Lewis Base Activation of Lewis Acid: A Detailed Bond Analysis

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Supporting Information

ABSTRACT: The effect of a Lewis base (LB) on the nucleophilic attack on chalcogeniranium (chalcogen = sulfur and selenium) cations, the so-called LB activation of a Lewis acid, has been studied coupling natural orbital for chemical valence decomposition of the orbital interaction energy with charge displacement analysis. This methodology provides a detailed and accurate description of all the interactions (LB-..chalcogen, chalcogen-..olefin and olefin-..ammonia) present in the system and leads to a deeper understanding of how they influence each other at all stages of the reaction: reactant complex, transition state, and product complex. In particular, the bond between the chalcogen and the olefin has been decomposed in terms of σ donation/π back-donation and the bond components quantified. This allowed determination of a linear relationship between the activation barrier of the nucleophilic attack and the net amount of charge donated by the olefin to the chalcogen.

INTRODUCTION

The interaction between a cationic ChR+ (Ch = S or Se) moiety and an unsaturated CC bond has been studied since 1950s,1,2 when the addition of PhChCl to polar and nonpolar alkenes was discovered. Such Lewis acids (LAs), called thiranium and seleniranium ions, are important intermediates in many chemical processes3−5 and have been isolated and characterized by NMR spectroscopy6−8 and, in some cases, by X-ray diffractometry.9 The interaction of selenium with an olefin has been often rationalized in terms of the Dewar−Chatt−Duncanson framework,15,16 with M ← olefin σ donation corresponding to the interaction between the olefin π system and an empty Se p orbital (or a σ* Ch−X orbital for RChX) and the M → olefin π back-donation being the model for interaction between a chalcogen π lone pair and the olefin π* orbital (Scheme 1).17 The back-donation concept has been recently applied also to selenium in selenoureas18 and phosphine chalcogenides.19

In particular, the Se ← olefin σ donation makes the olefin electron-poor and suitable for a nucleophilic attack.1 It has been recently observed that the presence of a Lewis base (LB), generally soft and in many cases containing another chalcogen as, for example, R3PCh (Ch = oxygen, sulfur or selenium), strongly increases the rate and the yield of the nucleophilic attack (LB activation of LA, LBLA).20,21 Even more importantly, if the LB is chiral it can induce excellent stereoselectivity to the entire process.22−24 The explanation for the stereoselectivity relies on the strong bond between the LA and the LB and the stability of the chalcogen−olefin interaction, which makes the configuration of the transition state (TS) stable enough to allow an efficient transmission of the chiral information.

Scheme 1. Orbital Interactions between the RSe+ Moiety and an Olefin

A theoretical analysis of the LBLA effect20,25,26 concluded that, despite the LB → LA donation of electron density, the electrophilicity of LA increases because of the increase of the coordination number and the redistribution of the charge to peripheral atoms bound to the electrophilic center (spillover effect27).

The recently introduced charge displacement (CD) function analysis28 allows an extremely detailed description of the metal−ligand coordinative bonds29 and an elegant rationalization of some experimental properties of complexes, such as the infrared spectrum of a coordinated carbonyl ligand,30−32 the rotational barrier33 and the geometrical arrangement34 of acyclic carbenes, and the 13C NMR chemical shift of cyclic...
systems. If the adduct shows enough elements of symmetry, the bond components can be decomposed according to their irreducible representations, otherwise an effective decomposition can be achieved according to the natural orbitals for chemical valence (NOCV) framework.37

Given the similarity between the seleniranium cation and a transition metal complex, it is interesting to apply such methodology to the adduct depicted in Scheme 2, as the CD methodology has already been shown to give reliable results for chalcogen-bonded adducts. Because in this case the adduct does not show any symmetry, the bond contributions will be decomposed through the NOCV method: the analysis of the electron density deformation (Δρ ′ maps) allows visualization for each contribution of the regions in which the electron density decreases or increases upon adduct formation and hence the electronic fluxes between the two fragments. These fluxes can be quantified by integrating the Δρ ′ functions (CD functions), obtaining both the direction of the flux and its intensity.

