomeric σ -allyl form of the ligand.

When the o -isopropenylphenyl(diphenyl)arsine (ipa) complex $\text{PtCl}_2(\text{ipa})$ is treated with silver acetate in chloroform the yellow solution initially formed turns orange over several hours and, on dilution with methanol, orange

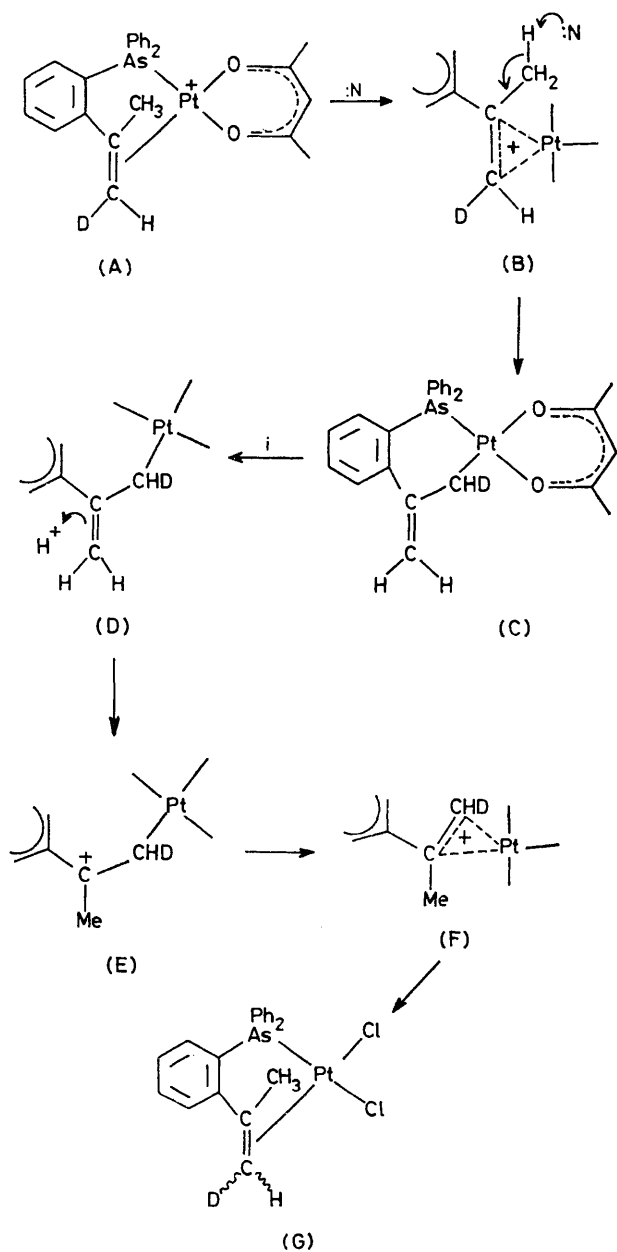
crystals of $[\text{AsPh}_2\text{C}_6\text{H}_4\text{-}o\text{-C}(\text{Me})=\text{CH}-\text{Pt}(\text{O}_2\text{CMe})_2]$ (I) are obtained. The molecule (I) has been shown by X-ray analysis to have an acetate-bridged dimeric structure (Figure) with the deprotonated olefin bonded to the platinum atom as a σ -vinyl group. ¹H N.m.r. studies of the formation of (I) in CDCl_3 solution indicate a reaction sequence in which $\text{Pt}(\text{O}_2\text{CMe})_2(\text{ipa})$ is initially formed and gradually loses acetic acid to give (I) [δ (I): 1.96 (s, Me), 1.43 (s, O_2CMe), and 7.21 (=CH); $\text{PtCl}_2(\text{ipa})$: 2.62 (s, Me, $J(\text{Pt-H})$ 37.8 Hz), 3.67 (s, =CH *trans* Me, $J(\text{Pt-H})$ 59.8 Hz), and 5.37 (s, =CH *cis* Me, $J(\text{Pt-H})$ 68.5 Hz); $\text{Pt}(\text{O}_2\text{CMe})_2(\text{ipa})$: 2.28 (s, Me), 3.52 (s, =CH *trans* Me), 4.72 (s, =CH *cis* Me), and 1.78 and 2.08 (2 \times s, O_2CMe)].



SCHEME 1. i, DCl.

When $[\text{Pt}(\text{acac})(\text{ipa})][\text{BF}_4]$ reacts with nucleophilic groups (acetate, methoxide, hydroxide, or triethylamine) the complex $[\text{AsPh}_2\text{C}_6\text{H}_4\text{-}o\text{-C}(\text{=CH}_2)\text{CH}_2-\text{Pt}(\text{acac})]$ (II) is formed. ¹H N.m.r. studies show that an isomeric form of the deprotonated ipa ligand is present, bonded to the platinum atom as a σ -allylic group, [δ 1.67 and 1.93 (2 \times s, acac Me groups), 2.99 (s, CH_2 , ² $J(\text{Pt-H})$ 121 Hz), 4.93 and 5.29 (2 \times d, = CH_2 , J (gem) 2.1 Hz), 5.36 (s, acacH), and 7.3—7.9 (ArH)].

