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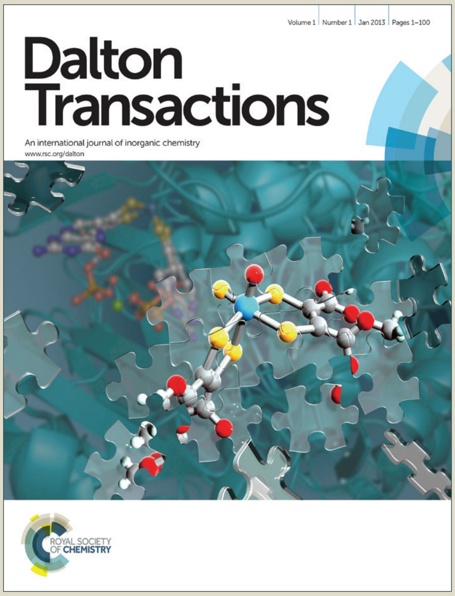

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Theoretical Treatment of One Electron Redox Transformation of Small Molecule using f-element Complexes

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Abstract

The theoretical treatment of the one electron redox (SET) chemistry mediated by f-element complexes is reviewed and summarized. The different computational strategies to account for the SET energy are presented and commented on the basis of the subsequent mechanistic investigation. Moreover, the mechanistic investigation of the subsequent reactivity, mainly in the field of heteroallene activation, using DFT-based approaches is also summarized. All reported reactivities are found to involve formation of bimetallic species and share in common the formation of the same key intermediate (where the substrate is doubly reduced and stabilized by two oxidized metal centers). Modern computational methods are found to efficiently account for such reactivity.

Introduction

The search for a secure clean energy supply is one of the major scientific challenges of our century calling for an important effort in fundamental research. Solar energy appears currently as the best option for clean energy production, but the cost-effective storage of the resulting energy is a critical step conditioning the future of solar electricity as primary energy source. One possible strategy, inspired by natural photosynthesis, is to store solar energy in chemical bonds. The use of solar energy in the conversion of carbon dioxide is an extremely attractive scenario that would impact the global carbon balance by recycling CO_2 into liquid fuel or fuel precursors such as CO/H_2 (synthesis gas). However, the efficient transformation of the very stable CO_2 molecule is one of the biggest challenges in synthetic chemistry, although plants are quietly doing it every day, and paths to low energy and selective reductive conversion of carbon dioxide into useful feedstock products such as formaldehyde, formic acid, methanol, or oxalic acid has proven elusive. Research in the field of carbon dioxide reduction has grown rapidly in the past few decades with some important steps forward in metal mediated conversion of carbon dioxide displaying the importance of basic research in inorganic chemistry for the advancement of this field.[1-9]

Metal complexes as catalysts for the transformation of carbon dioxide play a crucial role in advancing the utilization of carbon dioxide as a fuel. The use of such catalysts avoids high-energy intermediates often through the coordination of a carbon dioxide molecule to a highly reduced metal complex. The field of transition metal promoted reduction of carbon dioxide is relatively new with the first reports on metal bound carbon dioxide dating back to the 1970s.[10] This area has been growing rapidly in the past 30 years and is likely to increase exponentially in the near future as a result of the current demand for sustainable energy sources. The research of new systems based on f-elements for CO_2 fixation and activation is also in expansion. Nevertheless, structurally characterized examples of carbon dioxide reduction by lanthanides are limited to three/four examples in which Ln(II) complexes in different ligand environments promote CO_2 dimerization or disproportionation.[10-13]A part from few exceptions, early transition metals and lanthanides are difficult to reduce, and the reduced species are extremely reactive and difficult to handle. However, their high oxophilic character can be effective in promoting the cleavage of the C-O bond in carbon dioxide. Notably organometallic complexes of low valent titanium and zirconium were found to promote deoxygenation and disproportionation of CO_2 to yield CO and carbonate complexes respectively.[8,14]The reactivity of these systems is driven by the oxophilicity of the metal resulting in the formation of metal oxo complexes. Similar reactivity has also been observed with a 5f-element, uranium.[4,15] Notably, Meyer has taken advantage of the highly reducing character and oxophilicity of trivalent uranium to coordinate and activate carbon dioxide. This led to the isolation of the first complex in which a reduced CO_2 ligand is linearly coordinated to the metal through its oxygen atom and to some remarkable reactivity. A U(III) complex supported by a tripodal trisphenolate ligand reacts with carbon dioxide to form CO and an U(IV)/U(IV) oxo dimer in a concerted two ion mechanism.[16,17]The studies of Meyer have highlighted the importance of the ligand steric and electronic features on the reactivity of uranium complexes with CO_2.

