

## Synthesis and Crystal Structure of the $\eta^2$ -Bonded $\text{CSe}_2$ Complex [(triphos)RhCl( $\eta^2$ - $\text{CSe}_2$ )]· $\text{C}_6\text{H}_6$ [triphos = $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ ]. Metal-promoted Head-to-head Dimerization of $\text{CSe}_2$ to $\text{C}_2\text{Se}_4$

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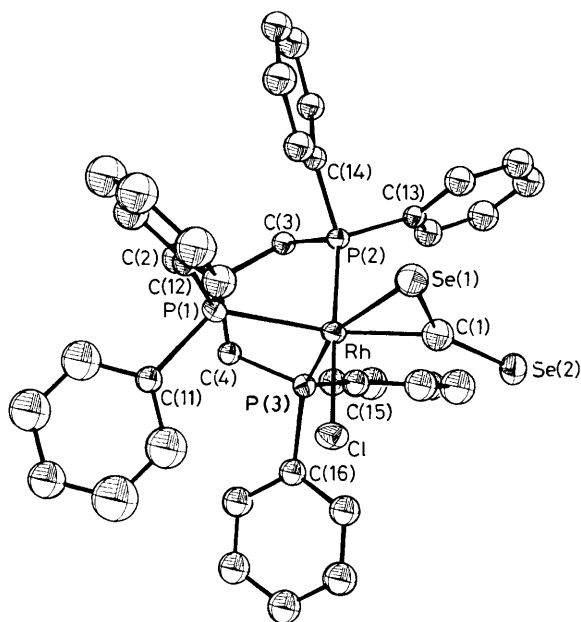
The reaction of  $\text{CSe}_2$  with  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and triphos [triphos =  $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ ] gives [(triphos)RhCl( $\eta^2$ - $\text{CSe}_2$ )]· $\text{C}_6\text{H}_6$ , X-ray analysis of which shows that  $\text{CSe}_2$  is  $\eta^2$ -bonded *via* C and Se; the action of Lewis acids on this  $\eta^2$ - $\text{CSe}_2$  compound leads to the unprecedented ethenetraselenolato-bridged complexes [(triphos)Rh( $\mu$ - $\text{C}_2\text{Se}_4$ )Rh(triphos)] $\text{Y}_2$  (Y = Cl,  $\text{BF}_4$ ,  $\text{PF}_6$ , or  $\text{BPh}_4$ ).

Owing to the pronounced tendency of carbon diselenide to polymerize when interacting with metal centres, few complexes containing  $\text{CSe}_2$  as a ligand have been reported.<sup>1</sup> The bonding mode of the  $\text{CSe}_2$  group has not been definitely established yet mainly because no appropriate X-ray structure determination has been made.

We report here the synthesis and the crystal structure of the complex [(triphos)RhCl( $\eta^2$ - $\text{CSe}_2$ )]· $\text{C}_6\text{H}_6$  (**1**) [triphos = 1,1,1-

tris(diphenylphosphinomethyl)ethane]. On addition of a three-fold excess of  $\text{CSe}_2$  to an equimolar mixture of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and triphos in benzene, a brown-orange precipitate is formed, which is transformed by heating into red crystals of (**1**) (yield 60%).<sup>†</sup>

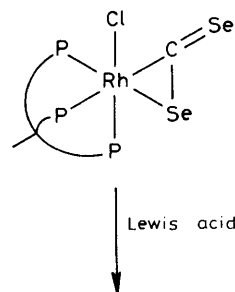
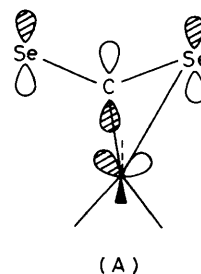
<sup>†</sup> Satisfactory elemental analytical data were obtained; i.r. (Nujol)  $\nu(\text{CSe})$  970  $\text{cm}^{-1}$ ; non-electrolyte.



**Figure 1.** ORTEP drawing of the (triphos)RhCl( $\eta^2$ -CSe<sub>2</sub>) molecule. Distances (Å): Rh–Se(1), 2.514(4); Rh–Cl, 2.429(7); Rh–P(1), 2.416(8); Rh–P(2), 2.265(7); Rh–P(3), 2.339(7); Rh–C(1), 2.08(3); C(1)–Se(1), 1.90(3); C(1)–Se(2), 1.71(3). Angles (°): Se(1)–Rh–P(1), 112.7(2); Se(1)–Rh–C(1), 47.9(8); Cl–Rh–P(1), 92.0(3); Cl–Rh–P(2), 176.1(3); Cl–Rh–P(3), 95.1(3); P(1)–Rh–P(2), 88.8(3); P(1)–Rh–P(3), 88.3(3); P(2)–Rh–P(3), 88.8(3); P(3)–Rh–C(1), 111.2(8); Rh–Se(1)–C(1), 53.9(9); Rh–C(1)–Se(1), 78(1); Se(1)–C(1)–Se(2), 132(2).

