

# On the Dewar–Chatt–Duncanson Model for Catalytic Gold(I) Complexes

Nicola Salvi, Leonardo Belpassi, and Francesco Tarantelli\*<sup>[a]</sup>

**Abstract:** We provide a rigorous model-free definition and a detailed theoretical analysis of the electron-charge displacements making up the donation and back-donation components of the Dewar–Chatt–Duncanson model in some realistic catalytic intermediates of formula L–Au<sup>I</sup>–S in which L is an N-heterocyclic carbene or Cl<sup>−</sup> and S is an  $\eta^2$ -coordinated substrate

containing a C–C multiple bond. We thus show, contrary to a widely held view, that the gold–substrate bond is characterized by a large  $\pi$  back-dona-

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tion component that is comparable to, and often as large as, the  $\sigma$  donation. The back-donation is found to be a highly tunable bond component and we analyze its relationship with the nature of the auxiliary ligand L and with structural (interdependent) factors such as metal–substrate bond lengths and carbon pyramidalization.

## Introduction

In recent years, homogeneous gold catalysis has been established as a powerful and versatile tool in chemists' hands.<sup>[1–6]</sup> The binding of Au<sup>I</sup> complexes to alkenes and, especially, alkynes enables the chemo-, regio-, and stereoselective activation of unsaturated carbon–carbon bonds, often more effectively than other transition metals.<sup>[7–12]</sup> A growing body of theoretical data exists on Au<sup>I</sup> chemistry,<sup>[13–15]</sup> but an understanding of the nature of the chemical bond between Au<sup>I</sup> and the reacting substrate in the catalytic intermediates and of its reactivity is still limited and lacking predictive capacity.<sup>[16]</sup> One significant, still unsettled, and much debated issue concerns the interpretation of the electronic structures of these species in terms of the well-known Dewar–Chatt–Duncanson (DCD) model,<sup>[17–20]</sup> which, ironically, was first introduced almost 60 years ago precisely to describe the  $\eta^2$  coordination of ethene to a coinage-metal atom. In short, the debate concerns the extent and relative importance of substrate-to-metal (S→M) donation and metal-to-substrate (M→S) back-donation.

Experimental clues are only indirect. Remarkably, for example, Au<sup>I</sup> carbonyls are “nonclassical” in that they display

a blueshift of the CO stretching frequency,<sup>[21]</sup> which is commonly associated with a lack of back-donation.<sup>[11,22,23]</sup> In the case of Au<sup>I</sup>–alkynes or Au<sup>I</sup>–alkenes, relevant unambiguous experimental evidence is more difficult to obtain due to the fact that both the S→M donation and M→S back-donation components tend to weaken the C–C bond,<sup>[24–26]</sup> but recently reported data were also deemed consistent with the lack, or marginal role, of back-donation.<sup>[27]</sup> The lack of back-donation may have an impact on the peculiar and powerful catalytic properties of Au<sup>I</sup> because, quite simply, it should tend to increase the electrophilicity of the coordinated substrate.<sup>[11]</sup>

Most of the available theoretical work involving DCD-type analyses of alkene and alkyne complexes of Au<sup>I</sup> deals with bare Au–ethene<sup>[25,28–32]</sup> or Au–ethyne<sup>[30]</sup> and generally tends to suggest that  $\sigma$  donation largely dominates over  $\pi$  back-donation. Only when the presence of ancillary ligands (F<sup>−</sup>, bipyridines) was studied by natural bond order (NBO) analysis of orbital populations was a significantly larger or even dominating  $\pi$  back-donation found.<sup>[25,31]</sup> However, the most recent investigations carried out on realistic Au<sup>I</sup>–alkene<sup>[33]</sup> and Au<sup>I</sup>–alkyne<sup>[26,34–36]</sup> catalytic intermediates using NBO orbital interaction energies all support the view of a dominating donation component.

Rather than on the basis of energy decompositions, a conclusive assessment of coordination bonds in terms of the DCD model requires a clear-cut and noncontroversial definition of the DCD components, donation and back-donation, which can only emerge as a result of a detailed analysis of the changes in electron density taking place upon forma-

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tion of the bond. Herein we report new theoretical results on the nature of the Au<sup>I</sup>-unsaturated C–C bond that clarify these issues as well as the significance and limits of the DCD model for Au<sup>I</sup> and other coinage-metal complexes. We have investigated a number of realistic catalytic intermediates, similar to some recently synthesized,<sup>[34,35]</sup> resulting from coordination of ethyne to AuCl and Au–nhc<sup>+</sup> (nhc = 2,3-dihydroimidazol-2-ylidene). The analogous Ag<sup>I</sup> and Cu<sup>I</sup> complexes have also been studied for comparison, as well as those of Au<sup>I</sup> with ethene. We have combined relativistic quantum chemical calculations with a detailed analysis of the change in electron density that occurs upon coordination. To free our results from any charge decomposition model, we have computed and examined, as detailed below, the spatial distribution of the S→M donation and M→S back-donation components of the electron-cloud displacement, which defines the metal–substrate interaction across the entire molecular region, and will show how this can be unequivocally related, with enlightening results, to the DCD model.

### Computational Details and Theoretical Aspects

We have investigated a series of coinage-metal bilinear complexes of formula [L–M(I)–η<sup>2</sup>S] in which M = Au, Ag, and Cu, the auxiliary ligand L is either the chloride ion or the N-heterocyclic carbene (nhc) 2,3-dihydroimidazol-2-ylidene, and S is either ethyne or ethene coordinated to the metal through a C–C π bond. Because the metal is formally a positive ion, the resulting complex is positively charged in the case of the neutral nhc ligand whereas it is neutral in the case of Cl<sup>–</sup>.

Equilibrium geometries, harmonic frequencies, and electron densities were calculated by using density functional theory (DFT) with Becke's exchange functional<sup>[37]</sup> in combination with the Lee–Yang–Parr correlation functional<sup>[38]</sup> (BLYP), as implemented in the ADF package.<sup>[39–41]</sup> An all-electron triple-zeta basis set with two polarization functions was used on all atoms (TZ2P).<sup>[39]</sup> Relativistic effects were included by means of the zeroth-order regular approximation (ZORA) Hamiltonian<sup>[42–44]</sup> with a small frozen core. The satisfactory accuracy of this approach was verified by both coupled-cluster and all-electron four-component Dirac–Kohn–Sham calculations on related systems.<sup>[45]</sup>

The changes in electron density that occur upon formation of the metal–substrate bond studied herein were analyzed through the charge-displacement (CD) function given by Equation (1). Δρ(x,y,z) is the difference between the electron density of a complex and that of its noninteracting fragments placed in the same position as they occupy in the complex. In the present case, the fragments are the L–M(I) moiety and the substrate, ethyne or ethene. The function Δq(z) was successfully introduced to study the chemical bond between gold and the noble gases<sup>[46]</sup> and also used to investigate charge transfer in weakly bound water adducts.<sup>[47,48]</sup> It defines, at each point z along a chosen axis, the

amount of electron charge that, upon formation of the bond between the fragments, moves across a plane perpendicular to the axis through the point z. A positive (negative) value corresponds to electrons flowing in the direction of decreasing (increasing) z. Charge accumulates where the slope of Δq is positive and decreases where it is negative. Thus, a positive (negative) difference between the Δq values computed at two points gives the amount of charge that has flowed into (away from) the region of space delimited by the two corresponding planes.

