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Catalysis Today 36 (1997) 99–106

CATALYSIS TODAY

Polycarbonyl cations of Cu(I), Ag(I), and Au(I): $[M(CO)_n]^+$

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Abstract

Recently published data for polycarbonyl complexes of monovalent copper, silver, and gold are reviewed and discussed within the context of metal–ligand bonding. For the dicarbonyl complexes $[M(CO)_2]^+$ the data indicate that (i) metal–carbonyl σ bonding is strongest for $M^+ = Au^+$ and weakest for $M^+ = Ag^+$, and (ii) metal–carbonyl π bonding is strongest for $M^+ = Cu^+$ and negligible for $M^+ = Ag^+$ and Au^+. These variations in M–CO σ- and π-bond strengths are explained in terms of the ionization energies and the electronic excited state energies of the three gaseous M^+ cations.

Keywords: Metal carbonyls; σ/π Bonding; Copper; Silver; Gold

1. Introduction

Carbon monoxide is one of the most important ligands in transition metal chemistry. Many industrial processes, from hydroformylation and the Fischer–Tropsch synthesis to the synthesis of acetic acid and the water–gas shift reaction, employ CO as a reagent and transition metal compounds as heterogeneous or homogeneous catalysts and involve the intermediacy of metal carbonyls [1]. The classical picture of metal–carbonyl bonding is well understood. It involves synergistic bonding, with carbon monoxide acting as a σ-donor and a π-acceptor for *d*-block metals [2,3]. For classical metal–carbonyl complexes such as $Cr(CO)_6$, $RhCl(CO)(PPh_3)_2$, and $CpFe(CO)_2I$, the average $\nu(CO)$ values are considerably lower than 2143 cm^{-1}, the value for free CO. It is generally accepted that the decrease in $\nu(CO)$ is due to π-backbonding, the transfer of metal d_π electron density to the CO π^* orbitals [2].

In the last few years, a number of cationic metal carbonyl complexes with average $\nu(CO)$ values higher than 2143 cm^{-1} have been isolated and studied [4]. We proposed the name *nonclassical metal carbonyls* for this growing class of complexes that seem to have an insignificant amount of π-backbonding [5]. Of particular interest are the cationic homoleptic carbonyls of monovalent copper, silver, and gold, which have been implicated in a number of important catalytic reactions [6]. In this paper we will focus our attention on the two-coordinate complexes $[Cu(CO)_2]^+$, $[Ag(CO)_2]^+$, $[Au(CO)_2]^+$, for which enough data have now been reported to allow for a meaningful discussion of the metal–ligand bonding.

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PII S0920-5861(96)00202-7

2. A survey of the available data

Historically, the first evidence for Cu(I) carbonyls was the observation by Leblanc and Berthelot [7] that acidic solutions of Cu(I) salts absorbed up to 1.0 equivalent CO (based on Cu). The solid compound Cu(CO)Cl was first prepared by Wagner, who treated solid CuCl with 100 atm CO [8]. Crystalline Cu(CO)Cl (ν(CO) = 2127 cm^{-1}, Cu–C = 1.86(2)Å) was subsequently isolated from solutions or suspensions of CuCl under 1 atm CO [9]. Other simple Cu(CO)X salts have been reported, including [Cu(CO)][AsF$_6$] (ν(CO) = 2180 ± 5 cm^{-1}) [10]. In addition, many Cu(I) carbonyl complexes with amine ligands are known [11]. With one exception, the CO/Cu stoichiometric ratio in all known Cu(I) carbonyl compounds, including all known carbonylated Cu(I)-containing proteins, is $\leq$ 1.0. The exception is the report by Souma et al. that solutions of Cu_2O in neat HSO_3F, $BF_3 \cdot H_2O$, and other strong acids absorbed up to 4 equivalents CO per equivalent Cu, the exact stoichiometry being dependent on temperature and pressure [12]. Based on this report, IR [12] and Raman [13] spectra of these solutions were interpreted in terms of the following set of equilibria (any or all of the cations may be solvated):

$$Cu^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Cu(CO)]^+ \underset{-2CO}{\overset{+2CO}{\rightleftharpoons}} [Cu(CO)_3]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Cu(CO)_4]^+.$$

None of these carbonyl complexes could be isolated. For reasons that are not clear, other possible interpretations of the data, especially the existence of the dicarbonyl complex $[Cu(CO)_2]^+$, were not considered.