The molecular structure of (1)† is shown in Figure 1. The complex can be viewed as assembled from a bent CSe<sub>2</sub> molecule  $\eta^2$ -linked to the fragment (triphos)RhCl. The CSe<sub>2</sub> group is almost in the equatorial plane of this L<sub>4</sub>M fragment having pseudo C<sub>2v</sub> symmetry. An interesting comparison can be made with the structure of a CS<sub>2</sub> complex of rhodium(I) having practically the same primary geometry, namely the complex cation [( $\eta^3$ )Rh( $\eta^2$ -CS<sub>2</sub>)]<sup>+</sup> (2).<sup>2</sup> The Rh–C bonds are almost identical [2.085(14) and 2.075(29) Å in (1) and (2) respectively]. The difference of ca. 0.12 Å between the Rh–S and Rh–Se bonds [2.387(5) vs. 2.514(4) Å] reflects the different covalent radii of S and Se. However, the observed differences between the C–S and C–Se bonds in (1) and (2) needs to be explained by more than just increase in radii. The unco-ordinated C–Se bond [1.71(3) Å] is about 0.17 Å longer than the corresponding C–S bond in (2). The co-ordinated C–Se bond is remarkably long [1.90(3) Å], considering also the fact that in [1,2-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]Pd( $\eta^2$ -CSeS),<sup>3</sup> the C–Se side of the M–C–Se triangle measures only 1.80(2) Å. Finally there is a noticeable bending of CSe<sub>2</sub> in (1) [the Se–C–Se angle is only 132(2)° vs. a S–C–S angle of 143(1)° in (2)]. The two

† Crystal data: C<sub>42</sub>H<sub>30</sub>ClP<sub>3</sub>RhSe<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, *M* = 1011.09, monoclinic, space group P2<sub>1</sub>/n, *a* = 21.151(6), *b* = 16.450(5), *c* = 13.500(3) Å,  $\beta$  = 90.81(3)°, *U* = 4696.6 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.429 g cm<sup>-3</sup>,  $\mu$ (Mo–K $\alpha$ ) = 20.8 cm<sup>-1</sup>. The structure was solved by heavy-atom methods and refined to *R* = 0.077 and *R<sub>w</sub>* = 0.082 for 1904 absorption-corrected reflections with *I* > 3 $\sigma$ (*I*) measured on a Philips PW 1100 diffractometer using Mo–K $\alpha$  radiation ( $\lambda$  = 0.71069 Å, 2.5 <  $\theta$  < 20°). The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Scheme 1**

latter structural features are indicative that the  $\pi$ -back donation from the metal is more effective in the  $\eta^2$ -CSe<sub>2</sub> complex. In fact, CSe<sub>2</sub> contributes to the MO with a strongly C–Se antibonding  $\pi^*$  orbital which is stabilized on bending the heteroallene molecule [see structure (A)]. Our previous MO studies on the bonding capabilities of heteroallenes, however, have clearly indicated that the bonding is complicated by a variety of factors so that it would be hazardous to draw final conclusions regarding the different MO bonding patterns for CS<sub>2</sub> and CSe<sub>2</sub> respectively.<sup>4</sup>

Treatment of solutions of (1) with Lewis acids such as HgCl<sub>2</sub>, HBF<sub>4</sub>, and NaPF<sub>6</sub>, led to green complexes of formula [(triphos)Rh( $\mu$ -C<sub>2</sub>Se<sub>4</sub>)Rh(triphos)]Y<sub>2</sub> (Y = Cl, BF<sub>4</sub>, or PF<sub>6</sub>), which contain an unprecedented ethenetetraselenolato bridging group (Scheme 1). Metathetical reaction with BPh<sub>4</sub><sup>-</sup> afforded the complex [(triphos)Rh( $\mu$ -C<sub>2</sub>Se<sub>4</sub>)Rh(triphos)]-[BPh<sub>4</sub>]<sub>2</sub>.<sup>§</sup> All the physical and chemical properties of this compound are identical to those of the sulphur analogue [(triphos)Rh( $\mu$ -C<sub>2</sub>S<sub>4</sub>)Rh(triphos)][BPh<sub>4</sub>]<sub>2</sub>, the structure of which has been established by X-ray analysis.<sup>5</sup>

The interaction of the Lewis acid with the exocyclic selenium atom of the  $\eta^2$ -CSe<sub>2</sub> group is believed to be responsible for the opening of the RhCSe ring. In this respect, we note that (NBu<sub>4</sub>)BPh<sub>4</sub> does not promote the conversion of (1) into the  $\mu$ -C<sub>2</sub>Se<sub>4</sub> dimer. Evolution to the dimeric cation could then proceed through the displacement of the chlorine

§ Satisfactory elemental analytical data were obtained; no i.r. bands in the C–Se region are observed; <sup>31</sup>P{<sup>1</sup>H} n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>, 293 K): 31.0 p.p.m. (d, *J*<sub>P–Rh</sub>, 105.2 Hz); molar conductance for 10<sup>-3</sup>M nitroethane solution: 95 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>.

ligands in two molecules of (1) by the originally uncoordinated selenium atoms and the formation of a C–C bond.

We are attempting to extend to other heteroallene molecules the present Lewis-acid assisted C–C bond formation, which would be of particular importance for carbon dioxide.

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