$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^z dz' \Delta \rho(x, y, z') \quad (1)$$

The systems studied herein have C<sub>2v</sub> symmetry and the z axis was chosen to coincide with the symmetry axis that passes through the gold atom and the middle of the substrate's C–C bond. This permits the separation of the Δρ function in components according to Equations (2) and (3) in which p represents the four irreducible representations A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, and B<sub>2</sub>. AB, A, and B represent the complex and its two fragments, respectively, and φ<sub>i</sub> are the Kohn–Sham orbitals. This gives rise to a separate CD function for each symmetry in each complex. We define the molecular plane (σ<sub>h</sub>) as that containing the metal center and the substrate's C–C bond. Thus, A<sub>1</sub> symmetry correlates with the in-plane component of the occupied π orbital of the free substrate and B<sub>2</sub> is the symmetry of the in-plane component of the unoccupied π\* orbital. In the case of ethyne, symmetry B<sub>1</sub> contains the out-of-plane π component of the C–C bond and A<sub>2</sub> contains the out-of-plane π\* component. In the case of ethene, the orbitals in symmetries A<sub>2</sub> and B<sub>1</sub> are engaged in carbon–hydrogen bonds. As will be clear in the following, this simple approach permits the unambiguous separation of the components of the DCD bond model and, most important, a detailed analysis of their spatial distribution over the whole molecular region.

$$\Delta \rho = \sum_p \Delta \rho_p \quad (2)$$

$$\Delta \rho_p = \sum_{i \in p} |\phi_i^{(AB)}|^2 - \sum_{i \in p} |\phi_i^{(A)}|^2 - \sum_{i \in p} |\phi_i^{(B)}|^2 \quad (3)$$

## Results and Discussion

**Catalytic gold–alkyne complexes: L–Au<sup>I</sup>–ethyne (L = N-heterocyclic carbene, Cl<sup>–</sup>):** As representative examples of catalytic intermediates formed in the gold(I)-promoted activation of triple bonds,<sup>[12]</sup> we studied the neutral complex [Cl–Au–ethyne] (1) and the cationic complex [nhc–Au–ethyne]<sup>+</sup> (2) in which nhc is the N-heterocyclic carbene 2,3-dihydroimidazol-2-ylidene. Closely related complexes have been experimentally characterized by Wu et al.<sup>[34]</sup> and Flügge et al.<sup>[35]</sup> The computed energy for the dissociation of com-

plex **1** into AuCl and ethyne is  $34.8 \text{ kcal mol}^{-1}$ , in line with those of previous DFT calculations using different exchange correlation functionals<sup>[34,35,49]</sup> and with those computed for other complexes of AuCl with simple alkynes ( $37.5 \text{ kcal mol}^{-1}$  for cyclododecyne<sup>[35]</sup> and 3-hexyne<sup>[34]</sup>). For the cationic complex **2** we obtained a dissociation energy of  $36.9 \text{ kcal mol}^{-1}$ .

Our focus in this work was an in-depth comparative analysis of the changes in electron density that take place upon formation of the bond between L–Au<sup>I</sup> and ethyne. Figure 1

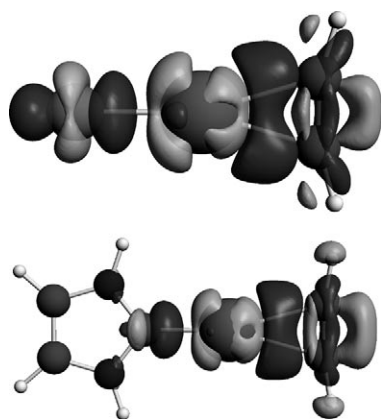


Figure 1. Contour plot of the change of electronic density upon formation of the complexes [Cl–Au–ethyne] (upper) and [nhc–Au–ethyne]<sup>+</sup> (lower). Light grey isosurfaces identify regions in which the electron density decreases whereas zones of density accumulation are marked by dark isosurfaces. Density value at the isosurfaces:  $\pm 0.003 \text{ a.u.}$  See also Figure S1 in the Supporting Information.

shows a 3D contour plot of the differences between the electron density of the complexes and of the corresponding noninteracting fragments (AuCl or Au–nhc<sup>+</sup> and ethyne, respectively) placed in the same positions as they occupy in the complexes.<sup>[50]</sup> It evidences a significant and widespread density rearrangement on formation of the adducts with alternating regions of electron loss and accumulation. The extended zone of increased density between the gold atom and the alkyne is clearly suggestive of a pronounced covalency of the bond. Even in the region of the triple bond a quite complex pattern of density change is exhibited such that its impact on the C–C bond strength cannot easily be deduced. There is a clear increase in density closest to the C–C bond, but also a decrease to the right and left of it. Note in particular the extensive depletion of density on the external side (right) of the C–C bond, which may be related to its activation towards nucleophilic attack. A weakening of the alkyne C–C bond upon coordination is clearly indicated by the computed frequencies and geometries (see Table 1) and, in this respect, interesting differences begin to appear between **1** and **2**. In both complexes, the computed C–C stretching frequency is smaller than that of free ethyne, but this redshift is more pronounced in **1** ( $176 \text{ cm}^{-1}$ ) than in **2** ( $119 \text{ cm}^{-1}$ ). Consistent with this, the ethyne C–C bond is found to elongate slightly more upon coordination in **1** than

Table 1. Computed structural and spectroscopic data for the L–M(I)–S complexes.<sup>[a]</sup>

M =		Au		Ag		Cu	
L =		Cl	nhc	Cl	nhc	Cl	nhc
S = C <sub>2</sub> H <sub>2</sub>	$R_{CC} [\text{Å}]^{[b]}$	1.24	1.23	1.22	1.22	1.24	1.23
	$R_{MC} [\text{Å}]$	2.09	2.17	2.20	2.25	1.90	1.96
	$\theta [^\circ]$	163	168	169	171	164	169
	$\omega [\text{cm}^{-1}]^{[b]}$	1815	1872	1884	1912	1825	1871
	$D_e$ [kcal mol <sup>-1</sup> ]	34.8	36.9	20.2	26.1	34.9	37.3
S = C <sub>2</sub> H <sub>4</sub>	$R_{CC} [\text{Å}]^{[c]}$	1.39	1.37				
	$R_{MC} [\text{Å}]$	2.11	2.20				
	$\theta [^\circ]$	164	168				
	$\omega [\text{cm}^{-1}]^{[c]}$	1526	1550				
	$D_e$ [kcal mol <sup>-1</sup> ]	37.5	38.8				