Theoretical investigations on uranium carbonate formation carried out by Castro *et al.* using DFT calculations have shown that the preferred pathway for carbonate formation is a three mechanism involving the coordination of CO_2, CO release and formation of a bridging uranium oxo-dimer followed by the insertion of carbon dioxide in the U-O bond to yield the final carbonate.[18] Gardiner[12] has demonstrated a similar carbon dioxide reduction with samarium(II) affording a carbonate bridged dinuclear porphyrinogen-based Sm(III)/Sm(III) dimer. An oxalate intermediate was proposed on the basis of the dinuclear oxalate complex of samarium previously isolated by Evans in the reaction of a divalent samarocene complex with carbon dioxide.[18] In these systems the Sm(II) centre is likely to act as one-electron donor in a concerted two ions mechanism. Notably, out of the 14 lanthanide elements compounds reported, molecular complexes with divalent europium, samarium, and ytterbium have been known for more than 90 years, whereas the first molecular species of divalent lanthanum, thulium, dysprosium, holmium, erbium and neodymium have only been recently reported;[19-23] their isolation being extremely challenging due to their much higher reducing potential.

The utilization of ligands with readily accessible oxidation states such as diazabutadiene,[24,25] arenes,[26] diimines[27,28] or terpyridine,[29,30] for governing electron transfer processes in divalent lanthanides has attracted a wide range of structural, spectroscopic, magnetic, and computational studies directed to assess the valence localization. Recent results obtained from the thorough study of the electronic properties of Yb(II) complexes associated to redox active ligands carried out in the group of Andersen in collaboration with Eisenstein and Maron[24,27] clearly show the importance of allying theory and experiment in the analysis of these systems. Arenes have also been shown to act as redox active ligands when combined to low-valent uranium affording dinuclear inverted-sandwich complexes where two uranium ions are bridged by arene dianions[31-35] or tetraanions.[36] While the assignment of metal oxidation state and of the arene charge remains under debate in these unconventional systems, the few reported examples of reactivity studies have shown that these compounds can act as multi-electron reductants with different oxidizing substrates.[31,35-37] Surprisingly the reactivity of these systems with CO_2 has not been investigated. Studies on ligand centered reactivity are less developed for lanthanide systems.[38] The most conspicuous example of ligand centered reactivity has been developed by Evans who discovered that triscyclopentadienyl complexes of trivalent lanthanides have similar reductive reactivity to that of the divalent complex.[39,40] This reactivity is induced by steric crowding around the lanthanide center which can be controlled by tuning the lanthanide size and cyclopentadienyl ring substituents. The reactivity does not involve a change of the metal oxidation state but is centered on the ligand and involves a $(C_5Me_5)/(C_5Me_5)^-(Cp^*/Cp^{*-})$ redox couple. However, these interesting systems can only perform one electron redox reactions or eventually two-electron reduction if associated to a lanthanide metal having an accessible divalent oxidation state.

Alongside such an amount of experimental studies, theoretical chemistry can be of great help in understanding the mechanisms of the observed reactions. Density functional theory (DFT) in particular has been an important tool for the prediction of structures, energies, mechanisms of transition-metal, lanthanide and actinide complexes in the last decade.