We recently reported that $CuAsF_6$ absorbs up to 3 equivalents of CO *in the solid state* at $\leq$ 1 atm CO pressure [14]. Vibrational spectra and manometric titrations of neat samples recorded under precise pressures of CO demonstrated the existence of [Cu(CO)][AsF$_6$] (ν(CO) = 2178 cm^{-1}), [Cu(CO)$_2$][AsF$_6$] (ν(CO) = 2164 (IR) and 2177 (Raman) cm^{-1}), and [Cu(CO)$_3$][AsF$_6$] (ν(CO) = 2183 (IR) and 2179 and 2206 (Raman) cm^{-1}). The complexes are stable only under CO pressure. Spectra taken at 200 Torr CO, at which pressure the tricarbonyl complex $[Cu(CO)_3]^+$ was formed, are shown in Fig. 1.

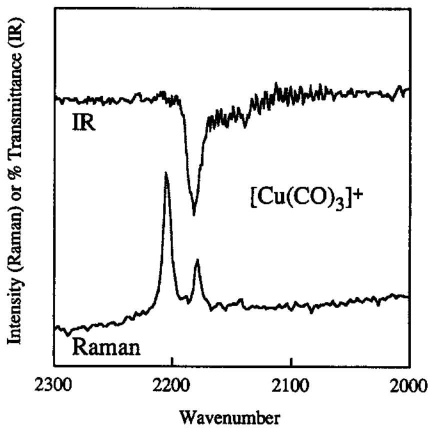

Fig. 1. IR and Raman spectra of [Cu(CO)$_3$][AsF$_6$], generated in situ from $CuAsF_6$ and 200 Torr CO.

Until recently, isolable Ag(I) carbonyls were unknown. In 1925, Manchot et al. reported that a solution of Ag_2SO_4 in conc. H_2SO_4 reversibly absorbed carbon monoxide [15]. A limiting CO/Ag stoichiometric ratio of 0.5 was achieved when $T = 0°C$ and $P_{CO} \sim 1$ atm [15]. Later, Souma et al. found that this phenomenon was general for a variety of Ag(I) salts in a variety of strong protic acids (e.g., HSO_3F, $BF_3 \cdot H_2O$) [12,16]. These authors were able to achieve a CO/Ag ratio of 2.0, but only at low temperatures (e.g., −40°C at 1 atm) or high pressures (e.g., 19 atm at 24°C). In neither Manchot's nor Souma's work were silver carbonyls isolated from solution.

Using a variety of $OTeF_5$-containing weakly coordinating anions, we isolated a number of compounds containing the $[AgCO]^+$ and $[Ag(CO)_2]^+$ ions, and have structurally characterized two of them, [Ag(CO)][B(OTeF$_5$)$_4$] (ν(CO) = 2204 cm^{-1}; Ag–C = 2.10(1)Å) and [Ag(CO)$_2$][B(OTeF$_5$)$_4$] (IR ν(CO) = 2198 cm^{-1}; Ag–C = 2.06(5), 2.14(5), 2.16(4), and 2.20(4)Å for three unique cations, all of which exhibited the expected two-coordinate, pseudo-$D_{\infty h}$ geometry) [5]. Infrared and Raman spectra of $[Ag(CO)_2][Nb(OTeF_5)_6]$ exhibited ν(CO) bands at 2196 and 2220 cm^{-1}, respectively [5]. Like the series of compounds $[Cu(CO)_n][AsF_6]$, these silver carbonyls are stable only under CO pressure. We recently reported that the tricarbonyl $[Ag(CO)_3][Nb(OTeF_5)_6]$ is formed under 13 atm CO [17]. The IR spectrum of this compound exhibited a ν(CO) band at 2192 cm^{-1} [17]. These results can be summarized by the following set of equilibria:

$$Ag^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Ag(CO)]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Ag(CO)_2]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Ag(CO)_3]^+.$$

