

## Organic Selenium Compounds

## XII.\* Coordination Compounds of Carbon Diselenide

K. A. JENSEN and E. HUGJENSEN

*Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark*

The interesting investigations by Wilkinson *et al.*<sup>1</sup> have demonstrated that carbon disulfide is able to function as a ligand in coordination compounds. Within the compass of our investigations of the chemical reactions of carbon diselenide we have tried to prepare the corresponding compounds of carbon diselenide. This has, however, a pronounced tendency to polymerize, and in most experiments we were only able to isolate poly(carbon diselenide)<sup>2</sup> or compounds that probably contain a tetraselenooxalate ion (see below).

Only in one case did we isolate a substance containing monomeric carbon diselenide, namely the compound  $[\text{Pt}(\text{Ph}_3\text{P})_2(\text{CSe}_2)]$ , which was obtained as a light green solid by the interaction of tris(triphenylphosphine)platinum(0) at room temperature with exactly the calculated amount of carbon diselenide. As soon as an excess of carbon diselenide was added the green compound was transformed into a brown solid.

The above mentioned complex has a strong band in the infrared spectrum at  $995\text{ cm}^{-1}$ , which is attributed to the stretching frequency of the carbon-selenium double bond. Free carbon diselenide has the corresponding band at  $1270\text{ cm}^{-1}$  (in  $\text{CCl}_4$ ). The shift is similar to that found for coordinated carbon disulfide ( $1157\text{ cm}^{-1}$ ) versus free carbon disulfide ( $1522\text{ cm}^{-1}$ ). Otherwise the infrared spectrum differs from that of triphenylphosphine practically only in the intensities of the bands. The  $1090\text{ cm}^{-1}$  band of triphenylphosphine (the "X-sensitive" phenyl band, *cf.* Ref. 3) appears at  $1100\text{ cm}^{-1}$  with increased intensity in the spectrum of the platinum compound.

From  $[\text{Ni}(\text{Ph}_3\text{P})_2(\text{CO})_2]$  or  $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$  and carbon diselenide we have only been

able to isolate compounds which analytically contain 2 mol of carbon diselenide. The reaction of  $[\text{Ni}(\text{Ph}_3\text{P})_2(\text{CO})_2]$  with carbon diselenide shows convincingly that no compound containing 1 mol of carbon diselenide can be formed. When carbon diselenide is added to a benzene solution of the nickel compound, CO is evolved and the solution first becomes dark red and later almost black, and a blackred solid precipitates. When only 1 mol of carbon diselenide had been added, the filtered solution still contained half of the  $[\text{Ni}(\text{Ph}_3\text{P})_2(\text{CO})_2]$  unchanged; when 2 mol of carbon diselenide was added a practically insoluble compound with the composition  $[\text{Ni}(\text{Ph}_3\text{P})_2(\text{CSe}_2)_2]$  was obtained in almost quantitative yield. Similarly, the rhodium compound obtained from  $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$  analytically corresponds to the formula  $[\text{Rh}(\text{Ph}_3\text{P})_2\text{Cl}(\text{CSe}_2)_2]$ .

The infrared spectra of these two compounds do not exhibit the absorption band near  $1000\text{ cm}^{-1}$ , found in the spectrum of the platinum compound. The main difference between the infrared spectra of the starting materials and those of the  $\text{CSe}_2$  compounds is the appearance of a strong band at  $870\text{ cm}^{-1}$ . Since the asymmetric stretching vibration of a diselenocarboxylate group occurs near  $900\text{ cm}^{-1}$ ,<sup>4</sup> we conclude that these compounds probably contain a coordinated tetraselenooxalate ion. The reduction of 2  $\text{CSe}_2$  to  $(\text{CSeSe}^-)_2$  would correspond to an oxidation of Ni(0) to Ni(II) and of Rh(I) to Rh(III). The properties of the nickel compound (colour, diamagnetism) also indicate that it is a square-planar complex. Poly(carbon diselenide) exhibits an absorption in the same range<sup>5</sup> but the stoichiometric composition of the compounds isolated makes it improbable that they contain polymeric carbon diselenide.

Our efforts to obtain a definite proof of the presence of a tetraselenooxalate group in these compounds have not been successful. It has not been possible to get crystals suited for an X-ray structural analysis, and it has not been possible to prepare complexes with aliphatic phosphines which might be more soluble. Various attempts have been made to prove the presence of tetraselenooxalate in a purely chemical way. So far these have been unsuccessful, but they will be pursued further.

*Experimental.* *Tris(triphenylphosphine)platinum(0)*,  $[\text{Pt}(\text{Ph}_3\text{P})_3]$ , was prepared es-

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essentially according to the directions given by Malatesta and Cariello,<sup>5</sup> but the starting material,  $[\text{PtI}_2(\text{Ph}_3\text{P})_2]$ , was prepared in a simpler way.