Results and Discussion

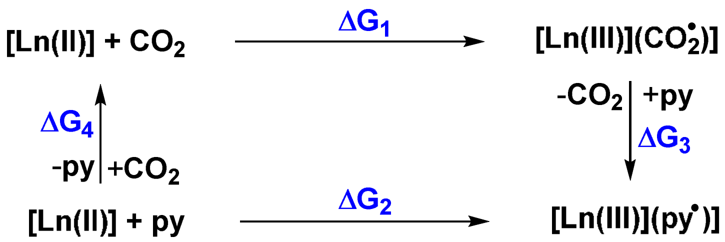
Theoretical approaches have been extensively used to predict for instance the nature of the ground state of several Yb(II) complexes, using the multireference CASSCF method.[24,27] However, this computational approach is hardly tractable for bimetallic complexes and reactivity studies involving divalent lanthanide complexes as previously described, thus DFT methodologies must be adopted. However, DFT poorly describes the Single Electron Transfer (SET) process that necessarily precedes reactivity. This leads to the requirement for simplified, largely DFT-based that accounts for the SET step while retaining computational precision.

Single Electron Transfer energy determination in divalent lanthanide chemistry using DFT

A first attempt to compute the SET process in divalent lanthanide chemistry using DFT was recently achieved on the reductive dimerization of pyridine promoted by $(Cp^*)_2Tm^{II}$ and the CO_2reduction mediated by $(Cp^*)_2Sm^{II}$ (Cp* refers to C_5Me_5).[41]DFT appeared to describe the Tm system relatively well, since the electronic configuration (EC) of the Cp^*_2Tm(pyridine) adduct is $4f^{13}\pi^{*0}_{py}$ (S =1/2), while after single electron promotion to pyridine its EC becomes$4f^{12}\pi^{*1}_{py}$(S = 3/2). Thus small-core RECP calculations (which include f electrons explicitly)at the B3PW91 level of theory (Scheme **1**) allow the SET energy to be determined by a simple difference between the two spin state energies(19.9 kcal mol^{-1}). The DFT computed SET energy compares well with that derived from CASSCF calculations. The situation is somewhat different with samarium: the $(Cp^*)_2Sm^{II}$-CO_2 adduct has the same spin state in the ground state ($4f^6\pi^{*0}_{CO_2}$ (S =3))as after the SET ($4f^5\pi^{*1}_{CO_2}$

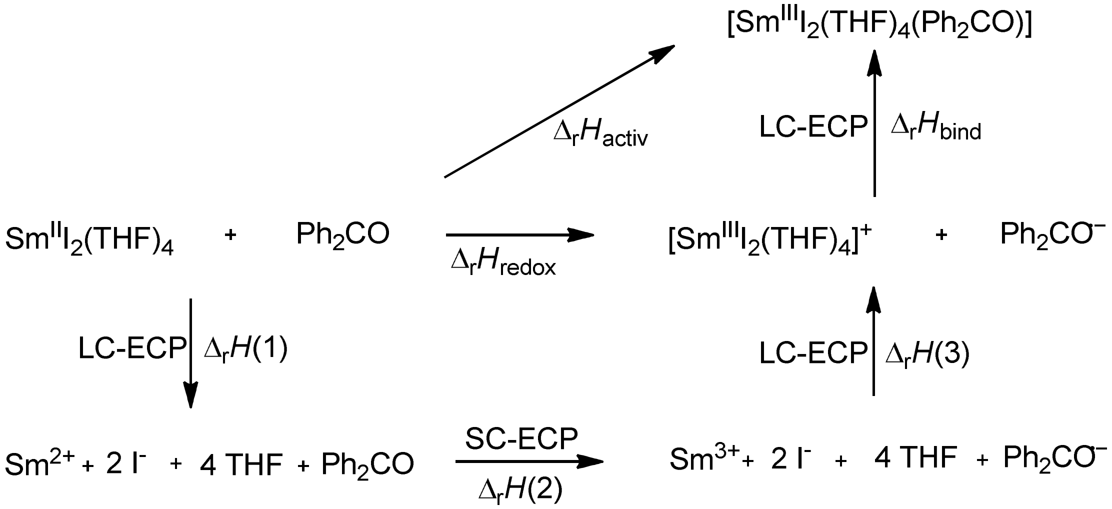
(S =3)). At first sight, this precludes determination of the SET energy in the same way as for Tm. Fortunately however, the case of the CO_2reductionis peculiar because population of the lowest unoccupied molecular orbital of CO_2 results in a first-order Jahn-Teller effect, leading to the bending of the molecule. The latter geometrical change allows the direct estimation of the energetics of the SET process.

