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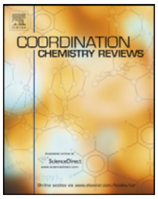

Review

Theory meets experiment: Gas-phase chemistry of coinage metals

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ABSTRACT

The close interaction between experiment and theory is a key motif in contemporary transition-metal chemistry with mechanistic orientation. As an illustration of this aspect, we present selected examples from the gas-phase chemistry of the coinage metals (Cu, Ag, Au). The topics range from seemingly simple systems, such as hydrated metal ions, via the role of formal and real charge states in gaseous species to several case studies which demonstrate that modern mass spectrometry can contribute to the understanding of important processes in applied chemistry, such as C—C bond formations using organocuprates, the epoxidation of ethylene on silver contacts, and the recent achievements in catalysis with gold compounds.

1. Introduction

The gas-phase ion chemistry of the coinage metals has attracted quite some attention in recent years. In part, this interest is associated with the facts that coinage metals are relatively easy to study experimentally, reasonably well treatable by contemporary quantum theory, and moreover offer the option to probe trends within the series of Cu, Ag, and Au. The latter aspect is of particular interest with respect to relativistic effects [1–3]. In addition to this fundamental interest, the attraction of coinage metals lies in their relevance in chemistry; in the case of copper particularly also biochemistry. Copper- and silver-oxide catalysts are, for example, used in a variety of oxidation reactions [4], such as the production of ethylene oxide on silver contacts which is performed in a megaton scale [5], and also gold oxides have recently attracted increased interest due to cluster-size-selective activity in oxidation reactions [6,7]. Further, copper plays an outstanding role in many C—C coupling reactions in organic synthesis and is of prime importance in many metalloenzymes. Last but not least, the interest in

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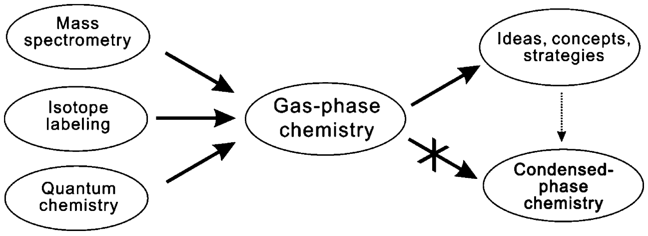


Scheme 1.

homogeneous gold catalysts has recently experienced a renaissance [8].

The results of gas-phase chemistry, i.e. the combination of mass spectrometric methods with isotope labeling and modern quantum chemistry, cannot be applied to condensed-phase chemistry in a direct manner, but yet gas-phase experiment may help to develop a conceptual understanding for the chemistry of transition metals, thereby providing concepts, strategies, and ideas for applied chemists (Scheme 1). Due to their particular position at the end of the d-block and thus limited number of unpaired d-electrons, coinage metals are especially well-suited for comparisons between experiment and theory. Rather than providing a comprehensive review, we here present examples of recent experimental and theoretical efforts in the coordination and organometallic chemistry of coinage metals in the gas phase including cluster chemistry and bond-activation reactions. Particular attention is paid to those cases in which experiment and theory either fruitfully complement each other or disagree and point out the perspectives for future research as well as methodological developments. As far as copper is concerned, the gas-phase chemistry has been reviewed recently by Tureček with a focus on biologically relevant molecules [9]. The theoretical chemistry of gold has been summarized by Pyykkö with an excellent coverage of experimental aspects as far as gas-phase chemistry is concerned [10–12]. If not indicated by the particular circumstances of a specific example presented below, we will not dwell upon either experimental or theoretical methods and details. Nevertheless, it is important to point out that without the rapid progress in density functional theory within the last 15 years (hybrid methods in particular) [13], the huge steps forward towards a merger of theory and experiment could not have been achieved.

2. Simple systems

We begin our overview with a discussion of selected coinage-metal ions with simple coordinative ligands L, e.g. L = H_2O, or covalent ligands X, e.g. X = F, where the distinction between L and X is particularly useful with respect to the formalism of oxidation states. Binding of a metal to merely coordinative and thus closed-shell ligands L does not involve a change of the metal's formal oxidation state (unless oxidative addition takes place, but this fundamentally alters the nature of L), whereas binding to a covalent and thus open-shell ligand gives rise to a change of the formal oxidation state (provided that the electronegativities of M and X differ sufficiently). This distinction between different types of ligands – although not always unambiguous – is a quite useful concept in the rationalization of the gas-phase chemistry of transition-metals and relies on a long tradition in coordination chemistry. Instead of providing an excessive coverage of the rich work which has been performed in the last three decades, we deliberately restrict ourselves in this section to a detailed discussion of a few, selected cases with particular attention to those systems in which experiment and theory are either in close concert or reveal an obvious disagreement and thus request for new efforts on either side.

Table 1
Sequential bond energies (most recent experimental values in kJ mol^{-1}) of the first and second water molecules binding to atomic M^+ cations (M = Cu, Ag, Au)

	Cu	Ag	Au
$D(H_2O–M^+)$	161 ± 8 [17]	134 ± 8 [18]	168 ± 10 [19][a]
$D(H_2O–M(OH_2)^+)$	170 ± 7 [17]	127 ± 8 [18]	188 ± 14 [19][a]

[a] Also see ref. [20].

2.1. Hydrated coinage-metal ions

One of the most simple, but nevertheless extremely important interactions of metal ions with the surrounding is their solvation in water. The sequential ligation of "naked" metal cations with water molecules, i.e. $M(H_2O)_n{}^{z+}$ species, is an important topic in contemporary research [14]. A major motivation of these studies is the attempt to close the gap between ion solvation from a molecular viewpoint (microsolvation) and the behavior of metal salt solutions in the bulk (macrosolvation). With increasing number of water molecules, these do not anymore only act as ligands directly attached to the metal cation, but also form extended networks among each other via hydrogen bonding. Due to the resulting structural richness and fluxionality of larger $M(H_2O)_n{}^{z+}$ ions, the combination of experiment and theory is particularly important in this area [15,16].

With regard to the coinage metals, there are several interesting aspects to discuss in the context of solvation by water. At first, let us consider the sequential binding energies of Cu^+, Ag^+, and Au^+ to one and two water molecules (Table 1). For the monoligated systems, $M(OH_2)^+$, the binding energies are similar for copper and gold, whereas that of silver is significantly lower. This trend in binding energies is generally observed for coinage metals and can be attributed to the interplay of the differential overlap between the orbitals of the metal and the ligand (which is maximal for copper) and relativistic effects (which reach a maximum for gold), whereas silver occupies an intermediate position in both respects. A similar ordering is observed for the bond dissociation energies (BDEs) of a second water ligand, but particularly notable is that the second BDEs exceed the first BDEs in the case of Cu and Au. This phenomenon was first discovered by Marinelli and Squires in an experimental study of $M(H_2O)_n{}^+$ cations of 3d metals [21] and attributed to the reorganization energy which is necessary to disturb the electron configuration of the metal ion upon approach of the first ligand, whereas the second ligand enters an already disturbed arrangement [22,23]. In other words, the first ligand already pays the bill of the second [24]. This situation occurs for copper as well as gold (Table 1); for the latter, also a "skewed" orbital overlap has been invoked as an explanation of the larger BDE of the second water ligand [25]. In contrast, $D(H_2O–Ag^+)$ exceeds $D(H_2O–Ag(OH_2)^+)$ and silver is thus more similar, although not identical to alkali metals [26].

Another notable aspect concerns the structure of $Au(H_2O)^+$ because it is the only singly charged metal-ion hydrate known so far with a non-planar geometry as predicted already in 1994 (Fig. 1) [27] and as confirmed by several subsequent computational

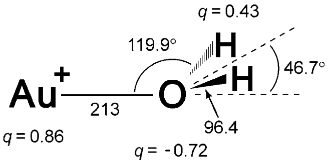


Fig. 1. Calculated geometry (bond lengths in pm and angles in degrees) of $Au(OH_2)^+$ and the partial charges (q) of the atoms [27].