[a]  $R_{CC}$  is the substrate's C–C bond distance,  $R_{MC}$  is the distance of M from the C–C midpoint,  $\theta$  is the C–C–H angle for ethyne and the dihedral angle between the two HCCH planes for ethene,  $\omega$  is the C–C stretching frequency, and  $D_e$  is the energy for the dissociation to L–M(I) and S. [b] In free ethyne,  $R_{CC} = 1.21 \text{ Å}$ ,  $\omega = 1991 \text{ cm}^{-1}$ . [c] In free ethene,  $R_{CC} = 1.33 \text{ Å}$ ,  $\omega = 1628 \text{ cm}^{-1}$ .

in **2**. Concerning the distortion from linearity, the geometry of the ethyne is more perturbed in **1** than in **2**: The C–C–H bond angle is bent by  $17^\circ$  (away from the gold site) in **1** and by  $12^\circ$  in **2**. Note also that the computed distance between the gold atom and the middle of the triple bond is  $0.08 \text{ Å}$  shorter in **1** than in **2**. This greater perturbation of the alkyne when it is coordinated to neutral AuCl than to the Au–nhc<sup>+</sup> cation is somewhat surprising and we shall discuss it again later. We note in passing that our computed structural data are consistent with those of previous theoretical calculations on some related systems and with reported X-ray crystallography data.<sup>[34,35]</sup>

Returning now to the changes in density in Figure 1, we finally note that alkyne coordination also induces a significant perturbation of the system on the side of the ligand L, with an evident polarization of the Au–L bond, of the chlorine atom and of the carbenic carbon atom directly bound to the gold. The far side of the nhc ligand seems by contrast only marginally affected.

**Charge displacement curves:** A more detailed and quantitative view of the nature of the alkyne coordination bond is provided by the CD curves defined in the Computational Details section and shown in Figure 2. Let us begin by analyzing the total CD curves (labeled “Total” in Figure 2). The curves for the two complexes display an overall quite similar shape but, especially in the bond region between the gold atom and ethyne and in the region around the latter, the CD curve of **1** is noticeably shifted to smaller values than that of **2**. As a result, both curves are positive everywhere except for a narrow region in the middle of the Au–ethyne bond of **1**. We recall that a positive CD value corresponds to charge transfer from right to left at that point, that is, in this case, in the direction from ethyne to L–Au<sup>I</sup>. One notices, in both cases, two evident zones of charge accumulation: One between the gold atom and the alkyne and the

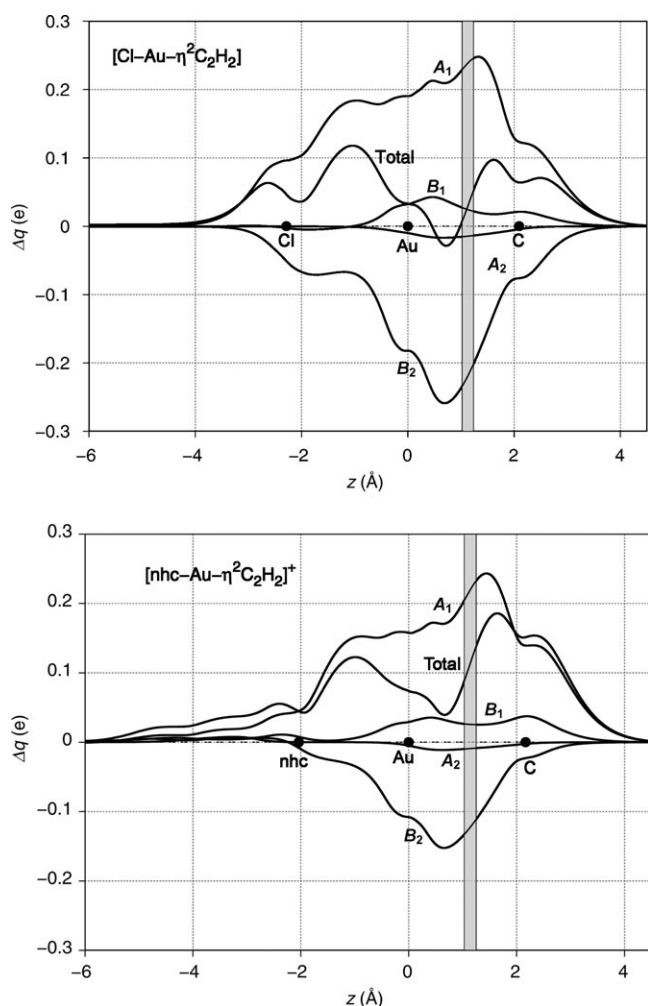


Figure 2. Charge displacement curves for the complexes  $[\text{Cl}-\text{Au}-\text{ethyne}]$  and  $[\text{nhc}-\text{Au}-\text{ethyne}]^+$ . The black dots represent the  $z$  coordinate of the atoms. The vertical band identifies a suitable boundary between the  $\text{L}-\text{Au}^{\text{I}}$  and ethyne fragments (see the text for details and Figure S2 in the Supporting Information).

other between the auxiliary ligand  $\text{L}$  and gold. However, in the region delimited by the positions of gold and ethyne there is a global net electron influx, whereas this is essentially absent in the region between  $\text{L}$  and gold, the charge accumulation near  $\text{L}$  being almost exactly compensated by a decrease near the gold atom. Thus, the latter region may be characterized by significant charge polarization caused by alkyne coordination. A region of charge polarization is also visible on the far side (left) of the chlorine ligand, whereas the electron density over the  $\text{nhc}$  ligand is less affected. We also note, as already hinted at earlier, an evident region of charge depletion to the right of ethyne, in the zone where an external nucleophile may attack. This depletion appears significantly more pronounced in the  $\text{nhc}$  complex owing to the shift between the two curves noted above. Taking as a reference the point on the  $z$  axis corresponding to the position of the alkyne carbon atoms, we see that 0.08 electrons have been transferred towards gold in **1** and nearly twice as

many (0.15) in **2**. This puts in a quantitative perspective the electrophilic character of the alkyne when coordinated to a  $\text{L}-\text{Au}^{\text{I}}$  group (either charged or neutral)<sup>[35]</sup> and is also consistent with the fact that complexes containing an  $\text{nhc}$  ligand are widely known and used to effectively activate triple bonds towards nucleophilic attack.<sup>[51]</sup> A similar analysis on  $\text{Au}^{\text{I}}$  complexes containing a phosphine as secondary ligand shows an even higher charge depletion at the alkyne.<sup>[52]</sup>