For some substrates however, the spin state is also the same before and after the SET but populating the LUMO of the substrate does not induce a first order Jahn-Teller effect. The use of the large core RECPs (adapted to a given oxidation state, II or III for samarium by in-core treatment of valence f-electrons) offers an alternative strategy by allowing computation of the complexes before and after the SET step. But, due to the differing number of electrons in the system, the results of these calculations are not directly comparable. To circumvent this issue, a Hess cycle involving CO_2 for the oxidation step followed by a substrate exchange reaction from the oxidized species, was proposed as is shown in Scheme **1**. This method was validated by computing the SET energy to pyridine promoted by $(Cp^*)_2Tm^{II}$ complex for which the direct method also works (19.5 vs. 19.9 kcal mol^{-1}).



Scheme 1. Hess cycle to determine the SET energy(ΔG_2) using DFT methods.

In a recent contribution, the estimation of the energetics of the redox step of the reduction of benzophenone (Ph_2C=O) by SmI_2 in neat THF was studied[42] and all reported methods for SET estimation failed. Thus, a different thermodynamic cycle was proposed (Scheme 2): it involves the complete disruption of $SmI_2(THF)_4$ into Sm^{2+}, free iodide and THF, $\Delta_rH(1)$, the oxidation of Sm^{2+} to Sm^{3+} and the concomitant reduction of benzophenone($Ph_2^{\cdot}C$–O radical formation), $\Delta_rH(2)$, and finally the formation of $[SmI_2(THF)_4]^+$ from separated fragments $\Delta_rH(3)$.



Scheme 2.A schematic representation of the SET energy determination using DFT.

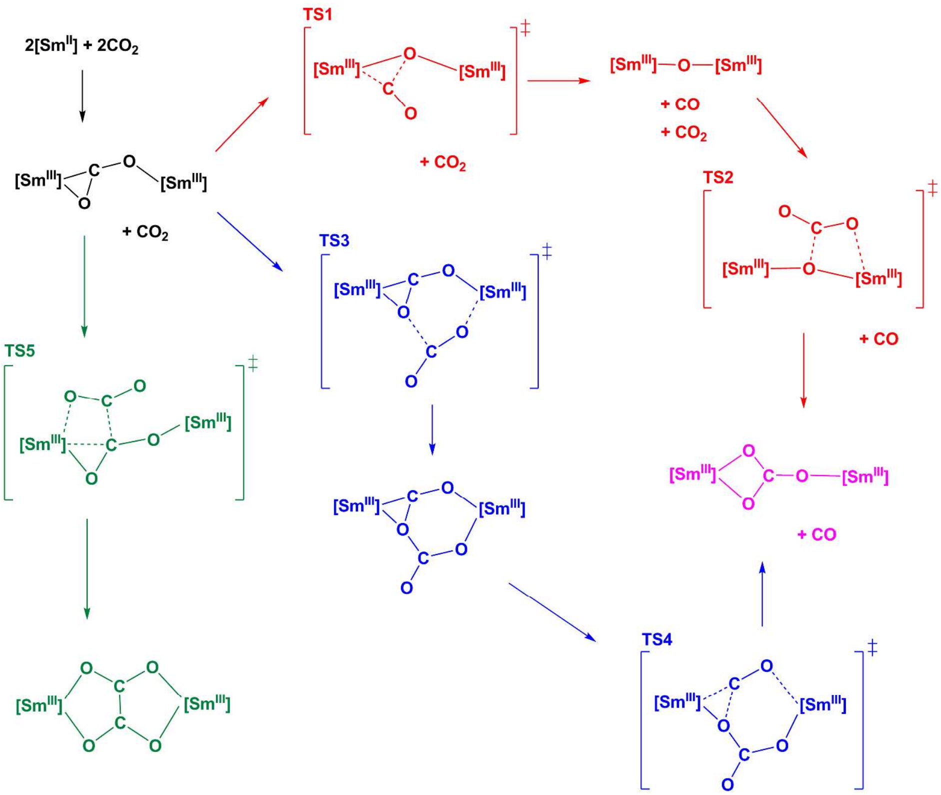
The computed enthalpy for the redox step was found to be in good agreement with the experimental value, $\Delta_r H_{redox}$.[43] However, the $\Delta_r H_{activ}$, which is the sum of the reduction energy of the substrate and the binding energy, was found to be higher than the experimentally estimated one. The latter inconsistency further highlights the totally different behavior of the SmI_2 systems with respect to other lanthanide congeners and makes more imperative than ever the need for finding a general method or strategy that will be simple and effective.