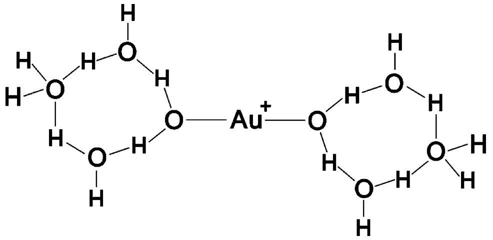


Fig. 2. Sketch of the calculated dumbbell structure of $Au(H_2O)_8{}^+$ [33].

studies [25,28–33]. This deviation is essentially caused by relativistic effects of gold which increase the covalent character of the bonding as reflected by the significant charge transfer (see Fig. 1) and revealed a detailed analysis of the bonding [34]. In chemical terms, the non-planar geometry of $Au(H_2O)^+$ re-iterates the seminal conclusion that Au(I), particularly the $Au(PR_3)^+$ fragment [35], is isolobal [36] to a proton and thus behaves similarly [10,37–39]. In this sense, the bent arrangement of $Au(H_2O)^+$ is thus parallel to the structure of the hydronium ion H_3O^+ [40]; likewise, also $Au(H_2S)^+$ is predicted to be non-planar [41].

Of interest are also the higher hydrates of the coinage metals, in particular those of Au^+. In general, sequential hydration of metal ions leads to octahedral coordination in $M(H_2O)_6{}^+$, or even higher coordination numbers in the case of heavy elements, before water molecules begin to form a second solvation shell [14–16]. Comparison of $M(H_2O)_n{}^+$ ions for M = Cu, Ag, and Au with n up to 10 reveals notable differences between these metals, however. Thus, according to MP2 and coupled-cluster calculations, silver(I) behaves similar to alkali cations with coordination numbers of 3 in $Ag(H_2O)_3{}^+$, $Ag(H_2O)_4{}^+$, as well as $Ag(H_2O)_5{}^+$, with one and two outer water ligands for the two latter, respectively, and a coordination number of 4 in $Ag(H_2O)_6{}^+$ which has two outer water ligands [26]. The same study revealed, however, that density functional theory prefers a coordination numbers of only 2 for all $Ag(H_2O)_n{}^+$ complexes studied in that work (n = 1–6). Irrespective of the theoretical method used, the coordination number 2 is strongly preferred in $Cu(H_2O)_n{}^+$ and $Au(H_2O)_n{}^+$ (n = 1–6) [32], which is fully confirmed by a recent study of $Au(H_2O)_n{}^+$ (n = 1–10) by Khanna and co-workers [33]. Thus, unlike other main-group and transition metals, copper and gold show a strongly directed bonding to two water ligands to which additional ligands are attached in the outer sphere. A particularly intriguing structural motif was found for $Au(H_2O)_8{}^+$ which exhibits a dumbbell-like structure with a linear $[H_2O{-}Au{-}OH_2]^+$ unit in the core with the six additional water ligands added to the polarized protons at both peripheries via hydrogen bonds (Fig. 2); for n = 9 and 10, the further water molecules form a hydrogen-bond network bridging the balls of the dumbbell [33]. The theoretical findings of Khanna and co-workers agree well with the experimental data available for $Au(H_2O)_n{}^+$ (n = 1–10) [19,20]. We note in passing that also anionic $M(H_2O)^-$ clusters (M = Cu, Ag, Au) have been studied recently [42].

Another system which has attracted quite some attention is hydrated copper(II). In marked contrast to the analogous copper(I) species, much like in solution, copper(II) prefers higher coordination numbers in the gas phase [43–46] as well as in solution [47]. Due to the pronounced Jahn–Teller effect in Cu(II), octahedral coordination is not ideal, however, and instead a special significance has been attributed to $Cu(H_2O)_8{}^{2+}$ species [44,48] in which according to theoretical predictions four water molecules directly coordinate to copper in a square-planar manner with four additional water ligands bridging the four former via hydrogen bonds [49]. Quite some debate dealt about the lower limit of stability for gaseous $Cu(H_2O)_n{}^{2+}$ species, for which n of about 15 has been suggested as the lowest possible size in 1990 [50]. With subsequent progress in research, $Cu(H_2O)_n{}^{2+}$ dications with lower coordination numbers were observed [43,48] and culminated in the theoretical prediction of a stable monoligated $Cu(H_2O)^{2+}$ dication by El-Nahas et al. [51], for which a weak signal was observed in previous mass spectrometric experiments dealing with a different context, namely neutral $Cu(H_2O)_n$ molecules [52]. Based on consideration of competing electron- and proton-transfer processes which limit the stability of gaseous, hydrogen-containing dications [53], Stace et al. questioned [54,55] the reliability of the theoretical prediction [51] and further argued that the earlier experimental observation of a weak signal for $Cu(H_2O)^{2+}$ might be due to instrumental artifacts [52,56]. In two independent studies, shortly afterwards the existence of the genuine $Cu(H_2O)^{2+}$ dication as a long-lived species in the gas phase has been established beyond any doubts [57,58]. Subsequent theoretical work has further substantiated the existence of long-lived $Cu(H_2O)^{2+}$ as a stable molecular dication in the gas phase [59], even though this species has been termed to be a particularly difficult case for theory [60].

It is instructive to consider this scientific debate in some more detail, because it can serve to illustrate the different points of view in chemistry, here particularly with regard to the term "stability". Thus, within the original context, i.e. ion solvation in aqueous media, the comment of Stace et al. is correct in its essence in that $Cu(H_2O)_n{}^{2+}$ dications with small n are not stable in aqueous environment. In the idealized case of the infinitely diluted gas phase, however, even the monoligated $Cu(H_2O)^{2+}$ dication can exist as a metastable species with a quasi-infinite lifetime. To understand this situation, several general features relevant for the chemistry and physics of gaseous dications [53,61–64] and the specific aspects in the particular case of $Cu(H_2O)_n{}^{2+}$ need to be considered.

Even though copper is a transition metal, the second ionization energy of atomic copper (20.29 eV) is much larger than the ionization energy of water (12.62 eV). As a consequence, single-electron transfer from water to Cu^{2+} according to reaction (1) is exothermic by 7.67 eV.

$$Cu^{2+} + H_2O \rightarrow Cu^+ + H_2O^+ \tag{1}$$

Despite this huge exothermicity, electron transfer is hindered by a kinetic barrier whose occurrence becomes apparent upon consideration of the reverse reaction, because the monopositive products $Cu^+ + H_2O^+$ lead to a purely repulsive potential dictated by the Coulomb law. This kinetic hindrance in the dissociation of a molecular dication into two, thermochemically more stable fragments is also referred to as Coulomb barrier. On the other hand, the attractive potential between the Cu^{2+} dication and the dipolar water molecule gives rise to a favorable interaction with a binding energy of about 400 kJ mol^{-1}. In conjunction with $D(H_2O{-}Cu^+) = 161$ kJ mol^{-1}, a thermochemical Born–Haber cycle with reference to the $Cu^{+/2+} + H_2O$ asymptotes implies a significant lowering of the second ionization energy from $IE(Cu^+) = 20.29$ eV for the bare atomic cation to $IE(Cu(H_2O)^+) = 17.8$ eV for the monohydrated cation. The same effect occurs upon ligation with a second water molecule in that $D(H_2O{-}Cu(H_2O)^{2+}) = 310$ kJ mol^{-1} [51] significantly exceeds $D(H_2O{-}Cu(H_2O)^+) = 170$ kJ mol^{-1}, leading to a further decrease of $IE(Cu(H_2O)_2{}^+)$ to ca. 16.3 eV. Continued ligation with water may then decrease $IE(Cu(H_2O)_n{}^+)$ below $IE(H_2O) = 12.62$ eV such that for larger values of n the hydrated copper dications $Cu(H_2O)_n{}^{2+}$ become stable with respect to electron transfer according to reaction (2).

