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# Novel Complexes of Rhodium(I) Containing Bridging $SO_2$ Ligands

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The recently reported complex, [1] $[Rh_2(CO)_2(\mu\text{-}CO)(\mu Cl)(DPM)_2]BPh_4$, (**1**), (DPM = bis(diphenylphosphino)methane; Ph = $C_6H_5$), is the first structurally characterized example of an "A-frame" complex containing a ligand in the proposed "active site", bridging the two metal atoms. This carbonyl-bridged cationic complex is obtained by the reversible addition of CO to the parent complex, $[Rh(CO)_2(\mu\text{-}Cl)(DPM)_2]BPh_4$, (**2**) and conclusively establishes that small molecules can coordinate to the active site in "A-frame" complexes as first suggested by Kubiak and Eisenberg [2]. We wish now to report the reaction of $SO_2$ with **2**, which yields initially the $SO_2$-adduct, believed to be analogous to the CO-bridged complex, **1**. In addition, however, a variety of new and interesting chemistry is observed. The crystal structure of one of the products in this reaction is also reported.

Treatment of an acetone or dichloromethane solution of **2** with $SO_2$ gave initially a red solution. Addition of petroleum ether or slow evaporation of the solvent gave a red-brown crystalline product, $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2][BPh_4]$, (**3**), with $\nu(CO)$ at 2015 (vs) and 1986 (ssh) $cm^{-1}$, $\nu(SO_2)$ at 1229 (m) and 1070 (m) $cm^{-1}$ [3]. The presence of $BPh_4^-$ was indicated by a band at 610 $cm^{-1}$. The above formulation for **3** is based on:

1) the similarity in the infrared spectra of **3** and **1**, the analogous CO-bridged complex; 2) the $^{31}P\{^1H\}$ n.m.r. spectrum, indicating only one phosphorus environment and a strong metal–metal interaction (*vide infra*); 3) the displacement of $SO_2$ from solutions of **3** under a stream of $N_2$, generating **2** and replacement of $SO_2$ by CO generating **1** (see Scheme); 4) the values of $\nu(SO_2)$ are in the region observed for other $SO_2$ ligands bridging metal–metal bonds [4, 5]; and 5) the elemental analysis: Calcd. for $Rh_2BClC_{76}H_{64}O_4P_4S$: C, 62.98; H, 4.45. Found: C, 61.85; H, 4.44. On prolonged treatment of the red acetone, dichloromethane or THF solutions of **3** with $SO_2$ a brown microcrystalline precipitate, $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$, (**4**), was obtained along with a yellow solution. Slow evaporation of the ultimate red dichloromethane or THF solutions produced well-formed red crystals of **4**. This ultimate product has $\nu(SO_2)$ at 1190 (m) and 1060 (m) $cm^{-1}$ [3]. No CO or $BPh_4^-$ band is observed.

The $^{31}P\{^1H\}$ n.m.r. spectra of solutions **3** and **4** in dichloromethane-$d_2$ (–50° to +30 °C) each showed a single second-order pattern (**3**: $\delta_P$ = 24.6 p.p.m. (all shifts measured downfield from 85% $H_3PO_4$ are positive) $|^1J_{RhP} + {}^xJ_{RhP}|$ = 91.3 Hz; **4**: $\delta_P$ = 19.6 p.p.m., $|^1J_{RhP} + {}^xJ_{RhP}|$ = 115.0 Hz). Therefore each complex contains only one environment for phosphorus. A solution of **3**, allowed to stand for 24 hours, gave a $^{31}P\{^1H\}$ n.m.r. spectrum with signals due to **3**, **4** and an as yet unidentified product (**5**) which will be the subject of further investigations.

Complex **4** crystallizes in the space group $C^5_{2h}$–$P2_1/c$ with $a$ = 118.228(1), $b$ = 13.526(1), $c$ = 19.632(2) Å, $\beta$ = 104.72(1)°, V = 4862 Å$^3$ ($Z$ = 4,

*Scheme*

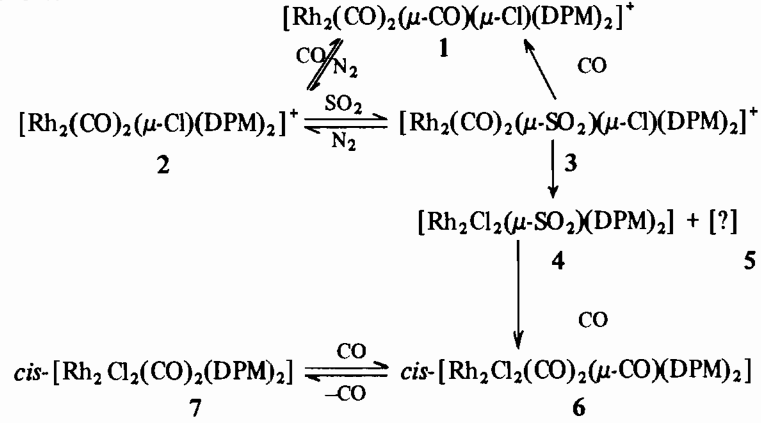

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TABLE. Selected Bond Distances (A) and Angles (deg).

| Atoms | Distance | Atoms | Distance | Atoms | Distance |
|---|---|---|---|---|---|
| Rh(1)–S | 2.169(2) | Rh–P (av) | 2.331(8) | P–C (phenyl) | 1.827(8) |
| Rh(2)–S | 2.169(2) | Rh(1)–Rh(2) | 2.7837(8) | P–C (methylene) | 1.829(9) |
| Rh–Cl (av) | 2.342(2) | S–O (av) | 1.452(6) | | |

| Atoms | Angle | Atoms | Angle | Atoms | Angle |
|---|---|---|---|---|---|
| Cl(1)–Rh(1)–S | 143.33(9) | Cl(2)–Rh(2)–P(4) | 86.11(8) | Rh(1)–S–Rh(2) | 79.84(7) |
| Cl(2)–Rh(2)–S | 142.44(8) | S–Rh(1)–P(1) | 95.23(8) | O(1)–S–O(2) | 111.9(4) |
| Cl(1)–Rh(1)–P(1) | 85.98(9) | S–Rh(1)–P(3) | 96.04(8) | P(1)–C(1)–P(2) | 111.6(4) |
| Cl(1)–Rh(1)–P(3) | 86.45(9) | S–Rh(2)–P(2) | 95.37(8) | P(3)–C(2)–P(4) | 110.5(5) |
| Cl(2)–Rh(2)–P(2) | 86.75(7) | S–Rh(2)–P(4) | 94.91(8) | | |

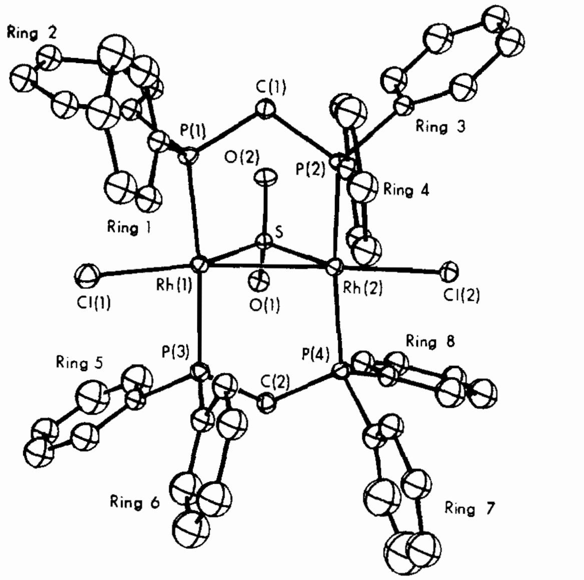

Figure. A perspective view of $Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2$ showing all non hydrogen atoms with 20% thermal ellipsoids.

$\rho_{calc}$ = 1.574, $\rho_{obs}$ = 1.59(2) g cm$^{-3}$). Data were collected on an automated Picker four-circle diffractometer using nickel-filtered CuK$\alpha$ radiation ($2\theta \leqslant 123°$, scan range, 1.5° in $2\theta$ with correction for K$\alpha_1$–K$\alpha_2$ separation). Of the 7690 unique reflections measured, 5207 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the solution and refinement of the structure. The heavy atoms were located by conventional Patterson techniques and the light atoms located in subsequent Fourier maps. The structure was refined by full-matrix, least-squares techniques to R = 0.058 and $R_w$ = 0.067 [6] based on 216 parameters varied.

