



George Cady's contribution to noble-metal chemistry

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While George Cady's contributions to Main-Group chemistry, particularly fluorine chemistry, are widely known, his contribution to noble-metal chemistry has been highly significant. His publications in this area have opened up new opportunities and paved the way for new insights and developments.

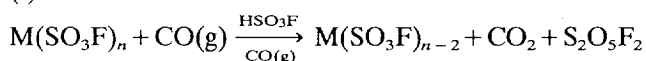
The use of AgF_2 as a catalyst has led to many novel fluorine compounds, such as bis(fluorosulfonyl)peroxide, $\text{S}_2\text{O}_6\text{F}_2$ [1]. An attempt by us to elucidate the role of AgF_2 in this reaction resulted in the synthesis and characterization first of silver(II) fluorosulfate [2] and then of $\text{Pd}(\text{SO}_3\text{F})_2$ and the mixed valency compound $\text{Pd}^{\text{II}}[\text{Pd}(\text{SO}_3\text{F})_6]$ [3,4] with paramagnetic, octahedrally coordinated Pd^{II} . Below 40 K [5], both palladium fluorosulfates and $\text{Ag}(\text{SO}_3\text{F})_2$ become ferromagnetic.

The syntheses of $\text{Au}(\text{SO}_3\text{F})_3$ and $\text{Pt}(\text{SO}_3\text{F})_4$ [6] by metal oxidation with bromine(I) fluorosulfate proceeded via the intermediates $\text{Au}(\text{SO}_3\text{F})_3 \cdot 2\text{BrSO}_3\text{F}$ and $\text{Pt}(\text{SO}_3\text{F})_4 \cdot 4\text{BrSO}_3\text{F}$. The binary fluorosulfates formed on pyrolysis of these solvates were weakly paramagnetic, while $\text{Au}(\text{SO}_3\text{F})_3$ and $\text{Pt}(\text{SO}_3\text{F})_4$ obtained via metal oxidation by $\text{S}_2\text{O}_6\text{F}_2$ were diamagnetic. The bromine fluorosulfate solvates were found to contain the anions $[\text{Au}(\text{SO}_3\text{F})_4]^-$ and $[\text{Pt}(\text{SO}_3\text{F})_6]^{2-}$ and the polybromine cations Br_3^+ and Br_5^+ . This, in turn, led to the development of the noble-metal superacid systems $\text{HSO}_3\text{F}-\text{Au}(\text{SO}_3\text{F})_3$ [7,8] and $\text{HSO}_3\text{F}-\text{Pt}(\text{SO}_3\text{F})_4$ [9].

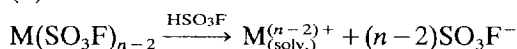
The observation of paramagnetism in $\text{Au}(\text{SO}_3\text{F})_3$ has resulted in the generation and identification (by electron spin resonance spectroscopy) of true Au^{2+} cations, both in the radical anion $[\text{Au}(\text{SO}_3\text{F})_4]^{2-}$ [10] and as lattice defect in oligomeric $[\text{Au}(\text{SO}_3\text{F})_{3-x}]_n$ [11]. The detection of Au^{2+} was aided by the molecular structure determination of $[\text{Au}(\text{SO}_3\text{F})_3]_2$ [12].

An attempt to utilize the protonating ability of the noble-metal superacids towards CO resulted in the discovery of thermally stable noble-metal carbonyl cations: linear $[\text{Au}(\text{CO})_2]^+$ [13,14], square-planar $[\text{M}(\text{CO})_4]^{2+}$ [15,16] ($\text{M}=\text{Pd}$ or Pt) and cyclic $[\text{Pd}_2(\mu\text{-CO})_2]^{2+}$ [17] with $\text{Sb}_2\text{F}_{11}^-$ as anions and the fluorosulfates $\text{Au}(\text{CO})(\text{CO}_3\text{F})$ [18] and *cis*- $\text{M}(\text{CO})_2(\text{SO}_3\text{F})_2$

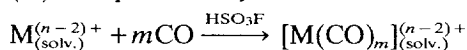
(i) Reduction



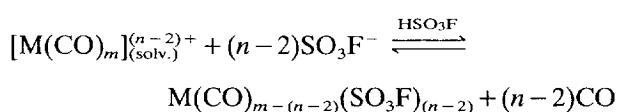
(ii) Ionic dissociation



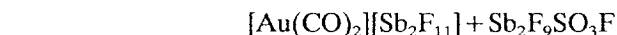
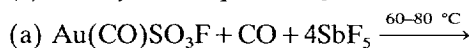
(iii) Complexation by CO



(iv) Ligand exchange (CO versus SO_3F^-)



(v) Solvolysis in liquid SbF_5



($\text{M}=\text{Pd}$ or Pt)

Scheme 1. The formation of metal carbonyl cations in HSO_3F – an attempt at a rationalization.

[19] ($\text{M}=\text{Pd}$ or Pt), all examples of unusual metal-to-CO bonding, where π -back-donation is insignificant and the effective atomic number rule is not obeyed. A rationale for the formation of the 'non-classical metal carbonyl' derivatives is offered in Scheme 1.

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