For more than 65 years, the only isolable Au(I) carbonyl was Au(CO)Cl, first prepared by Manchot and Gall in 1925 [18]. In 1992, Aubke, Willner et al. reported the isolation and characterization of $[Au(CO)_2][Sb_2F_{11}]$, which unlike the Cu(I) and Ag(I) systems described above is stable indefinitely in the absence of a CO atmosphere [19]. The compound $[Au(CO)_2][Sb_2F_{11}]$ exhibited mutually exclusive ν(CO) bands in IR and Raman spectra at 2217 and 2254 cm^{-1}, respectively [19]. We determined that a new IR band at 2212 cm^{-1}, assigned to $[Au(CO)_3][Sb_2F_{11}]$, appears when the dicarbonyl complex is exposed to 100 atm CO pressure [20]. In this case, the relevant equilibrium is:

$$[Au(CO)_2]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Au(CO)_3]^+.$$

No observable tricarbonyl complex was observed when the CO pressure was only 13 atm.

Armentrout et al. have reported metal–carbonyl bond energies for the *gas phase* complex ions $[Cu(CO)_n]^+$ and $[Ag(CO)_n]^+$ ($n = 1$–4): $(CO)_xCu^+$–CO bond energies at 0K were found to be 36(2), 41(1), 18(1), and 13(1) kcal mol^{-1} for $x = 0$, 1, 2, and 3, respectively; $(CO)_xAg^+$–CO bond energies at 0K were 21(1), 26(1), 13(2), and 11(4) kcal mol^{-1} for $x = 0$, 1, 2, and 3, respectively [21]. The first three bond energies for silver are in excellent agreement with earlier theoretical values of Veldkamp and Frenking (VF) [22]. They calculated (MP2 level of theory) $(CO)_xAg^+$–CO bond energies to be 21, 27, and 12 kcal mol^{-1} for $x = 0$, 1, and 2, respectively. VF also calculated $(CO)_xAu^+$–CO bond energies to be 45, 50, and 9 kcal mol^{-1} for $x = 0$, 1, and 2, respectively.

3. Discussion

The results listed above are summarized in Table 1. For the purposes of our discussion, we will assume that all three $[M(CO)_2]^+$ complexes have $D_{\infty h}$ symmetry. Although the structures of $[Cu(CO)_2]^+$ and $[Au(CO)_2]^+$ salts have not yet been determined by X-ray crystallography, the mutual exclusion of their IR and Raman ν(CO) values leaves little doubt that they share the two-coordinate linear structure found for the $[Ag(CO)_2]^+$ complex in $[Ag(CO)_2][B(OTeF_5)_4]$ [5]. Furthermore, we will assume that all three $[M(CO)_3]^+$ complexes have D_{3h} symmetry. The vibrational data support this structure for $[Cu(CO)_3]^+$ [5], and VF's calculations predict this structure for the silver and gold homologues [22].

The three unique $[Ag(CO)_2]^+$ cations in $[Ag(CO)_2][B(OTeF_5)_4]$ have a number of weak, secondary bonding contacts with fluorine atoms

Table 1
Summary of data for group IB metal carbonyl cations

Carbonyl complex	ν(CO) (cm^{-1})		$(CO)_xM$–CO bond enthalpy (kcal/mol) [a]
	IR	Raman	
$[Cu(CO)]^+$	2178		36(2) exp.
$[Ag(CO)]^+$	2208	2206	21(1) exp., 21 theo.
$[Au(CO)]^+$			45 theo.
$[Cu(CO)_2]^+$	2164	2177	41(1) exp.
$[Ag(CO)_2]^+$	2196	2220	26(1) exp., 27 theo.
$[Au(CO)_2]^+$	2217	2254	50 theo.
$[Cu(CO)_3]^+$	2183	2179, 2206	18(1) exp.
$[Ag(CO)_3]^+$	2192		11(4) exp., 12 theo.
$[Au(CO)_3]^+$	2212		9 theo.

[a] exp. = experimental values [21]; theo. = theoretical values [22].

