

Stepwise Metal-promoted Conversion of η^2 -CS₂ into η^2 -SO. Synthesis and Crystal Structure of the Complex [(triphos)Rh(μ -SO)₂Rh(triphos)][BPh₄]₂·HCONMe₂ [triphos = MeC(CH₂PPh₂)₃]

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

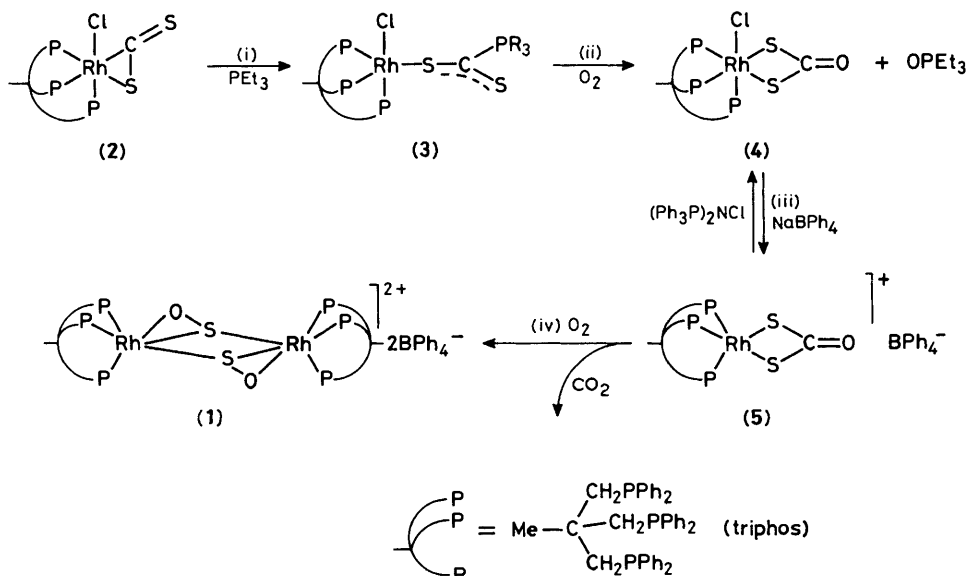
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R., Via F. D. Guerrazzi, 27, 50132 Firenze, Italy

Nucleophilic attack by PEt₃ at the carbon atom of the η^2 -CS₂ ligand in (triphos)RhCl(η^2 -CS₂) [triphos = MeC(CH₂PPh₂)₃] yields the η^1 -phosponiodithiocarbonylate complex (triphos)RhCl(S₂CPEt₃), which reacts with dioxygen to give the η^2 -dithiocarbonate complex (triphos)RhCl(S₂CO), treatment of which with NaBPh₄ gives [(triphos)Rh(S₂CO)]BPh₄; reaction of the latter with O₂ generates the novel μ -SO complex [(triphos)Rh(μ -SO)₂Rh(triphos)][BPh₄]₂·HCONMe₂, X-ray analysis of which shows that each bridging SO molecule is η^2 -bonded to one metal centre *via* O and S, and η^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 molecule¹ are extremely rare.² The only authenticated compounds are Fe₃(S)(SO)(CO)₉^{2d} and IrCl(PPR₃)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 η^2 -S,O: η^1 -S SO ligand. The complex [(triphos)Rh(μ -SO)₂Rh(triphos)][BPh₄]₂



Scheme 1

(1) [triphos = MeC(CH₂PPh₂)₃] is obtained as air-stable red-brown crystals from (triphos)RhCl(η²-CS₂)³ (2) through the reactions in Scheme 1.† Intermediary steps for the formation of (1) are: (i) nucleophilic attack by PEt₃ at the carbon atom of the η²-CS₂ group of (2) to yield the blue air-sensitive phosphoniodithiocarboxylate complex (triphos)RhCl(S₂CPEt₃) (3) (yield 65%) [i.r.(Nujol) 1030m: C-CH₃ rocking, PEt₃; 1045m cm⁻¹: ν(C=S), S₂CPEt₃]; (ii) reaction of (3) with dioxygen to give OPET₃ and the yellow η²-dithiocarbonate complex (triphos)RhCl(S₂CO) (4) (yield 70%) [i.r.(Nujol) 1720m and 1600vs cm⁻¹: ν(C=O), S₂CO²⁻; ³¹P{¹H} n.m.r. (CD₂Cl₂, 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(S₂CO)]BPh₄ (5) (yield 95%) by chloride ion elimination with NaBPh₄ [i.r.(Nujol) 1685vs and 1600s cm⁻¹: ν(C=O), S₂CO²⁻; ³¹P{¹H} n.m.r. (CD₂Cl₂, 293 K) 35.22 p.p.m. (s, *J*_{P-Rh} 98.7 Hz)] [reversible on addition of (Ph₃P)₂NCl]; (iv) finally, reaction of (5) with dioxygen to generate the title compound (yield 40%). [No absorption attributable to ν(SO) modes is present in the i.r. spectrum of complex (5). Its ³¹P{¹H} n.m.r. spectrum in dimethylformamide (DMF) at 293 K exhibits a typical AB₂X pattern]. During this process CO₂ is evolved almost quantitatively. Compound (1) can be obtained in one step by exposing to air a CH₂Cl₂ solution of the phosphoniodithiocarboxylate complex (3) in the presence of NaBPh₄. 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 O₂⁴ and Se₂.⁵ 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)⁶ and in the previously mentioned iron and iridium complexes [1.47(2)^{2d} and 1.32(2)^{2e} Å, respectively].

