A computational study of the effects of ancillary ligands on copper(I)–ethylene interaction

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A set of $[Cu^{(I)}L_n(C_2H_4)]^q$ (q = -1, 0, or 1) complexes modelling systems of experimental interest were studied by DFT calculations to analyze the $Cu^{(I)}$-ethylene bonding using NBO and CDA analyses. All complexes are better viewed as donor-acceptor complexes between a d^{10} $Cu^{(I)}$ center and ethylene. Back-donation depends significantly on the nature and number of the ancillary ligands, hence on the coordination sphere at copper. Back-donation is shown to vary more with the nature of the ligands than donation and to increase significantly with the number of ancillary ligands. However, even with strongly donating ligands such as alkyl (modelled by CH_3), there is no tendency of forming a metallacyclopropane. This can lead to reconsider the mechanisms of alkylation of olefin catalyzed by copper complexes.

Introduction

Formation of complexes between $Cu^{(I)}$ and unsaturated substrates S is essential in organic synthesis since it is postulated in numerous stoichiometric and catalytic reactions.[1-4] It is proposed to be essential for the activation and functionalization of unsaturated species. Alkene complexes have been isolated and structurally characterized.[5] A π-complex between the $Cu^{(I)}$ fragment and S can be described by the Dewar-Chatt-Duncanson (DCD) model, *i.e.* involving donation of the π-bond of the organic moiety to a vacant metal orbital and back-donation from an occupied metal orbital to a low-lying empty π* orbital of the substrate.[6] In the case of copper(I), which has a full d^{10} configuration, donation can only take place to the empty 4s and 4p orbitals of $Cu^{(I)}$, and thus essentially to the former since the 4p are higher in energy. Back-donation, which occurs from the highest occupied d orbital, delocalizes the metal density on the π* orbital of the substrate resulting, at the limit, in a formal oxidation of $Cu^{(I)}$ to $Cu^{(III)}$. The π-complex is then viewed as a metallacyclopropane.[7] As such, the interaction of a multiple bond with copper is commonly considered as an oxidative addition.[8] Early computational studies of the coordination of π ligands with $Cu^{(I)}$ species highlighted the formation of $Cu^{(III)}$ complexes on the basis of structural parameters of the Cu-CC moiety in a limited number of systems.[4,9-10] The formation of $Cu^{(III)}$ metallacyclopropane derivatives is also commonly considered when discussing experimental results, in particular for the reaction of alkylation of olefin catalyzed by copper complexes. Several analyses of the bonding scheme in specific $Cu^{(I)}$ complexes (with ethylene as substrate) were reported.[11-14] Nevertheless, no systematic study on a large panel of structures was reported.

In this work, we aim at evaluating in which cases and to which extend the coordination of $Cu^{(I)}$ to an unsaturated ligand can be considered as an oxidative addition. For this purpose, we consider a large representative set of Cu-ethylene complexes with different total charge, ancillary ligands and coordination spheres. Calculations of these complexes and systematic use of electron density analysis tools allow to better assign the bonding between Cu and the substrate. This study participates also to the need of developing a quantitative structure/property relationship for this family of complexes. This is the first attempt to build a ligand knowledge base for Cu complexes following previous studies for different metals and ligand sets.[15-19]

Results

Models. A set of twenty cationic, anionic or neutral ethylene Cu complexes, with monodentate or bidentate L- or X-type ligands (phosphine, carbene, alkyl or heteroalkyl, halide …) was selected (see Scheme 1 where ancillary ligands are organized according to charge). The study focuses on the interaction between ethylene and the Cu moieties. Complex **1**, in which ethylene is coordinated to a naked $Cu^{(I)}$ cation, is the simplest system. Generic ligands either neutral like PH_3 or monoanionic like CH_3, F, Cl, Br, OCH_3, and CN were selected. Related ligands of synthetic interest in catalytic copper chemistry were also used. N-heterocyclic carbenes (NHC) with unsaturated or saturated carbon backbones are introduced as in **2-3**, **13-14, 16-17** and **25-26**.[20] Complexes **2** and **3** carry the simplest NHC ligands. Complexes **16** and **17** are models of systems developed in catalytic asymmetric alkylation by Mauduit *et al.*[21] Complexes **13-14** and **25-26** are alkylated forms of **2-3** and **16-17**. These alkylated complexes are proposed as intermediate during the catalytic cycles.[22] Mono- and bi-phosphine ligands of experimental interest were considered: they include BINAP (**6**) (BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)[23] and DiPPAM (**18**) (DIPPAM: DiPhenylPhosphinoAzoMethinylate).[24] These complexes are also examined in their native and alkylated forms. The structure of these Cu-ethylene complexes was computed (see Computational details), the bond dissociation energy of ethylene from these complexes was determined, and several correlations between structural features and electronic properties (in particular associated with the electron density transfer between Cu and