In this “proof of concept” paper, the chemical system has been reduced to a minimal model, containing all the elements of the real process (a base, a chalcogeniranium cation, and a nucleophile), in order to easily vary the nature of the LB and LA and follow evolution of the reaction for each combination.

In this framework, the association energy (E_int), which is the difference of electronic energy between the adduct and the relaxed fragments (the olefin and the [PhSe]+ cation), is −57.6 kcal/mol. According to the EDA (see Theoretical Details), E_int can be decomposed into the interaction energy, E_int, which is the difference of energy between the adduct and the unrelaxed fragments (−75.8 kcal/mol), and the deformation energy, E_int, which is the energy needed to distort the fragment from their relaxed geometry to the geometry they assume in the adduct (18.2 kcal/mol). E_int in Table 1 can be further decomposed in the following components: orbital (E_orb), steric (E_st), and dispersion (E_disp) energies, −222.9, 152.6, and −5.3 kcal/mol, respectively (Table 1). It is evident that the bond between the selenium and the olefin is quite strong and dominated by the orbital contribution.

More information can be derived from the decomposition of E_int in the natural orbital for chemical valence (NOCV)

Table 1. EDA for Selected Systems (The Complete List Can Be Found in the Supporting Information): Interaction Energy (E_int), Orbital Energy (E_orb), Steric Energy (E_st), and Dispersion Contribution (EDisp)

| system | fragments | E_int | E_orb | E_st | EDisp |
|--------|-----------|-------|-------|------|-------|
| Se1    | [PhSe]−...-[C2H4] | −75.8 | −222.9 | 152.6 | −5.3 |
| Se1_RC | [PhSe]−...-[C2H5(NH3)] | −93.0 | −199.3 | 112.0 | −5.5 |
| Se1_TS | [PhSe]−...-[C2H5(NH3)] | −97.7 | −191.5 | 101.9 | −5.5 |
| Se1_PC | [PhSe]−...-[C2H5(NH3)] | −125.8 | −222.2 | 89.9 | −5.3 |
| OSe1_RC | [Ph(O)−[PhSe]−...-[C2H5(NH3)] | −17.2 | −14.1 | 4.2 | −7.3 |
| OSe1_TS | [Ph(O)−[PhSe]−...-[C2H5(NH3)] | −75.6 | −189.4 | 119.9 | −5.8 |
| OSe1_PC | [Ph(O)−[PhSe]−...-][NH3] | −8.7 | −4.7 | −2.2 | −1.7 |
| SSe1_RC | [Ph(O)−[PhSe]−...-[C2H5(NH3)] | −82.3 | −167.3 | 91.1 | −5.9 |
| SeSe1_RC | [Ph(O)−[PhSe]−...-[C2H5(NH3)] | −125.5 | −198.6 | 79.4 | −6.4 |
| S1     | [PhSe]−...-[C2H4] | −83.2 | −299.1 | 221.3 | −5.1 |

*All values are in kcal/mol.

Results and Discussion

The first system discussed is the seleniranium cation, [PhSe(C2H5)]+ (Se1). The latter can be considered as an olefin “coordinated” through its π system on a cationic selenium, which is bound only to one substituent (the phenyl group). According to the NBO analysis, such a resonance structure counts for the 6.2%, whereas the most important one is obviously the one in which the selenium has a single bond with each carbon of the olefin and the C−C bond of the latter is single (79.0%). Nonetheless, the chosen fragmentation of the system is useful to analyze the electronic rearrangement upon the formation of the Se···C=C bond.

In this framework, the dissociation energy (E_diss) is −5.3 kcal/mol.

More information can be derived from the decomposition of E_int in the natural orbital for chemical valence (NOCV)
framework.\textsuperscript{38} Such a decomposition leads to a series of $\Delta \rho_i^k$ functions, which are essentially density difference maps (red = depletion, blue = accumulation) between a specific NOCV pair (see Theoretical Details). Generally, only a few functions ($k < 4$) are enough to completely characterize the interaction.

