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

THE DETERMINATION OF PALLADIUM IN ORGANOMETALLIC COMPLEXES

F. R. HARTLEY and J. L. WAGNER

Department of Chemistry, The University, Southampton, SO9 5NH (Great Britain)

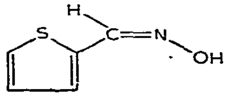
(Received March 20th, 1972)

SUMMARY

Use of 2-thiophene-*trans*-aldoxime as the precipitating agent provides an improved method for gravimetric determination of palladium.

INTRODUCTION

The most frequently cited method for the determination of palladium in organometallic complexes is the gravimetric method based on precipitation of the metal as its dimethylglyoxime salt[1]. However, even with very careful control of both the pH of the solution and the concentration of both the palladium salt and the dimethylglyoxime, we have consistently obtained low results and have met many other workers who have also found the same. This is due to the tendency of bis(dimethylglyoxime)palladium(II) solutions to exhibit supersaturation[2]. Accordingly we report here a satisfactory method for the determination of palladium by a gravimetric method using 2-thiophene-*trans*-aldoxime (I) as the precipitating agent.



(I)

EXPERIMENTAL AND RESULTS

Organometallic palladium complexes are most conveniently decomposed by heating with aqua regia and removing the excess nitric acid by boiling with concentrated hydrochloric acid. In the present method this solution is diluted with dilute hydrochloric acid and treated with the precipitating reagent. Although it has previously been stated[3] that precipitation is complete after 2–3 hours when the pH of the precipitating solution is between 0.2 and 0.8 in the present work, where the final pH is about 0.3, it was found that after 3 hours only about 92 per cent of the precipitation was complete. However, on standing overnight complete precipitation occurred.

The detailed experimental procedure used was as follows. Sufficient of the complex to contain about 10 mg of palladium was accurately weighed out and heated with aqua regia (4 ml) in a Kjeldahl flask. The volume was maintained at about 4 ml by adding concentrated hydrochloric acid at intervals, and heating was continued until no more brown fumes were evolved. After cooling, the solution was quantitatively transferred to a beaker and diluted to 125 ml using 0.25*M* hydrochloric acid. 12 ml of a 2 per cent solution of 2-thiophene-*trans*-aldoxime in 95 per cent ethanol (8 fold excess) were added with stirring. (2-Thiophene-*trans*-aldoxime (m.p. 132–132.5°) was prepared from 2-thiophenecarboxaldehyde and hydroxylamine hydrochloride[3]). After heating for 15 minutes on a steam bath the beaker was covered with a watch-glass and allowed to stand overnight before filtering off the precipitate of dichloro[bis-(2-thiophene-*trans*-aldoxime)]palladium(II) using a G4 sintered glass filter. After washing with cold 1 % v/v hydrochloric acid (25 ml) and cold water (25 ml) the precipitate was heated to constant weight at 115° and weighed as $[Pd(C_5H_5NOS)_2Cl_2]$.

The present gravimetric method of analysis was tested on a number of palladium complexes. Six independent samples of each complex were analysed and the results were within one per cent both of their own mean and of the calculated palladium content.

ACKNOWLEDGEMENTS

We thank the S.R.C. for a studentship (to J. L. W.) and Johnson Matthey and Co. Ltd. for the generous loan of the palladium salts used during this investigation.

REFERENCES

1 L. J. Kanner, E. D. Salesin and L. Gordon, *Talanta*, 7 (1961) 288.
2 R. Belcher, C. L. Wilson and T. S. West, *New Methods of Analytical Chemistry*, Chapman and Hall Ltd., London, 2nd Ed., 1964, p. 234–236.
3 S. G. Tandon and S. C. Bhattacharya, *Anal. Chem.*, 32 (1960) 194.