$$Cu(H_2O)_n{}^{2+} + H_2O \rightarrow Cu(H_2O)_n{}^+ + H_2O^+ \tag{2}$$

$$Cu(H_2O)_n{}^{2+} + H_2O \rightarrow Cu(OH)(H_2O)_{n-1}{}^+ + H_3O^+ \tag{3}$$

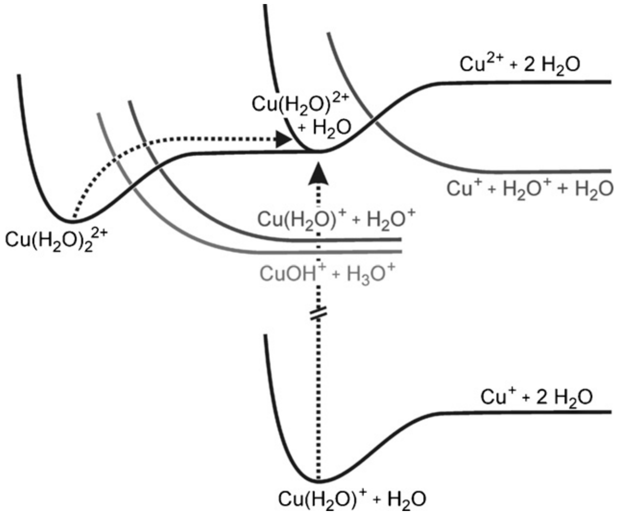


Fig. 3. Schematic potential-energy surface of $Cu(H_2O)^{2+}$ and its precursors $Cu(H_2O)_2{}^{2+}$ and $Cu(H_2O)^+$, respectively, with the relevant processes which may lead to charge separation under destruction of the dications (electron transfer, dark grey, and proton transfer, light grey) and the realized paths for the formation of $Cu(H_2O)^{2+}$ (dotted).

According to CCSD(T) calculations of Glusker and co-workers [65], also proton transfer from the hydrated dication to water according to reaction (3) is quite exothermic, e.g. $\Delta_rH(3) = -5.0$ eV compared to $\Delta_rH(2) = -5.2$ eV for $n = 1$. The possibility of reaction (3) thus increases the number of n required for thermochemical stability of $Cu(H_2O)_n{}^{2+}$ in the presence of excess water even further. It is of prime importance to note, however, that also this charge-separation process in inherently hindered kinetically by a Coulomb barrier because two singly charged and thus repelling cations are formed.

For illustration of these aspects, it is referred to the simplified scenario in Fig. 3, which describes the situation with regard to the two independent pathways which were successfully applied for the generation of isolated $Cu(H_2O)^{2+}$ in the gas phase. More closely related to ion solvation is the approach of Shvartsburg and Siu [58] who subjected $Cu(H_2O)_n{}^{2+}$ dications to a multiple collision event in which the water ligands are removed sequentially. In the last of the successive steps towards $Cu(H_2O)^{2+}$, i.e. the dissociation of $Cu(H_2O)_2{}^{2+}$, the considerably endothermic loss of a water ligand from the dication has to compete with the very exothermic channels leading to electron- and proton-transfer, respectively. Nevertheless, as both routes associated with charge separation are subject to a kinetic hindrance caused by the Coulomb barriers, the continuously exothermic and thus entropically favored loss of neutral water to afford monoligated $Cu(H_2O)^{2+}$ can be achieved to a small, but yet significant extent, as demonstrated by Shvartsburg and Siu [58]. Conceptually different is the alternative approach to $Cu(H_2O)^{2+}$ via ionization of the mass-selected $Cu(H_2O)^+$ monocation in a charge-stripping experiment at keV energies. In this case, collisional ionization of the mono- to the dication has to compete with collision-induced dissociation of the singly charged precursor. As $IE(Cu(H_2O)^+)$ is much larger than $D(H_2O–Cu^+)$, the charge-stripping process has a low efficiency, but the sensitivity of the experiment is still perfectly sufficient for its detection and the exclusion of instrumental artifacts such as overlapping isobaric ions [57]. In this context, we note that at the time the charge-stripping study of $Cu(H_2O)^+$ has been performed, the threshold of electron transfer in keV collisions was believed to be associated with the respective vertical transition, whereas experimental evidence meanwhile indicates that adiabatic thresholds are sampled in energy-resolved charge-stripping experiments [66].

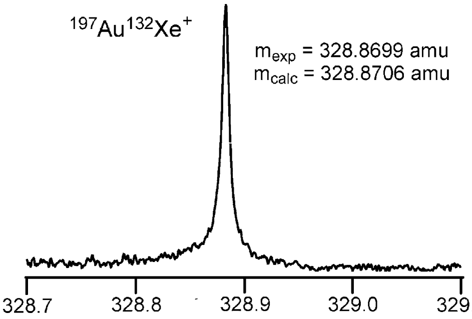


Fig. 4. High-resolution mass measurement of the $^{197}Au^{132}Xe^+$ cation generated via thermal ligand exchange of mass-selected $Au(C_6F_6)^+$ with neutral xenon. The deviation between the measured and the predicted mass is less than 0.001 amu.

2.2. *Other ML^+ ions with M = Cu, Ag, Au*

A success story of theory is the prediction of the rare-gas compounds $AuXe_n{}^+$ ($n = 1, 2$) by Pyykkö in 1995 with $D(Au^+–Xe) = 88$ kJ mol^{-1} for the diatomic complex [67]. This suggestion inspired a collaboration with experiment leading to the first generation of $AuXe^+$ which was identified by its characteristic isotope pattern and high-resolution mass measurements (Fig. 4) [68]. Evaluation of the experimental data by help of the theoretical results also revealed an important entropic contribution in ligand-exchange reactions involving atomic ligands which has subsequently found application in other areas [69–71]. Shortly afterwards, these gas-phase studies were followed by the isolation of the first gold-xenon compound in the condensed phase [72], and also triatomic XeAuF has been detected in the gas phase via microwave rotational spectroscopy [73]. Most recently, the binding patterns of $AuXe^+$ and related gold/rare-gas compounds have been analyzed in detail by Belpassi et al. [74] who quantified the significant amount of charge transfer in these compounds by means of relativistic four-component calculations [75]. Also the $CuXe^+$ cation has been observed experimentally, which has a significant binding energy of $D(Cu^+–Xe) = 98$ kJ mol^{-1} [76], whereas the silver analog $AgXe^+$ could not be generated under similar conditions [18,77], suggesting that $D(Ag^+–Xe)$ is much lower than $D(Cu^+–Xe)$ and $D(Au^+–Xe)$.

Further above, we introduced the classification of ligands L and X, of which the former do not change the formal oxidation state of the coordinating partners. This seemingly straightforward concept encounters some ambiguity with closed-shell ligands L, if the transition metal can easily change its oxidation state. A metal–olefin complex, for example, can also be viewed as a metallacyclopropane in which the metal formally undergoes a two-electron oxidation.

