

The use of fluorosulfuric acid, magic acid and liquid antimony(V) fluoride as media to generate, stabilize and study metal carbonyl cations

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With synthetic routes to the unusual non-classical metal carbonyl cations [1], i.e. $[\text{Au}(\text{CO})_2]^+$ [2,3], $[\text{M}(\text{CO})_4]^{2+}$ (M = Pd or Pt) [4,5], cyclo- $[\text{Pd}_2(\mu\text{-CO})_2]^{2+}$ [6], and to the fluorosulfate derivatives $\text{Au}(\text{CO})\text{SO}_3\text{F}$ [2] and *cis*- $\text{M}(\text{CO})_2(\text{SO}_3\text{F})_2$ [7] (M = Pd or Pt) established, we wish to focus attention on their spectroscopic, structural and bonding features, and provide a rationale for their existence in highly acidic media.

Most notable is the shift of $\bar{\nu}(\text{CO})$ to higher wavenumbers relative to CO itself and the very high CO stretching force constants f_r , summarized in Table 1. Likewise, the ^{13}C chemical shifts in the NMR spectra of isotopically enriched species are shifted to lower frequencies relative to CO, while classical transition-

metal carbonyls resonate at higher frequencies [8]. It appears that metal-to-CO π -back-donation is drastically reduced with increasing charge on the central metal and decreasing basicity of the counteranion.

Two recent molecular structures determined by us support this view. In $[\text{Pd}_2(\mu\text{-CO})_2](\text{SO}_3\text{F})_2$ [6], a cyclic $[\text{Pd}_2(\mu\text{-CO})_2]^{2+}$ cation with symmetrically bridging CO groups and short CO bonds is found. In this cation, $\bar{\nu}_{\text{as}}(\text{CO})$ is, at 2002 cm^{-1} , about 200 cm^{-1} higher than in classical metal carbonyls [9]. In *cis*- $\text{Pd}(\text{CO})_2(\text{SO}_3\text{F})_2$ [10], terminal CO groups with very short CO bond distances are encountered. More significantly, inter- and intra-molecular $\text{SO}\cdots\text{CO}$ contacts between the carbonyl cation and terminal oxygens of the fluorosulfate group are observed and appear to provide some charge compensation for the C atom.

It appears that in these predominantly σ -bonded carbonyls, secondary contacts in the solid state and solvation in strong acidic media provide stabilization for the electrophilic carbon.

It is concluded that without significant π -back-donation and a failure of the 18-electron rule, not only transition and noble metals should form stable carbonyl derivatives. We have very recently reported on the first syntheses of post-transition-metal carbonyl cations $[\text{Hg}(\text{CO})_2]^{2+}$ and $[\text{Hg}_2(\text{CO})_2]^{2+}$ [11]. Both cations are stabilized by $\text{Sb}_2\text{F}_{11}^-$ anions; their $\bar{\nu}(\text{CO})$ and f_r values are included in Table 1.

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Table 1
Bonding properties of CO in noble metal carbonyls and related species

Compound	ν (cm^{-1})	$10^2 f_r$ (N m^{-1})	r (pm)
CO	2143	18.6	112.8
CO^+	2184	19.3	111.5
$\text{NaCl}(100)\cdots\text{CO}$	2155	18.8	
$\text{FH}\cdots\text{CO}$	2162	18.9	
HCO^+	2184	21.3	110.5
$\text{Cu}(\text{CO})\text{AsF}_6$	2180	19.2	
$[\text{Ag}(\text{CO})_2][\text{B}(\text{OTeF}_5)_3]$	2200	19.5	108.0
$[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]$	2235	20.1	
$\text{Au}(\text{CO})\text{Cl}$	2163	18.9	111.3
$[\text{Pd}(\text{CO})_4][\text{Sb}_2\text{F}_{11}]_2$	2259	20.6	
$\text{Pd}(\text{CO})_2(\text{SO}_3\text{F})_2$	2218	19.8	110.8
$[\text{Pt}(\text{CO})_4][\text{Sb}_2\text{F}_{11}]_2$	2261	20.6	
$[\text{Hg}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$	2280	21.0	110.4
$[\text{Hg}_2(\text{CO})_2][\text{Sb}_2\text{F}_{11}]_2$	2248	20.4	

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