

## New Reactions of Precious Metals and their Binary Compounds in Solvents containing Carbon Halides

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Several precious metals and their binary compounds react with  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CPh}_2\text{Cl}_2$ ,  $\text{CPhCl}_3$ , or  $\text{C}(\text{CN})_2\text{Cl}_2$  in dimethyl sulphoxide, dimethylformamide, or dimethylacetamide, and with carbon halides in ethanol or acetaldehyde containing added ligand.

Precious metals are well known for their general resistance to attack by solvents. We report several new reactions which precious metals and their binary compounds undergo with the solvents dimethyl sulphoxide (dmsO), dimethylformamide (dmf), and dimethylacetamide (dma) containing dissolved  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CPh}_2\text{Cl}_2$ ,  $\text{CPhCl}_3$ , or  $\text{C}(\text{CN})_2\text{Cl}_2$ . Parker<sup>1</sup> has described how redox reactions involving copper(II) or iron (III) allow the ready dissolution of silver and gold in dmsO or dmf.

We find that addition of  $\text{CCl}_4$  speeds up the reaction of Ag or  $\text{Ag}_2\text{O}$  with oxidants  $\text{Cu}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Ru}^{\text{III}}$ ,  $\text{Rh}^{\text{III}}$ , and  $\text{Ir}^{\text{IV}}$  in dmsO or dmf in the presence of added halide. The oxidant is continuously regenerated under such conditions, even in the absence of added halide, with consumption of  $\text{CCl}_4$ , according to Scheme 1. In the case of  $\text{Ag}_2\text{O}$ , oxygen is evolved.

Solutions of  $\text{CCl}_4$  in a range of solvents oxidise  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$  (see ref. 2) and also oxidise many base metals.<sup>3</sup> At slightly elevated temperatures, we have found that solutions containing carbon halides react directly with several precious metals and their compounds. Ag reacts readily with  $\text{CCl}_4$  or  $\text{CBr}_4$  in dmsO at 80 °C to form  $\text{AgX}_2^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ), but Au reacts only with  $\text{CBr}_4$  in dmsO, forming  $\text{AuBr}_4^-$ . Pd reacts slowly with  $\text{CCl}_4$  in dmsO, forming  $\text{PdCl}_2 \cdot 2\text{dmsO}$ , and with  $\text{CBr}_4$  in dmf, forming  $\text{PdBr}_2 \cdot 2\text{dmf}$ . The carbon halide solutions do not react with Ru, Rh, or Pt. PdO and  $\text{PtO}_2$  react slowly with  $\text{CBr}_4$  in dmf at 100 °C, forming  $\text{PdBr}_2 \cdot 2\text{dmf}$  and  $\text{PtBr}_4 \cdot 2\text{dmf}$ , respectively.  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_2\text{Se}$ , and  $\text{Ag}_2\text{Te}$  react with  $\text{CBr}_4$  in dmf, forming  $\text{AgBr}_2^-$ .  $\text{Au}_2\text{O}_3$  also reacts with  $\text{CBr}_4$  in dmf, to form  $\text{AuBr}_4^-$ . No reaction was observed between  $\text{CCl}_4$  in dmf

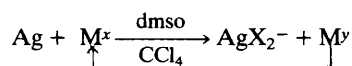
and Ru, Rh,  $\text{Rh}_2\text{O}_3$ ,  $\text{Rh}_2\text{S}_3$ ,  $\text{Ir}_2\text{S}_3$ , PdO, PdS,  $\text{PtO}_2$ ,  $\text{PtS}_2$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_2\text{Se}$ , or  $\text{Ag}_2\text{Te}$ , or between  $\text{CBr}_4$  in dmf and  $\text{Rh}_2\text{O}_3$ ,  $\text{Rh}_2\text{S}_3$ ,  $\text{Ir}_2\text{O}_3$ ,  $\text{Ir}_2\text{S}_3$ , PdS, or  $\text{PtS}_2$ .