ethylene) were analysed.
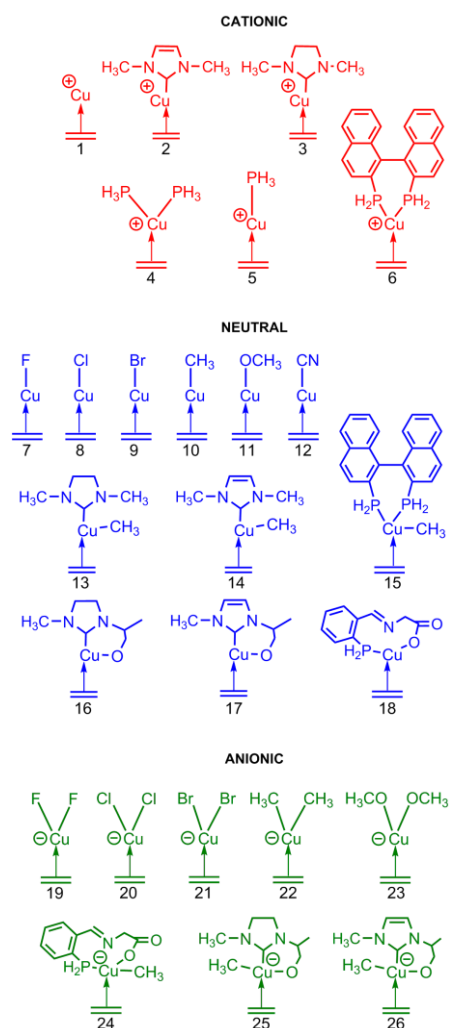
Scheme 1 Schematic representation of ethylene complexes (color code refers to the total charge of complexes. Red: cationic; Blue: neutral; Green: anionic).

Geometries. The geometry of the complexes shown in Scheme 1 was optimized and selected parameters, associated with the coordinated ethylene are shown in Table 1. We define <Cu-C> as the average of the two Cu-C distances and the average HHCC dihedral angle (180° in free ethylene and 120° in a pure sp^3 carbon) as a measure of the non planarity of coordinated ethylene.

The coordination mode at the metal (described by considering ethylene as a single ligand) depends on the denticity of the ancillary ligands (see Fig. 1). The n = 1 complexes have the expected structure with ethylene coordinated trans to L (the L-Cu-ethylene centroid angle is close to 180°). The n = 2 complexes have the two ancillary ligands, the metal and the two ethylene carbon atoms in a plane. This forms a trigonal planar geometry if ethylene is viewed as a single neutral ligand and a square planar geometry if ethylene is viewed as a bidentate X_2 ligand (Fig. 1, **22** and **16**). For n = 3, where a methyl group is always present, a

trigonal based pyramid is obtained (considering ethylene as a neutral ligand). In all cases, the ethylene and the CH_3 group occupy two basal sites while the apical site is occupied by the weakest σ-donor, namely the alcoholate arm (pointing toward the back in Fig. 1, in **25** and **26**), or the carboxylate arm (in **24**), or one of the two phosphines in **15** (thus leading to unequal Cu-phosphine distances (2.470 *vs* 2.304 Å).
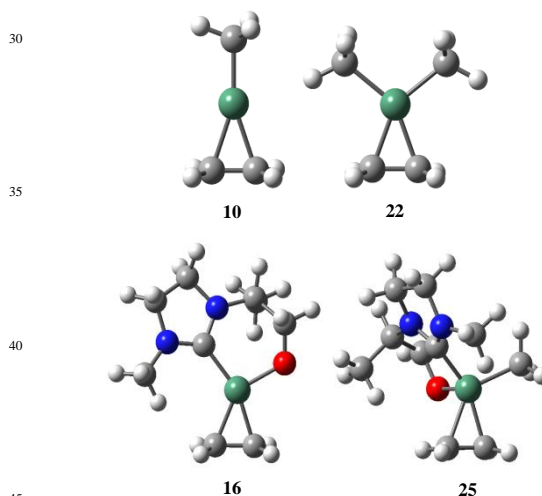

Fig. 1 Geometries of ethylene-Cu complexes depending on the denticity for n = 1 (**10**), n = 2 (**22** and **16**) and n = 3 (**25**).

The [Cu(C₂H₄)]⁺ complex has <Cu-C> and C=C bond distances of 2.045 and 1.395 Å, respectively, which agree with previous theoretical studies.[11,13,25] The calculated C=C bond distance of 1.388 Å in [CuCl(C₂H₄)] is also in good agreement with a recent theoretical and experimental study.[26] For the structures that have been considered, the C=C distances range from 1.375 Å in **3** (saturated NHC ligand) to 1.428 Å in [Cu(CH₃)₂(C₂H₄)]⁻ (**22**). Thus, as expected, the C=C bond distance is longer for all complexes than the value of 1.341 Å calculated at the same computational level in free ethylene.

Strong pyramidalization of the carbon of the ethylene ligand is characteristic of a metallacyclopropane. A study by Morokuma *et al.* [27] and an analysis by Uddin *et al.*[28] have used an alkene with steric strain to define a reference of a metallacyclopropane (Pt in their study). We thus selected complex **27** (Scheme 2) to complete the study. The calculated distance of 1.453 Å for the CC bond in **27**, which is longer that in all other complexes, can serve as upper limit, whereas full sp^3 hybridization is ensured by the strained pyramidalization (120° in **27**). In comparison, complexes **1-26** are significantly closer to planar ethylene, as evidenced in Fig. 1. This can be quantified by the HHCC dihedral angle averaged over the two ends of ethylene whose values vary from 169.8° to 158.3° for complexes **1-26**. A correct linear correlation (R^2 = 0.83) is obtained between the HHCC dihedral angle and the C=C bond elongation with small values of HHCC being associated with long CC bond (See Supporting Information).

Scheme 2 Schematic representation of the strained olefin complex to copper(I), used as a reference for metallacyclopropane.

The C=C distance depends on the total charge of the complex as already proposed by Frenking *et al.* for copper-acetylene complex.[25d] In the **1-26** set, the C=C bond distance of 1.382 Å obtained by averaging over the cationic complexes is shorter than that of 1.394 Å for the neutral complexes, which is itself shorter than that of 1.406 Å for the anionic systems. In others words the metallacycle character of the C=C coordination increases from cationic to anionic complexes. In contrast, there is no apparent correlation between the C=C bond distance and the denticity of the ancillary ligands. For instance, for the structures with n = 3, the average C=C bond distance is 1.397 Å. This value is smaller than that for n = 2 ligands (1.404 Å) but longer than that for n = 1 (1.383 Å). No trend involving the coordination number could be established.