Finally, a quantitative way to estimate the SET energy in various of lanthanide(II) complexes having alkynes (phenylacetylene, hex-1-yne) or hetero-aromatic compounds was proposed by computing the SOMO-LUMO gap energy of the orbitals of these complexes.[44] Interestingly, by carefully inspecting the Restricted Open-Shell Hartree-Fock orbitals, it was found that the π* of the substrate was already occupied, and that the LUMO orbital is a pure 4*f*, in line with the picture of the orbitals of a reduced substrate. The same holds true at the DFT(B3PW91) level. This coordination induced SET was further verified on different samarium complexes with substrates as bipyridine or terpyridine, and found to be reminiscent to the phenylacetylene case, but also on $SmI_2(THF)_4(Ph_2CO)$ system, for which all the previous methodologies failed to give coherent results. Indeed, in this case the computed SOMO-LUMO energy gap is in very good agreement with that derived from the electrochemical experiments. Finally, the method also works for other lanthanide atoms (europium or ytterbium).[44]

By applying one of the previously described methods to estimate the SET energy, it is possible provide a detailed assessment of subsequent reactivity. It should also be noted that similar methods for SET energy determination were proposed for the low valent actinide chemistry.

Reduction of CO_2

As mentioned previously, CO_2 is a peculiar substrate but also a highly attractive target for chemical transformation. Experimentally, it was reported by Evans that $[(Cp^*)_2Sm^{II}]$ reacts with CO_2in THF at room temperature to form an oxalate-bridged bimetallic complex $[\{(Cp^*)_2Sm^{III}\}_2(\mu\text{-}\kappa^2\text{:}\kappa^2\text{-}O_2CCO_2)]$ in more than 90% yield.[13] In order to understand why an oxalate complex is formed instead of an oxo or a carbonate complex, Castro *et al.* investigated three different pathways at the DFT level that are depicted in Scheme 3.[45]All begins with the formation of the same compound (referred as the "key intermediate" in the following), a bimetallic CO_2 sandwich complex in which both samarium centers have been oxidized to Sm^{III} and CO_2 has been doubly reduced. The red pathway consists of the release of a CO molecule leading to the formation of an oxo intermediate. A free CO_2 molecule can subsequently insert into one Sm-O bond in order to form the bimetallic carbonate product. In the blue pathway, the electrophilic addition of CO_2 (C-O coupling) occurs after the formation of the first bimetallic intermediate. CO is released afterward to form the carbonate product. The green pathway is the C-C coupling of a CO_2 molecule with the CO_2^{2-} moiety of the first intermediate to form the bimetallic oxalate complex.



Scheme 3. Three different reaction mechanisms for the reaction of $(Cp^*)_2Sm^{II}$ with CO_2. $(Cp^*)_2Sm^{II}$ is noted $[Sm^{II}]$ and $(Cp^*)_2Sm^{III}$ is noted $[Sm^{III}]$.

