Pd-Dissolution through a mild and effective one-step reaction and its application for Pd-recovery from spent catalytic converters†

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We describe here an innovative method for Pd-dissolution using the reagent *N*,*N*′-dimethylperhydrodiazepine-2,3-dithione diiodine adduct which, being safe and powerful, is appealing for practical applications: remarkably almost quantitative Pd-recovery from model spent three-way catalysts has been obtained, showing that the effectiveness of the method is maintained when palladium is contained in a complex system such as a car catalyst, a ceramic material which has undergone severe thermal stress.

The use of dihalogen adducts as oxidising reagents with σ-donors (D) towards metals[1] still seems little explored, despite the findings of the McAuliffe group which has shown since the 1990s that dihalogen adducts of tertiary phosphines (PR_3) can activate crude metal powders and even metal gold.[2] This may be related to the fact that $PR_3{\cdot}I_2$ adducts are unsuitable for practical applications, being very sensitive to air and moisture and use unattractive donors. The perspectives opened by these results prompted us to search for more safe but effective dihalogen adducts for the dissolution of noble metals (NMs), due to their wide use in advanced technologies (mainly in catalysis and electronics), their high cost and the unattractiveness of reagents still used for their dissolution (aqua regia, cyanides, *etc.*). Moreover, the novel world-wide legislation promotes the increase of NM recycling from NM-rich accumulating waste to preserve environment and limit the exhaustion of natural sources.[3] On the basis of our previous studies,[4] we decided to prepare and investigate the properties of the class of the diiodine adducts of cyclic dithio-oxamides. The softness of the donor atoms, as well as the chelating properties of the two vicinal thiones is expected to stabilise the oxidised NMs in the d^8 configuration, favouring the dissolution of the metal. The adduct $Me_2dazdt{\cdot}2I_2$ (**1**) (Me_2dazdt = *N*,*N*′-dimethylperhydrodiazepine-2,3-dithione),† has shown to be capable of dissolving metallic gold to produce the gold(III) square-planar complex $[Au(Me_2dazdt)I_2]I_3$ in mild conditions,[5] and also to be an optimal reagent for the dissolution of gold in micro-electronic devices for "Failure Analysis".[6] This reagent is air and moisture stable, and recent results show that **1** has no cytotoxical activity.[7] The X-ray structure of **1** has been solved now[8] and the molecular structure is shown in Fig. 1. The two thionic sulfur atoms act as donors towards two diiodine molecules. Almost linear S–I(1)–I(2) fragments with *d*[S–I(1)] and *d*[I(1)–I(2)] equal to 2.786(2) and 2.818(2) Å respectively are found. The I–I vector is elongated with respect to that in the free I_2 molecule [2.715(1) Å]. Different features in diiodine adducts have been used to distinguish them between three types which depend on the strength of the donor: D···I–I (I), D–I–I (II), $D{-}I^+{\cdots}I^-$ (III) (the notations ··· and – refer to charge transfer interactions and covalent bonding respectively).[4] Accordingly the system can be described by a MO picture which changes within the limiting forms I–III. The obtained results allow classification of **1** as a type I adduct (medium–weak donor). The simplest MO model, where the σ lone pair of the sulfur atoms donates part of its electron density into the relatively low lying σ* level of I_2, can explain the shortening of the S–I distance proportional to the lengthening of the I–I distance.[4] $PR_3{\cdot}I_2$ adducts belong to type III (strong donor);[4] the behaviour of **1** towards gold shows that the activation of NMs is not confined to type III adducts.

Accordingly, **1** has been reacted with Pd-metal, as powder or foils, and complete metal dissolution is observed with formation of **2** in relatively short times (about 1 h to dissolve 12.3 mg of Pd powder, by using THF as solvent) at room temperature and without protection from air and/or moisture in a one-step reaction, according to Scheme 1.†

Crystals of **2** have been recovered from the reaction mixture and fully characterised. X-ray results[8] show that in **2** the palladium ion is coordinated by two bidentate Me_2dazdt ligands in a square-planar geometry and two different triiodide ions balance the charge of the cation (Fig. 2). By using the same reaction conditions with platinum and rhodium, no dissolution of the metals was

