

Synthesis and Crystal Structure of the η^2 -Bonded CSe_2 Complex $[(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)]\cdot\text{C}_6\text{H}_6$ [triphos = $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$]. Metal-promoted Head-to-head Dimerization of CSe_2 to C_2Se_4

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The reaction of 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 $[(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)]\cdot\text{C}_6\text{H}_6$, X-ray analysis of which shows that CSe_2 is η^2 -bonded *via* C and Se; the action of Lewis acids on this η^2 - CSe_2 compound leads to the unprecedented ethenetraselenolato-bridged complexes $[(\text{triphos})\text{Rh}(\mu\text{-C}_2\text{Se}_4)\text{Rh}(\text{triphos})]\text{Y}_2$ ($\text{Y} = \text{Cl}, \text{BF}_4, \text{PF}_6$, or BPh_4).

Owing to the pronounced tendency of carbon diselenide to polymerize when interacting with metal centres, few complexes containing CSe_2 as a ligand have been reported.¹ The bonding mode of the 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 $[(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)]\cdot\text{C}_6\text{H}_6$ (**1**) [triphos = 1,1,1-

tris(diphenylphosphinomethyl)ethane]. On addition of a three-fold excess of 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%).[†]

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

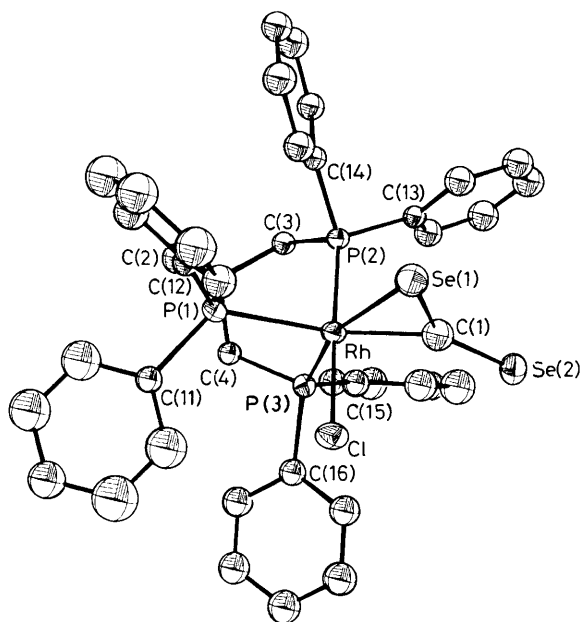
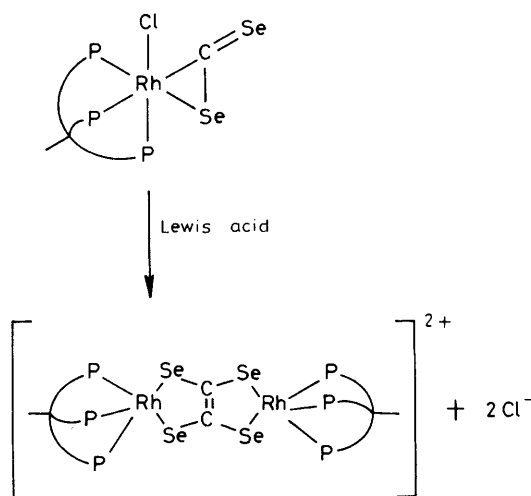
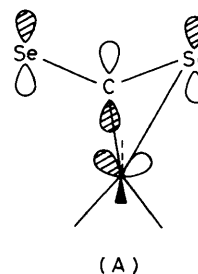


Figure 1. ORTEP drawing of the (triphos)RhCl(η^2 -CSe₂) molecule. Distances (Å): Rh–Se(1), 2.514(4); Rh–Cl, 2.429(7); Rh–P(1), 2.416(8); Rh–P(2), 2.265(7); Rh–P(3), 2.339(7); Rh–C(1), 2.08(3); C(1)–Se(1), 1.90(3); C(1)–Se(2), 1.71(3). Angles (°): Se(1)–Rh–P(1), 112.7(2); Se(1)–Rh–C(1), 47.9(8); Cl–Rh–P(1), 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 CSe₂ molecule η^2 -linked to the fragment (triphos)RhCl. The CSe₂ group is almost in the equatorial plane of this L₄M fragment having pseudo C_{2v} symmetry. An interesting comparison can be made with the structure of a CS₂ complex of rhodium(I) having practically the same primary geometry, namely the complex cation [(η^3)Rh(η^2 -CS₂)]⁺ (2).² 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-C₆H₄(CH₂PPh₂)₂]Pd(η^2 -CSeS),³ the C–Se side of the M–C–Se triangle measures only 1.80(2) Å. Finally there is a noticeable bending of CSe₂ in (1) [the Se–C–Se angle is only 132(2)° vs. a S–C–S angle of 143(1)° in (2)]. The two



Scheme 1

latter structural features are indicative that the π -back donation from the metal is more effective in the η^2 -CSe₂ complex. In fact, CSe₂ contributes to the MO with a strongly C–Se antibonding π^* 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 CS₂ and CSe₂ respectively.⁴

Treatment of solutions of (1) with Lewis acids such as HgCl₂, HBF₄, and NaPF₆, led to green complexes of formula [(triphos)Rh(μ -C₂Se₄)Rh(triphos)]Y₂ (Y = Cl, BF₄, or PF₆), which contain an unprecedented ethenetetraselenolato bridging group (Scheme 1). Metathetical reaction with BPh₄[–] afforded the complex [(triphos)Rh(μ -C₂Se₄)Rh(triphos)]-[BPh₄]₂.[§] All the physical and chemical properties of this compound are identical to those of the sulphur analogue [(triphos)Rh(μ -C₂S₄)Rh(triphos)][BPh₄]₂, the structure of which has been established by X-ray analysis.⁵

The interaction of the Lewis acid with the exocyclic selenium atom of the η^2 -CSe₂ group is believed to be responsible for the opening of the RhCSe ring. In this respect, we note that (NBu₄)BPh₄ does not promote the conversion of (1) into the μ -C₂Se₄ dimer. Evolution to the dimeric cation could then proceed through the displacement of the chlorine

† Crystal data: C₄₂H₃₀ClP₃RhSe₂·C₆H₆, *M* = 1011.09, monoclinic, space group *P*₂₁/*n*, *a* = 21.151(6), *b* = 16.450(5), *c* = 13.500(3) Å, β = 90.81(3)°, *U* = 4696.6 Å³, *Z* = 4, *D*_c = 1.429 g cm^{–3}, μ (Mo–K α) = 20.8 cm^{–1}. The structure was solved by heavy-atom methods and refined to *R* = 0.077 and *R*_w = 0.082 for 1904 absorption-corrected reflections with *I* > 3 σ (*I*) measured on a Philips PW 1100 diffractometer using Mo–K α radiation (λ = 0.71069 Å, 2.5 < θ < 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.

§ Satisfactory elemental analytical data were obtained; no i.r. bands in the C=Se region are observed; ³¹P{¹H} n.m.r. (CD₂Cl₂, 293 K): 31.0 p.p.m. (d, *J*_{P–Rh}, 105.2 Hz); molar conductance for 10^{–3} M nitroethane solution: 95 cm² ohm^{–1} mol^{–1}.

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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