(Ag...F ≈ 3Å) [5]. Since weakly coordinating fluoroanions have been used for all three metals, it is sensible to conclude that all of the di- and tricarbonyl complexes contain similar weak, but specific, cation–anion interactions. Furthermore, although the anions used in the three systems, AsF_6^-, $Nb(OTeF_5)_6^-$, and $Sb_2F_{11}^-$, are not identical, they are expected to be sufficiently similar in coordinating ability so that the differences in IR and Raman spectra for the *compounds* $[Cu(CO)_n][AsF_6]$, $[Ag(CO)_n][Nb(OTeF_5)_6]$, and $[Au(CO)_n][Sb_2F_{11}]$, are intrinsic differences between the *cations*. In future work we plan to verify this assumption by studying $[Cu(CO)_n]^+$, $[Ag(CO)_n]^+$, and $[Au(CO)_n]^+$ salts of a common weakly coordinating anion.

At first glance, there are no apparent trends in the data. All three metal–carbonyl bond energies for Cu(I) are approximately 50% larger than for Ag(I). For the dicarbonyl complexes, Au(I) forms the strongest metal–ligand bonds and Ag(I) the weakest. However, Cu(I) forms the strongest bond to the third carbonyl and Au(I) the weakest. (Note that the listed bond energies are consistent with the pressures of CO necessary to form the tricarbonyl complexes: ~ 200 Torr for Cu(I), 13 atm for Ag(I), and ~ 100 atm for Au(I)). For the dicarbonyl complexes, the average value of $\nu(CO)$ is highest for Au(I) and lowest for Cu(I). On the other hand, the frequency of the IR band *increases* by 19 cm^{-1} on going from $[Cu(CO)_2]^+$ to $[Cu(CO)_3]^+$ but *decreases* by ca. 5 cm^{-1} on going from $[Ag(CO)_2]^+$ or $[Au(CO)_2]^+$ to $[Ag(CO)_3]^+$ or $[Au(CO)_3]^+$, respectively.

The C–O stretching force constant is a useful indicator of the magnitude of metal–ligand σ- and π-bonding in metal carbonyls [23]. However, in the absence of a complete vibrational force-field analysis for all of the complexes listed in Table 1, we will use the simplifying assumption that the bands observed in the 2100–2300 cm^{-1} region of the IR and Raman spectra correspond to pure C–O stretching vibrations. This is a good approximation and is frequently invoked, since the normal modes that are largely C–O stretching are relatively free of changes in other internal coordinates [23]. Therefore, $[\nu(CO)]^2 \propto k(CO)$, and we will discuss the relative $\nu(CO)$ values in Table 1 as being a direct consequence of changes in metal–ligand σ- and π-bonding.

The C–O bond is strengthened, and $\nu(CO)$ is raised, by σ-donation of the carbon atom "lone pair" to an empty orbital on another species, such as a metal ion or other Lewis acid (the 5σ HOMO, or "lone pair," of CO is slightly C–O σ-antibonding). For example, $\nu(CO)$ is 2184 and 2165 cm^{-1} for HCO^+ [24] and BH_3CO [25], respectively. Another effect that would raise $\nu(CO)$ is electrostatic in nature: the carbon–oxygen bond in CO becomes stronger, and $\nu(CO)$ rises, if the molecule is placed in an electric field with the carbon atom facing the direction of increasing positive charge (e.g., towards a cation like H^+ or Ag^+) [26]. In contrast to M–C σ-bonding, $M \rightarrow CO$ $d \rightarrow \pi^*$ π-backbonding lowers $\nu(CO)$ by populating one or both of the CO 2π (π*) orbitals, decreasing the carbon–oxygen bond order [2]. For classical metal carbonyls, the effect of π-backbonding on $\nu(CO)$ is larger than the effect of σ-bonding since classical metal carbonyls (by definition) exhibit CO stretching frequencies considerably lower than free CO.

Let us start with the hypothesis that there is little or no π-backbonding in the $[Ag(CO)_n]^+$ complexes. In other words, silver(I) is behaving predominantly or exclusively as a Lewis acid, albeit a soft one. The Ag–C σ-bond raises $\nu(CO)$ from 2143 cm^{-1} to ~ 2200 cm^{-1}, and there is no countervailing Ag–C π-bond to lower $\nu(CO)$. This conclusion is in harmony with metal–carbon distances. Consider the two monovalent, soft, period 5 cations Rh^+ and Ag^+. There are ample vibrational data demonstrating that the former metal ion participates in π-backbonding. The Ag–C bond distances of ~ 2.1Å in $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ are 0.3Å longer than the ~ 1.8Å Rh–C distances in $RhH(CO)(PPh_3)_3$

[27] and $[RhCl(CO)_2]_2$ [28]. A lack of π-backbonding has been shown to be commensurate with an unusually long M–C distance: a theoretical study by Sherwood and Hall led to the prediction that if a Cr–C bond in $Cr(CO)_6$ was stretched 0.25Å longer than its equilibrium distance, Cr–C π-backbonding would be negligible and CO would act as a σ-only ligand [29]. Under these circumstances, Sherwood and Hall also found that ν(CO) would increase relative to free CO.

