Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

A sulfur dioxide insertion reaction into palladium–oxygen bonds

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(Received November 17th, 1970; in revised form December 31st, 1970)

Few examples of d^8 metal ion complexes containing metal–oxygen bonds have been reported, at least in the case of monodentate ligands, probably owing to the "hard" character of oxygen. In the case of palladium, to the best of our knowledge only one Pd–O bonded complex has been described, *viz.* *trans*-$[Pd(PEt_3)_2(OCH_3)(CN)]$[1]. However labile Pd–OR bonded intermediates have been proposed as intermediates in the oxidation of alcohols catalyzed by palladium chloride, according to the following equation[2]:

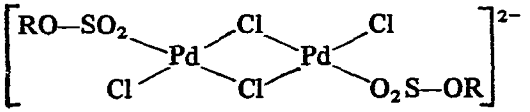
$$PdCl_2 + ROH \rightarrow -\overset{|}{\underset{|}{Pd}}-OR + HCl \qquad (1)$$

We have now succeeded in trapping this type of intermediate by forming a stable sulfinato-complex through insertion of sulfur dioxide into the Pd—OR bond ($OR = OCH_3$, OC_2H_5);

Upon bubbling SO_2 through an alcoholic suspension of $PdCl_2$ an orange-red solution is obtained, from which the $[Pd_2Cl_2(SO_3R)_2]^{2-}$ anions can be precipitated as tetraphenylarsonium salts. In nitromethane they behave as bi-univalent electrolytes.

The nature of the coordination of sulfur dioxide to the metal has been deduced from the infrared spectra of these complexes ($R = CH_3$, $\nu(SO)$ 1260, 1100 cm^{-1}; $R = C_2H_5$, $\nu(SO)$ 1260, 1120 cm^{-1} in Nujol mull). The shifts to lower wavelengths of the $\nu(SO)$ absorption bands relative to the position of these bands in the corresponding organic sulfonates $R—SO_2—OR$[3,4] show that sulfur dioxide is inserted in the metal—oxygen bond and S-bonded to the palladium.

The spectra in the region 200—400 cm^{-1} show bands at 355, 270 and 240 cm^{-1} for the methyl derivative and at 350, 265 and 230 cm^{-1} for the ethyl complex. Thus we tentatively formulate the complex as a chloro bridged complex, having the following structure:



The NMR spectrum shows the expected absorption for the methyl ethyl and phenyl groups, respectively.

Distillation of the reaction mixture gives palladium metal and the appropriate dialkylsulfate, which can be identified by GLC.

REFERENCES

1 F. Glockling and E.H. Brooks, *Preprints, Div. Petr. Chem.*, 14, no. 2, B 135 (1969).
2 V.C. Lloyd, *J. Org. Chem.*, 32 (1967) 2816.
3 E.A. Robinson, *Can. J. Chem.*, 39 (1961) 247.
4 R.D. Guthrie and H. Spedding, *J. Chem. Soc.*, (1960) 953.