

Gd(III) as MRI contrast agents. The spectacular growth in use of MRI as a diagnostic tool would not have occurred without the use of contrast agents. Radioactive nuclei, for example, Rh, described in Chapter 20, by S. Z. Lever, J. D. Lydon, C. S. Cutler and S. S. Jurisson, have been a vital part of medicine for a much longer period but developments are still being made through coordination chemistry in modifying the distribution of the elements. Chapter 21, by S. Faulkner and J. L. Matthews, describes the use of fluorescent compounds in diagnosis. A different method of cancer treatment is discussed in Chapter 22 on Ru, Pd and Pt complexes for photodynamic therapy. This area is dominated by porphyrin complexes.

## Conclusions

In summary this book certainly is a comprehensive overview of the applications of coordination chemistry, and in particular the use of pgms in catalysis, in dyes for optical applications,

and in medicinal and biomedical applications. It is an informative read and the individual chapters offer good introductions to the various areas.

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## References

- 1 A. K. Keep, *Platinum Metals Rev.*, 2004, 48, (2), 64
- 2 J. H. Jones, *Platinum Metals Rev.*, 2000, 44, (3), 94

## The Reviewers

Janet Fisher, who reviewed Chapters 1–9 and 11, is a Principal Scientist at the Johnson Matthey Technology Centre, Sonning Common, U.K. Her primary interests are in catalyst preparation and characterisation.

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# Sonochemical Asymmetric Hydrogenation with Palladium

Enantioselective hydrogenation is one of the most versatile methods of asymmetric synthesis, with heterogeneous catalysis, using chiral modifiers, rapidly becoming an alternative to the “traditional” homogeneous methods. The role of modifiers in asymmetric hydrogenations is to enhance catalysis, with the bonding mode and geometry of adsorption being important, as well as the modifier concentration and the type and position of the substituent groups in the aromatic ring.

Ultrasonic irradiation (sonication) is known to be beneficial in catalytic asymmetric hydrogenations. Sonication removes catalyst surface impurities, and gives enhanced adsorption to the chiral modifiers.

Now a team from Michigan Technological University, Houghton, U.S.A. (S. C. Mhadgut, I. Bucsi, M. Török and B. Török, *Chem. Commun.*, 2004, (8), 984–985; DOI: 10.1039/b315244h) has revisited the Pd-catalysed, proline-modified, asymmetric hydrogenation of isophorone (3,3,5-trimethyl-2-cyclohexen-1-one (with a C=C bond)). They examined the catalyst, the modifier and the effects of sonication.

Pd/Al<sub>2</sub>O<sub>3</sub> was found to give a better, though low, enantiomeric excess (ee) than Pd/C. Proline

and its derivatives (isomeric hydroxyl-prolines, prolinols and proline esters) were tested as chiral modifiers for Pd/Al<sub>2</sub>O<sub>3</sub>. Proline was the best modifier, and both enantiomers gave ee ≤ 35%.

Presonication was found to enhance the enantioselectivity when both the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and the proline modifier were present. “Modifier-free” presonication and the presence of substrate during pretreatment decreased the enantioselectivity.

The reaction was performed at 50 bar pressure and 25°C. Presonication for 20 minutes gave the highest optical yields, and increased optical yields across all the H<sub>2</sub> pressure range. Maximum ee occurred at a 1:2 isophorone:proline ratio, and with optimised conditions and presonication, the ee for the Pd/Al<sub>2</sub>O<sub>3</sub>-(S)-proline catalytic system was ≤ 85%.

Ultrasonic cleaning of the catalyst enhanced both the adsorption of the modifier and the modifier-induced surface restructuring of the Pd. The high ee was due to proline adsorption on the Pd surface. New catalysts that can strongly adsorb proline could thus become important in heterogeneous catalysis for C=C double bond hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds.