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Preliminary communication

THE COORDINATION AND ACTIVATION OF CARBON DISULFIDE IN BINUCLEAR RHODIUM COMPLEXES

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Summary

The reaction of *trans*-[RhCl(CO)(DPM)]$_2$ (DPM = $Ph_2PCH_2PPh_2$) with CS_2 yields an interesting series of CS_2 complexes culminating in the condensation of two CS_2 molecules yielding the unusual, asymmetric species [Rh_2Cl_2(CO)-(C_2S_4)(DPM)$_2$]. This novel C_2S_4 species is also produced in the reaction of [Rh_2Cl_2(μ-CO)(DPM)$_2$] with CS_2. The structural determination of the C_2S_4 complex indicates that the C_2S_4 moiety bridges the rhodium atoms such that it forms a Rh—S—C—S—C metallocycle with one rhodium atom while simultaneously bonding through a sulfur atom to the second rhodium atom forming a Rh—C—S—Rh metallocycle. A scheme for the reactions of the above complexes with CS_2 is presented.

Much of the recent interest in carbon disulfide chemistry stems from the close similarity of the molecule to CO_2. Although several transition metal-CS_2 complexes have been structurally characterized [1—5], only one structure is known for Rh [6] and none has been reported for Ir. For these metals the common η^2, side-on CS_2 bonding mode has often been inferred [7,8] based on analogies with other metal complexes, even though the CS_2 stretching frequencies in many of the Rh and Ir complexes are ca. 100 cm^{-1} lower than in those structurally characterized complexes [1—5]. Owing to this apparent discrepancy in infrared results and because of the demonstrated ability of Rh and Ir to activate small molecules towards condensation reactions [6,9—11], the present study was undertaken to establish the basis for much needed infrared and structural correlations and to gain a better understanding of transition metal activation of CS_2 and related molecules.

We now report on the reactions of *trans*-[RhCl(CO)(DPM)]$_2$ (1) and [Rh_2Cl_2-(μ-CO)(DPM)$_2$] (2) with CS_2 and the structural characterization of one of the products, [Rh_2Cl_2(CO)(C_2S_4)(DPM)$_2$] (3). A scheme for these reactions, based on infrared, ^{31}P and ^{13}C NMR spectral data is also presented.

Treatment of a suspension of 1 (200 mg in 20 ml of CH_2Cl_2) with 7 ml of CS_2 under a nitrogen atmosphere for 24 h yields a clear red solution from which red crystals of $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ were obtained by addition of diethyl ether and slow cooling. Complex 3, as a Nujol mull, has $\nu(CO)$ at 2040(sh) and 2020m cm^{-1} and has $\nu(CS)$ at 1050s, 995(sh) and 980vs cm^{-1}. It also shows a complex multiplet $^{31}P\{^1H\}$NMR pattern, consistent with an AA'BB'XY spin system and characteristic of an asymmetric species, centered at $\delta = 7.5$ ppm*. Although satisfactory elemental analyses were obtained for C, H and Cl, suitable results for S were never obtained**.

$[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ crystallizes in the space group $P2_1/c$ with $a = 22.311(3)$, $b = 22.843(3)$, $c = 22.838(3)$ Å, $\beta = 115.21(1)°$, $V = 10526$ Å^3 and $Z = 8$. Intensity data were collected on an automated Picker four circle diffractometer using nickel filtered Cu-K_α radiation in the range $2° \leqslant 2\theta \leqslant 100°$; beyond this few reflections were observed. Of the 11195 unique reflections measured 5929 had $I \geqslant 3\sigma(I)$ and were used in subsequent calculations. The structure was solved by a combination of MULTAN, trial and error methods (used in conjunction with the Patterson map to fix the origin) and conventional least-squares and Fourier techniques***. Refinement by full matrix, least-squares methods converged at $R = 0.114$ and $R_w = 0.145$ for 337 parameters varied, using isotropic thermal parameters for all atoms, rigid group refinement for the phenyl rings† and data which is corrected for absorption effects. Although the crystallographic residuals are rather high at this stage of refinement there is no ambiguity about the correctness of the structure. Both independent dimers are very similar with good agreement in the molecular parameters, all of which are chemically reasonable. The high residuals are a consequence of the poor diffraction quality of the crystals which furthermore underwent loss of solvent of crystallization during data collection. A full anisotropic refinement would have been preferable, however the extremely high cost involved does not justify such a refinement to us, since the important details of the structure are already clear.