The triad of the ethylene complexes of the coinage metals, $M(C_2H_4)^+$ with M═Cu, Ag, and Au, provides a particularly instructive example in this respect. By using Bader's atoms-in-molecules (AIM) analysis [78], the bonding schemes of these $M(C_2H_4)^+$ complexes have been analyzed in detail [79]. $Ag(C_2H_4)^+$ is a T-shaped π-complex with genuine Ag(I) as revealed by a single bond-critical point between silver and ethylene (Fig. 5). In contrast, $Au(C_2H_4)^+$ exhibits an auracyclopropane structure with a triangular bonding scheme, bond-critical points on both Au–C axes, and a ring-critical point in the middle. Formation of covalent bonding between gold and carbon is further revealed by a significant elongation of the C═C bond in $Au(C_2H_4)^+$ compared to free ethylene as well as $Cu(C_2H_4)^+$ and $Ag(C_2H_4)^+$, and the change in carbon hybridization is reflected in a considerable pyramidalization of the methylene

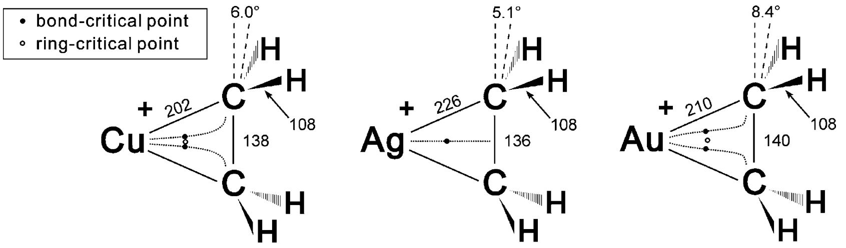


Fig. 5. Sketch of the calculated geometries of $M(C_2H_4)^+$ complexes (bond lengths in pm and angles in degrees) and the location of the bond-critical and ring-critical points [79].

groups. Given that carbon is considerably more electronegative than gold, within the conceptual framework of formal valences, the auracyclopropane structure thus corresponds to an Au(III) compound, which has also been characterized spectroscopically [80,81]. For $Cu(C_2H_4)^+$, the situation is in-between the extremes in that the two bond-critical points are very close to the ring-critical point in the center of the CuCC unit [82]. Qualitatively, these trends of the bonding schemes were also experimentally verified by a detailed theoretical analysis of experimentally measured H/D equilibrium isotope effects in $M(C_2H_{4-n}D_n)^+$ (M = Cu, Ag, Au; n = 0, 2, 4) [83].

As stated above, we concentrate on systems for which experimental as well as theoretical information is available for all three coinage metals. Although only dealing with Cu^{2+}, however, a series of studies by Yáñez and co-workers is particularly worth to be mentioned here due to the conceptual implications [84–86]. Thus, for gaseous Cu^{2+} complexes of several biologically relevant molecules, e.g. nucleobases, theoretical studies, also including AIM analysis, indicate a significant amount of charge transfer from the neutral ligand to the metal dication, leading to a bonding situation in which the copper is reduced from Cu(II) to Cu(I), whereas the ligand is oxidized from its neutral form to the radical cation. Despite this bonding scheme with two spatially separated charge centers in the dicationic species, the coordination complexes are still well-bound towards Coulomb explosion into a pair of monocationic fragments. A spectacular consequence of this particular bonding situation are bond energies $D(Cu^{2+}–L)$ in the order of 1000 kJ mol^{-1} for L = uracil and its thio derivatives (Fig. 6). In addition to the conceptual quest for experimental probes of this unusual bonding scheme of a molecular dication, the occurrence of such an intimate electron transfer may have consequences for the chemical reactivity of biomolecules complexed by Cu(II). It is added that the effects of ligation in more complicated biomolecules mostly behave additively such that reasonable estimations can be made even for large systems [87].

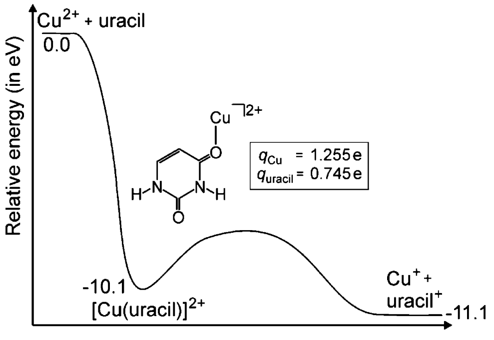


Fig. 6. Schematic potential-energy surface of $[Cu(uracil)]^{2+}$ with energetics given in eV (1 eV = 96.5 kJ mol^{-1}) according to density functional calculations [85]. In the most stable coordination geometry, the metal is attached to the carbonyl oxygen at the 4-position in conjunction with considerable charge transfer from the uracil ligand to the copper atom as indicated by the NBO charges. Despite the partial charge transfer, a sizable barrier of about 2 eV height prevents the exothermic Coulomb explosion of $[Cu(uracil)]^{2+}$ into the monocations Cu^+ and uracil$^+$.

2.3. Halides $MX_n{}^{-/0/+}$ ions with M = Cu, Ag, Au

The prototype covalent ligand X is fluorine, the most electronegative element, but the other halides (X = Cl, Br, I) behave similar in their binding to Cu, Ag, and Au, if relativistic effects and the differential electronegativities of the halides are acknowledged [88–90]. Fluorine allows formation of highest oxidation states, and in the case of silver even solid AgF_3 has been isolated [91], although Ag(III) otherwise is an unstable oxidation state [92,93]. Conceptually, the valence state of the metal hence can be adjusted by the number of halido ligands in conjunction with the net charge of the species. The $CuCl_2{}^-$ anion, for example, contains Cu(I), neutral $CuCl_2$ is a Cu(II) compound, and the cation $CuCl_2{}^+$ is an example of the elusive Cu(III) state which is proposed to be involved in a series of important copper-mediated transformations [94–96]. In the gas phase, these three species are connected to each other by electron transfer and the determination of the electron affinity (EA) of $CuCl_2$ and its ionization energy (IE) hence allows to assess the stabilities of the various valence states by mass spectrometric means [97,98].

Gold halides have attracted considerable interest and especially the fluorides still need further exploration [99]. A particular challenge has been the gold(I) fluoride AuF [100], whose first preparation employed neutralization of a mass-selected beam of the corresponding cation AuF^+ in a neutralization–re-ionization experiment (NRMS [101]). Later, neutral AuF has also been prepared in plasma-like processes [102–104], and most recently theory has suggested a viable route for a synthesis of gold(I) fluoride in the bulk phase [105].

NRMS has also been applied for the investigation of the redox chemistry of the anionic, neutral, and cationic gold dihalides $AuCl_2{}^{-/0/+}$ and $AuBr_2{}^{-/0/+}$, which cover the oxidation states gold(I), gold(II), and gold(III) (Fig. 7) [106,107]. Particularly useful with respect to the redox thermochemistry of the various oxidation states are energy-resolved NRMS experiments in conjunction with photoelectron detachment. In a NRMS experiment under sequential charge inversion of an anion M^- into a cation M^+ according to reaction (4), the energy required for the two-fold electron losses is provided by the kinetic energy of the projectile anion M^- having a kinetic energy of several kiloelectron Volt in the collision of the projectile ion with a quasi-stationary target gas (often a rare gas).

$$M^- \rightarrow M + e^- \quad \text{then} \quad M \rightarrow M^+ + e^- \qquad (4)$$

The energy deficit $\Delta E(4)$ can be determined from the kinetic energies $T(M^-)$ and $T(M^+)$ and corresponds to the sum of the $EA(M)$ and $IE(M)$, that is $\Delta E(4) = T(M^-) - T(M^+) = EA(M) + IE(M)$ [108,109]; recent work has demonstrated that despite the involvement of high-energy collision, and thus occurrence of mostly vertical redox transitions, the threshold values determined in this kind of energy-resolved measurements correspond to adiabatic transi-