In general, one considers that the Cu-C bond distance decreases when the C=C bond distance increases (from olefin complexes to metallacyclopropanes) if no other factor intervenes. In the present case, this correlation between the <Cu-C> and C=C bond distances is not simple. A rough correlation can be found for a set of ligands of a given denticity (see Supporting Information for graphical information), for which a given range of Cu-C bond distances is observed. Nevertheless, these ranges overlap and, for given denticity (see for instance n = 2), strong σ-donating groups like methyl or carbene (for instance complexes **13**, **14** and **22**) do not fit the behaviour of the other complexes as they lengthen the Cu-C bonds to which they are essentially transoid.

Energetics. The ethylene bond dissociation energy (D_e), the interaction energy (IE) and the deformation energy (Def which is the sum of the deformation energies of the two fragments [CuL$_n$] and ethylene) energies are given in Table 1 for all complexes. The bond dissociation energy D_e, calculated with respect to the energies of the relaxed fragments can be decomposed in the deformation energy (Def) and the interaction energy (IE). Def evaluates the energy cost to bring each fragment from its optimized structure as an isolated species to that in the complex. The interaction energy (IE) is that between fragments in the structures they have in the complexes. For convenience, we will usually discuss the absolute values of IE, |IE|, large absolute value of IE being associated with large stabilizing interaction energy. The bond dissociation energy is related to |IE| and Def as shown in eq 1 (all values being positive in this definition).

$$D_e = |IE| + Def \qquad (1)$$

The D_e energy of 45.6 kcal/mol calculated for [CuF(C$_2$H$_4$)] (**7**) is similar to the value of 38.6 kcal/mol, previously reported.[12] For n > 0 complexes, the bond dissociation energy ranges from 1.6 (**22**) to 45.6 kcal/mol (**7**). These values can be divided in three

groups determined by the total charge of the complex. The cationic complexes have D_e averaging at 43.9 kcal/mol for complexes (**2-6**). Neutral complexes have lower D_e averaging at 25.9 kcal/mol (**7-18**), and anionic complexes have the lowest D_e (averaging at 4.3 kcal/mol for **19-26**). This is in line with the important electrostatic contribution to the binding highlighted for [Cu(C$_2$H$_4$)]$^+$.[11]

The large range of D_e values is associated with a large range of deformation energy. Large Def energies are associated with small values of D_e. For instance, D_e of less than 10 kcal/mol (between 1.6 and 9.1 kcal/mol) is associated with Def larger than 18 kcal/mol (between 18.5 and 42.7 kcal/mol). Remarkably, Def for the [CuL$_n$] moiety can reach values as high as 32.9 kcal mol^{-1} (in **22**) while Def for ethylene varies over a more limited energy range (upper limit of 9.8 kcal mol^{-1} in **22**). Large deformation energies within the metal fragment has been mentioned previously for Cu$^{(I)}$ complexes.[29]

The range of the absolute values of IE, |IE|, is significantly smaller with values between 26.0 and 50.2 kcal/mol, for **24** and **7,** respectively (**1** and **27** are not included), compared with the corresponding ranges of values for D_e (3.9 to 45.6 kcal/mol). The largest value of |IE| (71.1 kcal/mol) in **27**, highlights the role of strain in increasing the interaction energy.[28]

Electronic properties. A tempting way to evaluate the "Cu$^{(III)}$" character of a complex would be to consider the charge on the copper centre (see Table 1). As expected, the charges on Cu are significantly less than the formal charge of +3. However, this is not a valid criteria since it is well recognized that "charges" and "oxidation state" have no reason to be identical.[31] Nevertheless, the computed charge on copper(I) atom is reported to be much less than +1,[4] while it may be just around +1 for Cu$^{(III)}$.[30] In the set of complexes of Scheme 1 the Natural Population analysis (NPA) charge at Cu ranges from 0.623 in **10** to 1.097 in **19**. The charge is 0.779 in **27,** which is viewed as a reference model for Cu$^{(III)}$ metallocyclopropane, and higher (0.871) in **1**, which has no ancillary ligand and no strain. Therefore, charge at Cu cannot be used as a significant reporter.

We next considered properties associated with the electron transfer between [CuL$_n$] and ethylene as analyzed by the Natural Bond Orbital (NBO) and the Charge Decomposition Analysis (CDA). The NBO analysis provides a description of chemical species in term of Lewis structures through covalent bonds and donor-acceptor interactions.[32] The NBO analysis of donation and back-donation, between phenanthroline copper complexes and ethylene was previously used.[13] The CDA method of Frenking *et al* constructs the wave function of the complex in term of linear combination of donor and acceptor orbitals (See computational details for further information). These two methods are currently used to analyze interactions between chemical fragments (here [CuL$_n$] and ethylene). They analyze the wave functions in different ways. In particular, NBO uses a localization procedure while CDA uses canonical orbitals. It is thus of interest to discuss the analogies and differences that emerge from these two methods.

Copper, which is a 3d transition metal has only its 4s orbital for establishing covalent bonding since its 3d shell is fully occupied and since its 4p shell is considered as unable to provide covalent

bonds as shown by Weinhold and Landis.[32] The NBO supports this proposal for all systems, **1-27**. The covalent bond with copper involves the ancillary ligands L (for n=1). For n = 2 and higher, the situation is slightly more complicated and the 4s orbital appears to be involved in donor-acceptor interactions with all ligands. The key point for this study is that in none of the complexes a covalent Cu-C bond is formed between the metal and ethylene, as it would be expected in a metallacyclopropane form. All complexes are formed by donor-acceptor interactions between neutral ethylene and a $[CuL_n]$ fragment carrying the total charge of the complex. This also means that in this donor (ethylene)-acceptor ($[CuL_n]$) interaction, the accepting orbitals on the metal side are the $\sigma^*(CuL)$ orbitals (ω bond following the NBO terminology).

