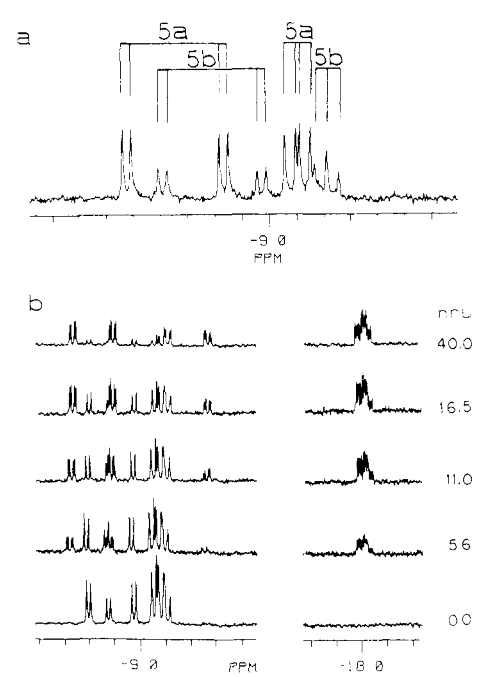


Figure 1. Hydride region of the ^1H NMR spectrum of IrBr(CO)(chiraphos) (**4**) plus H_2 in acetone-d_6: (a) expanded view at -25 °C; (b) spectra taken over 40-h period monitoring the conversion from diastereomers **5** to **6** at 25 °C.

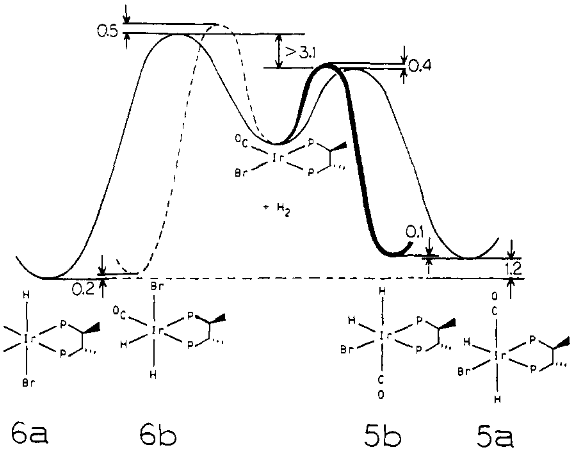


Figure 2. Reaction coordinate diagram for the system IrBr(CO)(chiraphos) (**4**) + H_2. Values of $\Delta\Delta G$ and $\Delta\Delta G^{*}$ are given in kcal/mol.

The results described above show that kinetic and thermodynamic differentiation of metal-centered chirality in simple cis oxidative additions by chiraphos is significant.[9] The results also provide a sensitive probe to the transition-state structure in these systems through observed differences in the extent of kinetic and thermodynamic differentiation for the diastereomers in these cis oxidative additions. On the basis of these differences, it appears that for both H_2 and Ph_3SiH oxidative addition, the transition state in these reactions is not very product-like.

Acknowledgment. We thank the National Science Foundation (CHE 83-08064) and the Office of Naval Research for support of this work and Johnson Matthey Co., Inc., for a generous loan of iridium salts.

---

(9) (a) While diastereomeric cis dihydrides have been seen previously for $[IrH_2(dipamp)_2]BF_4$, the stereoselectivity of the oxidative addition was not reported. Brown, J. M.; Dayrit, F. M.; Lightowler, D. *J. Chem. Soc., Chem. Commun.* **1983**, 414. (b) For the oxidative addition of H_2 to [Ir(cod)-(diop)](PF_6), only one set of hydride resonances was discernible. Presumably the diastereomers were not resolved. Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183.