$[\text{PtI}_2(\text{Ph}_3\text{P})_2]$ . A solution of 2 g of  $\text{K}_2\text{PtCl}_4$  in 20 ml of water was mixed with a solution of 4 g of KI in 20 ml of water. After 15 min a solution of 5.2 g of triphenylphosphine in 50 ml of abs. ethanol was added to the mixture with stirring. The yellow precipitate was filtered off, washed with water and ethanol, collected, dried and crystallized from chloroform. This product is  $[\text{Pt}(\text{Ph}_3\text{P})_4][\text{PtI}_4]$ , m.p. ca. 290°C (decomp.). On boiling with water for 1 h it was transformed into  $[\text{PtI}_2(\text{Ph}_3\text{P})_2]$ , m.p. 258°C.

$[\text{Pt}(\text{Ph}_3\text{P})_3]$ . Anhydrous hydrazine (1 ml) was added to a suspension of  $[\text{PtI}_2(\text{Ph}_3\text{P})_2]$  in 10 ml of abs. ethanol and the mixture was refluxed for 10 min. The hot solution was decanted from a little precipitate and yielded on cooling and standing a yellow precipitate which was isolated by centrifugation, washed with warm ethanol, water and again with warm ethanol and dried in vacuum. Yield almost quantitative. M.p. 125–130°C in accordance with lit.<sup>5</sup> (Found: C 66.2; H 4.69. Calc. for  $\text{C}_{54}\text{H}_{45}\text{P}_3\text{Pt}$ : C 66.2; H 4.58).

$[\text{Pt}(\text{Ph}_3\text{P})_2(\text{CSe}_2)]$ . Carbon diselenide (43 mg) was added with stirring to a suspension of  $[\text{Pt}(\text{Ph}_3\text{P})_3]$  (250 mg) in dry ether (10 ml). The yellow solid soon became green. The green product was isolated by centrifugation, washed three times with ether and dried in vacuum. M.p. 158–163°C (decomp.). (Found: C 50.15; H 3.39; Se 17.77. Calc. for  $\text{C}_{37}\text{H}_{30}\text{P}_2\text{PtSe}_2$ : C 50.00; H 3.38; Se 17.75). Infrared spectrum:  $\text{CSe}_2$ -band at 995  $\text{cm}^{-1}$  (s).

The compound was insoluble in ether or ethanol. It dissolved in benzene or dichloromethane but was thereby transformed into a brown product. A similar product was also obtained when excess carbon diselenide was added to a solution of  $[\text{Pt}(\text{Ph}_3\text{P})_3]$  in ether. The selenium content of the brown products was higher than that of the green compound but lower than calculated for a compound containing 2 mol of  $\text{CSe}_2$ . In the infrared spectrum of the brown products the intensity of the 995  $\text{cm}^{-1}$  band had decreased considerably and a rather weak and broad band had appeared in the 850–870  $\text{cm}^{-1}$  region. According to these results it is doubtful whether a compound analogous to the nickel and rhodium compounds, described below, was formed or whether the product only contained polymeric carbon diselenide.

$[\text{Ni}(\text{Ph}_3\text{P})_2(\text{CSe}_2)_2]$ . Carbon diselenide (220 mg) was added to a solution of 400 mg of  $[\text{Ni}(\text{Ph}_2\text{P})_2(\text{CO})_2]$ <sup>6</sup> in 10 ml of benzene. The solution instantly turned red and CO was evolved; after 1 h the mixture was opaque and a reddish-black precipitate had formed. The precipitate was isolated by centrifugation,

washed with ether and dried in vacuum. Yield 470 mg (83 %). M.p. 167°C (decomp.). (Found: C 49.00; H 3.31; Se 34.16. Calc. for  $\text{C}_{38}\text{H}_{30}\text{NiP}_2\text{Se}_4$ : C 49.43; H 3.25; Se 34.24).

The complex is slightly soluble in chloroform with a red colour. Absorption maxima of a  $\text{CHCl}_3$  solution (0.1 mg/ml): 454 nm ( $\log \epsilon$  3.61) and 550 nm ( $\log \epsilon$  3.45). Infrared spectrum:  $\text{CSe}_2$ -band at 870  $\text{cm}^{-1}$  (s).

$[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CSe}_2)_2\text{Cl}]$ . Carbon diselenide (85 mg) was added to a suspension of  $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$ <sup>7</sup> (231 mg) in benzene (10 ml). The colour changed from red to dark brown. After 1 h the precipitate was isolated by filtration, washed with ether and dried in vacuum. Yield 150 mg (60 %). (Found: C 45.51; H 3.31; Cl 3.54; Se 31.10. Calc. for  $\text{C}_{38}\text{H}_{30}\text{ClP}_2\text{RhSe}_4$ : C 45.49; H 2.99; Cl 3.54; Se 31.52). Infrared spectrum:  $\text{CSe}_2$ -band at 865  $\text{cm}^{-1}$  (s).

From a solution of  $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$  in benzene and carbon diselenide a brown-black product was obtained which still contained CO ( $\nu\text{CO}$  1970  $\text{cm}^{-1}$ ) and approximately had the composition of the starting material with 1 mol  $\text{CSe}_2$  added. It was, however, unstable and was transformed into the above-mentioned compound.

Infrared spectra of KBr discs were recorded on a Perkin Elmer model 337 grating spectrophotometer and visible spectra on a Unicam SP. 800 A instrument.

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