The CDA analysis of these ethylene complexes carried out using ethylene and $[CuL_n]$ as fragments, provided the following terms: (i) the donation from ethylene to $[CuL_n]$ (term d in Table 2), (ii) the back-donation from $[CuL_n]$ to ethylene (term b in Table 2) (iii) the repulsion associated with the interaction between the occupied orbitals of the two fragments (term r in Table 2). The appropriateness of this analysis is established when the sum of these densities is equal to the total density and the residual term Δ, close to zero (See computational details for further details). Indeed, this residual term is small for the entire set **1-27**. This feature is a characteristic of species that can be viewed as donor-acceptor complexes.

NBO and CDA analyses confirm the Cu retains a d^{10} electronic structure in all complexes with a maximum of 0.7 e transferred to ethylene. They also consider that binding between ethylene and $[CuL_n]$ is of the type donor-acceptor and follows the Dewar-Chatt-Duncanson model.[28] This is even the binding description found for **27**, which is poorly compatible with a $Cu^{(III)}$ complex.

NBO results can be further analyzed by quantifying the electron population of ethylene π and π^* (Table 1). The NBO electron occupancies of the π orbital range from 1.733 e in **1** to 1.902 e in **26** indicating that 0.267 to 0.098 e are donated from π orbital to Cu fragment. These values are smaller than that in **27** for which the ethylene π gives 0.396 e. The complexes with phosphine ligands are associated with larger π-ethylene $\rightarrow$ Cu donation (0.152, 0.192, 0.155, and 0.127 e in **4**, **5**, **6** and **18**, respectively), which is consistent with an electron withdrawing behavior of these phosphine ligands. Back-donation into the ethylene π^* orbital, are fluctuating over a larger scale: 0.103 e in **5** and 0.652 in **22**. To be noted the electron occupancy of π^* in the strained olefin complex **27** is not the highest in the whole series as it would be expected if it was a metallacyclopropane. In fact, it has an intermediate value of 0.392 e. Back-donation thus appears to vary more (by a factor of 5) than donation (by a factor of less than 2) with the nature of the complex. This agrees with previous results that donation is less sensitive to ligand variation as shown on a series of ethylene copper complexes with polydentate ancillary ligands (bipyridine, …).[14] In general, back-donation is larger for the anionic systems (averaging around 0.457 e) than for the neutral and cationic systems (average value of 0.271 e). In contrast, donation is less influenced by the charge since the average value of 0.186 e for the cationic complexes is similar to that of 0.129 e for neutral and anionic systems.

Quantification of donation and back-donation is also a direct result obtained from CDA analysis (Table 2). CDA and NBO agree in the quantification of the back-donation part. A very good linear correlation ($R^2 = 0.94$) appears between back-donation computed with the CDA approach and the NBO π^* population (see Supporting Information for a graphical representation) except for complex **27**. This is due to the fact that the π^* of this strained olefin, is already partially occupied (0.138 e) in its non-coordinated state. An improved correlation is thus obtained when subtracting 0.138 e from the NBO π^* population. (Supporting Information).

The NBO and CDA analyses give somewhat different information on the amounts of donation. The NBO analysis showed that donation and back-donation are rather comparable in magnitude and that often the back-donation dominates (such as in **11**, **13-18** and **19-26**). This is not the information provided by CDA, which indicates that donation dominates significantly over donation. Ratio d/b which is higher ≥ 4 for **1-5**, decreases to around 2 for many complexes and is not smaller than 1.4 (set **22-26**). These differences are most likely due to the different manners in calculating the electron transfer from either localized or canonical orbitals and may be also from the different methodologies used for calculating the density (DFT *vs* MP2, see Computational details). These differences also involve the nature of the donating orbitals. Thus, while the DCD model usually considers that only the ethylene π orbital donates electron density in the interaction with $[CuL_n]$ fragment, CDA involves also the C=C σ bond in the donation. In fact, the CDA analysis for **10** shows that 50% of the donation is associated with the π orbital, 36% with the σ orbital (Fig. 2) and the 14% is spread over other ethylene orbitals. The NBO analysis does not indicate any donation of density from the σ orbital of ethylene, which remains fully occupied in all complexes. Since the orbitals are not defined in the same manner in the two methods, the electron transfers calculated by the two methods have no reasons to be identical and it is not possible to go further in this analysis.

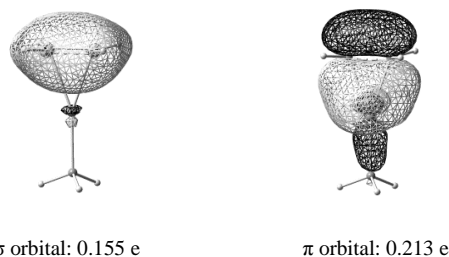

σ orbital: 0.155 e   π orbital: 0.213 e

Fig. 2 Donating orbitals (left, σ CC orbital, and right π CC orbital) according to the CDA analysis for complex **10**.

Table 2 Charge Decomposition Analysis (d: donation, b:back-donation, b/d ratio, r: repulsive part, Δ: residual term) for olefin complexes.