The Gibbs energy profiles corresponding to these pathways are presented in Figure 1. The red pathway appears to be strongly disfavored compared to the two others, its rate determining activation barrier being much higher in free energy (22.2 kcal mol^{-1}vs 8.9 and 6.4 kcal mol^{-1} for the green and the blue pathways respectively). The formation is endergonic by +1.2 kcal mol^{-1} with respect to the bimetallic CO_2 sandwich intermediate (at -7.9 kcal mol^{-1}). This is noteworthy since there is a strong entropy gain due to the release of CO. For example, for the complex $[((^{tBu}ArO)_3mes)U^{III}]$, the formation of the oxo complex was calculated to be exergonic by -12.8 kcal mol^{-1} with respect to the previous intermediate.[18] These high energy values are mainly explained by the steric hindrance of the Cp* ligands. All along the pathway, the Sm-Sm distance is rather short because an oxo complex has to be formed. This leads to a strong steric repulsion between the ligands. In the blue pathway, the Sm-Sm distance remains long during the reaction, leading to smaller activation barriers. It is noteworthy that the intermediate of this pathway is not in a deep well, which allows for a concerted electrophilic attack of CO_2 and the release of CO. Formation of the carbonate product is exergonic by -39.3 kcal mol^{-1} with respect to separated reactants. The C-C coupling is also a very easy reaction, as can be seen in the green profile: it is kinetically accessible (8.9 kcal mol^{-1}) and very favorable thermodynamically (-66.4 kcal mol^{-1}). The activation barriers of the blue and green pathways differ by just 2.5 kcal mol^{-1}, which is within the error of the DFT method (ca. 5 kcal mol^{-1}).[46] Thus, it is not possible to conclude which pathway would be preferred kinetically. The oxalate-bridged species (product of the green pathway, C-C coupling) is computed to be far more thermodynamically stable than the carbonate, in excellent agreement its experimental data observation.

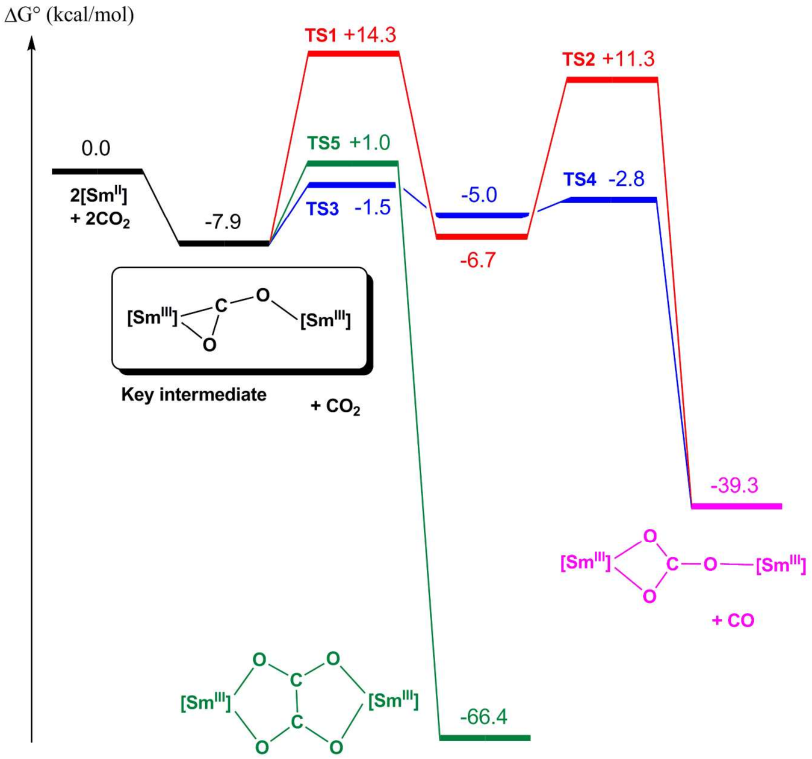


Figure 1. Gibbs energy profiles of the three different pathways of the reaction of $(Cp^*)_2Sm^{II}$ with CO_2. The colors of the profiles correspond to the pathways presented in Scheme 3.