We are now ready to compare and understand the data for the dicarbonyl complexes, $[M(CO)_2]^+$. A plot of average bond energies vs. average ν(CO) values is shown in Fig. 2. Why are the $\nu(CO)_{av}$ values for Au(I) and Cu(I) higher and lower, respectively, than the value for Ag(I)? The data show that Cu(I) forms significantly stronger bonds to carbonyl ligands than Ag(I), and if these bonds were purely σ-bonds in both cases, $\nu(CO)_{av}$ would be not lower but *higher* for the $[Cu(CO)_2]^+$ complex. Therefore, the lower $\nu(CO)_{av}$ value for the Cu(I) complex signals some π-backbonding (although not enough to lower ν(CO) below 2143 cm^{-1}). It follows that the high $\nu(CO)_{av}$ value for $[Au(CO)_2]^+$ is a consequence of much stronger σ-bonding in the gold complex.

Why are the Ag–C bonds, at ~2.1Å, so long and so weak (compare Cu–C in Cu(CO)Cl, 1.86(2)Å [9a], and Au–C in Au(CO)Cl, 1.93(2)Å [30]) and why are the Au–C bonds so strong? The main reason may be variations in σ-repulsion due to the interaction of the filled CO 5σ MOs with the filled metal z^2 (d_σ) atomic orbital. For two-coordinate d^{10} metal complexes, sd_σ mixing results in a shift of electron density from the z axis (the metal–ligand axis) to the xy plane, and decreases the σ-repulsion which allows for shorter, stronger metal–ligand σ-bonds [31]. The amount of sd_σ mixing depends on the s–d_σ energy gap, and although this cannot be measured directly, others have estimated it to be equal to the lowest energy $d^9s^1 \leftarrow d^{10}$ electronic transition energy [31]. The s–d_σ energy gaps [32] and d-subshell energy levels for Cu(I), Ag(I), and Au(I) are depicted in Fig. 3 (the d-subshell energies correspond to the the second ionization potentials of the neutral atoms). Note that there is no corresponding $4z^2$ σ-repulsion for two-coordinate d^8 Rh(I): *ab initio* calculations predict that Rh–CO bonds in $[Rh(CO)_2]^+$ are ~50% stronger than the Ag–CO bonds in $[Ag(CO)_2]^+$,

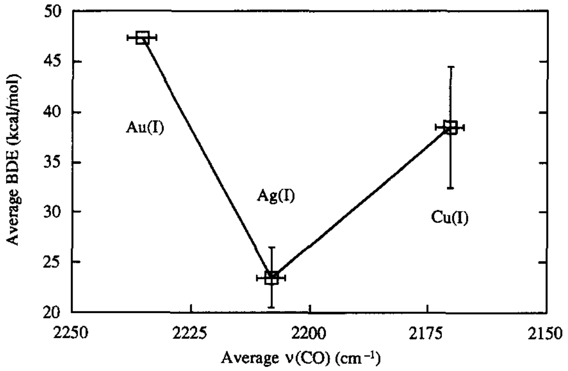

Fig. 2. Plot of the average of the two M–CO bond dissociation energies vs. the average of ν_{sym}(CO) and ν_{asym}(CO) for $[M(CO)_2]^+$ complexes (M = Cu, Ag, Au). Error bars for measured values are $\pm 3\sigma$ or ± 2 cm^{-1}.

