Electronic Supplementary Information (ESI)

Gold and palladium oxidation/complexation in water by the thioamide-iodine system

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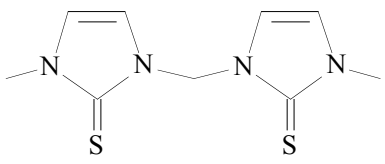
Table S1. Structurally characterised metal complexes obtained by using IX-adducts (X = I, Br) of *S*-donor molecules[a,b] as oxidising reagents towards metal powders.

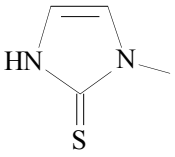
Adduct	Metal	Solvent	Main product/s	Ref.
bmitm·$2I_2$	Sn	Et_2O	$[Sn(bmitm)_2I_2](I_3)_2·2/3I_2$	3
Me_2dazdt·$2I_2$	Au	THF	$[Au(Me_2dazdt)I_2]I_3$	1
Me_2dazdt·2IBr	Au	THF	$[Au(Me_2dazdt)Br_2]IBr_2$	4
Me_2dazdt·$2I_2$	Hg	THF	$[Hg(Me_2dazdt)I_2]$	2
Me_2dazdt·$2I_2$	Pd	THF	$[Pd(Me_2dazdt)_2](I_3)_2$	5
$HN(SPPh_2)_2·I_2$	Sb	Et_2O	$[(N(SPPh_2)_2)Sb(\mu–S)(\mu –I)_2Sb(N(SPPh_2)_2)]$	6
$HN(SPPh_2)_2·I_2$	Co	Et_2O	$[Co(N(SPPh_2)_2)_2]$	7
$HN(SPPh_2)_2·I_2$	Cu	Et_2O	$[Cu(HN(SPPh_2)_2)_2]I_3·MeCN$	8
			$[Cu_4(N(SPPh_2)_2)_3]I_3$	
$HN(SPPh_2)_2·I_2$	Au	Et_2O	$[Au(N(SPPh_2)_2)I_2]$	9
$HN(SPPh_2)_2·I_2$	In	Et_2O	$[In(N(SPPh_2)_2)I_2]$	10
$HN(SPPh_2)_2·I_2$	Hg	Et_2O	$[Hg(HN(SPPh_2)_2)I_2]$	11
			$[Hg(N(SPPh_2)_2)_2]$	11
$HN(SPPh_2)_2·I_2$	Pd	Et_2O	$[Pd(HN(SPPh_2)_2)I_2]$	12
			$[Pd(N(SPPh_2)_2)_2]$	12
$HN(SPPh_2)(OPPh_2)·I_2$	Co	Et_2O	$[Co(\{HN(SPPh_2)(OPPh_2)\}_2I_2]$	13
			$[Co(N(SPPh_2)(OPPh_2))_2]$	13
MeImSH·I_2	Hg	CH_2Cl_2	$[Hg_2I_4(MeImSH)_2]$	14
MeImSH·I_2	Zn	CH_2Cl_2	$[Zn(MeImSH)I_2$	15
PTU·I_2	Hg	CH_2Cl_2	$[Hg(PTU)_2I_2·HgI_2]$	14
mbtt·I_2	Au	Et_2O	$[Au(mbtt)_2]I_3$	16

[a] *S*-donors molecules: bmitm = 1,1'-bis(3-methyl-4-imidazoline-2-thione)methane; Me_2dazt = *N*,*N'*-dimethylperhydro-1,4-diazepine-2,3-dithione; $HN(SPPh_2)_2$ = tetraphenyldithioimidodiphosphine; $HN(SPPh_2)(OPPh_2)$ = tetraphenylthiooxoimidodiphosphine; MeImSH = methimazole, 1-methyl-3*H*-imidazole-2-thione; PTU = propylthiouracil, 6-propyl-2-sulfanylpyrimidin-4-one; mbtt = 3-methyl-benzothiazole-2-thione

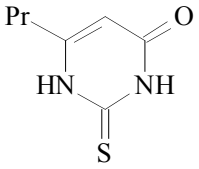
[b] *S*-donor molecules chemical structure:



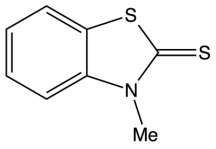
bmitm



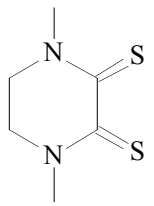
MeImSH



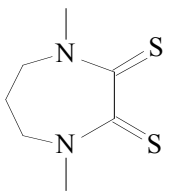
PTU



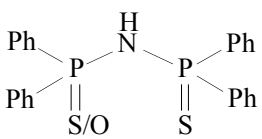
mbtt



Me_2pipdt



Me_2dazdt



$HN(SPPh_2)_2$
HN(SPPh)(OPPh)