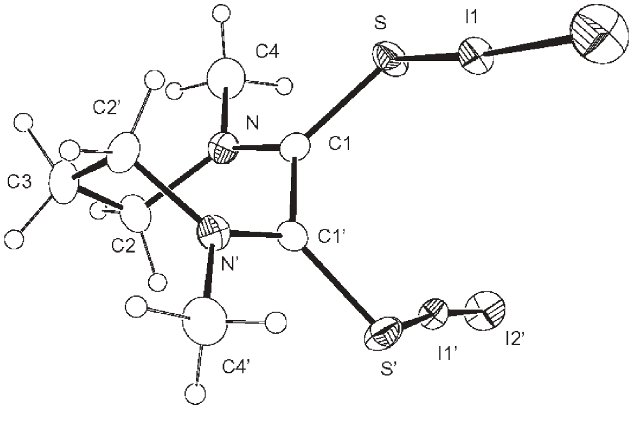

Fig. 1 X-ray molecular structure of $Me_2dazdt{\cdot}2I_2$.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation of **1** and **2**, materials and methods, X-ray characterisation, synthesis and XRD characterization of model three-way catalysts. See http://www.rsc.org/suppdata/cc/b4/b415799k/

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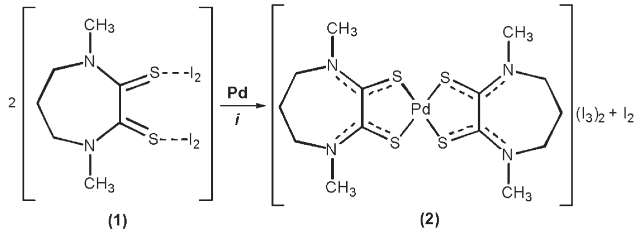

Scheme 1 i = THF or acetone or acetonitrile or methyl ethyl ketone (MEK), rt, quantitative yield.

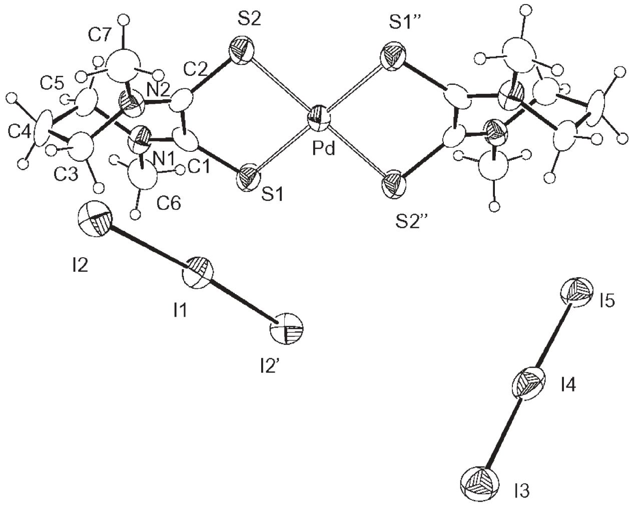

Fig. 2 Molecular structure of $[Pd(Me_2dazdt)_2](I_3)_2$. Average values: *d*(Pd–S) 2.305(3) Å; (S–Pd–S) 90.00(11)°.

observed, even in refluxing solvents. The results, summarised in Scheme 1, prompted us to apply reagent **1** to Pd-recovery from spent three-way car converters (TWC), one of the fields where the metal is most extensively used. Notably, Pd-only technology has been introduced in catalytic converters in the last few years.[9] The car industry, which puts on the market 40 million new cars each year with a limited lifetime, could save an annual \$1 billion resource *via* Pd-recovery.[10] Currently still low Pd-recovery (12%)[10] is performed by high temperature thermal treatment or by non-selective unattractive methods involving, for the crucial metal-dissolution step, a pyrometallurgical chlorination[11] or dissolution with strong oxidising acids.[12] In order to check the effectiveness of the method in Pd-recovery from spent TWC, samples containing Pd in the range 0.5–3.0 wt% (typical loading in commercial wash-coats), supported both on Al_2O_3 and CeO_2–ZrO_2/Al_2O_3 have been employed: Al_2O_3 represents the typical support employed in the 1980s and in the early 1990s, CeO_2–ZrO_2/Al_2O_3 is the most advanced support in current technologies.[9,13] An accelerated ageing protocol has been employed (1050 °C/200 h) to simulate the thermal deactivation of TWC. Textural and structural characterisation shows that the nature of the model aged catalysts mimics that of the real systems.†[13] The aged catalysts have been reacted with a solution of **1** in MEK or CH_3CN under stirring at reflux while varying the concentration of the reagent (1.1×10^{-3}–2.5×10^{-3} M) and the reaction times (72–168 h).[14] The solution containing **2** has been separated from the catalyst support through a glass microfibre thimble (0.8 μm particle retention) in a Soxhlet apparatus, and its Pd-content determined by ICP analysis. The best yields have been obtained working with a 2.5×10^{-3} M concentration of **1** and with a 168 h reaction time. The extraction yields with the two solvents are similar but MEK seems preferable being safer and less expensive than CH_3CN. In these conditions, the satisfactory extraction yields reported in Table 1 are achieved. Notably, **1** is also capable of dissolving PdO, ubiquitously present in spent TWC, and this contributes to obtaining these high yields.

