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**In the Lab**

# The Use of Recovered Metal Complexes in Catalysis

***Johnson Matthey Technology Review* features laboratory research**

**NON-PEER REVIEWED FEATURE**

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Research in the group led by James Wilton-Ely focuses on catalysis, imaging and sensing. All of this work involves *d*- and *f*-elements and is underpinned by the group's wide-ranging expertise in synthesis. Collaborations with researchers in engineering, medicine and bioimaging allow these discoveries to be used to address major healthcare and sustainability challenges. Professor Wilton-Ely is the author of more than 100 publications and was the recipient of the 2021 Sir Geoffrey Wilkinson Award from the Royal Society of Chemistry for his work on metal-based carbon monoxide sensing. He has a strong interest in sustainability, having directed the MRes Green Chemistry course at Imperial College for over 12 years (2010–2022). He has published on the use of recovered metals in catalysis (1–5), the catalytic transformation of biomass to platform chemicals (6–11) and magnetically-recoverable nanoscale catalysts (12, 13). Elemental sustainability is a pressing concern for all researchers using precious metals and this has led Wilton-Ely to work with colleagues to explore the potential for using gold (3) and palladium (4, 5) complexes recovered from end-of-life products in catalysis.

## The Researcher

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## About the Research

Catalysis using precious metals is a cornerstone of synthetic chemistry, yet many of these metals are extremely scarce. Palladium is found in concentrations of 1–10 parts per trillion in the earth's crust in only a few locations. The demand for this metal is driven by its use in automotive three-way catalysts (TWCs) and the limited

supply has resulted in a significant palladium deficit, rendering current palladium consumption unsustainable. An attractive solution is to recycle and reuse rather than continuing to draw on primary sources, thereby also reducing waste. Johnson Matthey has played a leading role in adopting this approach through their pyrometallurgical and chemical leaching process for recovering and reusing spent TWCs. However, only around 20–30% of palladium is currently recovered worldwide. New technologies, such as those investigated in the Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS) programme, offer promising alternatives to the current energy-intensive processes for the recovery of TWC metal content for reuse in new automotive TWCs.

In contrast, there has been relatively little research aimed at the recovery of precious metals for use in the catalytic transformations needed to make fine chemicals, pharmaceuticals and fertilisers (1, 2) with the majority of these catalysts still being sourced directly from mining. While efforts have been made to use catalysts based on more abundant metals, the use of palladium catalysts in industry and academia is well established due to its high activity and reliability. Professors Angela Serpe and Paola Deplano (University of Cagliari, Italy) have pioneered low-energy, environmentally-benign processes for the recovery of palladium from TWCs and gold from waste electrical and electronic equipment (WEEE) in the form of molecular recovery compounds. While almost quantitative recovery of the metal can be achieved from these products by cementation or electrowinning, this treatment increases the environmental and economic costs of the recovery process. Instead, the Wilton-Ely group is working with Professor Serpe and a synthetic organic chemist, Professor Christopher Braddock (Imperial College London), to valorise these products directly in catalysis (**Figure 1**).

End-of-life TWCs contain around 4 g of palladium (200 times the concentration in mined ore) and this metal content can be recovered in high yield through the use of *N*,*N*-dimethylperhydrodiazepine-2,3-dithione ($Me_2$dazdt) and iodine to form the recovery product $[Pd(Me_2dazdt)_2]^{2+}$ (**Figure 1**). This complex was found to catalyse important C–H oxidative functionalisation transformations in higher yield, more rapidly and under milder conditions than those previously reported (4). The related recovery product, $[PdI_2(Me_2dazdt)]$ was then shown to undergo ligand exchange with dithiocarbamate ligands with trimethoxysilyl-terminated units suitable for the functionalisation of silica-coated $Fe_3O_4$ nanoparticles. The resulting catalyst system was used to transform benzo[*h*]quinoline to 10-methoxybenzo[*h*]quinoline before being magnetically recovered and reused (5). These reports demonstrated the great potential for valorising the molecular recovery products obtained from TWCs using benign, low-energy solvometallurgical routes. This will become even more significant with the planned end to the sale of new petrol and diesel cars in the UK in 2030, necessitating a range of recovery solutions for the millions of existing TWCs.

Most WEEE is currently sent to landfill with little attempt to recover the valuable metal content. This is despite the fact that the amount of gold in printed circuit boards (50−700 g $tonne^{-1}$) is far higher than that found in primary mined ores or concentrates (1−10 g $tonne^{-1}$), which rely on highly polluting and environmentally damaging processes. Serpe and Deplano have patented (14) a low-energy process to recover gold as the molecular product $[AuI_2(Me_2dazdt)]I_3$ using $Me_2$dazdt and iodine as part of a selective, three-stage metal leaching and recovery approach from WEEE. This solvometallurgical method employs common organic solvents and environmentally-friendly reagents under mild conditions.

Very recently (3), it has been demonstrated that this recovery product can be used as an effective homogeneous catalyst for a range of catalytic reactions, allowing an existing mild and effective recovery process to be connected with a major catalytic application of gold. Using SIM cards as the e-waste source, $[AuI_2(Me_2dazdt)]^+$ was produced and found to show comparable catalytic activity to current Au(III) catalysts for a range of important gold-catalysed transformations. These included cyclisation of propargylic amides, addition reactions of electron-rich arenes to carbonyl compounds and oxidative cross-coupling reactions of arenes with aryl silanes. This was the first example of the direct application in homogeneous catalysis of gold recovery products sourced from e-waste. A preliminary indicative cost analysis suggests that even unoptimised, small-scale production of the catalyst, $[AuI_2(Me_2dazdt)]^+$, from certain types of WEEE leads to a significantly lower cost than commercial catalysts derived from environmentally-damaging mining.

The wider aim of these studies is to demonstrate that molecular recovery products from mild, low-impact processes based on end-of-life materials

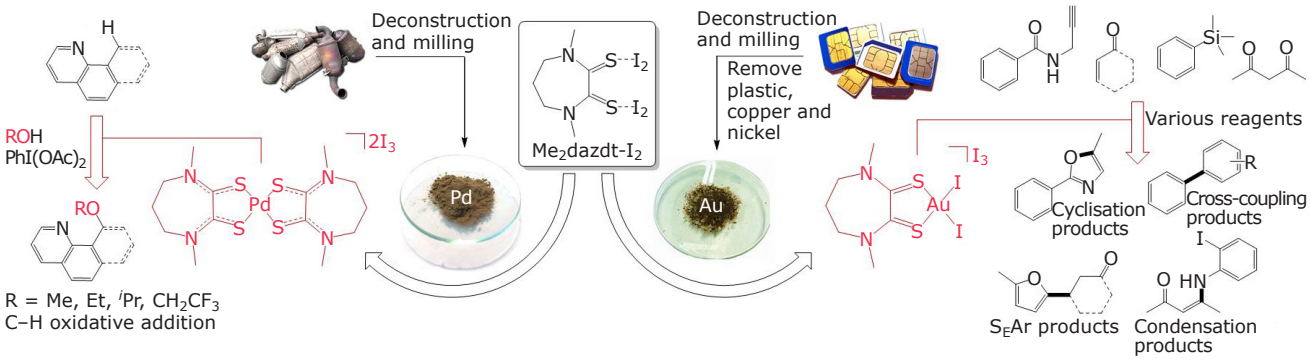


Fig. 1. Catalysis using palladium and gold compounds recovered from end-of-life sources

can be used to replace homogeneous catalysts derived from mining. If adopted more widely, this would not only improve sustainability, reduce waste and relieve pressure on primary sources, but also have cost and supply chain security benefits.

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