[$Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2$] is shown in the Figure to be a distorted, $SO_2$-bridged, "A-frame" complex. This is the first example of an $SO_2$-bridged rhodium "A-frame", and the first such complex of rhodium with terminal instead of bridging anionic ligands. Other similar complexes formed by the reaction of [$Pd_2Cl_2(DPM)_2$] with CNR [7], $N_2Ph^+$ [8], $SO_2$ [9] and [$Pd_2Cl_2(DAM)_2$] (DAM = bis(diphenylarsino)methane) with Co [10] have been reported and are similar to the title complex apart from the metal–metal bond in the latter. Moreover, the palladium adducts are the expected products resulting from ligand insertion into the Pd–Pd bond, whereas the present complex is the result of the disproportionation of the initial $SO_2$ adduct (3) (see scheme).

The coordination about each rhodium atom is best described as a significantly distorted trigonal bipyramidal geometry with the three equatorial sites occupied by a terminal chloro ligand, a bridging sulfur dioxide ligand and the other rhodium atom. The Rh(1)–Rh(2) distance of 2.7838(8) Å (see Table) is within the range considered to involve normal two-electron Rh–Rh bonds (2.617(3)–2.796(8) Å) [11]. The metal–metal bond is further substantiated by several observations: 1) The intraligand P(1)–P(2) and P(3)–P(4) distances (3.019(3) and 3.012(3) Å, respectively) are significantly larger than the Rh(1)–Rh(2) distance indicating a compression along the Rh–Rh axis [12]; 2) The acute Rh(1)–S–Rh(2) angle (79.85(7)°) again indicates compression along the Rh–Rh axis; 3) Conventional electron counting results in a 15 electron configuration without inclusion of the Rh–Rh bond which is necessary to account for the observed diamagnetism of the compound; 4) The second order $^{31}P\{^1H\}$ n.m.r. spectrum (*vide supra*) indicates significant Rh–Rh interaction.

The sulfur dioxide ligand symmetrically bridges the two rhodium atoms (Rh(1)–S = Rh(2)–S = 2.169(2) Å), with a dihedral angle between Rh(1)–S–Rh(2) and O(1)–S–O(2) planes of 92.3(2)°. The Rh–S distances are significantly shorter than the metal–sulfur distances observed in other $SO_2$-bridged complexes, ([$IrH(CO)_2(PPh_3)$]$_2$ $SO_2$ [4], Ir–S, 2.313(3) Å; $Pd_3(SO_2)_2({}^tBuNC)_5$ [5], Pd–S, 2.261(9) Å) implying strong Rh–S interactions.

The "active site" opposite the $SO_2$ ligand is effectively blocked by four phenyl rings; in particular rings 4 and 6. The Rh–*ortho* hydrogen interactions involving the latter two rings are unusually short (Rh(1)–H(66), 2.70 Å; Rh(2)–H(46), 2.73 Å). Compare for example the analogous distances in the red and orange isomers of Wilkinson's catalyst [13] (Rh---H; 2.77 and 2.84 Å, respectively). The sites adjacent to the $SO_2$ ligand are, however, conspicuously vacant and open to attack.