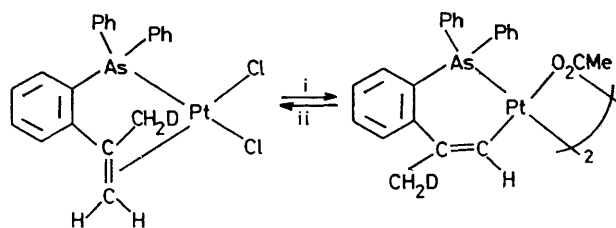
Conditions for interconversion of the two isomeric deprotonated forms of the ipa ligand have been found. Treatment of a solution of (I) with acetylacetonone and sodium carbonate in an attempt to prepare $\text{AsPh}_2\text{C}_6\text{H}_4\text{-}o\text{-C}(\text{CH}_3)=\text{CH-Pt}(\text{acac})$ resulted in a mixture of the desired product and (II). When (II) is treated with acetic acid, (I) is formed and this latter isomerism of the ligand has been shown by ^1H n.m.r. spectroscopy to occur *via* the intermediate $\text{Pt}(\text{O}_2\text{CMe})_2(\text{ipa})$.



SCHEME 2. :N = Nucleophile; i, 2HCl , $-\text{Hacac}$.

Both (I) and (II) react with HCl to give the protonated compound $\text{PtCl}_2(\text{ipa})$ and with DCl the deuteration is stereospecific giving the products (III) and (IV) respectively (Scheme 1). The deuterium labelled forms of $\text{PtCl}_2(\text{ipa})$ are being used in an investigation of the mechanism of formation of the isomeric deprotonated ligand compounds and their subsequent protonation.

The ^1H n.m.r. results indicate that in the formation of (II) (Scheme 2, A—C) the proton is lost from the methyl group and that there is a movement of the double bond position in the ipa ligand; this process is reversed on reprotonation (Scheme 2, C—G) and is well accounted for by a stabilised carbonium ion pathway.² This appears the best evidence to date for the application of this mechanism in a reaction of a co-ordinated olefin. In contrast, the formation of (I) involves no shift in the double bond position and the proton is lost from the terminal olefinic carbon atom (Scheme 3).



SCHEME 3. i, AgO_2CMe ; ii, HCl .

Crystal data: (I), $\text{C}_{46}\text{H}_{42}\text{As}_2\text{O}_4\text{Pt}_2$, monoclinic, space groups $C2/c$; $a = 31.633(5)$, $b = 11.345(3)$, $c = 18.450(4)$ Å, $\beta = 141.37(2)^\circ$, $U = 4133.6$ Å³, $Z = 4$. Intensity data were collected with a Phillips PW1100 four-circle diffractometer using $\text{Mo-K}\alpha$ radiation from a graphite monochromator. The non-chelating phenyl rings were treated as rigid groups (C—C, 1.395 Å) and the platinum and arsenic atoms were assigned anisotropic temperature factors. Full-matrix least-squares refinement using 2093 reflections with $I/\sigma(I) > 3.0$ has given a final R -value of 0.059.†

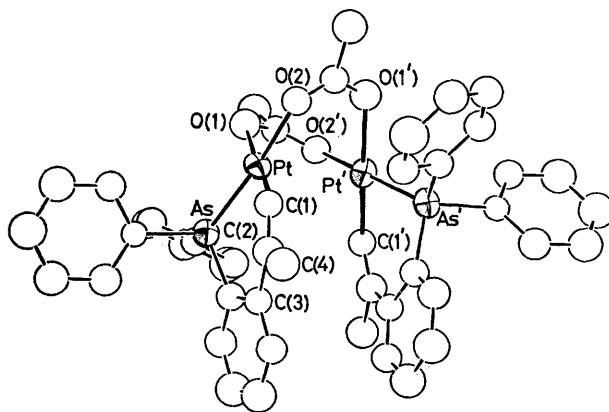


FIGURE. The structure of the acetate bridged σ -vinyl platinum complex (I). Important bond lengths and angles are: Pt—C(1), 1.99(2); Pt—As, 2.267(2); Pt—O(1), 2.16(2); Pt—O(2), 2.10(1); C(1)—C(2), 1.27(3); C(2)—C(3), 1.51(3); and C(2)—C(4), 1.57(3) Å; C(1)—C(2)—C(3), 128(2); C(3)—C(2)—C(4), 113(2); and C(1)—C(2)—C(4), 119(2)°.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The Pt-Pt distance in the dimeric molecule is 2.989 Å, much longer than the average of 2.495 Å observed in tetrameric platinum(II) acetate where considerable metal-metal bonding occurs.³ The Pt-As distance is the shortest so far reported.⁴ The structure of the molecule is shown in the Figure.

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