In the case of Se1 and using the same fragmentation scheme used for the EDA, $\Delta \rho_i^k$ describes the formation of the two C-Se bonds, with depletion regions at the $\pi$ system of the olefin and accumulation regions at the Se atom. The phenyl ring is the recipient is the $\sigma$ function, which are essentially density difference maps (red = depletion, blue = accumulation) between a specific NOCV pair (see Figure 1a). The energy associated with $\Delta \rho_i^k (\Delta E_0)$ is a large part of the total orbital energy $E_{\text{orb}} = -142.3$ out of $-222.9 \text{ kcal/mol}$ (64%).

![Figure 1](image.png)

Figure 1. (a) Isodensity surfaces ($\pm 0.007 \text{ e/au}$) for the most relevant $\Delta \rho_i^k$ ($k = 0$–$3$) for the [PhSe]$^+$–[C$_2$H$_4$] bond in Se1. Blue and red regions indicate accumulation and depletion of electron density, respectively. (b) Total CD curve and its most relevant CD components. Black dots indicate the $z$ position of the atomic nuclei. A yellow vertical band indicates the boundary between the fragments.

On the other hand, $\Delta \rho_i^0$ describes a flux from the selenium to the olefin. Analysis of the shape of the regions demonstrates that the source of the electron density (red-colored depletion regions in Figure 1a) is the filled $p_z$ orbital of the selenium and the recipient is the $\pi^*$ orbital of the olefin. This component could be called “back-donation” if a transition metal were present instead of the selenium, and indeed, the back-donation concept has been occasionally invoked in chalcogen chemistry.\textsuperscript{17–19} The energy associated with $\Delta \rho_i^0$ is smaller than $\Delta E_0$, but still significant, $-53.5 \text{ kcal/mol}$.

Finally, $\Delta \rho_i^2$ and $\Delta \rho_i^3$ describe very weak components, in which the two fragments are electrostatically polarized.

Such components can be quantified through the integration of the $\Delta \rho_i^k$ functions along the $z$ axis (defined as the axis passing through the selenium and the middle point of the double C=C bond), using the CD methodology,\textsuperscript{28} obtaining the corresponding CD$_k$ functions. The value of the CD$_k$ function at the isodensity boundary\textsuperscript{36} between the two fragments is called CT$_k$, and expresses, in electrons, the charge transfer associated with the $k$th bond contribution. For Se1, CT$_k$ values are $0.733, -0.435, 0.003$, and $-0.002$ for $k$ going from 0 to 3, respectively. These numbers are consistent with the qualitative picture presented above: $k = 0$ and 1 have opposite signs because the direction of the flux is opposite, $k = 2$ and 3 have no practical impact on the chemical bond, and the energy associated with each contribution ($\Delta E_0 = -142.3$ and $-3.3 \text{ kcal/mol}$ for $k = 0$ and 4, respectively, see Supporting Information). The total charge transfer from the olefin to the selenium cationic moiety is $0.303 \text{ e.}$

![Figure 2](image.png)

Figure 2. (a) Energy profile for the reaction Se1RC $\rightarrow$ Se1PC; (b) optimized geometries for Se1RC, Se1TS, and Se1PC.

It is important to note here that this CD analysis has been shown to be very stable with respect to the choice of exchange-correlation functional approximation used.\textsuperscript{34} Also in the present case, we find that the use of a hybrid functional instead of a generalized gradient approximation (GGA) one does not significantly change the results (Supporting Information).