Solutions of **3** and **4** in dichloromethane each react readily with CO. Complex **3** reacts rapidly with CO to form **1**, and **4** reacts with CO forming the novel neutral carbonyl species, *cis*-$[Rh_2Cl_2(CO)_2(\mu\text{-}CO)(DMP)_2]$ (**6**). This species reversibly loses CO in solution yielding the corresponding dicarbonyl species, *cis*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ (**7**). Only a few other examples in which CO reversibly binds to a bridging site have been reported [1, 7]. Crystals of **6** and **7** are yellow and yellow-orange, respectively. Complex **6** exhibits $\nu$(CO) at 2004(s), 1964(vs) and 1872(s) $cm^{-1}$ and **7** has $\nu$(CO) at 1994(s) and 1972(va) $cm^{-1}$. Elemental analyses are in agreement with these formulations (**6**: Calcd. for $Rh_2Cl_2C_{52}H_{44}O_2P_4$: C, 56.70; H, 4.03; Cl, 6.44; P, 11.25. Found C, 57.37; H, 4.55; Cl, 6.46; P, 10.99. **7**: Calcd. for $Rh_2Cl_2C_{53}H_{44}O_3P_4$: C, 56.36; H, 3.93; Cl, 6.28; P, 10.97. Found C, 56.29; H, 4.22; Cl, 6.43; P, 11.03). Furthermore, the $^{31}P\{^1H\}$ n.m.r. spectra show only one phosphorus environment in each case (**6**: $\delta_P = 8.21$ p.p.m., $|^1J_{RhP} + {}^xJ_{RhP}| = 116.0$ Hz. **7**: $\delta_P = 7.45$ p.p.m., $J_{RhP} = 113.5$ Hz).

The analogous *trans* dicarbonyl species, *trans*-$[Rh_2Cl_2(CO)_2(DPM)_2]$ [14], unlike the *cis* species, is insoluble in $CH_2Cl_2$ and does *not* react with CO under the same conditions even after prolonged exposure. The single sharp value for $\nu$(CO) at 1968 $cm^{-1}$ for the *trans* dicarbonyl species is in contrast to the two carbonyl bands observed in **7** as is expected for the *trans* and *cis* carbonyl arrangements, respectively. Further reactions of the above dinuclear complexes with small molecules are under investigation.

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## References

1 M. Cowie, J. T. Mague, and A. R. Sanger, *J. Am. Chem. Soc.*, in press.

2 a) C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc., 99*, 6129 (1977).
b) *Idem, Conference of the American Chemical Society, Anaheim,* California (1978) *Inor 32.*

3 Infrared spectrum in KBr pellet. All others in Nujol mulls.

4 M. Angoletta, P. L. Bellon, M. Manessero and M. Sansoni, *J. Organometal. Chem., 81*, C40 (1974).

5 S. Otsuku, Y. Tutsuno, M. Miki, T. Aoke, M. Matsumoto, H. Yoshioka and K. Nakatsu, *Chem. Commun.*, 445 (1973).

6 $R = \Sigma\||F_o|-|F_c\||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

7 M. M. Olmstead, H. Hope, L. S. Benner, and A. L. Balch, *J. Am. Chem. Soc., 99*, 5502 (1977).

8 a) A. D. Rattray and D. Sutton, *Inorg. Chim. Acta, 27,* L85 (1978).
b) *Idem,* Personal Communication.

9 L. S. Benner, M. M. Olmstead, H. Hope and A. L. Balch, *Conference of the American Chemical Society, Anaheim,* California (1978) *Inor 153.*

10 R. Colton, M. J. McCormick and C. D. Punnun, *Chem. Commun.*, 823 (1977).

11 O. S. Mills and J. P. Nice, *J. Organometal. Chem., 10,* 377 (1967); O. S. Mills and E. F. Paulus, *J. Organometal. Chem., 10,* 331 (1967); E. F. Paulus, *Acta Crystallogr., B25,* 2206 (1969); C. H. Wei, *Inorg. Chem., 8,* 2384 (1969); R. S. Dickson, S. H. Johnson, H. P. Kirsch and D. J. Lloyd, *Acta. Crystallogr., B33,* 2057 (1977); W. A. Herman, C. Kruger, R. Goddurd, and I. Bernal, *Angew. Chem. Int. Ed. Engl., 16,* 334 (1977).

12 This is to be contrasted with the situation in the related complex, $[Rh_2(CO)_2Cl_2(Ph_2AsCH_2AsPh_2)_2]$ where the Rh–Rh separation is 3.396(1) Å while the intraligand As---As distance is 3.288 Å. The Rh–Rh interaction here is clearly repulsive. See: J. T. Mague, *Inorg. Chem., 8,* 1975 (1969).

13 M. J. Bennett, P. B. Donaldson, P. B. Hitchcock and R. Mason, *Inorg. Chim. Acta, 12,* L9 (1975).

14 J. T. Mague and J. P. Mitchener, *Inorg. Chem., 8,* 119 (1969).