The complex crystallizes with two independent molecules per asymmetric unit, one of which (dimer A) is shown in Figure 1. Both dimers display similar, distorted octahedral coordination geometries about each rhodium atom. However subtle differences between the dimers are observed resulting mainly from the different orientations of the DPM phenyl groups. These in turn result in somewhat different orientations for the chloro and carbonyl ligands in the two dimers. In addition, the $Rh_2C_2S_4$ fragment is close to planar in dimer B whereas it is puckered slightly in dimer A. The corresponding bond lengths within the two $Rh_2C_2S_4$ fragments however compare well, as shown in Table 1. The C_2S_4 fragment bridges the Rh—Rh single bond such that it forms a five membered metallocycle with one rhodium atom (Rh(1)) while simultaneously bonding to the other rhodium atom through a sulfur atom forming a second, four membered metallocycle. Within the metallocycle rings the C—S distances (1.63(2) to 1.79(2) Å) indicate delocalization over the carbon-sulfur framework

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*Positive δ values are downfield from H_3PO_4.

**Elemental analyses: Found: C, 51.6; H, 4.56; Cl, 6.23; S, 4.11. $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ calcd: C, 51.9; H, 3.61; Cl, 5.78; S, 10.5%.

***Details of the solution of the structure will be published in a subsequent full paper.

†For a rigid body treatment, see for example ref. 12.

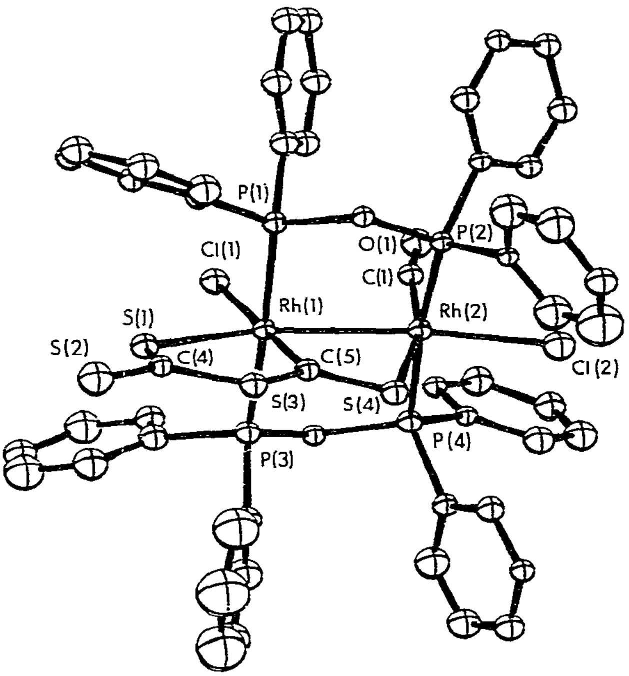


Fig. 1. A perspective view of $[Rh_2Cl_2(CO)(C_2S_4)(DPM)_2]$ (dimer A) showing 20% ellipsoids. The gross structural features of dimer B are similar.

TABLE 1

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES)