Stepwise Metal-Assisted Conversion of CSe_2 to Se_2 and CO_2. Novel Bonding Mode of the Diselenium Molecule in the Double-Se_2-Bridged Complex $[(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)](BPh_4)_2\cdot 2DMF$

Claudio Bianchini,* Carlo Mealli, Andrea Meli, and
Michal Sabat

Istituto per lo Studio della Sterochimica ed
Energetica dei Composti di Coordinazione
C.N.R., 50132 Firenze, Italy

Received February 26, 1985

Despite the academic, biological, catalytic, and synthetic interest in metal complexes containing chalcogens in their framework, surprisingly little is still known about the organometallic and coordination chemistry of CSe_2. Only very recent studies have revealed the potentially enormous reaction possibilities of CSe_2 complexes.[1] In this paper we report an unprecedented metal-promoted transformation of η^2-CSe_2 into η^2-Se_2 via η^1-Se_2CPEt_3 and η^2-Se_2CO intermediates (Scheme I).

It is well-known that, with adoption of the η^2-C,S coordination mode, the electrophilicity of the carbon atom of the sulfur analogue of CSe_2, CS_2, is enhanced thereby facilitating attack of a nucleophile.[2] Accordingly, we have found that PEt_3 reacts with (triphos)RhCl(η^2-CSe_2)[1e] (**1**) in CH_2Cl_2 to give green crystals of the phosphoniodiselenocarboxylate complex (triphos)RhCl-(Se_2CPEt_3)[3] (**2**) (yield 70%). The latter complex reacts immediately at room temperature in CH_2Cl_2 solution with dioxygen to give $OPEt_3$ and yellow crystals of (triphos)RhCl(Se_2CO)[5] (**3**) (yield 60%), the first example of a diselenocarbonate complex. The diselenocarbonate complex **3** is obtained also by simple exposure in air either of solid samples or of solutions of **2**. In this case, however, $OPEt_3$ cannot be collected as it is sensitive to moisture.

The chloride ligand in **3** is easily replaced by other monofunctional ligands like N_3^-, but can be also definitely removed from the complex by treatment of solutions of **3** with $NaBPh_4$ in ethanol. As a result, the 16-electron rhodium(III) complex $[(triphos)Rh(Se_2CO)]BPh_4$[6] (**4**) is quantitatively obtained. A preliminary X-ray crystal-structure determination[7] has shown that the diselenocarbonate ligand chelates the rhodium atom through both selenium donors with the oxygen atom remaining uncoordinated.

By bubbling molecular oxygen into a CH_2Cl_2 solution of **4** for 5 min, brown crystals of $[(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)](BPh_4)_2$ (**5**) are precipitated in 60% yield, whereas CO_2 is evolved (Scheme I). Crystals of **5**·2DMF suitable for an X-ray analysis are obtained by recrystallizing **5** from DMF/butanol. Alternatively, compound **5** can be synthesized either by exposure in air of solutions of the diselenocarbonate **4** or by treatment of solutions of **4** with H_2O_2. In the latter case, the reaction is immediate and it is possible to

---

(1) (a) Clark, G. R.; Grundy, K. R.; Harris, R. O.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1975**, *90*, C37. (b) Roper, W. R.; Town, K. G. *Ibid.* **1983**, *252*, C97. (c) Werner, H.; Ebner, M. *Ibid.* **1983**, *258*, C52. (d) Werner, H.; Kolb, O. *Ibid.* **1984**, *268*, 49. (e) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1647.

(2) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

(3) IR (Nujol mulls) 1030 (C–CH_3 rocking PEt_3), 970 cm^{-1} ν(C=Se); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 32.2 MHz) 30.45 (d, J_{PP} = 17.2, J_{PRh} = 127.6 Hz, triphos), 23.9 pp (m, $PCSe_2$). This pattern does not vary with the temperature and is consistent with triphos acting as a tridentate ligand in five-coordinate complexes.[4] The phosphoniodiselenocarboxylate ligand in **2** is monodentate probably to avoid a supersaturated 20-electron species. This is demonstrated by the existence of the complex $[(triphos)Rh(\eta^2\text{-}Se_2CPEt_3)]BPh_4$ obtained by chloride ion abstraction from **2**.