Se1 can now be attacked by a nucleophile, such as NH$_3$, to form the product, [PhSeCH$_2$CH$_2$NH$_3$]$^+$ (Se1PC, Figure 2). Generally, the nucleophile loses a proton after the attack, which in this case would give a selenoether with a $\gamma$-amino functionality, and the proton is taken by the ammonia from the seleniranium cation. As the first step of the reaction, Se1 and NH$_3$ form a stable complex (Se1RC) in which the ammonia is still far from the olefin ($\text{C}1$–$\text{N}$ distance $= 2.357 \text{ Å}$), but already close enough to induce an asymmetry in the two Se–C bonds, which are Se–C1 $= 2.294$ and Se–C2 $= 2.016 \text{ Å}, \Delta d = d(\text{Se–C}1) - d(\text{Se–C}2) = 0.278 \text{ Å}$ for Se1RC. In the TS (Se1_TS) geometry, the ammonia is closer to C1 ($2.208 \text{ Å}$), the asymmetry is more pronounced ($\Delta d = 0.484 \text{ Å}$), and $\Delta G^\ddagger = 2.9 \text{ kcal/mol}$ with respect to Se1RC. Finally, in the product (Se1PC), the C1–N bond is formed ($1.550 \text{ Å}$) and the selenium is bound only to C2 ($\text{Se–C}2 = 1.986 \text{ Å}, \Delta d = 0.850 \text{ Å}$), with $\Delta G = -6.3 \text{ kcal/mol}$ (Figure 2).

Decomposing the system into fragments [PhSe]$^+$ and [(C$_2$H$_4$)(NH$_3$)]$^-$ as described above, the effect of the ammonia on the Se–C$_2$H$_4$ bond can be quantified in detail. First, the
EDA reveals that the Se····C,H interaction is stronger, but this is not due to an enhancement of the orbital contribution, which decreases in absolute value by 23 kcal/mol (Table 1). Likely, the addition of the electron-rich ammonia makes the electrostatic contribution between the two fragments more negative. As well, the presence of the ammonia causes an increase in the Se····C1 bond length to 2.292 Å, reducing the Pauli repulsion between the two fragments. Both effects lead to a decreased $E_d$ and an increased $E_{int}$ despite the less favorable $E_m$ contribution.

From the orbital point of view, $\Delta \rho_{\sigma}$ in addition to the regions discussed above, also shows a depletion region at the nitrogen atom (Supporting Information), indicative of a N $\rightarrow$ C1 polarization and giving a larger CT$_\sigma$ value (0.789 e). $\Delta \rho_\pi$ shows essentially the same regions discussed before, but as the olefin is further from the selenium, the back-donation is less effective, resulting in a smaller absolute value of CT$_\pi$, $-$0.316 e (Figure 3).

More in general, the NOCV-CD analysis enables following the electronic changes that occur in the system during the nucleophilic attack. A similar approach has been used for the gold(I)-catalyzed functionalization of alkynes$^{37}$ and the nucleophilic attack. A similar approach has been used for the gold(I)-catalyzed functionalization of alkynes$^{37}$ and the nucleophilic attack. A similar approach has been used for the gold(I)-catalyzed functionalization of alkynes$^{37}$ and the nucleophilic attack.

Now, the effect of the LB on this LA-catalyzed reaction can be studied. First, the effect of a model phosphine oxide, PH$_3$O, will be discussed. Similar species, together with phosphine sulfides and selenides, have been used with success in this type of reaction.$^{21}$

The interaction between Se1 and PH$_3$O is quite strong and the Gibbs free energy of the adduct OSe1 is $-$6.8 kcal/mol with respect to the isolated components, denoting a good stability. The stability of this interaction allowed the use of a chiral auxiliary LB to effect enantioselective reactions.$^{24}$ In the optimized geometry of OSe1, the O−Se distance is 2.511 Å and the Se−O−P angle is 134.7°. The EDA reveals that $E_{int}$ is $-$18.3 kcal/mol, $E_{disp}$ is $-$19.6 kcal/mol, and $E_{dip}$ is 1.3 kcal/mol. The decomposition of $E_{int}$ leads to the following values of $E_{dis}$, $E_{disp}$, and $E_{dip}$: $-$16.7, 4.4, and $-$7.3 kcal/mol, respectively. The NOCV decomposition of $E_{int}$ shows that in this case $\Delta \rho_\sigma$ contributes $-$10.2 kcal/mol, much more than the other ones ($-$1.9, $-$1.3, and $-$1.0 for $k = 1$, 2, and 3, respectively). Analysis of the 3D maps of $\Delta \rho_\sigma$ reveals a depletion region at oxygen, an accumulation region between O and Se, a polarization pattern (depletion/accumulation) at the selenium atom and, finally, an accumulation region at the olefin (Figure 4a). This is coherent with a PH$_3$O $\rightarrow$ Se1 charge transfer from the filled $\pi$ orbital of the oxygen (lone pair) to the $\sigma^*$ (Se−C) orbitals. Also, the $\pi$ electrons of the P=O bonds participate in the donation, lowering the Mayer bond order,$^{43}$ which passes from 1.97 (bond distance 1.491 Å) for the isolated moiety to 1.74 (bond distance 1.510 Å) in OSe1. Similar results reported for selenourea.$^{46}$ $\Delta \rho_\pi$ is mainly localized on the PH$_3$O moiety and reveals the polarization of the $\pi$ electrons of the P=O bond toward the oxygen atom. The other contributions ($k > 1$) describe similar, weaker polarization contributions.