Entry	d	b	d/b	r	Δ

1	0.479	0.037	12.95	-0.095	-0.038
2	0.457	0.056	8.20	-0 .124	-0.033
3	0.456	0.048	9.5	-0.120	-0.031
4	0.451	0.094	4.80	-0.226	-0.021
5	0.446	0.033	13.52	-0.107	-0.035
6	0.443	0.123	3.60	-0.233	-0.026
7	0.468	0.168	2.79	-0.157	-0.034
8	0.458	0.109	4.20	-0.171	-0.025
9	0.455	0.103	4.42	-0.172	-0.023
10	0.427	0.082	5.21	-0.236	-0.013
11	0.476	0.168	2.83	-0.186	-0.028
12	0.422	0.075	5.63	-0.151	-0.024
13	0.459	0.259	1.77	-0.337	0.013
14	0.452	0.253	1.79	-0.340	0.015
15	0.432	0.207	2.09	-0.345	0.001
16	0.468	0.228	2.05	-0.281	-0.007
17	0.468	0.232	2.02	-0.277	-0.007
18	0.424	0.182	2.33	-0.261	-0.013
19	0.421	0.236	1.78	-0.267	0.005
20	0.397	0.170	2.34	-0.352	0.008
21	0.395	0.153	2.58	-0.369	0.005
22	0.437	0.293	1.49	-0.438	0.0371
23	0.464	0.267	1.74	-0.293	0.020
24	0.392	0.210	1.87	-0.405	0.012
25	0.355	0.250	1.42	-0.391	0.020
26	0.357	0.251	1.42	-0.406	0.023
27	0.555	0.079	7.03	-0.133	-0.036

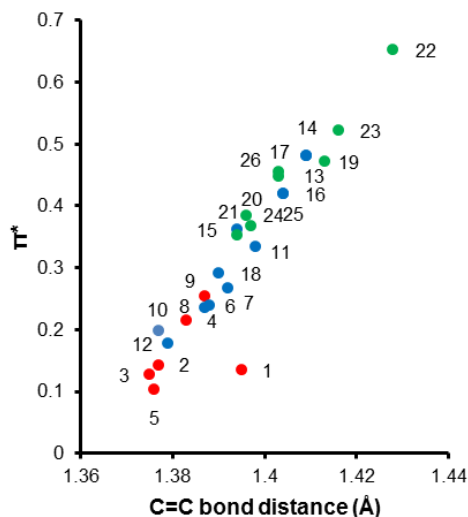**Fig. 3** Cu → Ethylene back-donation (NBO electron occupancy of ethylene π*) for **1-26** as a function of the C=C bond distance (Å) (the color code refers to the total charge of the complex. Red: cationic, Blue: neutral, Green: anionic).

Correlations. In donor-acceptor complexes, one expects a relation between the amount of electron transfers and the energetics of the complexes. However, the sum of donation and back-donation transfers was thus plotted as a function of D_e, IE and Def, indicating the absence of any correlation (Supporting Information). No better correlations were found using the amount of charge transfer associated with back-donation (selected because it varies the most within the set **1-27**). The same result applies to the amount of donation. This generalizes the proposal that the ethylene dissociation energy, D_e, is not a measure of the Cu-C covalent interactions resulting from the donation and back-donation transfers.[33] The electrostatic interaction between the metal fragment and ethylene appears an important factor, regardless of the total charge, even for the anionic systems.

The geometrical features appear to be correlated with the electron transfer between the two fragments. A good linear correlation (R^2 = 0.90) is found between back-donation and the C=C bond distance (Fig. 3). However, no correlation between the amount of donation and the C-C bond distance could be found (Supporting Information). Thus, in these complexes where the variation back-donation is important, the geometrical features of the coordinated ligand appear to depend more on the latter. This trend is often thought to apply to the coordination of unsaturated ligands to transition-metal complexes.[7]

Discussion

In Figure 3, the color code highlights that the complexes somewhat gather as function of their charge. All cationic complexes appear in the lower left corner (*i.e.* short CC distance and low back-donation, red in Fig. 3) whereas the anionic complexes are more on the upper right corner of the figure (medium to long CC distance and medium to large back-donation, green in Fig. 3) and spread over a larger range of values since the nature and denticity of the ancillary ligands are rather diverse. The neutral complexes appear to overlap and bridge the charged species, being spread over nearly the whole range of values (short to medium CC bond distances and small to medium back-donation, blue in Fig. 3).

Influence of the basicity of the X-type ligands. Computational studies for copper-(κ^2-phenanthroline) complexes highlighted that Cu→ethylene back-donation increases with the basicity of ancillary ligand.[13] This led us to consider this argument for our set of complexes. Basicity increases in the order halide < OCH_3 < alkyl. This argument accounts for the trends in the anionic complexes **19-23**. The metal orbital, which is involved in the back-donation, is σ-antibonding with the 2 X ligands (Fig. 4 left) and is thus hybridized towards the ethylene ligand and raised in energy with increasingly good donor (halide, alkoxy, alkyl).[34]

In contrast, the mono-ligated complexes (**7-12**) follow another trend since, according to the electron occupation of π* ethylene, the best donor is the alkoxy, the least are the alkyl and CN groups, the halide groups being intermediate. The nature of the d orbital involving in the back-donation (Fig. 4 right) rationalizes this trend. The orbital is σ-non-bonding but is π-anti-bonding with the lone pairs of the X group (and thus with the alkoxy or the halide). This creates a 4-electron repulsion between X and the d occupied which is known to increase the back-donation.[35] The alkoxy group appears to be a better π donor (probably good overlap associated with short distances and rather compact orbitals) than a halide, which accounts for the trend in this set. However, the amount of back-donation calculated for any member of the **7-12** set is not sufficient (<<1 electron) to justify a denomination of metallacyclopropane in contrast with the proposal to consider to [Cu(F)(C_2H_4)] as metallacycle.[12]
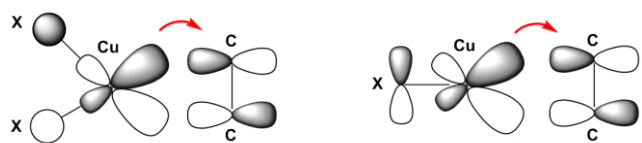
Fig. 4 Cu$^{(I)}$ d orbital involved in back-donation to ethylene (left) CuX$_2$, σ-antibonding with X, (right) CuX, π-antibonding with lone pair of X.