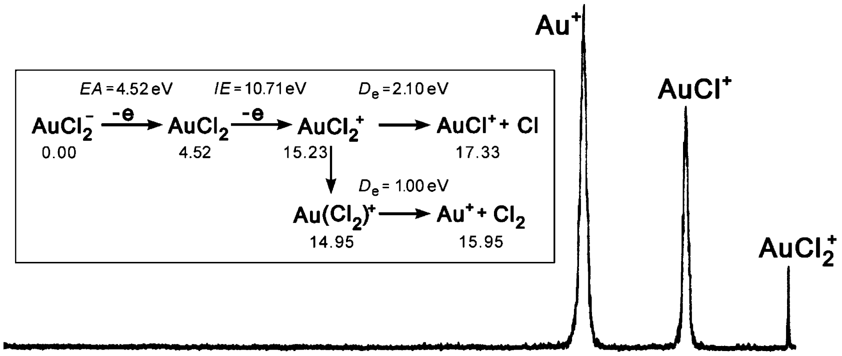


Fig. 7. Neutralization–re-ionization mass spectrum of mass-selected $AuCl_2^-$ which is neutralized in a first keV collision, then all ions are removed, and the remaining neutral species are subsequently re-ionized to cations. From the analysis of the kinetic energy deficits in conjunction with additional photoelectron detachment data, the redox chemistry of $AuCl_2^{-/0/+}$ can be assessed quantitatively (see insert, with relative stabilities in eV).

tions [66]. Combined with an independent determination of either *EA*(M) or *IE*(M) via photodetachment or photoionization experiments, for example, the redox-chemistry of $M^{-/0/+}$ can thus be assessed. For a complete understanding of the redox chemistry of the metal halides and the achievement of internal consistency in terms of Born–Haber cycles, some additional knowledge about the neutral metal halides is indispensable, however. With regard to the coinage metals, especially Hildenbrand and Lau have provided valuable data for copper- and silver-halides using high-temperature mass spectrometry, i.e. CuF [110], CuCl [111], AgF [110], AgCl [111], and AgBr [112], whereas most information about neutral AuX species has been gathered by ion-molecule reactions [100,113,114].

In addition to the thermochemical data, photoelectron detachment spectra of anions provide information of electronic structures in that excited states of the neutral species M can be populated upon electron detachment from a precursor anion M^-; with regard to metal compounds, the combination of photoelectron spectroscopy with electrospray ionization is particularly useful [115]. In the case of $AuCl_2^-$, the assignment of the bands in the photodetachment spectra has given rise to some discussion [116–118], and it has turned out essential to explicitly include spin–orbit coupling for a correct designation of the electronic states involved [117]. We note in passing that recently also molecular hydrides of copper, silver, and gold have been isolated in rare-gas matrices, including the formal gold(II) species AuH_2 and anions of the type MH_2^- (M = Cu, Ag, Au) [119–121].

2.4. *LMX*$^+$ *cations with M = Cu and Au*

In general, the presence of additional ligands L at the metal center of a charged species MX_n^{z+}, where X stands for a covalent ligand, increases coordination and lowers the charge density, thereby leading to a reduced or even completely quenched reactivity of the MX_n^{z+} core [122]. Of particular interest is the competition between covalent and coordinative ligand in the case of redox-active metals. Collisional activation of the copper(II) cations $[Cu(OH)(H_2O)_n]^+$, for example, leads to exclusive loss of water for $n > 2$, whereas for $n = 1$, a competition between loss of the coordinative ligand (reaction (5a)) and a hydroxy radical (reaction (5b)) is observed [48]. The latter reaction involves loss of an open-shell species and is thus associated with a formal reduction from copper(II) to copper(I). The experimentally observed competition of reactions (5a) and (5b) further implies that the associated BDEs, $D(Cu^+–OH)$ and $D(Cu^+–OH_2)$, respectively, are similar. This conclusion is fully supported by ab initio studies of Irigoas et al. [123] and Glusker and co-workers [65] from which $D(Cu^+–OH)$ of about 130 kJ mol^{-1} can be derived using supplementary thermochemical data [124].

$$(H_2O)Cu(OH)^+ \rightarrow CuOH^+ + H_2O \quad (5a)$$

$$(H_2O)Cu(OH)^+ \rightarrow (H_2O)Cu^+ + OH \quad (5b)$$

As another LMX^+ system, the $(phen)CuO^+$ cation (phen = 1,10-phenanthroline) may serve as an example for the stabilization of a formal Cu(III) compound by ligation [125]. The bare, diatomic CuO^+ cation itself is too high in energy and also too reactive to be generated in yields sufficient for gas-phase reactivity studies. The phen ligand stabilizes the Cu(III) center and thus allows generation of the cation in good yields. The crucial step in the gas-phase synthesis of $(phen)CuO^+$ is the homolytic decomposition of the nitrato ligand in the copper(II) precursor species $(phen)Cu(NO_3)^+$ according to reaction (6). The precursor cation $(phen)Cu(NO_3)^+$ is accessible in good yields by electrospray ionization of aqueous copper(II) nitrate in the presence of phenanthroline. Similar strategies have recently been applied for the gas-phase production of other reactive transition-metal-oxide cations, such as MgO^+ [126], FeO^+ [127], and Ag_2O^+ [128], from the corresponding nitrato cations. Interestingly, pyrolysis of metal nitrates has also successfully been applied for the production of bulk metal-oxide catalyst in the condensed phase [129].

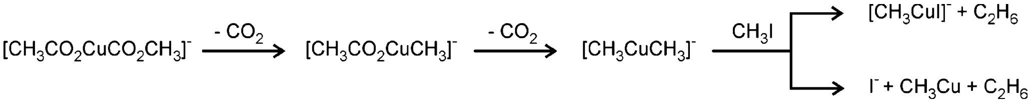
$$(phen)Cu(NO_3)^+ \rightarrow (phen)CuO^+ + NO_2 \quad (6)$$

$$(phen)CuO^+ + R–H \rightarrow (phen)CuOH^+ + R^\bullet \quad (7)$$

The $(phen)CuO^+$ cation is one of the few ligated metal-oxide cations which is capable of activating the C—H bonds of small alkanes with a prevalence of a radical-like hydrogen abstraction according to reaction (7). Parallel theoretical studies revealed that the bonding situation of the CuO moiety in $(phen)CuO^+$ resembles that in diatomic CuO^+ in that both ions exhibit high-spin ground states [123,130,131]. The mechanism of C—H bond activation of alkanes thus follows a two-state scenario [130,132–137]. Analogous dimeric gold species $[(phen)_2Au_2O_2]^{2+}$ have been shown to mediate oxidation of olefins in the condensed phase [138], and we have initiated a mass-spectrometric investigation of these compounds which can be transferred as intact dications into the gas phase using electrospray ionization of their hexafluorophosphates.

3. More complex systems as models for chemical reactivity

The course of chemical reactions in the condensed phase is influenced by many effects such that a detailed molecular description of all processes often is very demanding, if not impossible. Similarly, the theoretical treatment of large systems containing transition metals requires extremely large computational power and often is



Scheme 2.

possible only if drastic simplifications are employed. On the other hand, gas-phase studies of “reactive cores” bring often very useful insight to the reaction mechanisms while the systems are usually small enough to permit detailed mass-spectrometric as well as theoretical investigations.

Electrospray ionization (ESI [139,140]) brought very powerful technique for gas-phase mechanistic studies [115,141–143]. Using hard ionization conditions (large collision energies of the electrospray droplets with the drying gas [144]), highly reactive species can be generated and consequently used as models for catalysis. The soft mode of the ionization (small collision energies of the electrospray droplets with the drying gas) leads to a gentle transfer of the complexes from solution to the gas phase, which consequently allows studies of structures, reactivity, and of solvated reaction intermediates. In the following, some examples of successful symbiotic application of mass-spectrometry studies and theoretical calculations are presented.

3.1. Case study I: Gaseous organo-cuprates and -argentates

Organocuprates(I) are among the most selective and versatile reagents for C—C bond coupling reactions in organic chemistry [145]. Despite the huge success in the application of organocuprates as reagents in chemical synthesis, the precise nature of the reactive species at a molecular level represents still a hot topic [146–151].