The integration of the contributions quantifies the O−Se CT$_\sigma$ as 0.071 e. Furthermore, the presence of the LB induces an additional Se $\rightarrow$ C$_{def}$ charge shift of 0.054 e.
From an orbital point of view, the LB donates its electron density to the empty p orbital of the selenium, but the olefin also competes for the same orbital, forming a 3-center-4 electron bond.47

As the ammonia approaches, OSe1 RC forms, with a Gibbs free energy of 1 kcal/mol with respect to the isolated OSe1 and NH3. The N–C1 distance is 2.808, 0.45 Å longer than in the absence of the LB. This can be explained by the accumulation of electron density on the olefin induced by PH3O (Figure 4), which likely makes the electrostatic interaction with the ammonia weaker. This is confirmed by the natural population analysis for Se1 and OSe1, as the partial charge on the C1 passes from −0.449 to −0.459 e, respectively. In addition to this, the p character of the C1–C2 antibonding orbital increases from 67.5 to 68.4%, making the interaction with the lone pair of the ammonia less favorable. As the presence of the ammonia tends to make \( E_{\text{int}} \) stronger, as seen for Se1 RC, it is reasonable that if the ammonia is further away, \( E_{\text{int}} \) will decrease.

A similar effect, but less effective, is also exerted by the ammonia on the LB, as the O–Se distance changes from 2.511 to 2.566 Å. Noteworthy, the Se···olefin interaction is weaker in the presence of the LB, with \( E_{\text{int}} \) passing from −93.0 kcal/mol in Se1 RC to −75.6 in OSe1 RC (Supporting Information).

In OSe1 TS, the N–C1 distance is 2.298 Å, slightly longer than in the absence of LB, and O–Se is 2.587 Å. Interestingly, in OSe1 the oxygen of the C1–Se–O and C2–Se–O angles are very similar, 160.3° and 158.7°, respectively, while in OSe1 TS the former is smaller than the latter, 152.7 and 169.1°, respectively. This indicates an incipient \( \sigma \) hole opposite to C2, as discussed before. The Gibbs free energy of OSe1 TS is 3.7 kcal/mol, 0.8 kcal/mol higher than in the absence of PH3O (see later and Figure 5). For OSe1 PC, the Gibbs free energy is −2.6 kcal/mol and the C2–Se–O angle is 171.6, quite similar to the 180° typical of \( \sigma \)-hole interactions.44

In this case, from the orbital point of view, the LB donates its electronic energy to the \( \sigma^*(\text{Se}–\text{C}2) \) orbital (\( \omega \) bonding)

