Supporting Information

Oxidant/Complexing Properties of the Methimazole (MeImHS)/Iodine System Towards Palladium and Gold Metals. Crystal structure of the complex cation [Pd$^{II}$(MeImHS)$_4$]$^{2+}$ balanced by a tetraiodide/iodide mixture.

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Factors that influence the course of the reaction (1):

\[
\text{DS-I}_2 + M^0 \xrightarrow{\text{Et}_2O - \text{CH}_2\text{Cl}_2 - \text{H}_2\text{O}} \text{oxidized / complexed metal} \quad (1)
\]

- The thioamido DS unit should be stable enough to prevent its oxidation by iodine with formation of disulphides and (poly)-iodides derivatives (Scheme S1). Under these circumstances, the oxidation/complexation of metals is not observed. If the charge-transfer complex DS-I\(_2\) is in equilibrium with DS and I\(_2\) (Scheme S1), due to a low value of the equilibrium constant, the latter species can react with the oxidized/complexed metal, with the result that the outcome of reaction (1) becomes unpredictable.

- Even if the oxidation of metals often occurs under the experimental conditions outlined in reaction (1), with formation of “hard” ions [R. G. Pearson: “Hard and Soft Acids and Bases”. J. Am. Chem. Soc., 1963 85(22), 3533–3539], the corresponding complexes with the thioamido DS are difficult to isolate since the “soft” S-donor atom is intrinsically a poor coordinating agent towards these ions, and the formation of dense oils is commonly observed.

- Reaction conditions (solvent, temperature, reaction time, mode of stirring) and the DS/I\(_2\) to M\(^0\) molar ratio influence the outcome of the reaction and need to be optimised to favour both a high metal oxidation yield, and the formation of purer compounds.

**Scheme S1** Top: in non-polar solvents, compounds containing S-donor Lewis base (DS) generally form only 1 : 1 charge–transfer complexes with I\(_2\). The formation constant of the 1 : 1 complex (\(K_I\)) depends on the equilibrium molar concentrations according to the equation \(K_I = [\text{DS-I}_2]/[\text{DS}][\text{I}_2]\).\(^1\) Bottom: the interaction between DS and I\(_2\) to give 1 : 1 adducts containing an almost linear S–I–I fragment can be seen as a charge–transfer process n → σ\(^*\) (i.e. MO combination of a lone pair from the donor with the empty σ\(^*\) orbital of I\(_2\)). Depending on the charge density transferred by the DS donor molecule to I\(_2\) and the nature of the solvent, this can result in lengthening of the I–I bond and finally the breaking of this bond and formation of new species.\(^2\)

**Fig. S1** Fitting of the isotopic pattern for [Pd(L-H)L]+ (333 m/z), [Pd(L-H)L₂]+ (447 m/z) and [PdL₃]⁺ (575 m/z), red line calculated pattern, black line experimental pattern. L = MeImHS.

**Fig. S2** Palladium deposited on magnesium powder, image captured with a MOTIC BA210E, Epi-LED S Fluorescence attachment – Exciter 480SP Dichroic 505LP Barrier 520LP.
Fig. S3 Infrared spectrum of complex [Pd(MeImHS)₄][I₄]₀.₇₃[I]₀.₂₇.

Fig. S4 Infrared spectrum of complex [Au(MeImHS)₂]I₃.