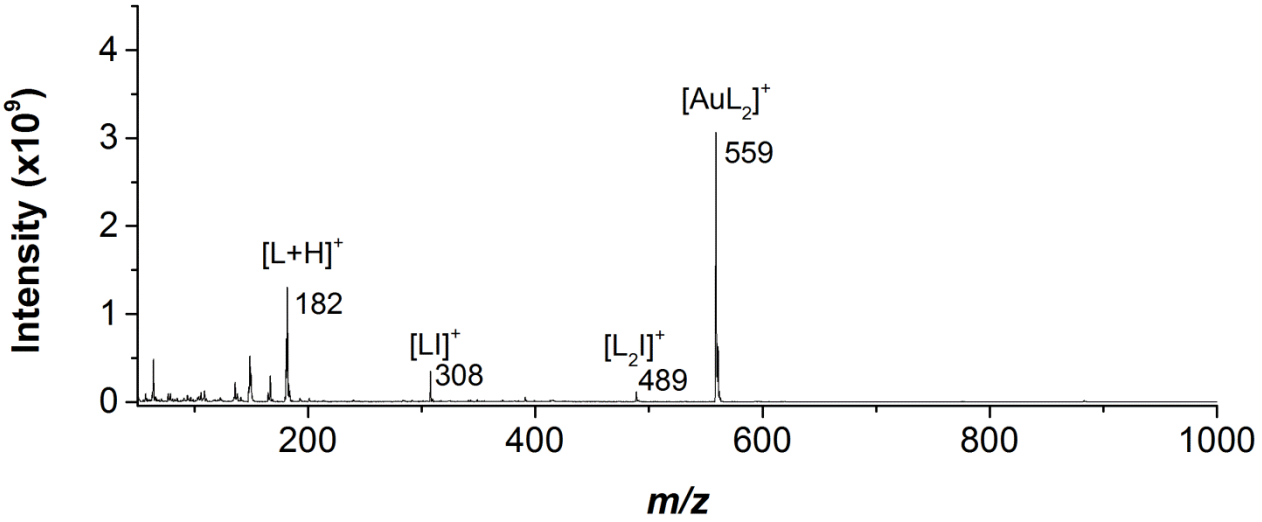


Figure S1. ESI-MS (+) spectrum of the solid obtained from the reaction in water of gold powder and the leaching mbtt + I_2 system (1/2/2 reaction molar ratio). Sample dissolved in CH_3OH:H_2O 1:1 (v/v).

