

Preliminary communication

REVERSIBLE INSERTION OF SULFUR DIOXIDE INTO PALLADIUM—PALLADIUM BONDS.

THE PREPARATION AND STRUCTURE OF $\text{Pd}_2(\mu\text{-SO}_2)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_2$

LINDA S. BENNER, MARILYN M. OLMSTEAD, HÅKON HOPE and ALAN L. BALCH*

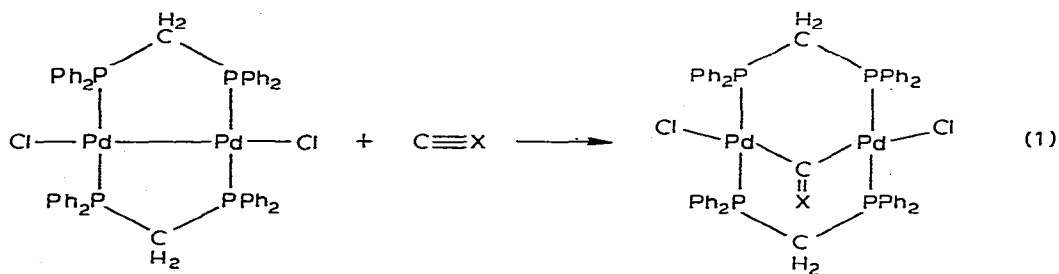
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received February 6th, 1978)

Summary

Addition of sulfur dioxide to $\text{Pd}_2(\text{dpm})_2\text{X}_2$, ($\text{dpm} = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$, $\text{X} = \text{Cl}$ or Br), $\text{Pt}_2(\text{dpm})_2\text{Cl}_2$ or $\text{Pd}_2[(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_2$ produces 1/1 adducts. The crystal structure of $\text{Pd}_2(\mu\text{-SO}_2)(\text{dpm})_2\text{Cl}_2$ shows two approximately planar palladium centers with coordination sites occupied by two phosphorus atoms from two bridging dpm ligands, a terminal halide ligand, and a bridging SO_2 ligand. The unit cell contains two crystallographically independent molecules. In most aspects the dimensions of the two molecules are similar. However, the ability of crystal packing forces to alter the Pd—Pd distance (3.383 and 3.221 for the two different molecules) reflects the lack of a direct Pd—Pd bond.

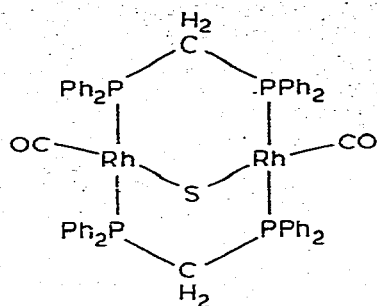
Recently we reported [1] that carbon monoxide and isocyanides insert into the palladium—palladium bond of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ ($\text{dpm} = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$) via eq. 1 to produce binuclear complexes in which three of the four planar



$\text{X} = \text{O}, \text{CH}_3\text{N}, p\text{-CH}_3\text{C}_6\text{H}_4\text{N}$

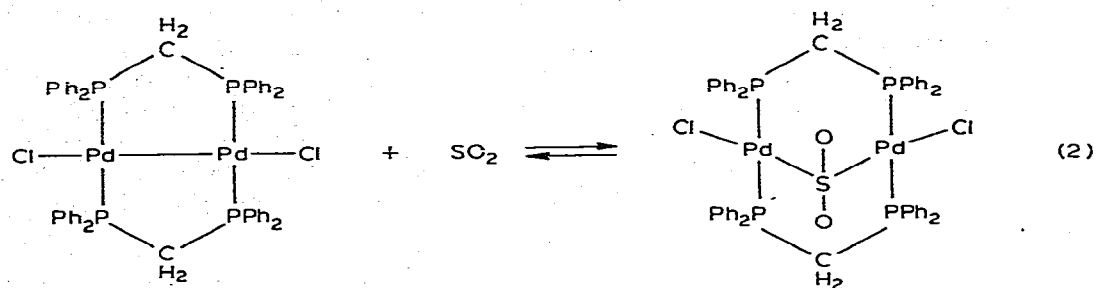
(1)

coordination sites of each metal are connected through bridging ligands. A related platinum carbonyl complex has been reported [2]. In studies of the structurally similar rhodium complexes II, Eisenberg and coworkers have termed



(II)

complexes with this novel bridging geometry molecular A-frames [3]. Here we report another group of A-frame complexes formed by the insertion of sulfur dioxide into metal-metal bonds (eq. 2).