The scope of any mechanistic model studies in the gas phase is determined by the possibility to generate the reactive organocuprates as gaseous ions. While less reactive organocuprates can be generated directly by electrospray ionization of solutions of Gilman reagents [152], the formation of the reactive dimethylcuprate anion cannot be achieved by a simple ionization of a precursor. Instead, dimethylcuprate needs to be “synthetized” in the gas phase by a sequential fragmentation of diacetatocuprate (Scheme 2) [153,154]. Thus, by electrospray ionization of a methanolic solution of copper(II) acetate O’Hair and coworkers could generate diacetato copper(I) as the precursor anion. Mass selection and subsequent collision-induced dissociation performed in an ion-trap mass spectrometer leads to the desired anion concomitant with elimination of two molecules of CO_2. Addition of another carboxylic acid to the solution leads to generation of hetero organocuprates in an analogous manner; likewise organoargentates can be prepared from carboxylate precursors [155].

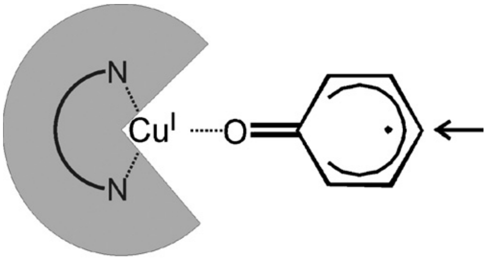
It has been demonstrated that dimethylcuprate anion is capable to react with methyl iodide under release of neutral ethane [154], which represents a gas-phase mimic of the reactive species in the C—C coupling reaction in organic synthesis. On the other hand, the same reaction with dimethyl argentate does not proceed, which might be due to a larger energy barrier for cleavage of the C—I bond. Another aspect of the reaction is the involvement of Cu^{III}/Ag^{III} intermediates, which in the first case represent rather unstable species leading rapidly to the product formation, whereas the Ag^{III} intermediates appear to be more stable and thus less effective with regard to C—C coupling [155]. Despite the indirect experimental evidence for the involvement of copper(III) intermediates in this reaction, it remains to be shown, whether copper(III) really plays a role or if metal clusters which would circumvent Cu^{III} are involved. In this respect, the effective and non-destructive ionization of sensitive organometallic reagents such as organocuprates remains a challenge for future instrumental development, and some recent results appear quite promising in this respect [156].

3.2. Case study II: Interaction of copper(II) with phenolates

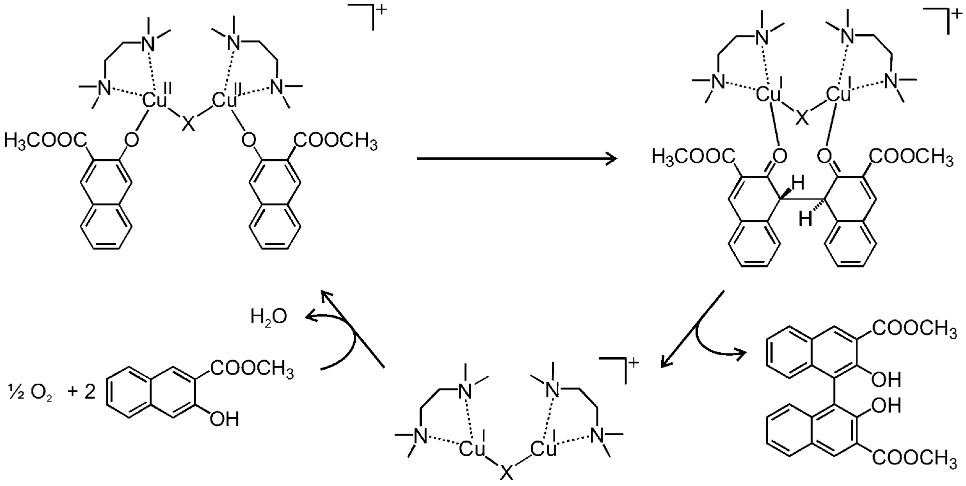
The motif of copper being bound to a phenol moiety can be found in the active centers of many copper-containing enzymes [157–162], where phenol is represented by a tyrosine ligand. This connection becomes especially important in enzymes, which contain a single copper atom and can still mediate oxidation by transfer of two electrons [163–165]. In this case, tyrosine takes an active role in the electron-transfer processes and is present as a radical, which can serve as an electron shuttle. The investigation of bonding relations between copper and phenolate, as a model for tyrosinate, revealed that phenolate interacts with copper via the oxygen atom, as expected [166–169]. Interestingly, the gas-phase study shows that the formation of the Cu—O bond is associated with electron transfer from phenolate to copper so that the resulting complex $(PhO)Cu^+$ corresponds to copper(I) bound to the phenoxy radical [166,170]. The formation of the radical site in the aromatic ring is also indicated by the reaction of $(PhO)Cu^+$ with dimethyl disulphide, which results in the activation of the S—S bond. The activation of the S—S bond in dimethyl disulphide is usually attributed to the presence of carbon-centered radicals due to a larger exothermicity of the C—S bond formation compared to bond formation between sulfur and a heteroatom [171].

The ability of the phenoxy ligand to bear the radical site in the complex with copper is not only interesting for the understanding of electron flow in the active centers of enzymes, but also for the radicalic polymerization of phenols [172,173]. It has been proposed that the copper-mediated polymerization of phenol involves “controlled” radicals as the reactive species [174,175], which means that the phenoxy radical is bound to the copper during the coupling reaction and no free radicals are generated. This mechanism is supported by the fact that the steric demands of additional ligands bound to the copper direct the selectivity of the coupling in that the bulkier ligands are bound to the copper center, the more selectively the coupling reaction occurs in the *para*-position of the phenoxy ligand (Scheme 3).

The distribution of spin density in the complex of copper and the phenoxy ligand is not significantly influenced upon addition of



Scheme 3. Sketch of the $(PhO)Cu^+$ complex bound to a sterically demanding nitrogen base; the arrow indicates the preferred position for the occurrence of bimolecular attack, e.g. C—O coupling.



Scheme 4. Simplified mechanism of naphthol coupling via binuclear copper clusters; X = bridging counterion (e.g. Cl or Br) [197].

a monodendate ligand to the copper center. It was shown that the radical site stays at the phenoxy ligand and only the bond energy between copper and the phenoxy ligand decreases. Interesting to note in this context is that the bonding between copper(I) and neutral phenol moiety does not take place via the oxygen atom, but copper is rather bound to the aromatic ring [176–180]. This remarkable feature was proved by calculations using density functional theory and infrared multiphoton dissociation (IRMPD) spectra of mass-selected ions [166], where the combination of these two modern techniques which is one of the most powerful tool available for the structural elucidation of gaseous ions [15,181–184].

The complex formed from copper(II) and phenolate should be analogous to that formed from copper(II) and naphtholate. The latter is proposed to play a major role in naphthol coupling mediated by copper [185–193]. However, a striking difference between these two systems evolves readily: The Cu-mediated coupling of phenol leads to poly(phenylene ether) with high selectivity [194], whereas the coupling of naphthols proceeds almost exclusively under C—C bond formation.

