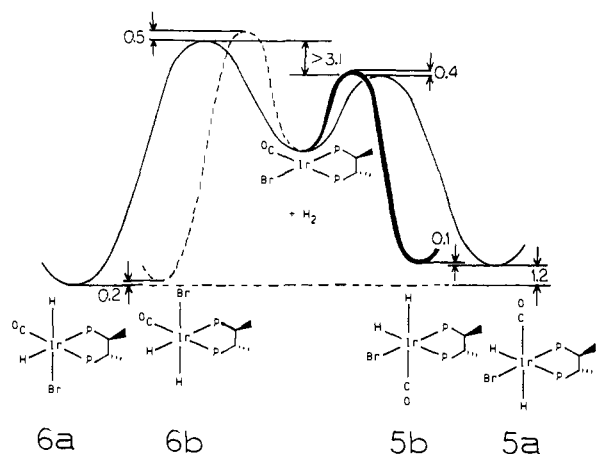


**Figure 1.** Hydride region of the  $^1\text{H}$  NMR spectrum of  $\text{IrBr}(\text{CO})(\text{chiraphos})$  (**4**) plus  $\text{H}_2$  in acetone- $d_6$ : (a) expanded view at  $-25^\circ\text{C}$ ; (b) spectra taken over 40-h period monitoring the conversion from diastereomers **5** to **6** at  $25^\circ\text{C}$ .



**Figure 2.** Reaction coordinate diagram for the system  $\text{IrBr}(\text{CO})(\text{chiraphos})$  (**4**) +  $\text{H}_2$ . Values of  $\Delta\Delta G$  and  $\Delta\Delta G^\ddagger$  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.<sup>9</sup> 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  $\text{H}_2$  and  $\text{Ph}_3\text{SiH}$  oxidative addition, the transition state in these reactions is not very product-like.

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(9) (a) While diastereomeric cis dihydrides have been seen previously for  $[\text{IrH}_2(\text{dipamp})_2]\text{BF}_4$ , 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  $\text{H}_2$  to  $[\text{Ir}(\text{cod})(\text{diop})](\text{PF}_6)$ , 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 $\text{CSe}_2$ to $\text{Se}_2$ and $\text{CO}_2$ . Novel Bonding Mode of the Diselenium Molecule in the Double- $\text{Se}_2$ -Bridged Complex $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)\text{Rh}(\text{triphos})](\text{BPh}_4)_2\cdot 2\text{DMF}$

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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  $\text{CSe}_2$ . Only very recent studies have revealed the potentially enormous reaction possibilities of  $\text{CSe}_2$  complexes.<sup>1</sup> In this paper we report an unprecedented metal-promoted transformation of  $\eta^2\text{-CSe}_2$  into  $\eta^2\text{-Se}_2$  via  $\eta^1\text{-Se}_2\text{CPEt}_3$  and  $\eta^2\text{-Se}_2\text{CO}$  intermediates (Scheme I).

It is well-known that, with adoption of the  $\eta^2\text{-C,S}$  coordination mode, the electrophilicity of the carbon atom of the sulfur analogue of  $\text{CSe}_2$ ,  $\text{CS}_2$ , is enhanced thereby facilitating attack of a nucleophile.<sup>2</sup> Accordingly, we have found that  $\text{PEt}_3$  reacts with  $(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)^{1e}$  (**1**) in  $\text{CH}_2\text{Cl}_2$  to give green crystals of the phosphoniodiselenocarbonylate complex  $(\text{triphos})\text{RhCl}(\text{Se}_2\text{CPEt}_3)^3$  (**2**) (yield 70%). The latter complex reacts immediately at room temperature in  $\text{CH}_2\text{Cl}_2$  solution with dioxygen to give  $\text{OPEt}_3$  and yellow crystals of  $(\text{triphos})\text{RhCl}(\text{Se}_2\text{CO})^5$  (**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,  $\text{OPEt}_3$  cannot be collected as it is sensitive to moisture.