(III)

Addition of sulfur dioxide to an oxygen-free, dichloromethane solution of $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ results in an immediate color change from orange to violet. Upon addition of methanol, violet crystals of the adduct $\text{Pd}_2(\mu\text{-SO}_2)(\text{dpm})_2\text{Cl}_2$ form. The air-stable adduct is characterized by infrared absorptions at 1028, 1041, 1157, and 1165 cm^{-1} ($\nu(\text{S}-\text{O})$) and at 277 cm^{-1} ($\nu(\text{Pd}-\text{Cl})$), and by electronic absorption maxima at 511 nm (ϵ 7300) and 345 nm (ϵ 16,500). Complexes analogous to $\text{Pd}_2(\mu\text{-SO}_2)(\text{dpm})_2\text{Cl}_2$ have been prepared from $\text{Pd}_2(\text{dpm})_2\text{Br}_2$, $\text{Pt}_2(\text{dpm})_2\text{Cl}_2$, and $\text{Pd}_2(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)_2\text{Cl}_2$. The addition of sulfur dioxide to $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$ is reversible; refluxing a dichloromethane solution of $\text{Pd}_2(\mu\text{-SO}_2)(\text{dpm})_2\text{Cl}_2$ under nitrogen forms $\text{Pd}_2(\text{dpm})_2\text{Cl}_2$.

To determine the details of the sulfur dioxide coordination, an X-ray structural determination was undertaken. Crystals of $\text{Pd}_2(\mu\text{-SO}_2)(\text{dpm})_2\text{Cl}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2 \cdot 1\text{CH}_3\text{OH}$ were obtained by slow diffusion of anhydrous methanol into a dichloromethane solution of III generated in situ. Crystal data (150 K): orthorhombic,

space group $P2_12_12_1$; cell dimensions a 15.582(4), b 16.457(3), c 19.184(5) Å; V 4919.45 Å³; ρ_{exptl} 298 K 1.57 g/cm³; $Z = 4$; $\mu(\text{Mo-K}\alpha)$ 10.74 cm⁻¹. Intensity data were collected on a Syntex P2₁ automated diffractometer using Mo-K α radiation (graphite monochromator), a peak searching ω scan, stationary background counts, and a variable scan speed (2 to 60° min⁻¹). A total of 3688 reflections were collected in the range of $2\theta \leq 45^\circ$. By Patterson, Fourier, and full-matrix least-squares methods, the structure was solved and refined isotropically for all atoms excluding the hydrogens and the methylene carbon of solvent dichloromethane. A final R index of 0.072 was obtained using 3220 reflections having $I_{\text{net}} > 3\sigma(I_{\text{net}})$.

The unit cell contains two pairs of crystallographically nonequivalent molecules in addition to two molecules of dichloromethane and four of methanol. An ORTEP drawing of one of these molecules is shown in Fig. 1. The crystal structure requires each molecule to have twofold rotation symmetry, with the sulfur atoms located on the respective symmetry axes. The bonds to the phosphorus atoms of the dpm ligands are essentially normal to the planes defined by sulfur and two palladium atoms. The terminal chlorine atoms are near these planes (deviations are 0.15 Å for molecule A, 0.08 Å for B). Selected interatomic distances and angles are listed in Table 1.

There are noteworthy differences between the two molecules. The metal-metal distances, which are longer than conventional Pd-Pd single bonds, differ

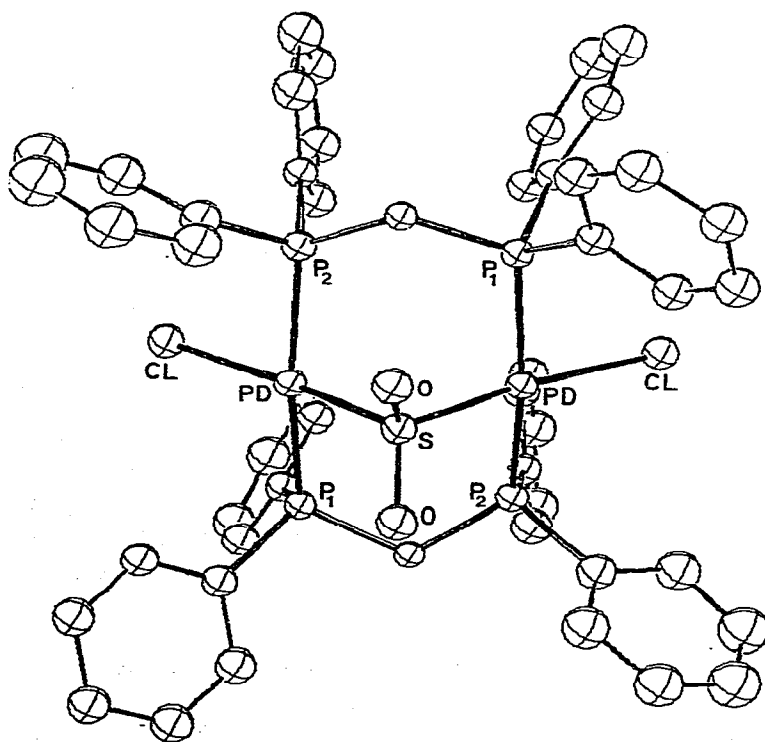


Fig. 1. An ORTEP drawing of $\text{Pd}_2(\mu\text{-SO}_2)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_2$ (molecule A) showing 50% thermal ellipsoids. The gross structural features of molecule B are similar.