The much smaller, and even negative,  $\Delta q$  value in the  $\text{Au}$ -ethyne region of the chlorine complex immediately appears to make, in at least one respect, the characterization of the bond in the two systems remarkably different. Indeed, while the presence of a net charge donation from the alkyne to gold in the cationic complex is entirely evident, this is much smaller if not altogether negligible in the neutral complex. To show this, we have drawn in Figure 2 a plausible boundary zone between the  $\text{L}-\text{Au}^{\text{I}}$  and ethyne fragments (grey vertical band), identified as the region (of width arbitrarily set at one tenth of the corresponding  $\text{Au}-\text{CC}$  distance) around the point on the  $z$  axis at which equal-valued isodensity surfaces of the isolated fragments are tangent. Across this boundary, the net charge transfer from ethyne to  $\text{Au}-\text{nhc}^+$  is 0.12 electrons (the values at the edges of the grey band are 0.09 and 0.14), whereas it is 0.03 electrons (between 0.01 and 0.05) from ethyne to  $\text{AuCl}$ . Note that NBO analysis has provided very similar charge transfer figures in analogous complexes with to cyclodecyne.<sup>[35]</sup> A smaller donation from the alkyne to a neutral group than to a cationic species might of course have been expected, but it appears somewhat inconsistent with the fact that, as we have noted above, in complex **1** ethyne undergoes a larger structural perturbation upon bonding and gets closer to the gold atom. Also, as already noted by Flügge et al.,<sup>[35]</sup> a vanishing charge transfer to  $\text{AuCl}$  is somewhat surprising in view of the nearly four-times larger NBO interaction energy computed for  $\sigma$  donation than for  $\pi$  back-donation.<sup>[35]</sup> Indeed,  $\text{AuCl}$  is an effective catalyst (see ref. [53] and examples reported in ref. [54]) and its adducts are experimentally stable, as confirmed by the fact that one such complex has been the first simple  $\text{L}-\text{Au}^{\text{I}}$ -triple-bond complex to be isolated and structurally characterized.<sup>[34]</sup>

**CD symmetry analysis and the DCD model:** A revealing insight into the above puzzling findings and into the electronic nature of the gold-alkyne bond in these complexes comes from an analysis of the symmetry components of the CD curves, also shown in Figure 2, which is the main focus of this work. Two components clearly dominate:  $A_1$  and  $B_2$ . The  $A_1$  symmetry correlates to the component of the occupied  $\pi$  orbital of ethyne lying in the  $\text{Au}$ -ethyne plane. The corresponding CD curve is positive and large everywhere and, in the  $\text{Au}$ -alkyne region, provides a rigorous and detailed picture of the  $\text{S} \rightarrow \text{M}$   $\sigma$  donation of the DCD model. The  $B_1$  CD curve is also positive in the  $\text{Au}$ -ethyne region but of much smaller magnitude. This symmetry correlates to the  $\pi$  component of ethyne lying outside the  $\text{Au}$ -ethyne plane, which is thus seen to give a small but non-negligible

contribution to  $S \rightarrow M$  donation. An energy component associated with this symmetry in the  $Au$ -ethyne<sup>+</sup> system has been discussed by Nechaev et al.<sup>[30]</sup> and was interpreted as being due to polarization. The  $B_2$  symmetry correlates to the in-plane component of the unoccupied  $\pi^*$  orbital of the free substrate and the corresponding CD curve is seen to be largely negative everywhere. This curve clearly provides the defining picture of  $M \rightarrow S$   $\pi$  back-donation. The curve associated with the  $A_2$  symmetry component of CD is nearly vanishing everywhere, its extremely small negative value in the  $Au$ -ethyne bond region describing a tiny  $M \rightarrow S$  back-donation into the substrate out-of-plane  $\pi^*$  component. It is thus a remarkable fact, which the symmetry CD curves illustrate in the clearest fashion, that the changes in electron density defining the coordination bond between a metal and a substrate are indeed made up of two charge flows with different symmetry properties going in opposite directions, which is precisely the tenet of the DCD model. Indeed, we would like to propose that such CD curves provide a rigorous definition, as well as the most detailed picture, of the DCD model.

The first eye-catching feature emerging from the symmetry CD curves is that  $Au \rightarrow$ alkyne  $\pi$  back-donation in these complexes, far from being negligible, constitutes a large component of the interaction. The  $B_2$  CD curve has indeed a pronounced negative peak in the region between the gold atom and ethyne. As a result, the global CD arises from cancellation between large opposite donation and back-donation components along the whole molecular axis. Focusing in particular on the  $Au$ -alkyne bond region, a quite clear picture emerges of the differences between the two complexes. We notice indeed the somewhat surprising fact that both systems exhibit nearly identical  $A_1$  and  $B_1$   $S \rightarrow M$  donation components, in spite of the difference in charge of the  $L-Au^I$  fragment. In contrast, quite remarkably,  $\pi$  back-donation is much larger, in fact roughly twice as large, in **1** and thus, as a result, it cancels here nearly exactly the  $\sigma$  donation. On the boundary defined earlier (middle of the grey band in Figure 2)  $\sigma$  ( $A_1$ ) donation in **2** is 0.22 electrons and  $\pi$  back-donation roughly half as much (0.12 electrons). For **1**, the corresponding figures are 0.24 and 0.22 electrons, respectively. As the Figure 2 clearly shows, this leaves in the latter complex a global net donation roughly equal to that of the sole  $B_1$  component, which is only about 10% of the total ( $A_1 + B_1$ ).

In summary, the symmetry decomposition of the CD curves indicates that donation from the alkyne to the  $L-Au^I$  moiety is surprisingly stable and independent of the latter's charge or the nature of the ancillary ligand  $L$ . Note in fact that, if at all, the neutral  $AuCl$  group appears to be an even slightly better  $\sigma$  acceptor than the  $Au-nhc^+$  ion. In contrast, and less surprisingly,  $\pi$  back-donation appears to be sensitive to the nature and charge of the activating gold complex, with the neutral  $AuCl$  back-donating almost twice as effectively as the charged complex. It may be interesting to observe that, compared with the bare  $Au$ -ethyne<sup>+</sup> complex,<sup>[45]</sup> the presence of the  $nhc$  auxiliary ligand causes  $S \rightarrow M$  dona-

tion to nearly halve but leaves the extent of  $\pi$  back-donation roughly unaltered. As a result, the ratio of total donation to back-donation changes from 3.1 in  $Au$ -ethyne<sup>+</sup> to 1.9 in **2** to 1.1 in **1**. In general, these results unequivocally indicate that the extent and role of  $\pi$  back-donation in  $Au^I$ -alkyne complexes is definitely more significant than previously thought.<sup>[34,35]</sup> More than anything else, it is in fact the variation in  $\pi$  back-donation that differentiates the  $Au^I$ -alkyne coordination bond and can be suitably tuned by an appropriate choice of the ancillary ligand. It may also be the case, as Figure 2 clearly shows, that the differences in  $\pi$  back-donation between the complexes are not limited to the region of the  $Au^I$ -alkyne bond but, much more than the small differences in  $\sigma$  donation, distinctly characterize the space around and beyond the  $C-C$  triple bond, even reaching the region of nucleophile approach to the coordinated alkyne. This picture finally offers a clear interpretation of the larger structural perturbation of ethyne and the tighter  $Au$ -ethyne bond in the  $AuCl$  complex: The larger  $\pi$  back-donation that characterizes the latter system weakens the  $C-C$  bond and pyramidalizes the carbon valence more pronouncedly.