(4) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 4125.

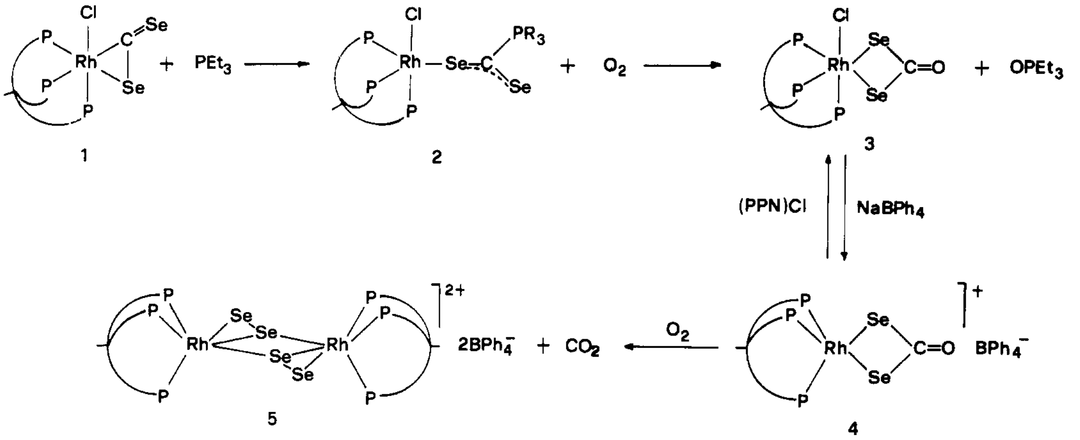
(5) IR (Nujol mulls) 1050 cm^{-1} ν(CO); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 32.2 MHz) 25.85 (t, J_{PP} = 27, J_{PRh} = 108.1 Hz), -6.24 ppm (d).

(6) IR (Nujol mulls) 1080 cm^{-1} ν(CO); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C, 32.2 MHz) 34.15 ppm (s, J_{PRh} = 98.3 Hz).

(7) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

0002-7863/85/1507-5317$01.50/0

Scheme I



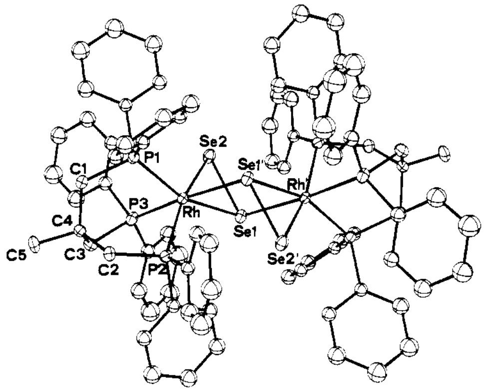


Figure 1. ORTEP drawing of the $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)_2\text{Rh}(\text{triphos})]^{2+}$ complex cation. Selected bond distances (Å) and angles (deg): Rh–Se(1), 2.531 (1); Rh–Se(2), 2.494 (1); Rh′–Se(1), 2.556 (1); Se(1)–Se(2), 2.298 (1); Rh–P(1), 2.313 (2); Rh–P(2), 2.342 (2); Rh–P (3), 2.343 (2). Se(1)–Rh–Se(2), 54.13 (4); Se(1′)–Rh–Se(2), 88.93 (5); Se(1)–Rh–P(1), 158.81 (8); Se(2)–Rh–P(2), 162.98 (8); Se(1′)–Rh–P(3), 173.03 (8); Se(1)–Rh–P(2), 109.90 (7); Se(1)–Rh–P(3), 95.65 (8); Se(2)–Rh–P(1), 105.42 (7); Se(2)–Rh–P(3), 87.76 (7); Rh–Se(1)–Rh′, 102.55 (5).

precipitate quantitatively CO_2 as $BaCO_3$.