$\text{CPh}_2\text{Cl}_2$  in dma at 110 °C reacts with Rh, Pd, Pt, and Ag, forming  $\text{RhCl}_3 \cdot 3\text{dma}$ ,  $\text{PdCl}_2 \cdot 2\text{dma}$ ,  $\text{PtCl}_2 \cdot 2\text{dma}$ , and  $\text{AgCl}_2^-$ , respectively. This system also reacts with PdO and  $\text{PtO}_2$ , forming  $\text{PdCl}_2 \cdot 2\text{dma}$  and  $\text{PtCl}_4 \cdot 2\text{dma}$ , but no reaction was observed with Ru,  $\text{Rh}_2\text{O}_3$ , or  $\text{Ir}_2\text{O}_3$ .  $\text{CPh}_2\text{Cl}_2$  in dma at 60 °C reacts readily with  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{Au}_2\text{O}_3$ .  $\text{CPh}_2\text{Cl}_2$  in dmf reacts readily with  $\text{Ag}_2\text{Se}$  and  $\text{Ag}_2\text{Te}$ , forming  $\text{AgCl}_2^-$ , but no reaction was observed with  $\text{Rh}_2\text{S}_3$ ,  $\text{Ir}_2\text{S}_3$ , PdS, or  $\text{PtS}_2$ . Pd dissolves in a solution of  $\text{CPh}_2\text{Cl}_2$  in thiophene, forming  $\text{PdCl}_2 \cdot 2(\text{C}_4\text{H}_4\text{S})$ , but no reaction occurs when a solution of  $\text{CPh}_2\text{Cl}_2$  in tetrahydrofuran is used.

$\text{Ag}_2\text{O}$  reacts very readily with  $\text{CPhCl}_3$  in dma, but not with  $\text{CPh}_3\text{Cl}$  in dma.  $\text{C}(\text{CN})_2\text{Cl}_2$  in dmf at 100 °C reacts with Rh, PdO, Pt, and  $\text{PtO}_2$ , forming  $\text{RhCl}_3 \cdot 3\text{dmf}$ ,  $\text{PdCl}_2 \cdot 2\text{dmf}$ ,  $\text{PtCl}_2 \cdot 2\text{dmf}$ , and  $\text{PtCl}_4 \cdot 2\text{dmf}$ , respectively, but no reaction occurs with Ru,  $\text{Rh}_2\text{O}_3$ , or  $\text{Ir}_2\text{O}_3$ .

PdO,  $\text{PtO}_2$ , and  $\text{Ag}_2\text{O}$  dissolve in solvents such as EtOH or MeCHO containing  $\text{CCl}_4$  and a ligand such as 1,10-phenanthroline (phen) or triphenylphosphine (tpp), forming complexes  $\text{PdCl}_2 \cdot \text{tpp}$ ,  $\text{PtCl}_2 \cdot 2\text{tpp}$ ,  $\text{AgCl} \cdot \text{tpp}$ ,  $\text{PdCl}_2 \cdot \text{phen}$ ,  $\text{PtCl}_4 \cdot \text{phen}$ , and  $2\text{AgCl} \cdot \text{phen}$ . No reaction was observed in the case of  $\text{RuO}_2$ ,  $\text{RuS}_2$ ,  $\text{Rh}_2\text{O}_3$ ,  $\text{Rh}_2\text{S}_3$ ,  $\text{Ir}_2\text{O}_3$ ,  $\text{Ir}_2\text{S}_3$ , PdS,  $\text{PtS}_2$ ,  $\text{Ag}_2\text{S}$ , or  $\text{Ag}_2\text{Se}$ .

Kleinberg<sup>2</sup> originally referred to the possible involvement of a carbene in the reaction of copper(I) with dmsO- $\text{CCl}_4$ , and Tezuka<sup>4</sup> recently supported this idea. We have isolated tetraphenylethylene from reactions of metals with dma- $\text{CPh}_2\text{Cl}_2$  and *trans*-dichlorostilbene from reactions of metals with dma- $\text{CPhCl}_3$ , in the absence of oxygen. This indicates that reaction proceeds through a carbene intermediate. In the presence of oxygen or air, reaction products include CO and



**Scheme 1.** For Cu,  $x = \text{II}$ ,  $y = \text{I}$ ; for Fe, Ru,  $x = \text{III}$ ,  $y = \text{II}$ ; for Rh,  $x = \text{III}$ ,  $y = \text{I}$ ; for Ir,  $x = \text{IV}$ ,  $y = \text{III}$ .

CO<sub>2</sub>, Ph<sub>2</sub>CO, and PhCOCl from solvents containing CCl<sub>4</sub>, CPh<sub>2</sub>Cl<sub>2</sub>, and CPhCl<sub>3</sub>, respectively.

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