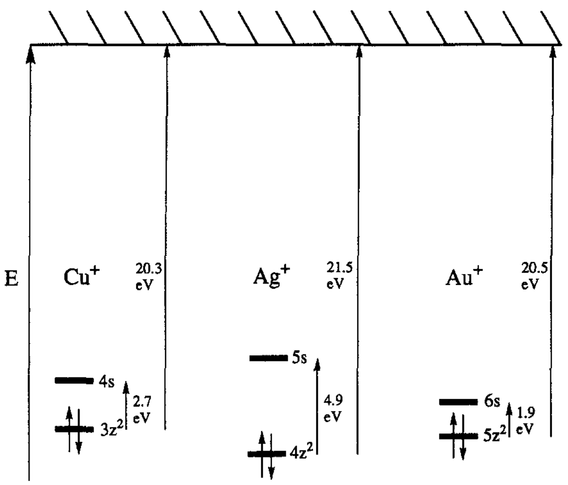

Fig. 3. Orbital energy diagram for monovalent copper, silver, and gold. The d subshell energies correspond to the second ionization potentials for the neutral atoms. The $s-d$ energy gaps correspond to the lowest energy $d^9s^1 \leftarrow d^{10}$ electronic transition energies for the gas-phase M^+ cations.

a consequence of stronger σ-bonding as well as π-backbonding [33]. The Ag^+ ion, with the largest s–d_σ energy gap, forms the weakest metal–ligand bonds, while the Au^+ ion, with the smallest energy gap, forms the strongest bonds.

Some have argued that the bonding in cationic metal–carbonyl complexes such as $[Ag(CO)_2]^+$ is primarily electrostatic (ionic) [34]. If true, this would preclude the σ-repulsion analysis presented above. However, the bonding is probably not primarily electrostatic: the ^{107}Ag–^{13}C NMR coupling constants for two different $[Ag(CO)_2]^+$ salts were found to be ~200 Hz, significantly larger than any previously reported values of $J(^{107}Ag^{13}C)$ [5]. Therefore, it is clear that there is significant $5s$–$2s$ overlap, and hence significant covalency, in the Ag–C bonds in $[Ag(CO)_2]^+$.

Since π-backbonding involves a shift of electron density from metal orbitals to carbonyl ligand orbitals, it is related to removal of electron density from the metal and hence is related to ionization potentials. The second ionization potential of silver (21.5 eV) is larger by ca. 25 kcal/mol than those for copper (20.3 eV) and gold (20.5 ev). In fact, silver has the highest second ionization potential of all metallic elements except for the alkali metals. Since π-bonding is a more sensitive function of distance than σ-bonding, the longer distances for the $[Ag(CO)_n]^+$ complexes greatly diminish or preclude π-backbonding in silver(I) carbonyls. It is now straightforward to understand why there is little or no π-backbonding in the $[Ag(CO)_n]^+$ complexes. The Ag^+ cation has two strikes against it: σ-repulsion leads to long Ag–CO bond distances *and* the second ionization potential for silver is too high for effective transfer of electron density from the metal to the carbonyl π^* orbitals. In contrast, the second ionization potential for rhodium is only 18.1 eV, some 20% lower than for silver. With no σ-repulsion from a filled $4z^2$ orbital and with a relatively low ionization potential for Rh^+, it follows that the Rh–C bonds in $[Rh(CO)_2]^+$ should have stronger σ- and π-components than the Ag–C bonds in $[Ag(CO)_2]^+$.

Since copper and gold have nearly identical second ionization potentials, it is not immediately apparent why there is no significant π-backbonding in $[Au(CO)_2]^+$, a conclusion consistent with the very high $\nu(CO)_{av}$ value [19] and with *ab initio* calculations [22]. It is tempting to conclude that the Au–C bonds in this species, which are undoubtedly longer than the Cu–C bonds in $[Cu(CO)_2]^+$, have less π overlap. This issue must be left unsettled, however. For group 6 hexacarbonyls, π overlap was found to be *larger* for tungsten than for chromium, not smaller [35]. Nevertheless, the CO π^* electron density was found to be smaller for tungsten than for chromium [35,36].