NHC and phosphine ligands. NHC and phosphine ligands are ubiquitous in Cu complexes. For such ligands, electron-donating power has been evaluated using either CO stretching frequency in [LNi(CO)$_3$][15] or experimentally by pK$_a$ measurement.[36] NHC ligands are imidazolylidene with an unsaturated aromatic backbone or imidazolidinylidene with a saturated backbone. These two ligands, which have similar electron-donating capability are slightly better electron donor than phosphine, but the difference is in total modest since the CO stretching frequencies in [LNi(CO)$_3$] are 30 cm^{-1} lower for NHC.[15]

In line with these studies, the two prototype NHC ligands, **2** and **3** (unsaturated and saturated NHC, respectively) lead to similar back-bonding and C-C bond length. The results are also similar in the presence of an additional chelating alkoxy-arm (**16** and **17**). Comparing NHC and phosphine ligands in cationic complexes **2** and **3** and **5** (PH$_3$), the amounts of back-donation and the C-C bond distances are similar although marginally higher for NHC ligands.

Changing mono to di-coordination for phosphines (**5** and **4**, respectively) essentially double the back-donation (Table 1). The reason has been already presented in Figure 4 where back-donation is shown to be always larger with two ancillary ligands. Complexes **4** and **6** address the influence of a chelating binaphtyl ligand simplified by replacing the phenyl substituent on phosphorus by hydrogen atoms. The present calculations, which give very similar results for the amount of back-donation and C-C bond distances, suggest that two monodentate phosphine and the chelating BINAP lead to similar Cu-ethylene complex. One should however not conclude that these two complexes would behave in similar ways in the catalytic reactions involving systems like **4** and **6**.

Another way to increase the coordination number at copper is illustrated in the (**2**, **3**) and (**16**, **17**) set. The two first complexes are monodentate NHC ethylene complexes while the two latter have an additional alkoxy arm. For the same reasons as before, the back-donation is larger (by about a factor of 2.5) in (**16**, **17**) than in (**2**, **3**). To be noted the coordination of an anionic ligand to form a neutral complex (**16** or **17**) from a cationic reactant (**2** or **3**) increases more the back-donation than adding a neutral ligand that does not modify the total charge (compare **5** and **4**).

Furthermore, as could be expected, coordination of a stabilized anion ligand like the carboxylate in the DiPPAM complex **18** increases much less the back-donation (compare **5** to **18**).

Additional alkyl groups. Copper catalysts are often used to assist the alkylation of unsaturated species. The formation of π alkene-[CuL$_n$(Alkyl)] complexes has been established as reactive intermediate[9] and complexes like **15**, **25-26** can illustrate situations in a number of experiments.[37] The effect of the alkyl group on the electronic properties of the π ethylene complex was thus studied with different ancillary ligands.

The alkyl group (modelled by CH$_3$) was thus added to [CuL$_n$(C$_2$H$_4$)] in which L is either a monodentate (n = 1) (**10** to **22**, [**2**, **3**] to [**13**, **14**]) or a bidentate ligand (n = 2) (**6** to **15**, **18** to **24**, [**16**, **17**] to [**25**, **26**]) (see values and notations in Fig 5). For n = 1, the methyl group added to [CuL(C$_2$H$_4$)] increases significantly the back-donation by about 0.4 e (**[2-3]** to **[13-14]** and **10** to **22** in Fig. 5). This can be associated to the favourable orbital arrangement already presented in Figure 4. Upon coordination of CH$_3$, the d orbital involved in back-donation goes from being non-bonded with a single ligand to be σ-antibonding with the 2 X ligands. The energy increase associated to this anti-bonding interaction is especially efficient as two very good donor ligands (CH$_3$ and NHC) are concerned.

The situation is different when the methyl group is added to a complex, which has already two ancillary ligands (n = 2). In this case, the 4-coordinated complex (counting always ethylene as a single ligand) takes the shape of a trigonal pyramid. The CH$_3$, the strongest electron-donor, is in the basal plane and the weakest is at the apical position, as described in the Geometries Section. The apical ligand, whose distance to Cu is rather long, has no overlap with the d orbital that is involved in the back-donation and its influence is thus indirect (Fig. 5). The increase in back-donation is thus essentially associated to the exchange of the weak donor by a better one (CH$_3$) and thus significantly smaller (< 0.11 e) than the direct effect seen in the monodentate case.