It is interesting to compare for different PH\( \text{Ch}_2 \) moieties the effect of chalcogen variation on both the bond components and the activation barrier. In fact, experimental studies revealed that passing from light to heavy chalcogen atoms, the yield of the selenolactonization increases.23 For this reason, the Ch\( \text{2} \)···Se and Se···C bond analyses and the reaction paths have been calculated using Ch\( \text{2} = \) O, S, and Se. Comparing the three different RC geometries (OSe1 RC, SSe1 RC, and SSe1 RC), many things can be noted: the C1–N distance decreases as the chalcogen mass increases (2.808, 2.721, and 2.679 Å for Ch\( \text{2} = \) O, S, and Se, respectively) and the \( \Delta d \) increases (0.061, 0.097, and 0.128 Å, respectively), making the RC more and more similar to the geometry of the TS. In addition to this, the \( E_{\text{int}} \) values decrease from −75.6 to −59.4 and −51.7 kcal/mol for Ch\( \text{2} = \) O, S, and Se, respectively (Table 1): the Se···olefin interaction is weaker in the presence of heavier Ch\( \text{2} \), as the Se···olefin distances increases.

All these facts impact on the Gibbs free energies of the TS structures, which decrease as the chalcogen weight increases: 3.7, 2.0, and 1.3 kcal/mol for Ch\( \text{2} = \) O, S, and Se, respectively (Figure 5a), in qualitative agreement with the experimental results.21

It has to be noted that \( \Delta G^\ddagger \) for the “assisted” attack becomes smaller than in the absence of an LB only for the heavier chalcogen S and Se. According to NBO second-order perturbation theory interaction energy analysis, the LB donates electron density directly into the antibonding orbitals \( \sigma^*(\text{Se}–\text{C}1) \) and \( \sigma^*(\text{Se}–\text{C}2) \) (\( \omega \) bonding: the more electron density the LB donates to Se, the weaker the Se···olefin bond becomes). The population of these orbitals favors the reaction, and according to NBO results the lowest population (0.29 e) is indeed seen with PH3O. In the absence of the LB the population is 0.39 e and in the presence of PH3S and PH3Se becomes 0.45 and 0.56 e, respectively. As a confirmation, the total population of \( \sigma^*(\text{Se}–\text{C}1) \) and \( \sigma^*(\text{Se}–\text{C}2) \) orbitals is seen to correlate linearly with \( \Delta G^\ddagger \) (\( r^2 = 0.974 \), Figure 5b).

On the other hand, the Ch\( \text{2} \)···Se interaction becomes stronger as the weight of Ch\( \text{2} \) increases, from −17.2 to −18.4 and −21.1 for Ch\( \text{2} = \) O, S, and Se, respectively, due to a large increase of the orbital contribution (Supporting Information). In other words, the LB···Se bond becomes progressively more covalent and less electrostatic in nature. This stabilization is of prime importance in the LBLA effect and likely prevents the decomposition of the active species. The same change in bonding can be quantitatively measured using the NOCV-CD analysis with the decomposition [PH3(Ch\( \text{2} \))···(PhSe)(C2H4)(NH3)]+. In this case, the value of CT\( \delta \) changes from −0.062 to −0.162 and −0.242 e, respectively (from Ch\( \text{2} = \) S to the seleniranium cation, Figure 6a).

Indeed, the nature of the chalcogen atom impacts also on the Se···olefin bond. In particular, the total curvatures in Figure 6b seem to be coincident for the three LBs, but it is important to remember that the olefin is progressively further away from the selenium, shifting the isoboundary further too (to 0.98, 1.02, and 1.04 Å for Ch\( \text{2} = \) O, S, and Se, respectively). Also, as the CD\( \delta \) functions are strongly dependent on the distance in this region, the increase of CT\( \delta \) is noticeable (0.319, 0.340, and 0.350 e, respectively).

The linear correlation between \( \Delta G^\ddagger \) and CT\( \delta \) looks good (\( r^2 = 0.9979 \)), but three data points are not enough to discuss a linear correlation. Therefore, the phenyl group at selenium was replaced by a methyl group, yielding three more structures: OSe2, SSe2, and SeSe2, bearing the same LB (PH3Ch\( \text{2} \)) and