In the region of the  $L-Au^I$  bond and around the ancillary ligand  $L$ , only the  $A_1$  and  $B_2$  curves remain appreciably different from zero. In the chlorine complex, noticeable CD extends even beyond the polarizable chlorine ligand whereas in the  $nhc$  system only the bond between the gold and carbenic carbon atoms is significantly affected by alkyne coordination. The fact that a small but non-negligible negative  $B_2$  component of the charge displacement is present between  $nhc$  and  $Au^I$  indirectly proves the presence of a component of  $\pi$  character in this bond.<sup>[51,55-60]</sup> Note the peculiar interplay between the  $A_1$  and  $B_2$  components in governing  $L-Au^I$  bond polarization. The  $A_1$  curve increases along the bond, quite rapidly close to  $L$  and much more slowly around the gold atom. In contrast, the  $B_2$  curve decreases with increasing slope on going from  $L$  to gold. As a consequence the charge accumulation in the metal- $L$  bond is mostly of  $\sigma$  symmetry whereas the electron depletion taking place closer to the gold atom is of  $\pi$  character and is essentially an early manifestation of the metal-to-alkyne  $\pi$  back-donation. As a further aspect of the structure of **2**, we investigated the rotation of the  $nhc$  ligand around the bond axis (a relatively low-energy motion of about  $1 \text{ kcal mol}^{-1}$ ) and found that it produces only small changes in the CD curves.

**Alkyne distortion and the  $Au^I$ -alkyne bond:** The extent of deformation of the substrate upon coordination is an important and well-recognized empirical clue to the nature of the interaction between a metal and a substrate.<sup>[61]</sup> A case in point is the bending of  $C-C-H$  in ethyne in the complexes studied herein, which, as we have argued, appears to be mostly related to the extent of  $M \rightarrow S$   $\pi$  back-donation. Our calculations have shown that a distortion from linearity of not more than 17 degrees is perfectly compatible with a large  $\pi$  back-donation in complex **1** and a deviation of 12 degrees characterizes complex **2**, in which  $\pi$  back-donation is smaller but still a quite important component of the bond.

Although at a very preliminary level, we have investigated this interesting relation in more detail by performing some simple computational experiments in which we constrained ethyne to remain linear upon coordination to AuCl. In a first calculation we simply straightened  $C_2H_2$  to linearity while keeping all the other geometrical parameters of the complex fixed at their equilibrium value. Under these conditions, the coordination energy decreased by  $5.0 \text{ kcal mol}^{-1}$ . In Figure 3 we show the CD curves for the constrained com-

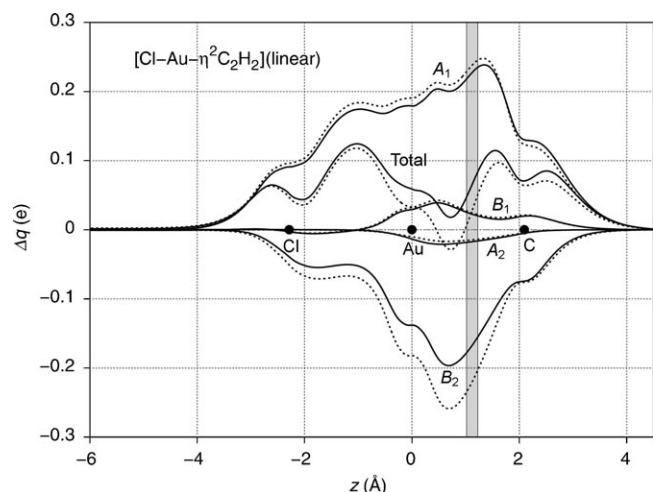


Figure 3. Charge-displacement curves for the complex [Cl-Au-ethyne] obtained when the alkyne is constrained to remain linear. For comparison, the curves for the fully optimized complex are shown as dotted lines. See also Figure S3 in the Supporting Information.

plex **1**. For easy comparison, the dotted lines show again the CD curves for the fully relaxed structure. The most evident change caused by the linearity constraint is the upward shift of the  $B_2$  CD curve in the Au-alkyne region, which means a decrease (by about 25% in the grey boundary zone) of the Au→alkyne  $\pi$  back-donation. In contrast, the  $\sigma$  donation component of the interaction decreases much less and the other symmetry components remain essentially unchanged. As a result, the total CD curve also shifts upward (becoming positive everywhere) and the net positive charge on ethyne, measured at the boundary, increases to about 0.07 electrons. The effects of distortion on the CD curves tend, however, to become negligible in the region of the triple bond. These results confirm the intuitive view that  $\pi$  back-donation is the DCD bond component most sensitively connected to carbon pyramidalization in the unsaturated substrate. However, they also show the important fact that even a negligible distortion is entirely compatible with the presence of a substantial  $M \rightarrow S \pi$  back-donation.

Of course, when alkyne pyramidalization is impeded, the optimal coordination geometry also changes and we have thus further investigated complex **1** when ethyne is kept linear but its C–C bond length and distance from the gold atom are allowed to relax. This leads to an increase in the Au–ethyne bond length of  $0.07 \text{ \AA}$ . Note that the relaxed dis-

tance of  $2.16 \text{ \AA}$  is thus very close to that found in **2** in which alkyne pyramidalization is in fact less pronounced. In contrast, the alkyne C–C bond length remains essentially unaffected by the linear constraint. In the relaxed geometry, the CD curves show that  $\pi$  back-donation is further reduced (by an additional 15% in the boundary region), whereas the other symmetry components of the CD curves remain practically identical to those obtained at the shorter Au–ethyne bond length represented in Figure 3. In this way, the ratio of  $\pi$  back-donation to  $\sigma$  donation is also close to that of complex **2**. It thus appears that  $\pi$  back-donation is significantly more sensitive than  $\sigma$  donation, in the range investigated, to structural parameters such as substrate distortion and distance from the metal. This is particularly interesting in so far as such parameters are, at least to some extent, controllable, for example, through substitution. A remarkable result of this, as the present case shows, is that a coordinated substrate may turn out to be more positively charged when its distance from the metal is longer. Further, more extensive studies on these crucial aspects of the bond in  $Au^I$  catalytic intermediates are in progress.