A gas-phase study of the reaction mechanism of copper(II)-mediated coupling of methyl ester of 2-hydroxy-3-naphthoic acid (NaphOH) in presence of the chelating ligand *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) [195,196] has shown that rather than mononuclear copper complexes [Cu(NaphO)(TMEDA)]$^+$, which do not exhibit any significant radical reactivity, binuclear clusters can serve as essential reaction intermediates [197,198]. In such complexes each naphthol molecule is bound to one copper atom and the coupling reaction occurs between two of these “controlled” radicals (Scheme 4). The C—C coupling of the naphthol molecules within the binuclear cluster is associated with simultaneous reduction of both copper(II) centers to the copper(I) state. This scenario is supported by a counterion effect found in parallel in the gas phase and the condensed phase, which shows that counterions with better bridging abilities for cluster formation lead to increased yields in the coupling reaction. Thus, for copper(II) catalysts, the reaction yield of naphthol coupling in the condensed phase increases in the row $Cu(NO_3)_2$–$CuCl_2$–$CuBr_2$ from less than 10% via 74% to 93%, respectively [192], and the amount of C—C coupling in the gas-phase experiments follows the very same trend. We note in passing that the binuclear mechanism also easily accounts for the high selectivity of the C—C bond formation in naphthol coupling, while it remains to be clarified further, why the difference between the seemingly similar phenolato- and naphtholato-ligands is so large.

3.3. *Case study III: Silver-mediated epoxidation of ethylene*

The partial oxidation of ethylene to ethylene oxide catalyzed by silver is a large-scale industrial processes [5]. The crucial point in the oxidations of alkenes is a balance between the epoxide formation and the over-oxidation, which leads essentially to the combustion of alkenes. Therefore, it is desirable to understand all steps in the reaction mechanism of the oxidation process in order to control and influence it towards the desired epoxide formation. The triatomic cation Ag_2O^+ can be considered as the smallest charged system potentially capable of oxygen transfer to olefin. Electrospray ionization of an aqueous solution of $AgNO_3$ allows the generation of the desired model ion by dissociation of the dinuclear nitrato cluster $Ag_2NO_3{}^+$ according to reaction (8) [128].

$$Ag_2NO_3{}^+ \rightarrow Ag_2O^+ + NO_2 \tag{8}$$

A detailed mechanistic study of the reaction between $Ag_2O^+ + C_2H_4$ shows that the reaction leads to the formation of ethylene oxide and therefore Ag_2O^+ can be seen as a minimalistic model of the active site of a catalyst for the epoxidation of ethylene. The small size of the model system allows quite sophisticated mass-spectrometric and theoretical investigations in conjunction with a kinetic analysis of the results. As the critical point, the branching between the formation of ethylene oxide and acetaldehyde, the first intermediate on the way to the complete combustion can be identified. Density functional calculations reveal that the reaction pathways lead via a common intermediate represented by a metallaoxetane structure [199–201], namely the intermediate $[Ag^\bullet c\text{–}AgOC_2H_4]^+$ (Fig. 8). This intermediate can either rearrange via a lower barrier to yield ethylene oxide, or the reaction pathway continues via a higher barrier to acetaldehyde, which is the more stable product. Thus, if the process is kinetically controlled, the desired product is formed, whereas the thermodynamic control leads via acetaldehyde to combustion. The reaction mechanism proposed on the basis of the gas-phase studies is in agreement with all findings reported for the condensed-phase catalysis and Ag_2O^+/C_2H_4 can thus be viewed as a minimalistic functional model of a large-scale industrial process.

Oxidation of the higher homologs propene, butane, and pentene cannot be efficiently controlled towards the formation of the desired epoxides and only the combustion products are vastly observed [202–205]. The failure of the desired process is ascribed to an additional channel, which leads to an abstraction of allylic hydrogen atoms [206–209]. Likewise, the gas-phase study of the reaction

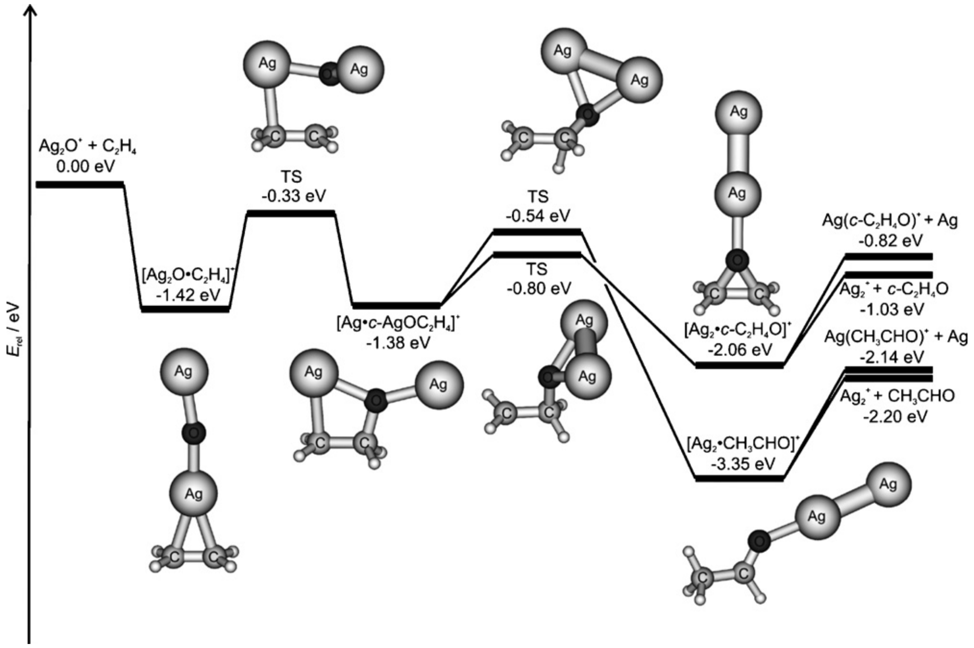


Fig. 8. Potential-energy surface for the oxidation of ethylene by Ag_2O^+ as predicted by DFT calculations (MPW1PW91 functional in conjunction with the SDD basis sets for silver and 6-311+G(2d,p) basis sets for other atoms) [127].

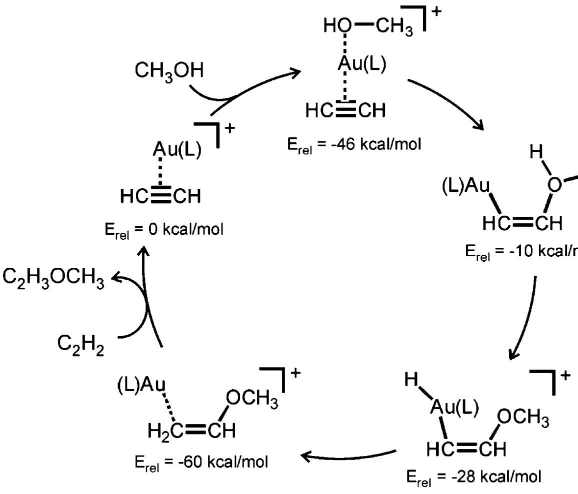
$Ag_2O^+ + C_3H_6$ consistently shows that the hydrogen abstraction from the methyl group of the propene prevails over two other channels leading to propylene oxide and propanal, respectively [128]. This undesired reactivity scheme can be suppressed if the silver catalyst is replaced by catalysts based on gold [210,211], and the search for a gas-phase analogue of this effect represents a future challenge.

3.4. Case study IV: Gold(I)-mediated coupling of alcohols and alkynes

Catalysis of chemical reactions by gold used to be considered as little effective due to the noble character of gold and therefore its small tendency for bond activations. However, ever since it has been shown that gold is capable to interact with multiple bonds and activate them towards a nucleophilic addition [212], gold as a catalyst attracts more and more attention of synthetic chemists [8], which has even been termed as a gold rush in catalysis [213]. It has been pointed out that the activity of gold in homogeneous catalysis is essentially caused by relativistic effects [214].