Figure 5. (a) Reaction paths for Se1, OSe1, SSe1, and SeSe1; (b) correlation between activation Gibbs energy and total occupancy of the NBO antibonding orbitals \( \sigma^*(\text{Se}–\text{C}1) \) and \( \sigma^*(\text{Se}–\text{C}2) \).
Figure 6. (a) CD\textsubscript{0} component for the \([\text{PH}_3\text{C}^+\text{H}^2\text{]}\)\(\rightarrow\)\([(\text{PhSe})(\text{C}_2\text{H}_4)\)\(\rightarrow\)\((\text{NH}_3)\)\(\rightarrow\)\] bond and (b) CD\textsubscript{tot} curve for the \([(\text{PH}_3\text{C}^+)\)\(\rightarrow\)\([(\text{PhSe})(\text{C}_2\text{H}_4)\)\(\rightarrow\)\((\text{NH}_3)\)\(\rightarrow\)\] bond in OSe\textsubscript{1} RC, SeS\textsubscript{1} RC, and SeSe\textsubscript{1} RC. Black dots indicate the \(z\) position or position range of the atomic nuclei. A yellow vertical band indicates the range of boundary between the fragments.

Figure 7. Linear correlation between \(\Delta G^\ddagger\) of the nucleophilic attack and CT\textsubscript{tot} of the \([(\text{PH}_3\text{C}^+)\)\(\rightarrow\)\(((\text{C}_2\text{H}_4)(\text{NH}_3)\)\(\rightarrow\)\] bond.

makes sense from the physical point of view, as a large CT\textsubscript{tot} means that the olefin is heavily depleted of electron density and will therefore easily be attacked by a nucleophile.

Finally, the same analysis has been conducted on the thiiranium cation \([\text{PhS}(\text{C}_2\text{H}_4)\)\(\rightarrow\)\] (S1), again in conjunction with \(\text{PH}_3\text{C}^+\text{H}^2\text{] as LB and NH}_3 as nucleophile. The \(S\)\(\rightarrow\)olefin bond is stronger than the Se\(\rightarrow\)olefin analyzed before, as \(E_{\text{tot}} = -83.2\) instead of \(-75.8\) kcal/mol and \(E_{\text{ai}} = -299.1\) instead of \(-222.9\) kcal/mol (Table 1). This is reflected also by the larger donation component (\(CT^1 = 0.792\) vs \(0.733\) e) and the larger CT\textsubscript{tot} (0.438 vs 0.303 e). When the nucleophile and PH\textsubscript{3}O are present (OS1 RC), the bond components are larger in terms of donation (0.684 instead of 0.649 e), back-donation (−0.315 instead of −0.400 e), and total transfer, (0.375 instead of 0.247 e). On the basis of Figure 7, one would expect a lower \(\Delta G^\ddagger\) value for OS1 RC than for OSe1 RC. Actually, we find \(\Delta G^\ddagger = 4.5\) kcal/mol, which is higher than the value for OSe1 RC.

Expanding the analysis to S1 and SeS1, we have the same trend and \(\Delta G^\ddagger\) decreases as CT\textsubscript{tot} increases (\(r^2 = 0.939\), Supporting Information), but the entire set of data is shifted to higher values of CT\textsubscript{tot}. Because the latter is the sum of two contributions, a real charge transfer and a polarization contribution,\(^50\) likely the latter is systematically different depending on the nature of the chalcogen atom and introduces such a constant difference between selenium and sulfur systems. As before, also the population of the \(\sigma^*(\text{S}\rightarrow\text{olefin})\) orbital correlates linearly with \(\Delta G^\ddagger\) (\(r^2 = 0.957\)), confirming the dual mode of action of the LBLA: the LB increases the population of the antibonding orbital, making the nucleophilic attack easier and, at the same time, it depletes the olefin of electron density, increasing the electrostatic attraction of the approaching nucleophile.

### CONCLUSIONS

In this paper, it has been shown that the NOCV method provides very detailed descriptions of what happens to the electron density when an olefin binds to a chalcogeniranium (seleno- or thiiranium) species and what happens when the resulting adduct interacts with an LB, decomposing the interaction in terms of chalcogen \(\rightarrow\) olefin \(\sigma\) donation and chalcogen \(\leftarrow\) olefin \(\pi\) back-donation. The description can be made more quantitative by integrating the separated components by CD analysis, which estimates the amount of charge shifted from one fragment to the other.