**Gold versus other coinage metals— $Cu^I$  and  $Ag^I$ :** It is widely recognized that  $Au^I$  complexes are generally superior  $\pi$ -activation catalysts, especially in promoting nucleophilic attack on triple bonds and especially when compared with analogous  $Cu^I$  and  $Ag^I$  complexes.<sup>[11,26]</sup> A complete and generalized understanding of this fact is a challenging task that involves not only an investigation of the nature and structure of the metal–substrate bond, but also of the dynamics of the chemical reactions, their transition states, solvent effects, and so on. However, a simplistic interpretation in terms of the DCD model of the bond between the metal and activated substrate may suggest that, in  $Au^I$  intermediates, such a bond is characterized by a particularly large  $S \rightarrow M \sigma$  donation and/or a correspondingly small  $M \rightarrow S \pi$  back-donation. Our analysis of the CD curves, which has shown that in the  $Au^I$  complexes both DCD components appear to play comparable roles in the bonding, allows us to explore in detail this particular aspect of the question by investigating analogous complexes of  $Cu^I$  and  $Ag^I$ . We thus show in Figures 4 and 5 the CD curves of the Cl–M–ethyne and  $[nhc-M-ethyne]^+$  complexes for  $M=Cu$  and  $Ag$  and compare them with those for  $M=Au$ . As a quick summary, we present in Table 2 the DCD charge transfer components determined from the curves at the metal–substrate boundary defined earlier for the gold analogues (middle of the grey strips in the figures).

Looking first at the total CD curves, one notices immediately that they are systematically extremely similar to those of the corresponding  $Au^I$  complexes in the region of the alkyne ligand, with appreciable differences only showing up around the metal center and in the region of the L–M(I) bond. The latter becomes invariably less polarized than L– $Au^I$  upon alkyne coordination. We thus see that the net charge on ethyne is roughly comparable in the corresponding complexes of all three coinage metals, if somewhat

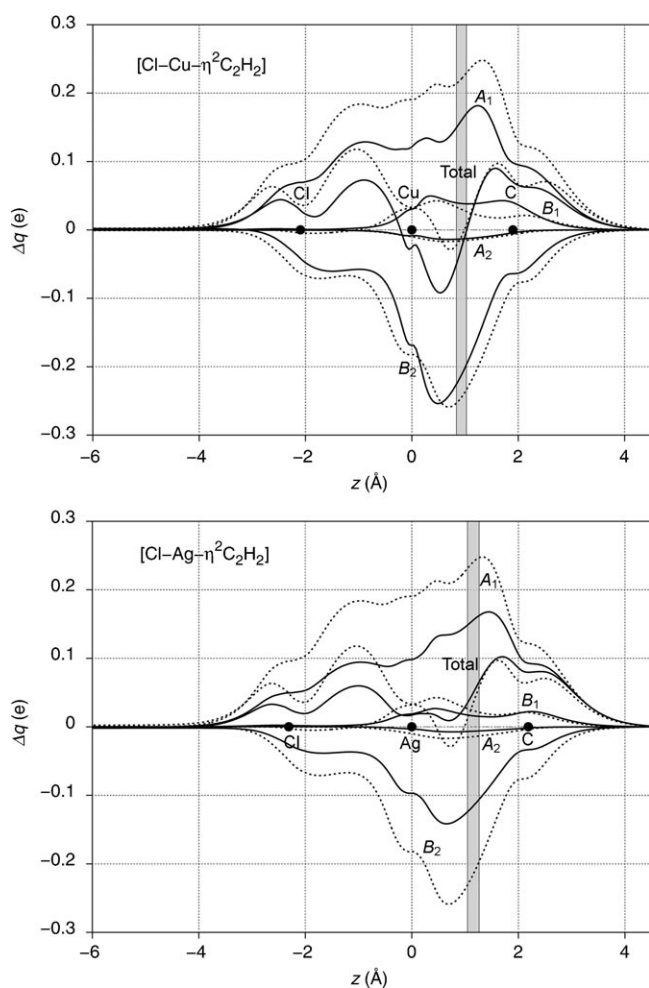


Figure 4. Charge-displacement curves for the complexes  $[\text{Cl-M-ethyne}]$  ( $M = \text{Cu, Ag}$ ). The curves for  $M = \text{Au}$  are also shown for comparison as dotted lines. See also Figure S4 in the Supporting Information.

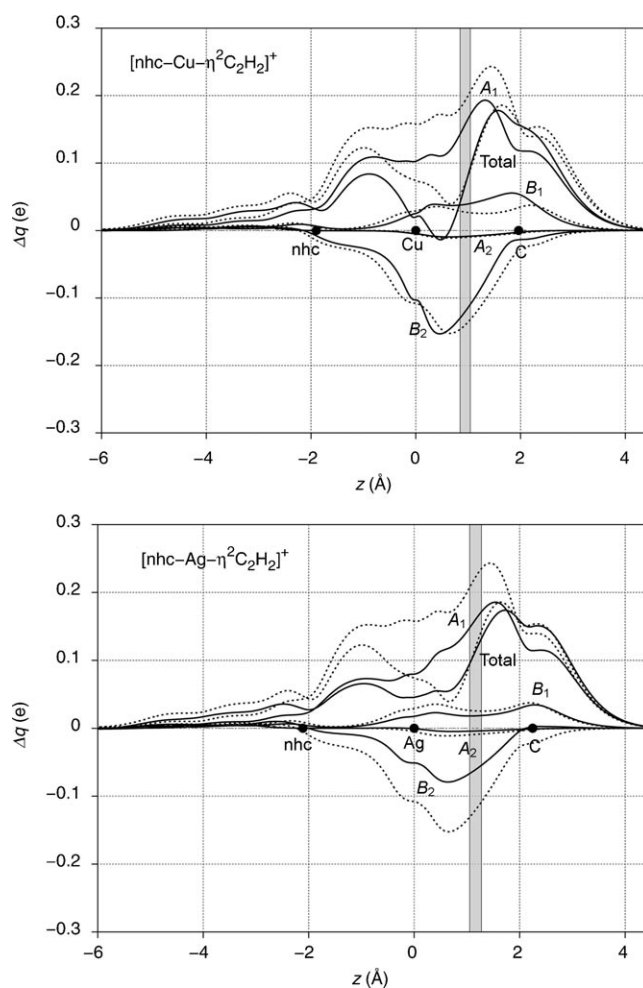


Figure 5. Charge-displacement curves for the complexes  $[\text{nhc-M-ethyne}]^+$  ( $M = \text{Cu, Ag}$ ). The curves for  $M = \text{Au}$  are shown for comparison as dotted lines. See also Figure S5 in the Supporting Information.

Table 2. Computed  $\text{S} \rightarrow \text{M}$  donation and  $\text{M} \rightarrow \text{S}$  back-donation values (in electrons) extracted from the CD curves of the  $[\text{L-M-ethyne}]$  complexes at the boundary between the fragments defined in the text.