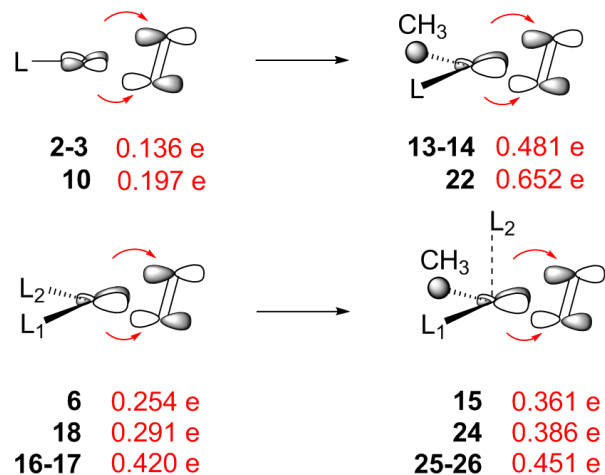|			
2-3	0.136 e	**13-14**	0.481 e
10	0.197 e	**22**	0.652 e
6	0.254 e	**15**	0.361 e
18	0.291 e	**24**	0.386 e
16-17	0.420 e	**25-26**	0.451 e

Fig. 5 Effect of additional alkyl group on the back-donation: in the case of monodentate (Me (**10** and **22**) and NHC ([**2,3**] and [**13,14**])) and bidentate ligands (BINAP, (**6,15**), DiPPAM, (**18**, **24**) alkoxy-NHC [**16,17**] and [**25,26**]). The [a, b] notation refers to the average values for the two complexes.

Conclusions

In this article, we considered a set of ethylene complexes that are representative of possible intermediates in the reaction of alkylation of olefin catalyzed by Cu$^{(I)}$ complexes. The set included model species similar to those that could occur in the experiments. Cationic, neutral and anionic complexes with ligands of variable donor strength and denticity were considered. Geometry optimization shows how the ethylene is oriented

relative to the ancillary ligands. For $[CuL(C_2H_4)]^q$, the ethylene ligand is trans to L. For $[Cu(L)_2(C_2H_4)]$ a planar structure is obtained. This can viewed as a 4-coordinated d^8 square planar complex in which the olefin has been reduced as X_2 ligand ($(C_2H_4)^{2-}$) and $Cu^{(I)}$ oxidized to $Cu^{(III)}$. Nevertheless, the computational analyses with NBO and CDA of the electronic structure of these complexes indicates that ethylene is bonded as a donor-acceptor ligand to a d^{10} $Cu^{(I)}$ metal in all cases. In no case these complexes appear as $Cu^{(III)}$ metallacyclopropane. The amount of donation and especially back-donation depends the nature of the ancillary ligands and most on the coordination of the complex determined by the number of ancillary ligands. In particular, the amount of back-donation in an ethylene complex with one ancillary ligand to form a linear $[CuL(C_2H_4)]$ complex, is modest even for ligands that are good electron donors. It is enhanced by the presence of lone pairs on the ancillary ligands so that alkoxy groups behave as a better donor than alkyl groups. With two ancillary ligands, the ethylene complex has a trigonal planar geometry, considering the ethylene as a single ligand. The back-donation is considerably larger with two ancillary ligands compared to one. It is controlled by the traditional trans influence so that an alkyl is a better donor than an alkoxy ligand. For three ancillary ligands, the ethylene complex is a trigonal pyramid with the weakest donor at the apical site. Calculations reveal that the back-donation in the trigonal pyramid is similar to that in the trigonal planar complex since the apical ligand does not interact with the d orbital involved in the back-donation. This information can be of importance to understand the behaviour of copper catalysts in the alkylation of unsaturated ligands.

Computational details

The calculations were carried out with the Gaussian09 package,[38] using the Density Functional Theory (DFT) with the exchange-correlation functional of Perdew and Wang, PW91.[39] Cu was represented with a quasi-Relativistic Effective Pseudopotential (RECP) from Stuttgart group[40] and the associated basis set augmented by an f polarization function.[41] A 6-31++G(d,p) basis set was used for all other atoms (H, C, N, O, F, P, Cl, Br).[42] The geometry optimizations were performed without any constraint and the nature of the minima were verified by analytical calculations of frequencies.

To select the functional, test calculations were carried out using $[Cu(tme)(C_2H_4)]^+$ whose solid state structure is known.[43] Calculations carried out with PW91,[39] B3LYP,[44] B3PW91,[44a,45] M06,[46] and PBE[47] indicated that PW91 gave the best compromise for all geometrical parameters (Supporting Information).

The bonding interaction between the metal moiety $[CuL_n]$ and the ethylene fragment was analyzed with the bond dissociation energy D_e defining as the energy difference between the complex $[CuL_n(C_2H_4)]$ and the two monomers $[CuL_n]$ and C_2H_4 separated at infinite distance in their electronic ground states and optimized geometry. The deformation energy Def is determined for each fragment, $[CuL_n]$ and C_2H_4, as the energy difference between their equilibrium structure and the geometries they have in the complex $[CuL_n(C_2H_4)]$. The interaction energy (IE) is the difference between the energy of the complex and the energies of the two fragments at the geometry they have within the complex. The bond dissociation energy, D_e, is the sum of IE and Def. For complexes 1 and 27, for which one of the fragment is a Cu^+ cation, MP2 – BSSE corrected values for IE were used and reported in Table 1 and not the De values, which we believe to be strongly biased.

The Natural Population Analysis (NPA) was used to evaluate the natural atomic charge of Cu.[48] The electronic properties of C=C bonding in the complexes were analyzed using the Natural Bond Orbital (NBO) method[49] which allows a description of the bonding in terms of Ethylene → Cu π-donation and Cu → Ethylene π-back-donation. All calculations were carried out with NBO-06 package[50] on the DFT optimized geometry.