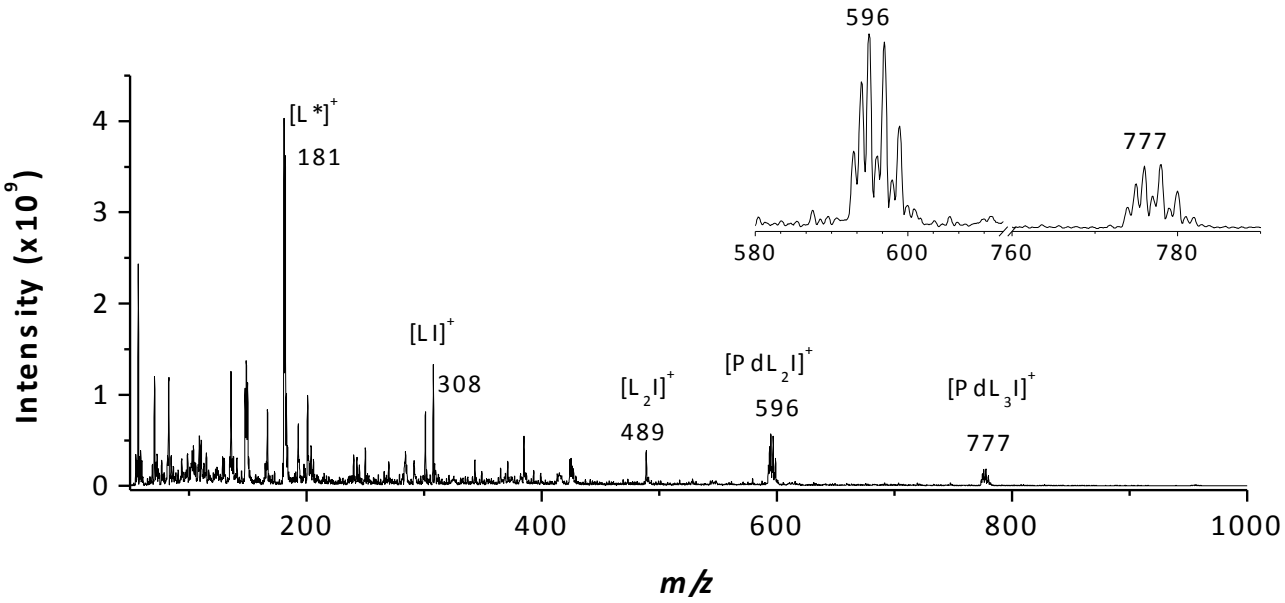


Figure S2. ESI-MS (+) spectrum of the solid obtained from the reaction in water of palladium powder and the leaching mbtt + I_2 system (1/2/2 reaction molar ratio). Sample dissolved in CH_3OH:H_2O 1:1 (v/v).

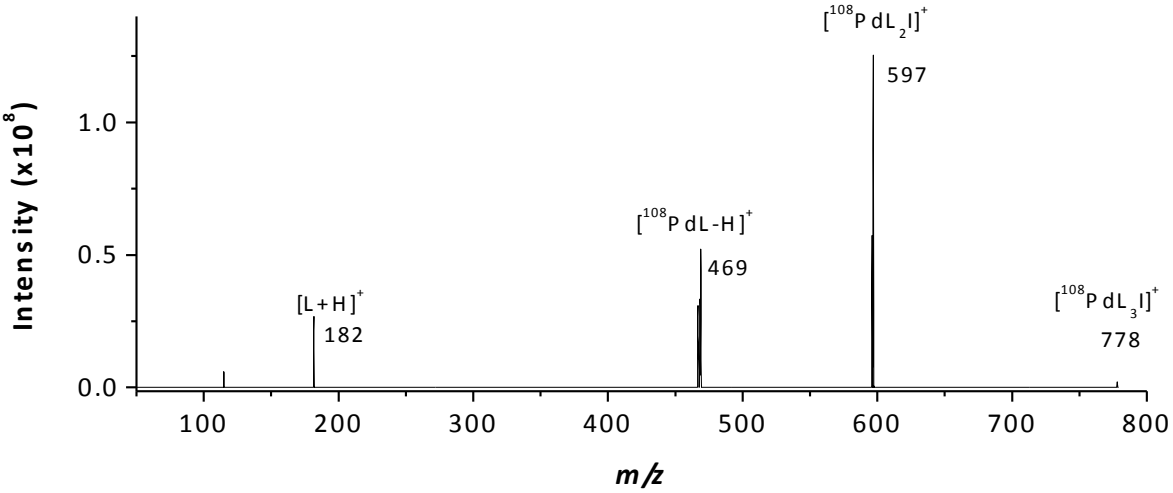


Figure S3. MS-MS spectrum of $[PdL_3I]^+$ (the *m/z* 778 signal is due to ^{108}Pd).

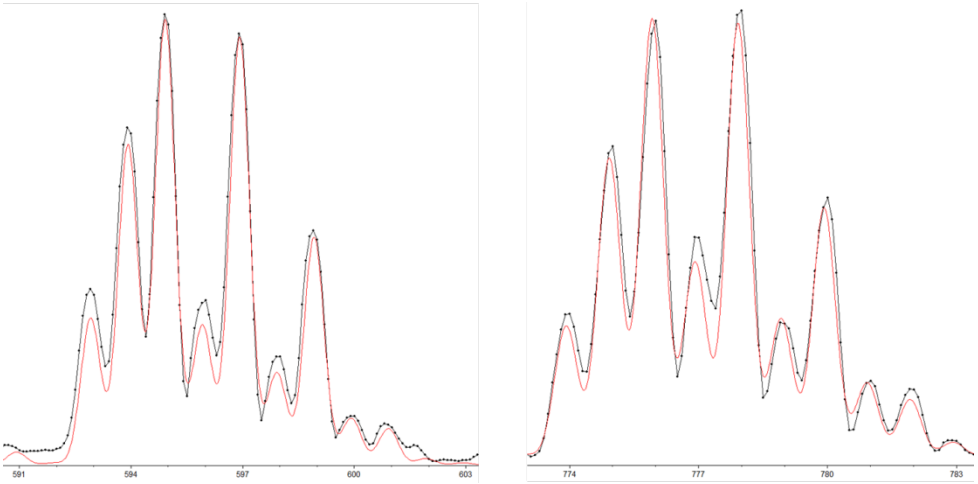


Figure S4. Calculated (red line) and experimental (black line) isotope distribution for $[Pd(mbtt)_2I]^+$ (*m/z* 596) and $[Pd(mbtt)_3I]^+$ (*m/z* 777).