The chloride ligand in **3** is easily replaced by other monofunctional ligands like  $\text{N}_3^-$ , but can be also definitely removed from the complex by treatment of solutions of **3** with  $\text{NaBPh}_4$  in ethanol. As a result, the 16-electron rhodium(III) complex  $[(\text{triphos})\text{Rh}(\text{Se}_2\text{CO})]\text{BPh}_4^6$  (**4**) is quantitatively obtained. A preliminary X-ray crystal-structure determination<sup>7</sup> 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  $\text{CH}_2\text{Cl}_2$  solution of **4** for 5 min, brown crystals of  $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)\text{Rh}(\text{triphos})](\text{BPh}_4)_2$  (**5**) are precipitated in 60% yield, whereas  $\text{CO}_2$  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  $\text{H}_2\text{O}_2$ . 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**, *258*, 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 ( $\text{C}-\text{CH}_3$  rocking  $\text{PEt}_3$ ), 970  $\text{cm}^{-1}$  ( $\nu(\text{C}=\text{Se})$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20  $^\circ\text{C}$ , 32.2 MHz) 30.45 (d,  $J_{\text{PP}} = 17.2$ ,  $J_{\text{PRh}} = 127.6$  Hz, triphos), 23.9 ppm (m,  $\text{PCSe}_2$ ). This pattern does not vary with the temperature and is consistent with triphos acting as a tridentate ligand in five-coordinate complexes.<sup>4</sup> The phosphoniodiselenocarbonylate ligand in **2** is monodentate probably to avoid a supersaturated 20-electron species. This is demonstrated by the existence of the complex  $[(\text{triphos})\text{Rh}(\eta^2\text{-Se}_2\text{CPEt}_3)]\text{BPh}_4$  obtained by chloride ion abstraction from **2**.

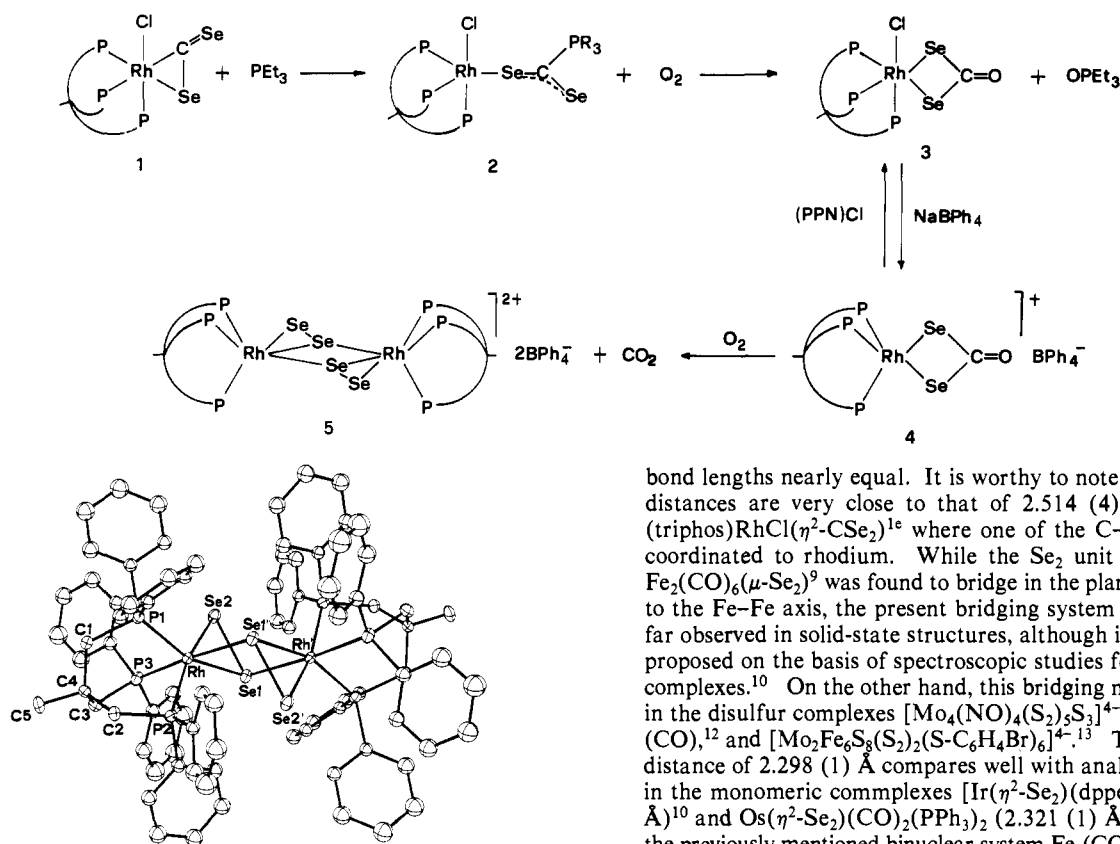
(4) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 4125.