Charge Decomposition Analysis (CDA) was used as described in the literature[51] considering that $[CuL_n(C_2H_4)]$ is formed of the union of two fragments $[CuL_n]$ and C_2H_4 (in the geometry they have in the complex). The wave function of a complex $[CuL_n(C_2H_4)]$ is expressed as a linear combination of the fragment molecular orbitals (MOs) of the ligand C_2H_4 and the metal fragment $[CuL_n]$. The orbital contributions of the fragments to wave function of the complex are divided into four parts: (i) mixing of the occupied MOs of C_2H_4 and the unoccupied MOs of $[CuL_n]$ (donation d); (ii) mixing of the unoccupied MOs of C_2H_4 and the occupied MOs of $[CuL_n]$ (back-donation b); (iii) mixing of the occupied MOs of C_2H_4 and of $[CuL_n]$ (repulsive polarization r) and (iv) mixing of the unoccupied MOs of C_2H_4 and of $[CuL_n]$ (residual term Δ).[52] This last term must to be ≈ 0 for donor-acceptor complexes otherwise the interaction between ethylene and $[CuL_n]$ is described as a covalent interaction. Calculations of CDA used MP2[53] level with the 6-31G(d,p) basis set for all atom.[42] Cu was represented at the same level as in the DFT calculations. All structures were optimized at the MP2 level and found to be very similar to that obtained with PW91.

Acknowledgments

Notes and references

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† Electronic Supplementary Information (ESI) available: Additional FIGURES showing various correlations. Cartesian coordinates and energies (E in a. u.) of all reported structures. See DOI: 10.1039/b000000x/

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TOC

Structural and electronic calculations on a ligand database are used to quantify the influence of the ancillary ligands and

coordinated mode on the electronic structure of Cu(I) ethylene complexes.
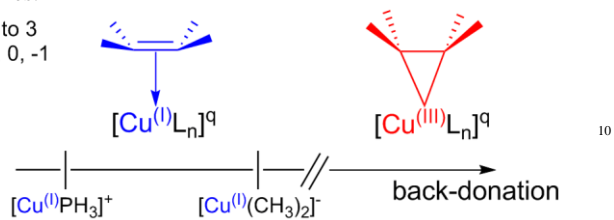
Table 1: Selected (C=C and <Cu-C>) bond distances (Å), <odp> angles (°), bond dissociation (D_e), deformation (Def) and interaction (IE) energies (kcal/mol), natural atomic charge (q_{Cu}) and electron occupancies of C_2H_4 (π and π^*) from NBO analysis (n refers to denticity and q to formal charge of complexes).

Entry	q	n	C=C	<Cu-C>	<opd>[c]	D_e	Def	IE	q_{Cu}	C₂H₄ (π)	C₂H₄ (π*)
Free ethylene			1.341		180.0					1.996	0.003
1	1	0	1.395	2.0445	167.3			-43.7[a]	0.871	1.733	0.135
2	1	1	1.377	2.089	169.2	39.4	3.7	-43.1	0.659	1.825	0.143
3	1	1	1.375	2.099	169.4	38.2	3.6	-41.8	0.657	1.828	0.128
4	1	2	1.383	2.111	166.0	19.1	18.7	-37.8	0.696	1.848	0.215
5	1	1	1.376	2.1055	169.8	43.3	3.6	-47.0	0.638	1.806	0.103
6	1	2	1.387	2.081	165.6	28.5	9.7	-38.2	0.707	1.845	0.254
7	0	1	1.392	2.004	165.7	45.6	4.7	-50.2	0.893	1.828	0.267
8	0	1	1.388	2.029	167.1	40.3	4.2	-44.5	0.754	1.833	0.238
9	0	1	1.387	2.035	167.3	38.9	4.1	-43	0.711	1.836	0.236
10	0	1	1.377	2.0935	169.6	24.0	3.8	-27.8	0.623	1.863	0.197
11	0	1	1.398	2.0005	164.4	41.4	7.0	-48.4	0.859	1.825	0.334
12	0	1	1.379	2.069	169.4	35.6	3.6	-39.1	0.683	1.850	0.178
13	0	2	1.409	2.041	161.0	4.1	33.5	-37.6	0.870	1.868	0.480
14	0	2	1.409	2.044	160.5	3.0	34.2	-37.2	0.864	1.872	0.482
15	0	3	1.394	2.1165	164.6	9.1	18.5	-27.6	0.805	1.885	0.361
16	0	2	1.404	2.0205	162.4	28.6	14.5	-43.1	0.944	1.870	0.419
17	0	2	1.404	2.0185	162.3	29.5	14.2	-43.7	0.941	1.870	0.420
18	0	3	1.390	2.0615	166.7	10.6	22.5	-33.1	0.880	1.873	0.291
19	-1	2	1.413	1.982	163.1	3.9	36.9	-40.8	1.097	1.890	0.471
20	-1	2	1.397	2.040	167.9	3.2	25.4	-28.6	0.875	1.897	0.367
21	-1	2	1.394	2.056	168.5	4.0	22.8	-26.8	0.809	1.898	0.352
22	-1	2	1.428	2.0185	158.3	1.6	42.7	-44.3	0.893	1.889	0.652
23	-1	2	1.416	1.985	161.0	4.0	39.4	-43.4	1.037	1.883	0.523
24	-1	3	1.396	2.1045	166.6	3.9	22.1	-26.0	0.890	1.898	0.386
25	-1	3	1.403	2.076	165.3	8.6	23.2	-31.7	0.970	1.899	0.448
26	-1	3	1.403	2.0765	164.6	5.5	26.3	-31.8	0.960	1.902	0.455
Strained C=C			1.375		121.3[b]					1.911	0.138
27	1	0	1.453	2.015	120.0[b]			-71.1[a]	0.779	1.604	0.392

[a] MP2-BSSE corrected values, see Computational Details. [b] C-C-C angles in degrees. [c] out-of-plane displacement, evaluated as the average of the HHC=C angle at the two ends of the ethylene.

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