As mentioned in the introduction, the reactivity of U(III) complexes with CO_2 have been of increasing interest in the last years both experimentally and theoretically.[47-51]All theoretical investigations converge on three different mechanisms in competition. Published reaction profiles share a common feature that is the formation of the bimetallic species $[U^{IV}]$-(CO_2^{2-})-$[U^{IV}]$. This complex can then evolve in three different directions depending on the nature of the ligand. The complex can readily expel a CO molecule, yielding the μ-oxo complex $[U^{IV}]$-(O^{2-})-$[U^{IV}]$. This may then remain inert or may further react with another CO_2 molecule to form the μ-carbonate product $[U^{IV}]$-(CO_3^{2-})-$[U^{IV}]$. The key intermediate can also achieve carbonate complex formation through an alternative mechanism wherein the attack of CO_2 and release of CO are concerted. The third mechanism would be the direct C-C coupling between free CO_2 and the CO_2^{2-} moiety of $[U^{IV}]\text{-}(CO_2^{2-})\text{-}[U^{IV}]$ to yield the *μ*-oxalate product $[U^{IV}]\text{-}(C_2O_4^{2-})\text{-}[U^{IV}]$ that is the thermodynamic product. The steric effects are found to control the reactivity as evidenced in Figure 2 for the reaction between CO_2 and $[((^{Me}ArO)_3mes)U^{III}]$ or the bulkier $[U^{III}(C_8H_6(1,4\text{-}Si^iPr_3)_2)(Cp^*)]$ complex. Steric hindrance thus dramatically increases the height of the barriers as well as the energy of the oxo intermediate, making the second mechanism, which avoids a μ-oxo intermediate (in red), more favorable.

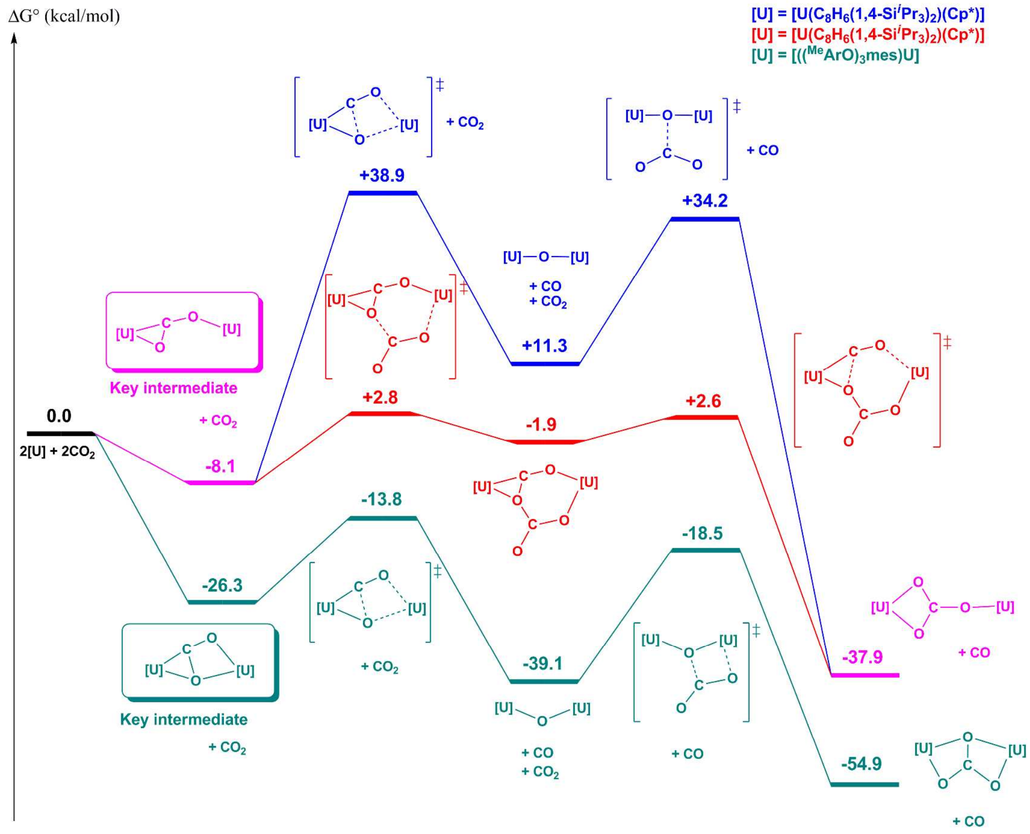


Figure 2. Gibbs free energy profiles of the reactions of U(III) complexes and CO_2. The green profile concerns $[((^{Me}ArO)_3mes)U^{III}]$ while the blue and red pathways concern $[U^{III}(C_8H_6(1,4\text{-}Si^iPr_3)_2)(Cp^*)]$. Both complexes are simplified as [U].