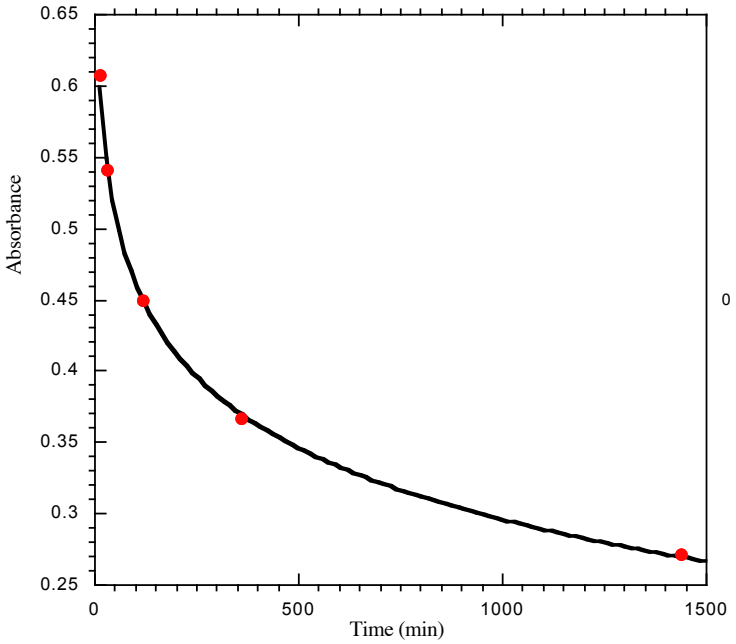


Figure S5. Absorbances recorded at different time for the reaction in water of I_2 with mbtt (1:1 reaction molar ratio, 23°C, λ = 460 nm), $[I_2] = 1.28 \times 10^{-3}$ M. [Time (min), Abs: 0, 0.960; 15, 0.607; 30, 0.541; 120, 0.449; 360, 0.367; 1440, 0.272].

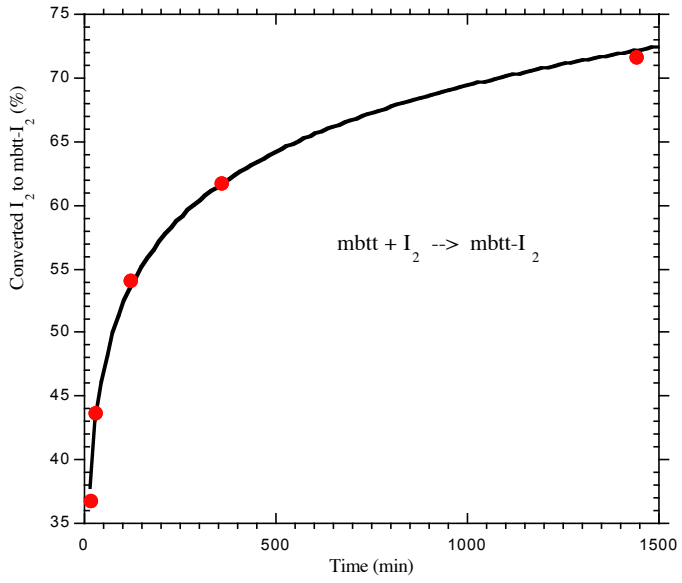


Figure S6. Calculated percentage of iodine that reacts in the course of 24 hours with mbtt to form the adduct mbtt-I_2. Data from caption Figure S5.

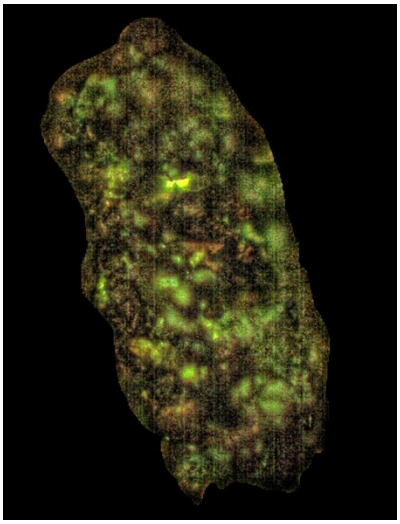


Figure S7. Image of gold deposited on magnesium powder.

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