The pioneering gold-mediated reaction between alkynes and alcohols [212] has been also approached by means of mass spectrometry combined with theoretical calculations [215]. The bare gold cation and a complex of the gold cation with trimethylphosphine were employed as models for the catalytically active species. The DFT calculations confirmed the mechanism proposed originally by Teles et al. [212] and showed that the reaction is in overall exothermic (Scheme 5). The individual reaction steps in the catalytic cycle lead over barriers close in energy to the initial reactant couple $[Au(C_2H_2)]^+/CH_3OH$ and therefore the reaction is subject to substantial kinetic constrains in the gas phase. Further, it has been shown that the gold cation, either bare or with a phosphine ligand, has a larger philicity to multiple carbon–carbon bonds than to the oxygen atoms of alcohols. Under thermal conditions, the initially formed $[Au(C_2H_2)]^+$ cation only slowly associates with methanol and the reaction does not proceed further, which is most probably due to the large energy barrier for the formation of the C—O bond, which exceeds the energy of the initial reactants $[Au(C_2H_2)]^+$ and CH_3OH. By reference to the concept of microscopic reversibility, the reaction can, however, be probed in the opposite direction. Thus, if the gold cation is reacted with methylvinylether, the complex $[Au(C_2H_2)]^+$ can be observed as one of the major products.

The analogous reactions of the gold cation bearing a phosphine ligand reveal the same reactivity pattern. The association of the initial complex of gold, phosphine, and alkyne with the molecule of an alcohol proceeds faster, most probably due to the larger size of the system, which enables accommodation of larger internal energy gained upon the complex formation in the gas phase. Similarly to above, the coupling reaction does not proceed further, whereas the reverse sequence starting from methylvinylether and $[Au(P(CH_3)_3)]^+$ can be again realized, but the yield is considerably lower than in the reaction with the bare gold cation. In summary, a conceptual model for the gold(I) catal-



Scheme 5. Catalytic cycle for the C—O coupling of acetylene and methanol according to DFT calculations [215]. The energy values refer to the corresponding intermediates without any ligand L and are given relative to the separated reactant couple $[Au(C_2H_2)]^+ + CH_3OH$.

ysis discovered by Teles et al. could be provided by gas-phase experiments.

4. Gas-phase reactions of coinage-metal cluster ions

The gas-phase chemistry of pure coinage-metal cluster ions $M_n{}^{-/0/+}$ (M = Cu, Ag, Au) is very rich and outside the topics covered in this review [216–218]. Instead, here we focus on recent achievements with regard to the gas-phase chemistry of substituted or heteronuclear cluster ions of copper, silver, and gold with particular attention to those studies which combine experiment and theory.

A series of functionalized silver clusters have recently been studied by O'Hair and co-workers, who discovered several examples for bond activation by these cluster ions, whereas bare silver clusters $Ag_n{}^+$ are much less reactive. A combined mass-spectrometric and theoretical study of the disilver acetate cation $CH_3COOAg_2{}^+$ unraveled a silver-mediated ester formation in the gas phase with allyl iodide (reaction (9)), whereas methyl iodide only undergoes adduct formation with $CH_3COOAg_2{}^+$ [219].

$$CH_3COOAg_2{}^+ + CH_2{=}CH{-}CH_2I \rightarrow Ag_2I^+ + CH_3COOCH_2CH{=}CH_2 \tag{9}$$

$$Ag_4H^+ + 3CH_2{=}CH{-}CH_2Br \rightarrow Ag(C_6H_{10})^+ + Ag_3Br_3 + C_3H_6 \tag{10}$$

In a comparative study of selected bare $Ag_n{}^+$ clusters and their hydrides Ag_nH^+ [220], several examples of C—O and C—H bond activations were observed, and as a representative example the reaction of $Ag_5{}^+$ with 2-iodoethanol was investigated using density functional methods [221]. The silver-hydride cluster Ag_4H^+ also enables a sequence of reactions with allyl bromide which inter alia lead to C—C bond coupling to afford hexadiene complexed to Ag^+ concomitant with degradation of the silver cluster to presumably afford neutral Ag_3Br_3 (reaction (10)) [222]. Calculations imply that the C—C coupling leads to 1,5-hexadiene and also reveal that the major driving force of reaction (10) is provided by the formation of Ag—Br bonds. In this context, the mechanism of formation of the Ag_4H^+ represents a challenge for both experiment and theory as the ion was generated by electrospray ionization of a solution of *N,N*-dimethylglycine and $AgNO_3$. The same strategy was recently also applied to generate dinuclear, phosphine-ligated clusters of the type $[(R_3P)_2Au_2H]^+$ from solutions containing $(R_3P)AuCl$, *N,N*-dimethylglycine, and $AgNO_3$ [223].

Oxide clusters of the coinage metals have received particular attention in recent years, and their gas-phase chemistry has been reviewed recently [224]. In addition to systematic studies of $Ag_mO_n{}^+$ clusters by Bréchignac and co-workers [225–228] and the Ag_2O^+/C_2H_4 system discussed in Section 3.3, recent work on the influence of the charge state on the mechanism of the oxidation of carbon monoxide by Bürgel et al. is particularly noteworthy [229]. By a combination of experiment and theory, also including molecular dynamics calculations, these authors compared the oxygen-atom transfer reactions of carbon monoxide with the mononuclear gold-oxide ions AuO^- as well as AuO^+ and the corresponding dinuclear species Au_2O^- as well as Au_2O^+. Although the two anionic species oxidize carbon monoxide significantly slower than the corresponding cations, all four species mediate oxygenation of CO, where the anions lead to the bare metal (reaction (11)), whereas the corresponding cations consume an additional equivalent of CO leading to the corresponding carbonyl complexes (reaction (12)).

$$Au_nO^- + CO \rightarrow Au_n{}^- + CO_2 \tag{11}$$

$$Au_nO^+ + 2CO \rightarrow Au_nCO^+ + CO_2 \tag{12}$$

The theoretical analysis of the experimental data suggests that the anions follow a Eley–Rideal-like mechanism, whereas the cations also proceed in a Langmuir–Hinshelwood mechanism. It remains to be shown, if these reactions are also suited to realize a catalytic sequence in the gas phase by reoxidation of the reduced species $Au_n{}^-$ and Au_nCO^+, respectively, by suitable oxidants such as O_2 [230,231], N_2O [232–234], or nitro compounds [235,236].

Theoretical methods are meanwhile even able to address systems as complex as mixed transition-metal clusters. Thus, experimental investigations of methane activation by heteronuclear $Pt_mM_n{}^+$ cluster cations (M = Cu, Ag, Au) and the subsequent coupling reactions with gaseous ammonia [237–239] were rapidly followed by detailed theoretical studies of the bare metal clusters themselves, the products formed with methane, and the subsequent reaction with NH_3, which provided a reasonable basis for understanding all of effects observed experimentally [240–244] – a remarkable performance of theory in almost incredibly short time!

5. Conclusions

The gas-phase chemistry of coinage-metal ions and their clusters is a rich field in chemical research with relevance for areas such as ion solvation, organic synthesis, oxidation catalysis, and even biochemistry. In particular, the mechanistic insight achieved in gas-phase studies can guide the further understanding of phenomena in condensed-phase chemistry. A highlight of the coinage metals in this respect is the close synergy between experiment and theory which can be achieved quite often. In fact, several of the experimental discoveries described above were crucially inspired by theoretical predictions (e.g. $Cu(H_2O)^{2+}$ and $AuXe^+$) and others still await a direct spectroscopic verification (e.g. the dumbbell-like structure of $Au(H_2O)_8{}^+$). On the other hand, some of the experimental findings described above form attractive and also challenging tasks for future theoretical studies (e.g. the copper(II)-mediated C—C coupling of naphthols). Both, experimental and theoretical gas-phase studies may also further elucidate the role of copper(III) intermediates in several synthetically important reactions and biochemical transformations. Finally, it is once more pointed out that the huge progress achieved in the last two decades with respect to the understanding of the chemistry of coinage metals in the gas- as well as the condensed phase is primarily due to the enormously increased performance of density functional methods which allow to accurately describe complex metal-containing systems of sizes which were thought to be much too large for such treatments in the earlier 1990s.

Acknowledgements

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