M =	$[\text{Cl-M-ethyne}]$			$[\text{nhc-M-ethyne}]^+$		
	Au	Ag	Cu	Au	Ag	Cu
$\text{S} \rightarrow \text{M}$ ( $A_1 + B_1$ )	0.26	0.18	0.20	0.25	0.18	0.20
$\text{M} \rightarrow \text{S}$ ( $A_2 + B_2$ )	0.23	0.13	0.22	0.13	0.06	0.13
net charge on ethyne	0.03	0.05	-0.02	0.12	0.12	0.07

smaller in the case of copper (and even slightly negative in  $\text{Cl-Cu-ethyne}$ ). Some significant differences in the metal-substrate bond begin, however, to emerge when we look at the DCD symmetry components of the charge displacement and their spatial distribution. In particular, one notices that the  $A_1$  component ( $\text{S} \rightarrow \text{M}$   $\sigma$  donation), although having an almost identical shape, is systematically significantly smaller in the copper and silver complexes than in the gold ones. At the proposed boundary between the  $\text{L-M}$  and ethyne fragments it is surprisingly quantitatively identical in the copper and silver systems (0.16 electrons both in the neutral and

cationic system) and about 30% smaller than in the gold case. The  $\text{M} \rightarrow \text{S}$  back-donation (essentially comprising the sole  $\pi$  component  $B_2$ ) shows a different pattern in that it is almost identical in the gold and copper complexes but about half as large in the silver ones. The small shift that is observed between the gold and copper  $B_2$  curves appears to be essentially due to the significantly different metal-alkyne bond lengths. Finally, the small out-of-plane component of  $\text{S} \rightarrow \text{M}$  donation ( $B_1$ ) shows some variation, compared with the gold case, only in the triple-bond region of the copper complexes, where it is larger. This effect may also be related to the smaller  $\text{Cu-ethyne}$  distance.

In summary, we may conclude that  $\text{L-Au}^{\text{I}}$  moieties are decidedly more effective  $\sigma$  acceptors than analogous  $\text{Ag}^{\text{I}}$  or  $\text{Cu}^{\text{I}}$  ones. In all coinage-metal systems,  $\pi$  back-donation is invariably found to be a large component of the metal-alkyne bond although it is significantly smaller in the  $\text{Ag}^{\text{I}}$  complexes. For all metals,  $\text{S} \rightarrow \text{M}$  donation is almost identical in the corresponding neutral and charged species, whereas  $\text{M} \rightarrow \text{S}$  back-donation is roughly half in the latter. Considering as a reference the boundary point defined earlier, the

ratio of  $S \rightarrow M$  donation to  $M \rightarrow S$  back-donation in the neutral complexes is 0.9, 1.1, and 1.4 for  $\text{Cu}^I$ ,  $\text{Au}^I$ , and  $\text{Ag}^I$ , respectively, whereas it increases to 1.5, 1.9, and 3.0, respectively, in the charged complexes. The corresponding NBO interaction energy ratios, computed in recent studies of related neutral<sup>[36]</sup> and charged<sup>[26]</sup> complexes, are two-to-three times larger and thus appear to grossly underestimate the relative magnitude of  $M \rightarrow S$   $\pi$  back-donation.

Finally, we comment on the fact that alkyne coordination in the  $\text{Au}^I$  complexes causes a much more pronounced effect on the bond between the metal and the auxiliary ligand than is observed in the corresponding  $\text{Cu}^I$  and, especially,  $\text{Ag}^I$  cases. This seems to generally suggest a much larger reciprocal effect of the left and right ligand coordination in binary  $\text{Au}^I$  complexes, which, in turn, would imply a higher sensitivity of the properties of the metal–substrate bond on the nature of the secondary donor, as recently also observed by Dias et al.<sup>[36]</sup> This aspect clearly calls for further investigation, which may be greatly helped by the CD analysis applied to the formation of the bond between the metal and ancillary ligand in the presence of the alkyne. We note that the structural data in Table 1 appear to be consistent with the present conclusions in that they show, for the  $\text{Au}^I$  systems, a somewhat larger variation of the computed parameters (especially the  $\text{C} \equiv \text{C}$  frequency and metal–substrate distance) upon switching from the chlorine to the nhc ligand. As we have shown here, these changes are mainly mediated by changes in  $\pi$  back-donation.

**Alkyne versus alkene substrates in  $\text{Au}^I$  complexes:** In homogeneous catalysis,  $\text{Au}^I$  catalysts are known to selectively activate alkynes even in the presence of alkenes or other functional groups (e.g., see refs. [8, 49, 62], and references therein). This “alkynophilicity” has been attributed to a kinetic rather than thermodynamic origin<sup>[49]</sup> on the grounds that  $\text{AuCl}$  is computed to bind ethene more strongly than ethyne, but an attacking group (e.g.,  $\text{OH}^-$ ) binds more strongly to the ethyne intermediate than to the ethene one. To our knowledge, with few exceptions,<sup>[63, 64]</sup> complete reaction profiles (i.e., transition states) have not been investigated. As mentioned in the Introduction, most available DCD analyses of the  $\text{Au}^I$ –alkene bond generally tend to support the view of a dominating  $\sigma$  donation component and a clear difference with the coordination of alkynes has not emerged. We have performed calculations on the  $[\text{Cl}–\text{Au}–\text{ethene}]$  and  $[\text{nhc}–\text{Au}–\text{ethene}]^+$  complexes analogous to those of ethyne. Some computed structural and spectroscopic parameters are presented in Table 1. As can be seen, ethene binds slightly more strongly than ethyne and our interaction energies agree with previous DFT results.<sup>[49]</sup> As with the alkyne, coordination activates the alkene and substrate deformation is more pronounced in the neutral  $\text{AuCl}$  complex.

In Figure 6 we show the CD curves for the two ethene complexes and make a comparison with those of the corresponding ethyne systems (dotted lines). Clearly, the differences in the CD curves between the ethene and ethyne sys-