TABLE 1
SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (Degrees)^a

Atoms	Molecule A	Molecule B
Pd—Pd	3.383(2)	3.221(2)
P(1)—P(2)	3.170(5)	3.111(5)
Pd—Cl	2.380(4)	2.381(4)
Pd—S	2.234(3)	2.240(3)
Pd—P(1)	2.346(4)	2.376(4)
Pd—P(2)	2.347(4)	2.343(4)
S—O	1.49(1)	1.45(1)
Pd—S—Pd	98.4(2)	91.2(2)
O—S—O	111.9(6)	109.4(6)
Pd—S—O	111.3(4)	115.5(4)
P(1)—C—P(2)	119.4(7)	114.8(8)
Cl—Pd—S	171.9(1)	175.5(1)
P(1)—Pd—P(2)	168.2(1)	175.2(1)
Cl—Pd—P(1)	87.1(1)	87.2(1)
Cl—Pd—P(2)	91.9(1)	95.7(1)
S—Pd—P(1)	92.3(1)	89.7(1)
S—Pd—P(2)	90.3(1)	87.5(1)

^aSee Figure 1 for atom numbering.

by 0.16 Å. The two molecules also differ in the degree of planarity of the palladium coordination. In molecule A the square around each palladium has suffered a digonal twist toward tetrahedral geometry so that the ligating atoms lie alternately 0.20 Å above and below the least-squares plane through PdP₂SCI. In molecule B the square about each palladium is much less distorted with all ligating atoms within 0.07 Å of the least squares plane. The greater distortion from planarity in molecule A is associated with the stretching apart of the two palladium atoms (3.383 Å). The metal—metal distance of 3.221 Å in molecule B is comparable to the metal—metal distances in two isoelectronic dpm containing A-frame molecules: Pd₂(dpm)₂(μ-CNCH₃)(CNCH₃)₂²⁺ (3.215 Å) [1] and Rh₂(dpm)₂(μ-S)(CO)₂ (3.155 Å) [3]. The ability of crystal packing forces to alter the Pd—Pd separation reflects on the lack of a direct Pd—Pd bond and on the flexibility of the bridging ligands.

The molecular A-frame geometry of these palladium complexes make them unique among sulfur dioxide-containing metal dimers. This work represents the first structural demonstration of direct sulfur dioxide insertion into a metal—metal bond with concurrent metal—metal bond cleavage; although it was previously proposed that sulfur dioxide inserts into M₂(CO)₁₀²⁻ (M = Cr or W) [4]. Other complexes containing bridging sulfur dioxide ligands include those where a metal—metal bond exists (e.g., Fe₂(CO)₈(μ-SO₂) [5], Ir₂(CO)₄(PPh₃)₂(μ-SO₂) [6], (η⁵-C₅H₅)₂Fe₂(CO)₂(μ-CO)(μ-SO₂) [7]), and those where the SO₂ unit serves as the sole bridge between the metals (e.g., (η⁵-C₅H₅)₂Fe₂(CO)₄-(μ-SO₂) [8,9]).

A table of atomic positions and isotropic thermal parameters is available*.

*A Table of atomic positions and isotropic thermal parameters and the table of observed and calculated structure factors has been deposited as NAPS Document No. 03257 (22 p.). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$ for photocopies or \$ for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Acknowledgement

We thank Mr. J. Labadie for experimental assistance, Matthey Bishop for a loan of precious metal salts and the National Science Foundation for support. Acquisition of the P2₁ diffractometer was made possible through a grant from the National Science Foundation.

References

- 1 M.M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, *J. Amer. Chem. Soc.*, **99** (1977) 5502.
- 2 R. Colton, M.J. McCormick, and C.D. Pannan, *J. Chem. Soc., Chem. Commun.*, (1977) 823.
- 3 C.P. Kubiak and R. Eisenberg, *J. Amer. Chem. Soc.*, **99** (1977) 6129.
- 4 J.K. Ruff, *Inorg. Chem.*, **6** (1967) 2080.
- 5 J. Meunier-Piret, P. Piret, and M. van Meerssche, *Bull. Sci. Chim. Belg.*, **76** (1967) 374.
- 6 M. Angoletta, P.L. Bellon, M. Manassero and M. Sansoni, *J. Organometal. Chem.*, **81** (1974) C40.
- 7 M.R. Churchill and K.L. Kalra, *Inorg. Chem.*, **12** (1973) 1650.
- 8 M.R. Churchill, B.G. DeBoer and K.L. Kalra, *Inorg. Chem.*, **12** (1973) 1646.
- 9 M.R. Churchill, B.G. DeBoer, K.L. Kalra, P. Reich-Rohrwig and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, (1972) 981.