In particular, the evolution of the electronic fluxes between the fragments can be followed during the reaction, as the NOCV-CD can be safely applied also to TSs, products, and even to non-stationary points at any position of the reaction coordinate. Here, as a model reaction, the nucleophilic attack of the ammonia on the ethylene moiety has been considered. As the ammonia approaches, the evolution of the Se–C chemical bond can be appreciated: \(\sigma\) donation increases and the \(\pi\) back-donation decreases as the ammonia approaches, consistent with the change in bonding from a Se–olefin interaction to a Se–C \(\sigma\) bond, strongly polarized by the cationic ammonium moiety.

Also, the effect of an LB, such as phosphine chalcogenides that have been experimentally used to activate the chalcogen-based LA, can be investigated by means of the same methodology. The results presented here show that soft LBS influence both the geometry and the bond components of the chalcogeniranium cation (which are mutually dependent). The net result is a decrease in electron density on the carbon atoms, favoring nucleophilic attack.

From the coupling of the NOCV-CD analysis with NBO results, it emerges that the LB increases the population of the CH–olefin anti-bonding orbitals, again favoring nucleophilic attack.

In conclusion, the present “proof of concept” demonstrates that the NOCV-CD analysis is a powerful tool to investigate chalcogen chemistry, revealing correlations between experimental and computational parameters and consequently...
Theoretical Details. If not otherwise specified, all the geometries were optimized with ORCA 4.0.1.251,52 using the BP86 functional53 in conjunction with a triple-$\zeta$ quality basis set (def2-TZVP). GGA functional was shown to be reliable for geometry optimizations,54,55 whereas single-point calculations using the double hybrid B2-PLYP were used for the computation of improved electronic energies.54 Dispersion corrections were taken into account using the Grimme D3-parametrized correction to the density functional theory energy (with Becke–Johnson damping).56 All structures were confirmed to be local energy minima (no imaginary frequencies) for intermediate species and saddle points (one imaginary frequency) for TSs.

Energy Decomposition Analysis. EDA41 allows the decomposition of the bond energy into physically meaningful contributions. The association energy ($E_{\text{as}}$), which is the difference of energy between the adduct and the relaxed fragments, is divided into two terms (eq 1)

$$E_{\text{as}} = E_{\text{int}} + E_{\text{def}}$$

where $E_{\text{int}}$ is the interaction energy, the difference of energy between the adduct and the unrelated fragments, and $E_{\text{def}}$ is the energy needed to distort the fragments form their relaxed geometry to the geometry they assume in the adduct. The interaction energy $E_{\text{int}}$ can be divided in contributions associated with the steric ($E_{\text{st}}$), orbital ($E_{\text{oi}}$) and dispersion ($E_{\text{disp}}$) interactions, as shown in eq 2

$$E_{\text{int}} = E_{\text{st}} + E_{\text{oi}} + E_{\text{disp}}$$

$E_{\text{st}}$ comprises the destabilizing interactions between the occupied orbitals and is responsible for any steric repulsion. $E_{\text{oi}}$ is generally further decomposed in Pauli and electrostatic contributions, but using ORCA this passage seems to be not possible at the moment. $E_{\text{disp}}$ is the contribution arising from allowing the wave function to relax to the fully converged one, accounting for electron pair bonding, charge transfer, and polarization.

CD Function Analysis. The CD function analysis is based on eq 3.30 $\Delta \rho^\prime(x,y,z)$ is the difference between the electron density of a complex and that of its non-interacting fragments placed in the same position as they occupy in the complex. In the present case, the choice of decomposition depends on the interaction being examined. The function $\Delta q(z)$ 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 $\Delta q$ is positive and decreases where it is negative.

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

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02243.

Optimized geometries (XYZ)

Energy decomposition analysis; charge transfer values; total CD curves; isodensity surfaces; computed electrostatic potential; $AG^\ddagger$ and CT_{tot} values for all the systems considered (PDF)

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Notes

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