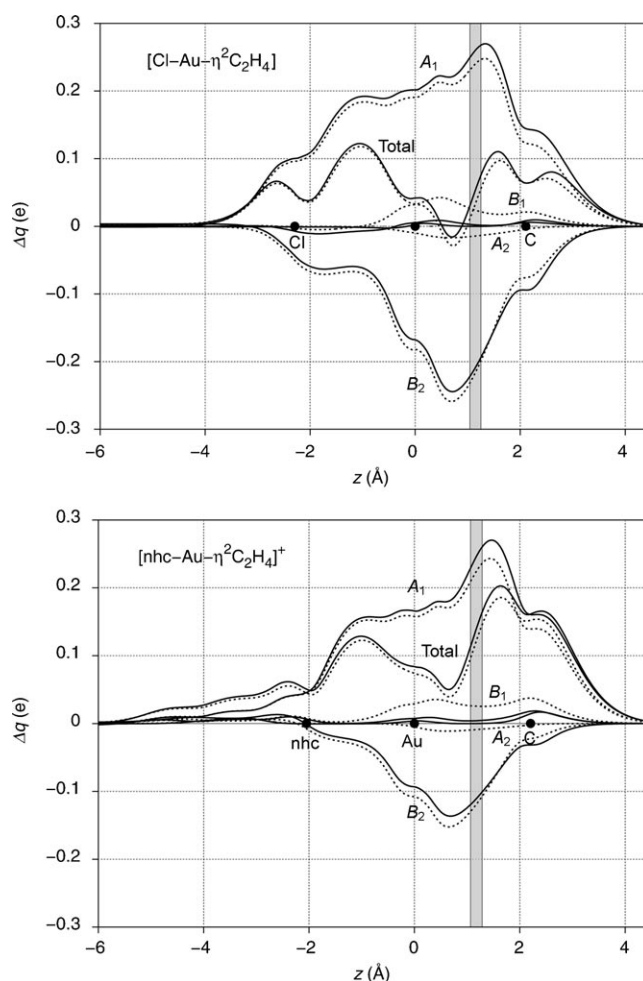


Figure 6. Charge-displacement curves for the complexes  $[\text{Cl}–\text{Au}–\text{ethene}]$  and  $[\text{nhc}–\text{Au}–\text{ethene}]^+$ . The dotted lines show for comparison the curves of the corresponding complexes with ethyne. See also Figure S6 in the Supporting Information.

tems are almost negligible, mainly due to the fact that the  $B_1$  and  $A_2$  CD symmetry components are essentially vanishing in the ethene complexes because the corresponding ethene density components are engaged in carbon–hydrogen bonding and are not available to the metal–substrate interaction. The vanishing  $B_1$  component is almost exactly compensated by a somewhat more positive  $A_1$  CD (thus a slightly larger  $\sigma$  donation) so that the total  $S \rightarrow M$  donation, measured at the boundary, coincides with that of the ethyne complexes (Table 2). The  $\pi$  back-donation curves appear to be very slightly shifted upward in the ethene complexes (except in the double-bond region) so that the global ratio of  $S \rightarrow M$  donation to  $M \rightarrow S$  back-donation (1.2 and 2.2 at the interfragment boundary of the neutral and charged systems, respectively) is a little larger than in the ethyne complexes.

In summary, the curves show that the nature of the bond in the  $\text{Au}$ –alkene complexes is similar to that of the complexes with the alkyne substrate. This clearly supports the view that the marked selectivity of the  $\text{Au}^I$  complexes to-



wards alkyne activation does not arise as a result of preferred bonding to the alkyne<sup>[26,49]</sup> but must have a kinetic origin. Further investigations of the actual reaction profiles in solution are needed to directly confirm this conclusion.

## Conclusion

We have carried out in this work an original and insightful theoretical analysis of the coordination  $\pi$  bond between Au<sup>I</sup> and unsaturated substrates (S) in catalytic intermediates of the form [L–Au<sup>I</sup>–S], with L an auxiliary ligand, Cl<sup>–</sup> or a N-heterocyclic carbene (nhc). We have studied ethene and ethyne as substrates and, in addition, the analogous complexes of other coinage metals, Ag<sup>I</sup> and Cu<sup>I</sup>, for comparison.

The analysis was based on a partial progressive integration of the changes in electronic density occurring in the systems upon formation of the coordination bond. This procedure defines the charge displacement occurring along the entire molecular axis and permits a reliable assessment, free of any theoretical model of charge decomposition, of the charge transfers taking place. Furthermore, and very importantly, molecular symmetry in the systems studied permits a rigorous definition and assessment of the CD components at the heart of the popular Dewar–Chatt–Duncanson model: Substrate-to-metal  $\sigma$  donation and metal-to-substrate  $\pi$  back-donation. This has allowed us to conclusively answer some long-standing questions concerning the nature of the Au<sup>I</sup>–carbon bond in these catalysts.

A first important conclusion is that, contrary to a widely held view mostly based on an inappropriate interpretation of experimental observations,  $\pi$  back-donation is a large and crucially important component of the Au<sup>I</sup>–substrate bond in all systems, even larger, in absolute terms, than for other coinage metals, especially Ag<sup>I</sup>. Thus, for example, in the neutral [Cl–Au<sup>I</sup>–ethyne] complex,  $\pi$  back-donation is essentially as large as  $\sigma$  donation, which explains the otherwise surprising result that the net charge donation from the substrate is nearly vanishing. Therefore the view that attributes the remarkable catalytic properties of Au<sup>I</sup> in activating multiple C–C bonds to a small, or even negligible,  $\pi$  back-donation must be abandoned. In fact,  $\pi$  back-donation is seen to penetrate the external side of the coordinated substrate at which nucleophilic attack is directed, thus partially mitigating the electron depletion caused by  $\sigma$  donation.

Secondly, in stark contrast to the surprisingly stable  $\sigma$  donation component,  $\pi$  back-donation is a sensitive and tunable bond component. For example, in going from the neutral [Cl–Au<sup>I</sup>–ethyne] complex to the charged [nhc–Au<sup>I</sup>–ethyne]<sup>+</sup>, the CD profile of  $\sigma$  donation remains essentially identical, whereas  $\pi$  back-donation nearly halves. Similarly,  $\pi$  back-donation appears to be much more sensitive to structural (interdependent) factors such as metal–substrate distance and substrate rigidity towards deformation (carbon pyramidalization). However, our specific investigations have clearly shown that even a totally undistorted alkyne binds with a large  $\pi$  back-donation. Hence, a lack of carbon pyra-

midalization should not be taken as an indicator of a corresponding lack of back-donation.

In comparison with the other coinage metals, Ag<sup>I</sup> and Cu<sup>I</sup>, gold is shown to be a 30–50% better  $\sigma$  acceptor when coordinating to an alkyne. The  $\pi$  back-donation component, however, is correspondingly larger only with respect to Ag<sup>I</sup> complexes, whereas it is comparable to that of Cu<sup>I</sup> complexes. These differences may tentatively be related to the superior catalytic properties of Au<sup>I</sup> species in activating triple bonds, especially when compared with Ag<sup>I</sup>, but only a detailed theoretical study of their impact on actual reaction profiles will provide a deeper understanding of this issue. The results presented herein also indicate that the properties and structural changes in the coordinated alkyne are more sensitive to the choice of ancillary ligand, through the tuning of  $\pi$  back-donation, in the case of Au<sup>I</sup> than for the other metals.

Finally, our CD curve analysis has shown that most details of the Au<sup>I</sup>–substrate bond are essentially the same when an alkene is substituted for an alkyne. This conclusively supports the view previously put forward that the origin of the marked selectivity of gold in activating triple bonds better than double bonds must be sought in the reaction dynamics.

The tools presented in this work appear to be particularly powerful for understanding the electronic structure of Au<sup>I</sup> catalytic complexes in terms of common chemical concepts such as the DCD model. Extending these investigations may be useful to guide the tuning of the Au<sup>I</sup>–substrate bond properties through a suitable combination of steric and donor/acceptor properties of the ligands. A deeper understanding of the charge displacement accompanying the formation of these coordination bonds may further provide a key to understanding and modeling other observables such as NMR chemical shifts. Work in this direction is in progress.

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