(5) IR (Nujol mulls) 1050  $\text{cm}^{-1}$  ( $\nu(\text{CO})$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20  $^\circ\text{C}$ , 32.2 MHz) 25.85 (t,  $J_{\text{PP}} = 27$ ,  $J_{\text{PRh}} = 108.1$  Hz), -6.24 ppm (d).

(6) IR (Nujol mulls) 1080  $\text{cm}^{-1}$  ( $\nu(\text{CO})$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20  $^\circ\text{C}$ , 32.2 MHz) 34.15 ppm (s,  $J_{\text{PRh}} = 98.3$  Hz).

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

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  $\text{CO}_2$  as  $\text{BaCO}_3$ .

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  $\text{Se}_2$  unit to another rhodium atom results in formation of a four-membered  $\text{RhSeRhSe}$  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  $(\text{triphos})\text{RhCl}(\eta^2\text{-CSe}_2)^{16}$  where one of the C–Se bonds is  $\eta^2$ -coordinated to rhodium. While the  $\text{Se}_2$  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.<sup>10</sup> On the other hand, this bridging mode occurs also in the disulfur complexes  $[\text{Mo}_4(\text{NO})_4(\text{S}_2)_3\text{S}_3]^{4-}$ ,<sup>11</sup>  $\text{Cp}_2\text{Fe}_2(\text{S}_2)_2(\text{CO})$ ,<sup>12</sup> and  $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{S}_2)_2(\text{S-C}_6\text{H}_4\text{Br})_6]^{4-}$ .<sup>13</sup> The Se(1)–Se(2) distance of 2.298 (1) Å compares well with analogous distances in the monomeric complexes  $[\text{Ir}(\eta^2\text{-Se}_2)(\text{dppe})_2]^+$  (2.312 (3) Å)<sup>10</sup> and  $\text{Os}(\eta^2\text{-Se}_2)(\text{CO})_2(\text{PPh}_3)_2$  (2.321 (1) Å)<sup>14</sup> 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  $\text{Se}_2$  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  $\text{CSe}_2$  is substituted for  $\text{CS}_2$ .<sup>7</sup>

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**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:  $\text{C}_{130}\text{H}_{118}\text{B}_2\text{P}_6\text{Rh}_2\text{Se}_4 \cdot 2(\text{CH}_3)_2\text{NCHO}$ ;  $M_r = 2555.7$ ; triclinic, space group  $P\bar{1}$ ;  $a = 16.950$  (5) Å,  $b = 13.710$  (4) Å,  $c = 13.379$  (4) Å,  $\alpha = 90.19$  (2)°,  $\beta = 98.53$  (2)°,  $\gamma = 104.03$  (2)°;  $Z = 1$ ;  $D_{\text{calc}} = 1.423$  g  $\text{cm}^{-3}$ ;  $\mu(\text{Mo K}\alpha) = 16.1$   $\text{cm}^{-1}$ . 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 K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $2.5 < \theta < 25^\circ$ ). Phenyl rings were treated as rigid bodies of  $D_{6h}$  symmetry.

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