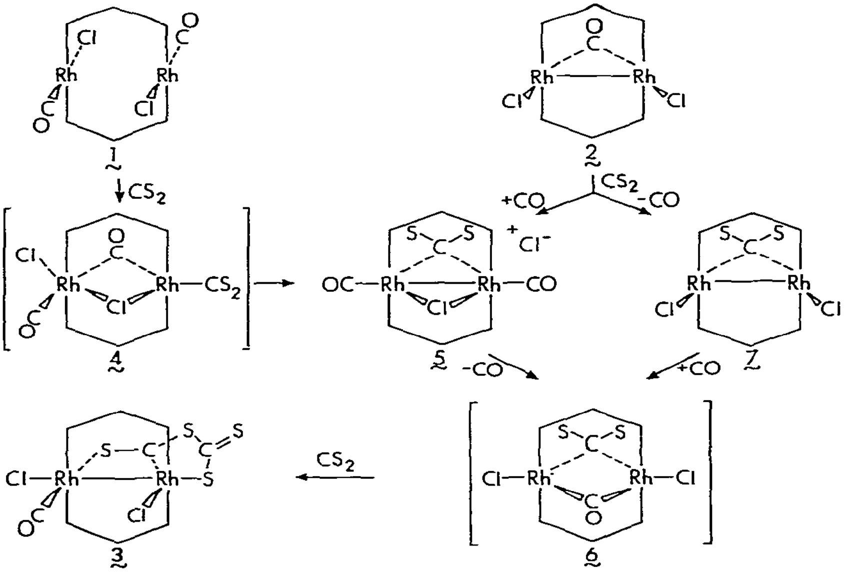
	Dimer A	Dimer B		Dimer A	Dimer B
Rh(1)—Rh(2)	2.810(3)	2.809(3)	Rh(2)—S(4)	2.388(7)	2.392(7)
Rh(1)—Cl(1)	2.427(6)	2.454(6)	Rh(2)—C(1)	1.86(2)	1.97(3)
Rh(2)—Cl(2)	2.507(8)	2.529(8)	S(1)—C(4)	1.67(2)	1.73(2)
Rh(1)—P(1)	2.353(7)	2.326(7)	S(2)—C(4)	1.63(3)	1.64(3)
Rh(2)—P(2)	2.359(7)	2.345(8)	S(3)—C(4)	1.79(2)	1.73(3)
Rh(1)—P(3)	2.367(8)	2.349(7)	S(3)—C(5)	1.76(2)	1.74(2)
Rh(2)—P(4)	2.346(8)	2.371(7)	S(4)—C(5)	1.68(3)	1.63(2)
Rh(1)—S(1)	2.351(7)	2.356(7)	C(1)—O(1)	1.13(2)	1.01(3)
Rh(1)—C(5)	1.89(2)	1.95(2)			
Rh(2)—Rh(1)—S(1)	163.0(2)	164.4(2)	S(4)—Rh(2)—C(1)	164.3(8)	171.8(8)
Rh(2)—Rh(1)—Cl(1)	104.1(2)	91.8(2)	Rh(1)—S(1)—C(4)	105.1(9)	104.5(9)
Rh(2)—Rh(1)—C(5)	74.7(8)	76.3(7)	S(1)—C(4)—S(2)	127(2)	123(1)
Rh(1)—Rh(2)—Cl(2)	172.9(2)	165.5(2)	S(1)—C(4)—S(3)	118(1)	119(2)
Rh(1)—Rh(2)—S(4)	72.6(2)	71.5(2)	S(2)—C(4)—S(3)	115(1)	117(1)
Rh(1)—Rh(2)—C(1)	91.9(8)	100.4(8)	C(4)—S(3)—C(5)	102(1)	104(1)
Cl(1)—Rh(1)—S(1)	92.9(2)	103.8(2)	Rh(1)—C(5)—S(3)	124(1)	124(1)
Cl(1)—Rh(1)—C(5)	177.5(8)	166.9(7)	Rh(1)—C(5)—S(4)	120(1)	117(1)
Cl(2)—Rh(2)—S(4)	101.2(2)	94.0(2)	S(3)—C(5)—S(4)	116(1)	119(1)
Cl(2)—Rh(2)—C(1)	94.4(8)	94.1(8)	Rh(2)—S(4)—C(5)	91.1(8)	95.1(8)
S(1)—Rh(1)—C(5)	88.3(8)	88.3(7)	Rh(2)—C(1)—O(1)	169(2)	165(3)

and range from values comparable to the C—S distances in ethylene thiourea (1.71 Å) [13] to single bond values (1.81 Å) [13]. The Rh—C distance in the $Rh_2C_2S_4$ fragment (average, 1.92(3) Å) is unusually short, being comparable to the rhodium—carbonyl distance (average, 1.92(6) Å). The slight bending of the carbonyl ligands (average Rh(2)—C(1)—O(1) = 167(3)°) results from close contacts with the phenyl groups.

Based on $^{31}P\{^{1}H\}$NMR and infrared spectra, on the present structure determination and on analogies with similar SO_2 [14] and acetylene [15] chemistry we propose the following scheme for the reaction of 1 with CS_2 (see Scheme 1). Initial CS_2 attack is probably terminal yielding a species such as 4 which then loses Cl^- readily and rearranges to 5. Species 5 is a 1:1 electrolyte and has a very similar infrared spectrum (ν(CO) = 1990 cm^{-1}; the CS_2 region is obscured by the bands due to the DPM ligands) and similar $^{31}P\{^{1}H\}$NMR spectral parameters (δ = 14.3 ppm; $|^{1}J(Rh—P) + {}^{x}J(Rh—P)|$ = 98.2 Hz) to the well characterized SO_2 analogue [14]. The loss of one carbonyl ligand yields compound 6 which although not observed, is exactly analogous to an acetylene complex which we have prepared by the same route and have structurally characterized [15]. Electrophilic attack at S(3) of the bound CS_2 molecule (see Figure 1) by another CS_2 molecule would then readily yield the final product (3).