The structure of the $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)_2\text{Rh}(\text{triphos})]^{2+}$ complex cation is shown in Figure 1. The system consists of two $(\text{triphos})\text{Rh}(\eta^2\text{-Se}_2)$ fragments related by a crystallographic inversion center. Binding of one of the selenium atoms, Se(1), from the side-on coordinated Se_2 unit to another rhodium atom results in formation of a four-membered $\overline{\text{RhSeRhSe}}$ ring with all Rh–Se bond lengths nearly equal. It is worthy to note that the Rh–Se distances are very close to that of 2.514 (4) Å observed in $(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)$[1e] where one of the C–Se bonds is η^2-coordinated to rhodium. While the Se_2 unit in the complex $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$[9] was found to bridge in the plane perpendicular to the Fe–Fe axis, the present bridging system has not been so far observed in solid-state structures, although its existence was proposed on the basis of spectroscopic studies for some iridium complexes.[10] On the other hand, this bridging mode occurs also in the disulfur complexes $[\text{Mo}_4(\text{NO})_4(\text{S}_2)_5\text{S}_3]^{4-}$,[11] $\text{Cp}_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$,[12] and $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}_2)_2(\text{S-C}_6\text{H}_4\text{Br})_6]^{4-}$.[13] The Se(1)–Se(2) distance of 2.298 (1) Å compares well with analogous distances in the monomeric commplexes $[\text{Ir}(\eta^2\text{-Se}_2)(\text{dppe})_2]^+$ (2.312 (3) Å)[10] and $\text{Os}(\eta^2\text{-Se}_2)(\text{CO})_2(\text{PPh}_3)_2$ (2.321 (1) Å)[14] as well as in the previously mentioned binuclear system $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ (2.293 (2) Å), thereby indicating that the Se_2 does not change significantly while making additional bonds with another metal center.

The major part of the chemistry presented in Scheme I is novel and rich of future implications. The facile cleavage of C–P and C–Se bonds by atmospheric oxygen as well as the new way of introducing a diselenium unit into a complex is particularly remarkable. In this respect, it is significant that all of the reactions of Scheme I work successfully also when CSe_2 is substituted for CS_2.[7]

Acknowledgment. Thanks are expressed to Dante Masi for his skillful technical assistance.

Supplementary Material Available: Fractional atomic coordinates and thermal parameters for compound **5** (3 pages). Ordering information is given on any current masthead page.

---

[8] Crystal data: $C_{130}H_{118}B_2P_6Rh_2Se_4\cdot 2(CH_3)_2NCHO$; M_r = 2555.7; triclinic, space group $P\bar{1}$; a = 16.950 (5) Å, b = 13.710 (4) Å, c = 13.379 (4) Å, α = 90.19 (2)°, β = 98.53 (2)°, γ = 104.03 (2)°; Z = 1; D_{calcd} = 1.423 g cm^{-3}; $\mu(\text{Mo K}\alpha)$ = 16.1 cm^{-1}. The structure was solved by Patterson and Fourier techniques and refined to a conventional R = 0.053 (R_W = 0.057) using 5488 absorption corrected reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer (Mo Kα radiation, λ = 0.71069 Å, $2.5 < \theta < 25°$). Phenyl rings were treated as rigid bodies of D_{6h} symmetry.

(9) Campana, C. F.; Lo, F. Y.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3060.

(10) Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. *Inorg. Chem.* **1982**, *21*, 3666.

(11) Mueller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 168.

(12) Giannotti, C.; Ducourant, A. M.; Chanaud, H.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1977**, *140*, 289.

(13) Kovacs, J. A.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1784.

(14) Farrar, D. H.; Grundy, K. R.; Payne, N. C.; Roper, W. R.; Walker, A. *J. Am. Chem. Soc.* **1979**, *101*, 6577.