ACTA CHEMICA SCANDINAVICA 7 (1953) 866–872

Short Communications

Platinum Compounds of Alkadienes (Diolefins)

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Zeise[1] in 1830 described some very interesting platinum compounds containing ethylene, *viz.* $K[PtCl_3C_2H_4]$ and $PtCl_2$, C_2H_4 *. Anderson[2] in 1934 found the latter compound to be dimeric. Other alkenes have yielded analogous compounds (see the review by Keller[3]), but until recently no compound containing more than one molecule of the alkene to one atom of platinum had been described. In 1950, however, Chatt and Wilkins[4] succeeded in preparing the compound $[PtCl_2(C_2H_4)_2]$ which is stable below −10°. Their recent publication[5] has prompted me to mention that in 1937 I prepared some platinum compounds of alkadienes in which one molecule appears to occupy two co-ordination places. This observation was not published because I intended to investigate these compounds further but pressure of other work prevented this.

When an excess of biallyl (1,5-hexadiene), $CH_2=CH-CH_2-CH_2-CH=CH_2$ is added to an aqueous solution of K_2PtCl_4, a precipitate slowly separates. This precipitate recrystallizes from chloroform to yield a pale yellow crystalline compound of composition $PtCl_2 \cdot C_6H_{10}$ and m.p. 173° (dec.). The corresponding iodide $PtI_2 \cdot C_6H_{10}$ is obtained in a similar way. The isomeric hexadiene, 2,4-hexadiene, behaves very differently: with K_2PtCl_4 only free platinum is obtained and with K_2PtI_4 a black precipitate consisting mainly of PtI_2. Compounds derived from the lower homologue butadiene have been prepared both by Gelman[6] and by Chatt and Wilkins[5], but the butadiene molecule seems only to occupy one co-ordination place in these compounds.

Diallylether gives a compound, $PtCl_2(C_6H_{10}O)$, which closely resembles the diallyl compound. Divinylether, on the other hand, reduces K_2PtCl_4 to free platinum. On addition of an excess of divinylether to K_2PtI_4, a dark red precipitate (resembling CrO_3) immediately separates, but this compound is very unstable and rapidly turns brown. Analysed as soon after formation as possible, it has the composition corresponding to platinum iodide with 1/2 molecule of divinylether, but the product smells of divinylether and may

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* It has not been generally recognised that Zeise prepared this compound. Anderson writes: "Zeise considered that he had obtained the basic compound of the series, $PtCl_2 \cdot C_2H_4 \cdots$ His product consisted probably of the more or less decomposed acid of the series". As a matter of fact, however, Zeise's analysis of his "*platinum chloridæ inflammabile*" (*l.c.* § 39) corresponds excellently with the composition he proposed: Found (Zeise): Pt 66.53; Cl 23.88; C 8.25; H 1.34. Calc. for $PtCl_2 \cdot C_2H_4$: Pt 66.34; Cl 24.14; C 8.16; H 1.36. Also the properties described by Zeise are in agreement with those of the compound $PtCl_2 \cdot C_2H_4$, with the exception that the colour is described by Anderson as orange and by Zeise as very slightly yellow ("*citrini coloris perquam pallidi*"). This may, however, simply be a question of crystal size (Anderson recrystallized his product from benzene).

have contained 1 molecule at the beginning.

The behaviour of biallyl and diallylether is thus very different from that of similar compounds with smaller distances between the double bonds. It thus seems probable that both double bonds in the longer diolefins are involved in complex formation giving chelated complexes. Other compounds of the type $PtCl_2 \cdot$ alkene are dimeric, but the compounds of biallyl and diallylether were found by cryoscopic measurements to be monomeric, in accordance with the view that these compounds are chelate compounds.

This conclusion is corroborated by measurement of the dipole moments of these compounds. Although the compounds are very slightly soluble in benzene it is possible to determine the order of magnitude of their dipole moments which was found to be 6—7 D. This high value is only compatible with the assumption that the compounds are *cis*-compounds, and this is the only possible configuration if the diolefins occupy two coordination places.

Biallyl also gives a palladium compound with the composition $PdCl_2 \cdot C_6H_{10}$ by reaction with the benzonitrile complex $[PdCl_2(C_6H_5CN)_2]$.

An attempt to determine the structures of the biallyl compounds using X-rays was frustrated by the decomposition of the compounds. They blackened in the X-ray beam and the only identifiable reflections were due to metallic platinum and palladium.

EXPERIMENTAL

Biallyl-dichloroplatinum(II). Biallyl (1 ml) was added to a solution of K_2PtCl_4 (2 g) in water (10 ml) and the mixture shaken vigorously for a few minutes. On standing a precipitate slowly separated, and after 2 days it was filtered off (yield 1.3—1.5 g). Further addition of biallyl caused the separation of a little more of the same compound and the yield was almost quantitative (calc. 1.7 g) the filtrate from the last precipitate was almost colourless. At 50° the reaction occurred more rapidly but the result was essentially the same. The compound was recrystallized from chloroform and obtained in pale yellow crystals, m.p. 172—73° (benzene gives a better recovery but more recrystallizations are necessary to obtain the pure compound); it was rather soluble in chloroform, less so in benzene and almost insoluble in ether. It dissolved somewhat in boiling water but soon decomposed with the separation of a brown precipitate. The melting point was sharp, and under the microscope the melting was seen to occur without decomposition, but the melt soon turned black. Found: C 20.51; H 3.05; Pt 56.1; Cl 20.17. Calc. for $[PtCl_2(C_6H_{10})]$, (348.3): C 20.69; H 2.89; Pt 56.0; Cl 20.36. Molecular weight (cryoscopically in bromoform solution): 369, 382, 364. Dipole moment, $\mu = 6.1$ ($c = 0.00385$ molar in benzene, $\Delta\varepsilon = 0.0180$).