Why does the IR $\nu(CO)$ band for $[Cu(CO)_3]^+$ appear at higher wavenumbers relative to $[Cu(CO)_2]^+$ when the corresponding bands for $[Ag(CO)_3]^+$ and $[Au(CO)_3]^+$ appear at lower wavenumbers relative to the respective dicarbonyl complexes? As discussed above, the silver and gold species have negligible π-backbonding. The complexes $[Ag(CO)_3]^+$ and $[Au(CO)_3]^+$ have three σ-bonded CO ligands, so each CO ligand is more weakly σ-bonded to the central metal ion than in the corresponding dicarbonyl complexes. Since σ-bonding raises $\nu(CO)$ above 2143 cm^{-1}, the result is lower $\nu(CO)$ values for the Ag(I) and Au(I) tricarbonyl complexes than for the dicarbonyl complexes. The same effect is operative in the copper system as well, but the presence of π-backbonding must also be considered. If each CO ligand in $[Cu(CO)_3]^+$ has less π^* electron density than the two CO ligands in $[Cu(CO)_2]^+$, $\nu(CO)$ should increase for $[Cu(CO)_3]^+$ relative to $[Cu(CO)_2]^+$. Consistent with observations for classical metal carbonyls, the loss of π-bonding on going from $[Cu(CO)_2]^+$ to $[Cu(CO)_3]^+$ has a larger effect on $\nu(CO)$ than the loss of σ-bonding.

For all three metal ions, why is the $(CO)M^+$–CO bond energy greater than the M^+–CO bond energy? The formation of the monocarbonyl

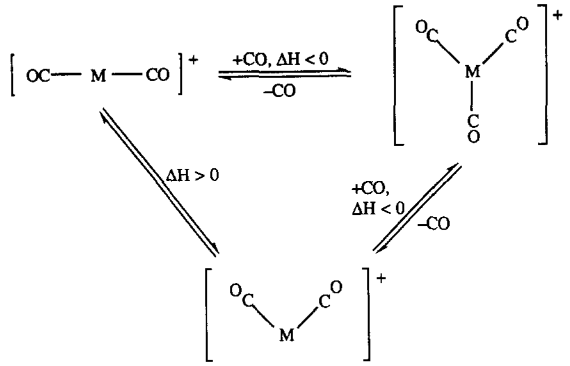

Fig. 4. The formation of $[M(CO)_3]^+$ from $[M(CO)_2]^+$ broken down into two steps, an endothermic reorganization and an exothermic bond formation.

cations requires significant electronic reorganization for the metal ion, including sd_σ mixing. Once sd_σ mixing occurs, the metal ion can effectively bond to two carbonyls on the z axis [37]. Thus, formation of the second M–CO bond does not involve as much endothermic reorganization as the formation of the first M–CO bond. Therefore, the second metal–carbonyl bond dissociation energy, which includes a relatively small endothermic term, is larger than the first.

Finally, why is the third metal–carbonyl bond so weak for gold? Of the three metals, Au(I) has the smallest s–d_σ energy gap, so the Au–C σ-bonds in $[Au(CO)_2]^+$ are particularly strong. As above, the reaction $[M(CO)_2]^+ + CO \rightarrow [M(CO)_3]^+$ can be broken down into two steps, an endothermic electronic/structural reorganization step and an exothermic bond formation step, as shown in Fig. 4. Even if the bond formation step is the most exothermic for Au(I), the reorganization step for Au(I) may be even more endothermic. In other words, d-orbital participation in M–C σ-bonding is so effective in $[Au(CO)_2]^+$ that bending the molecular framework is more destabilizing than for $[Cu(CO)_2]^+$ or $[Ag(CO)_2]^+$. This is consistent with the well-known observation that Au(I) has a much reduced tendency to form three-coordinate complexes relative to Ag(I) and Cu(I) [36].

4. Summary

Most of the variations in M–CO bond energies and in IR and Raman ν(CO) values for $[M(CO)_n]^+$ complexes ($M = Cu, Ag, Au$; $n = 1, 2, 3$) can be understood in terms of two quantifiable atomic properties, the second ionization potentials of the neutral metal atoms and the energies of the first excited states of the monovalent gas-phase metal ions. It is hoped that this analysis will lead to the design of improved catalysts based on Cu(I), Ag(I), and Au(I) carbonyls.

Acknowledgements

This research was generously supported by the US National Science Foundation (Grant CHE-9308583). We acknowledge the careful and thoughtful efforts of our co-workers and collaborators, who are listed in the references. J.J.R. thanks the US Department of Education for fellowship support under the Graduate Assistance in Areas of National Needs Program (Grant P200A10210).

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