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## Stepwise Metal-promoted Conversion of $\eta^2$ -CS<sub>2</sub> into $\eta^2$ -SO. Synthesis and Crystal Structure of the Complex [(triphos)Rh( $\mu$ -SO)<sub>2</sub>Rh(triphos)][BPh<sub>4</sub>]<sub>2</sub>·HCONMe<sub>2</sub> [triphos = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>]

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Nucleophilic attack by PEt<sub>3</sub> at the carbon atom of the  $\eta^2$ -CS<sub>2</sub> ligand in (triphos)RhCl( $\eta^2$ -CS<sub>2</sub>) [triphos = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>] yields the  $\eta^1$ -phosphoniodithiocarboxylate complex (triphos)RhCl(S<sub>2</sub>CPEt<sub>3</sub>), which reacts with dioxygen to give the  $\eta^2$ -dithiocarbonate complex (triphos)RhCl(S<sub>2</sub>CO), treatment of which with NaBPh<sub>4</sub> gives [(triphos)Rh(S<sub>2</sub>CO)]BPh<sub>4</sub>; reaction of the latter with O<sub>2</sub> generates the novel  $\mu$ -SO complex [(triphos)Rh( $\mu$ -SO)<sub>2</sub>Rh(triphos)][BPh<sub>4</sub>]<sub>2</sub>·HCONMe<sub>2</sub>, X-ray analysis of which shows that each bridging SO molecule is  $\eta^2$ -bonded to one metal centre via O and S, and  $\eta^1$ -bonded to the other metal via S.

The ligating properties of the lower sulphur oxides remain relatively unexplored in co-ordination chemistry. In particular, metal complexes with the short-lived sulphur monoxide molecule<sup>1</sup> are extremely rare.<sup>2</sup> The only authenticated compounds are  $Fe_3(S)(SO)(CO)_9^{2d}$  and  $IrCl(PPri_3)_2(SO)^{2e}$  where

SO bridges three metal centres through the sulphur atom, or acts as a terminal S-bonded ligand, respectively.

We now report the synthesis and crystal structure of the first example of a metal complex containing an  $\eta^2$ -S,O: $\eta^1$ -S SO ligand. The complex [(triphos)Rh( $\mu$ -SO)<sub>2</sub>Rh(triphos)][BPh<sub>4</sub>]<sub>2</sub>



Scheme 1

(1)  $[triphos = MeC(CH_2PPh_2)_3]$  is obtained as air-stable red-brown crystals from (triphos)RhCl( $\eta^2$ -CS<sub>2</sub>)<sup>3</sup> (2) through the reactions in Scheme 1.† Intermediary steps for the formation of (1) are: (i) nucleophilic attack by  $PEt_3$  at the carbon atom of the  $\eta^2$ -CS<sub>2</sub> group of (2) to yield the blue air-sensitive phosphoniodithiocarboxylate complex (triphos)RhCl( $S_2CPEt_3$ ) (3) (yield 65%) [i.r.(Nujol) 1030m: C-CH<sub>3</sub> rocking, PEt<sub>3</sub>; 1045m cm<sup>-1</sup>: v(C=S), S<sub>2</sub>CPEt<sub>3</sub>]; (ii) reaction of (3) with dioxygen to give OPEt<sub>3</sub> and the yellow  $\eta^2$ -dithiocarbonate complex (triphos)RhCl(S<sub>2</sub>CO) (4) (yield 70%) [i.r.(Nujol) 1720m and 1600vs cm<sup>-1</sup>: v(C=O), S<sub>2</sub>CO<sup>2-</sup>; <sup>31</sup>P{<sup>1</sup>H} n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>, 293 K) 23.30 p.p.m. (t,  $J_{P-P}$  28,  $J_{P-Rh}$ 107.1 Hz) and -5.04 p.p.m. (d), triphos]; (iii) conversion of (4) into the red-brown 16-electron species [(triphos)Rh- $(S_2CO)$ ]BPh<sub>4</sub> (5) (yield 95%) by chloride ion elimination with NaBPh<sub>4</sub> [i.r.(Nujol) 1685vs and 1600s cm<sup>-1</sup>:  $\nu$ (C=O),  $S_2CO^{2-}$ ; <sup>31</sup>P{<sup>1</sup>H} n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>, 293 K) 35.22 p.p.m. (s,  $J_{P-Rh}$  98.7 Hz)] [reversible on addition of  $(Ph_3P)_2NCl$ ]; (iv) finally, reaction of (5) with dioxygen to generate the title compound (yield 40%). [No absorption attributable to v(SO) modes is present in the i.r. spectrum of complex (5). Its  $^{31}P{^{1}H}$  n.m.r. spectrum in dimethylformamide (DMF) at 293 K exhibits a typical  $AB_2X$  pattern]. During this process  $CO_2$  is evolved almost quantitatively. Compound (1) can be obtained in one step by exposing to air a CH<sub>2</sub>Cl<sub>2</sub> solution of the phosphoniodithiocarboxylate complex (3) in the presence of NaBPh<sub>4</sub>. Crystals of (1) suitable for an X-ray analysis were obtained by recrystallization from DMF-n-butanol, and the structure is shown in Figure 1.‡