According to Gelman [7] biallyl can replace ethylene from $K[PtCl_3C_2H_4]$, probably with the formation of the compound $K_2[Cl_3PtC_6H_{10}PtCl_3]$. This compound was also formed as an intermediate in the preparation of the compound $[PtCl_2C_6H_{10}]$, especially when the reaction tookplace in acid solution or when no excess of biallyl was used.

Biallyl (1 ml) and 4 *N* hydrochloric acid (0.5 ml) were added to a solution of K_2PtCl_4 (2 g) in water (10 ml). A crystalline mustard-yellow precipitate soon began to separate. After two hours it was filtered off (yield 0.7 g). It was almost completely soluble in water at room temperature; on longer standing the yield was larger but more of the insoluble compound $[PtCl_2C_6H_{10}]$ was formed. The water-soluble substance could not be crystallized from water because it was partly decomposed in boiling water or by evaporation of an aqueous solution. The product was purified by extraction with boiling chloroform which dissolves $[PtCl_2C_6H_{10}]$. The yellow crystals have the composition $K_2[Pt_2Cl_6C_6H_{10}]$: Found: C 9.73; H 1.42. Calc. C 9.43; H 1.31. By addition of $[Pt(NH_3)_4]$ to an aqueous solution of this compound an insoluble cream-coloured precipitate, consisting of $[Pt(NH_3)_4]\,[Pt_2Cl_6C_6H_{10}]$, was formed. Found: C 7.59; H 2.32; N 5.90; Pt 61.73. Calc. C 7.72; H 2.49; N 6.04; Pt 62.75.

Biallyl-di-iodoplatinum(II). Biallyl (0.5 ml) was added to a solution of K_2PtCl_4 (1 g) and KI (1.5 g) in tepid water (10 ml). After 1 hour the precipitate was filtered off (yield 0.8 g), washed with water, dried and recrystallized from chloroform. The compound forms orange-red crystals; on heating it turns black without melting. Found: C 13.24; H 2.06;

Pt 35.75. Calc. for $[PtI_2C_6H_{10}]$ (547.2): C 13.17; H 1.84; Pt 35.67.

Biallyl-dichloropalladium(II). Biallyl (0.17 ml) was added to a solution of the benzonitrile complex[8] $[PdCl_2(C_6H_5CN)_2]$ (0.5 g) in benzene (10 ml). A brownishyellow, crystalline precipitate separated. The quantity was increased by addition of petroleum ether and cooling in ice (yield 0.30 g). Found: C 28.58; H 4.12. Calc. for $[PdCl_2(C_6H_{10})]$: C 27.74; H 3.88.

Diallylether-dichloroplatinum(II). Diallylether (0.80 g) was added to a solution of K_2PtCl_4 (2 g) in water (10 ml). An almost white precipitate soon began to separate. After 3 days the precipitate was filtered off (yield 1.00 g). The dry product was dissolved in warm chloroform (100 ml) and carbon tetrachloride (50 ml) added to until crystallization just started. As the solution cooled the compound separated as a fine, white crystalline powder, m.p. 180° (dec.). Found: C 20.05; H 2.94; Pt 53.71. Calc. for $[PtCl_2(C_6H_{10}O)]$ (364.3): C 19.78; H 2.77; Pt 53.57. Molecular weight (cryoscopically in bromoform): 344.

The assistance of Mr. Chr. Petersen in checking and completing my old observations is gratefully acknowledged. I also wish to thank Dr. J. Chatt, Welwyn, for reading the manuscript.

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Received April 29, 1953.

Platinum Compounds of *Cyclo*octatetraene *

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In the preceding article platinous complexes of some alkadienes were described. I have prepared similar derivatives of *cyclo*octatetraene. A compound of composition close to $PtCl_2$, C_8H_8 separates as an orange-yellow precipitate when *cyclo*octatetraene is added to an aqueous solution of K_2PtCl_4. It is insoluble in water and organic solvents and therefore could not be purified. However, the corresponding iodide could be recrystallised from chloroform and was obtained as a beautiful orange-red (dichromate-coloured) crystalline powder of the exact composition PtI_2, C_8H_8.

The platinum atom in these compounds is certainly co-ordinated to one or more double bonds. The unlikely possibility that the platinum atom be bound to all 4 double bonds is definitely ruled out because compounds of the type $[Pta_4]Cl_2$ are generally colourless, easily soluble in water, and contain ionised chlorine. This is not the case with the *cyclo*octatetraene compound. Neither can the platinum atom be bound to only one double bond because the compound would then be dimeric, as is generally true of platinum compounds of the type $PtCl_2a$ (a = amine, phosphine, alkyl sulphide, etc.). A cryoscopic determination of the molecular weight in bromoform solution shows that PtI_2,C_8H_8 is monomeric; thus it seems that *cyclo*octatetraene occupies two co-ordination places, in the same way as biallyl. According to the preceding paper a certain distance between the double bonds is necessary for the formation of chelate compounds by

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* Presented to the Danish Chemical Society, October 25th, 1949.