SCHEME 1

PROPOSED SCHEME FOR THE REACTIONS OF *trans*-[RhCl(CO)(DPM)]$_2$ AND [Rh$_2$Cl$_2$(μ-CO)(DPM)$_2$] WITH CS$_2$



The reaction of the monocarbonyl species 2 with CS_2, which also yields compound 3, was followed carefully by monitoring the infrared, $^{31}P\{^{1}H\}$ and $^{13}C\{^{31}P\{^{1}H\}\}$NMR spectra (using ^{13}CO enriched compound 2 for the ^{13}C NMR study) during the slow stepwise addition of CS_2. Initially the $^{31}P\{^{1}H\}$NMR spectrum shows two symmetric species in addition to the starting material 2: compound 5, which was previously characterized, and compound 7 (δ = 15.7 ppm; $|^{1}J(Rh—P) + {}^{x}J(Rh—P)|$ = 116.5 Hz). The $^{13}C\{^{31}P\{^{1}H\}\}$NMR spectrum at the same time shows only one additional resonance at δ = 186.5 ppm (doublet) with J(Rh—C) = 80.1 Hz, characteristic of a terminal carbonyl ligand. The corresponding infrared spectrum shows a band at 1990 cm^{-1} due to the terminal carbonyl groups in 5, and the bridging carbonyl of 2 at 1750 cm^{-1}. No other carbonyl bands are observed. These observations are consistent with species 5 and 7, shown in the scheme, resulting from CS_2 attack on 2 and CO transfer. Analogous species have been obtained and characterized in the reaction of 2 with SO_2 [16]. In these SO_2 studies we observed that these Rh dimers act as efficient CO scavangers. Therefore when 5 loses CO yielding 6, compound 7 picks up the CO also giving 6, which subsequently yields the final product. The spectral parameters of compound 3 are consistent with the structure observed in the crystal. In addition to the complex multiplet in the $^{31}P\{^{1}H\}$NMR spectrum (vide supra), compound 3 shows a doublet in the $^{13}C\{^{31}P\{^{1}H\}\}$NMR spectrum at 191.5 ppm with J(Rh—C) = 69.1 Hz and a terminal carbonyl band in its solution IR spectrum (2030 cm^{-1}; CH_2Cl_2). We postulate carbon-bound CS_2 species in complexes 5, 6 and 7, as shown in the scheme, since in each of species 5 and 7 the four phosphorus atoms are chemically equivalent at –50°C. A C—S bound species would give rise to a more complex ^{31}P NMR spectrum unless fluctional at this temperature, and no evidence for fluctionality was observed over the temperature range studied (20 to –50°C). Unfortunately lower temperatures could not be attained in this study owing to solubility problems.

This study presents one of the first structural characterizations [6] of a rhodium-CS_2 complex and based on its infrared spectrum, which is similar to other such complexes which are believed to contain π-bound CS_2, suggests that some previous formulations [7,8] could possibly be reformulated as C_2S_4 species. The similarities in the mode of CS_2 condensation to that of CO_2 in an iridium complex [11] support the argument that CS_2 is a useful model for studying CO_2 binding in metal complexes and suggest the possibility of analogous CO_2 binuclear chemistry which is currently under investigation.

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References

1 M.C. Baird, G. Hartwell, R. Mason, A.I.M. Rae and G. Wilkinson, Chem. Commun., (1967) 92.
2 R. Mason and A.I.M. Rae, J. Chem. Soc. A, (1970) 1767.
3 T. Kushiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakuda, S. Takahashi and N. Hagihara, Bull. Chem. Soc. Jap., 41 (1968) 296.
4 H. Werner, K. Leonhard and Ch. Burschka, J. Organometal. Chem., 160 (1978) 291.
5 H. LeBozec, P.H. Dixneuf, A.J. Carty and N.J. Taylor, Inorg. Chem., 17 (1978) 2568.
6 H. Werner, O. Kolb, R. Feser and U. Schubert, J. Organometal. Chem., 191 (1980) 283.
7 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.
8 D. Commereuc, I. Douek and G. Wilkinson, J. Chem. Soc. A, (1970) 1771.
9 M. Cowie and J.A. Ibers, Inorg. Chem., 15 (1976) 552.
10 K. Itoh, I. Matsuda, F. Ueda, Y. Ishii and J.A. Ibers, J. Amer. Chem. Soc., 99 (1978) 2118.
11 T. Herskovitz and L.J. Guggenberger, J. Amer. Chem. Soc., 98 (1976) 1615.
12 M. Cowie and S.K. Dwight, Inorg. Chem., 18 (1980) 209.
13 International Tables for X-ray Crystallography, The Kynoch Press, Birmingham, England, Vol. III, p. 276.
14 M. Cowie and S.K. Dwight, Inorg. Chem., 18 (1980) 209.
15 M. Cowie and T.G. Southern, J. Organometal. Chem., 193 (1980) C46.
16 M. Cowie and S.K. Dwight, Inorg. Chem., in press.