For comparison, the 2.8% Pd-content sample which furnishes the highest yield, has been submitted to a room temperature extraction, which gives lower but still satisfactory yield, and to a I^-–I_2 mixture treatment, previously proposed to dissolve NMs (Ag, Au, Pd),[1] which shows to be much less effective. The obtained results are particularly remarkable when taking into account: (i) the low Pd-content of the samples; (ii) the Pd-metal dispersion on the wash-coat where the metal strongly interacts with CeO_2–ZrO_2; (iii) the strong sintering of the catalyst; (iv) the presence of PdO crystallites. Since the reagent **1** is inactive towards metallic Pt and Rh, which are also present in several car catalysts, the reported Pd-recovery seems in principle to posses an intrinsic selectivity.[15] Moreover this method, based on a one-step oxidising/complexing reaction, is more convenient compared to those based on the use of complexing reagents, which require a non-selective time-consuming pre-treatment.[12,16] Pd-metal can be easily obtained from **2** through a conventional thermal treatment ($T < 600$ °C for a few minutes). Experiments in progress involve: the reagent recovery; the metal recovery from real spent catalysts; a structure/property study to rationalise the ability of the different adducts to discriminate and thus separate NMs. In this regard, on varying the donor by using a hexatomic ring in spite of the heptatomic one in **1**, the obtained reagent (**3**) is capable of dissolving Pt-metal too.[17] Thus a selective Pd/Pt extraction will be attempted employing consecutively **1** and **3**.

In conclusion: (i) the full characterisation of **1**, a type I diiodine adduct; (ii) the ability of **1** to dissolve metal palladium forming the fully characterised complex **2** in mild conditions and in a one-step reaction; (iii) a quite satisfactorily method for the selective

Table 1 Pd-recovery from aged Al_2O_3 and $Ce_{0.6}Zr_{0.4}O_2$ (10 wt%)/Al_2O_3 (CZ60/Al_2O_3)[a]

Sample	Pd-Content (wt%)	Support	Reagent	Temperature/°C	Pd-Extraction yield (%)
C1	2.8	CZ60/Al_2O_3	**1**	80	99
			1	rt	94
			I_2–I^-	80	11
C2	0.7	CZ60/Al_2O_3	**1**	80	92
C3	0.7	Al_2O_3	**1**	80	90

[a] Experimental conditions: **1** in approximately a 2 : 1 molar ratio towards the nominal Pd-content; [**1**] = 2.5×10^{-3} M; extraction solvent = MEK; time = 168 h.

Pd-recovery from model TWC, have been described. The novelty and effectiveness of the chemistry, the mildness of operative conditions, the low hazard for operators and the environment make the proposed method appealing to be tested for industrial employment.

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8 *Crystal data*: **1**: monoclinic, *P*2/*n* (no. 13), $a = 8.680(6)$, $b = 7.713(7)$, $c = 12.740(5)$ Å; $\beta = 94.38(2)^\circ$; $V = 850.4(1.0)$ Å^3; $Z = 2$; $R_1 = 0.0293$ $[I > 2\sigma(I)]$; $wR_2 = 0.0774$ (all data); $\rho_{calc} = 2.718$ Mg m^{-3}. **2**: monoclinic, *C*2/*c* (no. 15), $a = 27.354(5)$, $b = 10.429(7)$, $c = 10.823(7)$ Å; $\beta = 91.36(2)^\circ$; $V = 3087(3)$ Å^3; $Z = 4$; $R_1 = 0.0463$ $[I > 2\sigma(I)]$; $wR_2 = 0.1413$ (all data); $\rho_{calc} = 2.678$ Mg m^{-3}. CCDC 244743 and 244744. See http://www.rsc.org/suppdata/cc/b4/b415799k/ for crystallographic data in .cif or other electronic format.

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