The dimeric complex cation is located on a crystallographic inversion centre. The two (triphos)Rh(SO) subunits are linked together by the sulphur atoms of the SO moieties. The overall geometry of the bridging system closely resembles those found earlier for two rhodium complexes with  $O_2^4$  and Se<sub>2</sub>.<sup>5</sup> The S–O distance of 1.68(1) Å is significantly longer than the analogous separation for SO in the gas phase (1.48 Å)<sup>6</sup> and in the previously mentioned iron and iridium complexes [1.47(2)<sup>2d</sup> and 1.32(2)<sup>2e</sup> Å, respectively].

‡ Crystal data: C<sub>130</sub>H<sub>118</sub>B<sub>2</sub>O<sub>2</sub>P<sub>6</sub>Rh<sub>2</sub>S<sub>2</sub>·Me<sub>2</sub>NCHO, M = 2262.89, triclinic, space group P1, a = 16.028(4), b = 15.299(3), c = 13.126(3)Å,  $\alpha = 89.22(2)$ ,  $\beta = 91.01(2)$ ,  $\gamma = 65.26(2)^\circ$ , U = 2922(1) Å<sup>3</sup>, Z = 1,  $D_c = 1.286$  g cm<sup>-3</sup>,  $\mu$ (Mo- $K_{\alpha}$ ) = 4.43 cm<sup>-1</sup>. The structure was solved by Patterson and Fourier techniques and refined to an R factor of 0.080 ( $R_w = 0.085$ ) using 3058 absorption-corrected reflections with  $I > 3\sigma(I)$  measured on a Philips PW1100 diffractometer up to  $2\theta = 45^\circ$  with Mo- $K_{\alpha}$  radiation ( $\lambda = 0.710$  69 Å). During the refinement the phenyl rings were treated as rigid groups of  $D_{6h}$  symmetry. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Figure 1. ORTEP drawing of the [(triphos)Rh( $\mu$ -SO)<sub>2</sub>Rh(triphos)]<sup>+</sup> complex cation. The terminal phenyl rings (except for the connecting C atoms) have been omitted for clarity. Some relevant bond lengths (Å) and angles (°) are as follows: Rh–S, 2.323(5); Rh–S', 2.383(5); Rh–O, 2.296(10); Rh–P(1), 2.328(5); Rh–P(2), 2.292(5); Rh–P(3), 2.315(4); S–O, 1.68(1); S–Rh–S', 79.2(2); S–Rh–P(3), 150.9(2); S–Rh–O, 42.7(3); P(1)–Rh–O, 160.6(3); Rh–S–Rh', 100.8(2).

Most likely the reaction of (5) with dioxygen [step (iv)] is not a straightforward process. Spectroscopic studies indicate the production of at least one intermediate species before the final  $\mu$ -SO complex (1). In particular, the <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectrum of the reaction mixture in (CD<sub>3</sub>)<sub>2</sub>CO at 293 K changes from the initial singlet at 35.22 p.p.m. due to (5) to a singlet at 24.07 p.p.m. ( $J_{P.Rh}$  102.6 Hz) before the final AB<sub>2</sub>X pattern of (1) appears. We are now trying to isolate the intermediate. We note that the reaction of O<sub>2</sub> with [(triphos)Rh(Se<sub>2</sub>CO)][BPh<sub>4</sub>] under the same conditions yields the  $\mu$ -Se<sub>2</sub> dimer [(triphos)Rh( $\mu$ -Se<sub>2</sub>)<sub>2</sub>Rh(triphos)][BPh<sub>4</sub>]<sub>2</sub>.<sup>5</sup>

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 $<sup>\</sup>dagger$  All the reactions were routinely performed in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. When necessary the complexes were precipitated by addition of ethanol. Satisfactory elemental analytical data were obtained.