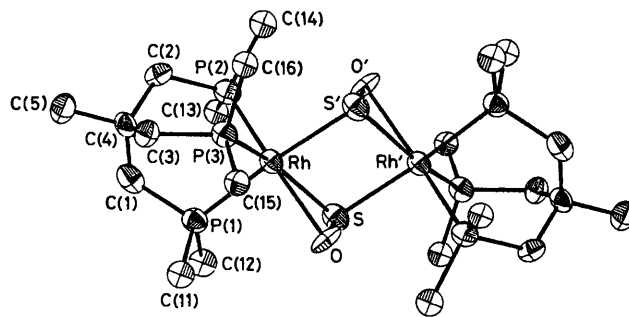


Figure 1. ORTEP drawing of the [(triphos)Rh(μ-SO)₂Rh(triphos)]⁺ complex cation. The terminal phenyl rings (except for the connecting C atoms) have been omitted for clarity. Some relevant bond lengths (Å) and angles (°) are as follows: Rh-S, 2.323(5); Rh-S', 2.383(5); Rh-O, 2.296(10); Rh-P(1), 2.328(5); 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 μ-SO complex (1). In particular, the ³¹P{¹H} n.m.r. spectrum of the reaction mixture in (CD₃)₂CO 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 AB₂X pattern of (1) appears. We are now trying to isolate the intermediate. We note that the reaction of O₂ with [(triphos)Rh(S₂CO)][BPh₄] under the same conditions yields the μ-Se₂ dimer [(triphos)Rh(μ-Se₂)₂Rh(triphos)][BPh₄]₂.⁵

Received, 18th April 1985; Com. 519

† All the reactions were routinely performed in CH₂Cl₂ at room temperature. When necessary the complexes were precipitated by addition of ethanol. Satisfactory elemental analytical data were obtained.

‡ *Crystal data*: C₁₃₀H₁₁₈B₂O₂P₆Rh₂S₂·Me₂NCHO, *M* = 2262.89, triclinic, space group *P*1̄, *a* = 16.028(4), *b* = 15.299(3), *c* = 13.126(3) Å, α = 89.22(2), β = 91.01(2), γ = 65.26(2)°, *U* = 2922(1) Å³, *Z* = 1, *D*_c = 1.286 g cm⁻³, μ(Mo-Kα) = 4.43 cm⁻¹. 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* > 3σ(*I*) measured on a Philips PW1100 diffractometer up to 2θ = 45° with Mo-Kα radiation (λ = 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.

References

- W. Genz and P. W. Schenk, *Z. Anorg. Allg. Chem.*, 1970, **309**, 300.
- (a) G. Schmid, G. Ritter, and T. Debaerdemaeker, *Chem. Ber.*, 1975, **108**, 3008; (b) M. Höfler and A. Baitz, *ibid.*, 1976, **109**, 3147; (c) K. S. Arulsamy, K. K. Pandey, and U. C. Agarwala, *Inorg. Chim. Acta*, 1981, **54**, L51; (d) L. Markó, B. Markó-Monostory, T. Medach, and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 226; (e) W. A. Schenk, J. Leissner, and C. Burschka, *ibid.*, 1984, **23**, 806.
- C. Bianchini, C. Mealli, A. Meli, and M. Sabat, *Inorg. Chem.*, 1984, **23**, 4125.
- M. J. Bennett and P. B. Donaldson, *J. Am. Chem. Soc.*, 1971, **93**, 3307.
- C. Bianchini, C. Mealli, A. Meli, and M. Sabat, *J. Am. Chem. Soc.*, in the press.
- F. X. Powell and D. R. Lide, Jr., *J. Chem. Phys.*, 1964, **41**, 1143.