In the same way, using versatile siloxides as supporting ligands in uranium(III)-mediated CO_2activationleads to the carbonate-bridged dinuclear product upon release of one CO molecule, through the same concerted mechanism (Figure3).[52] On the other hand, it is noteworthy that the reaction of the same complex with CS_2 only afford the highly stable bimetallic $(CS_2)^{2-}$ bridged complex, the key intermediate.

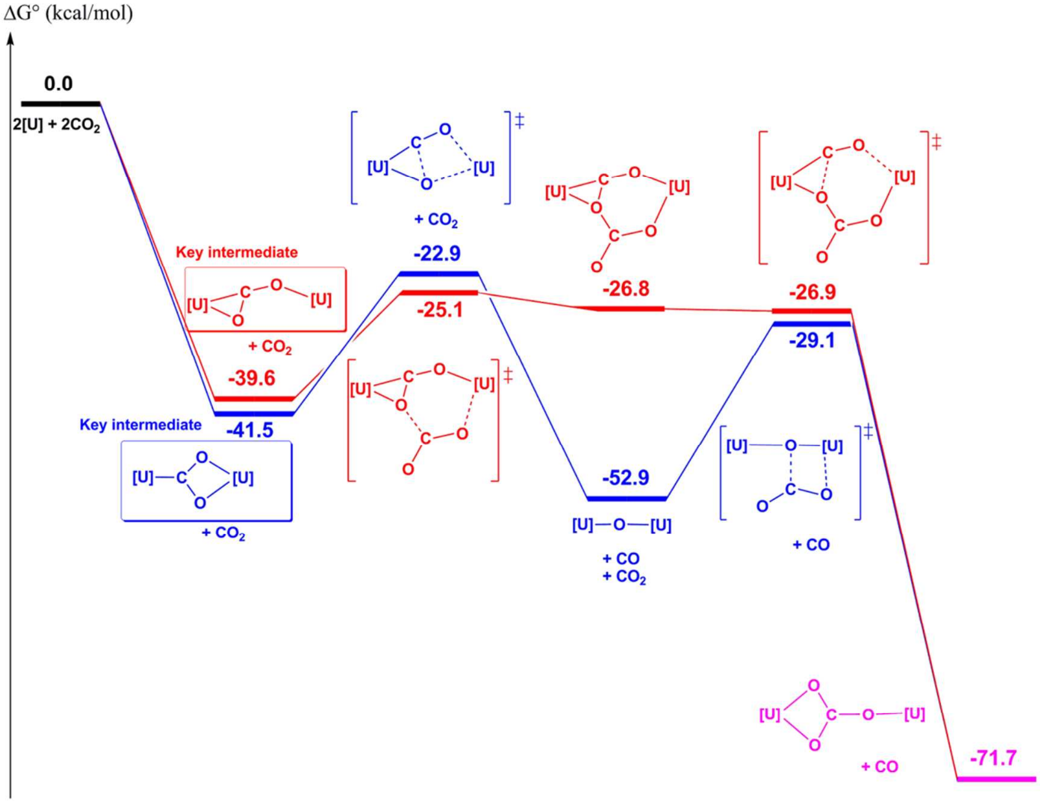


Figure 3. Gibbs free energy profiles of the reactions of [U^{III}(OSi(OtBu)$_3$)$_3$] complexes and CO$_2$.

Reduction of other heteroallenes

In 1986, Brennan and Andersen reported the first reaction of CS$_2$[53] and COS with Cp*$_3$U.[54] For the former at 0°C in diethyl ether, 1 equivalent of CS$_2$ is cleanly transformed onto a doubly reduced bridging fragment [Cp*$_3$U-(CS$_2$$^{2-}$)-UCp*$_3$] where the two metal centers have been oxidized by one unit each. Unlike the CO$_2$ reactivity, this intermediate does not react further. Castro and Maron investigated the mechanism of this reaction using DFT methods.[55] The Gibbs free energy profile was determined and putative subsequent reactivity from the bimetallic intermediate was studied (Figure 4). The formation of the key intermediate is highly exergonic, indicating a coordination induced reduction of CS$_2$. The disruption of one CS bond from this intermediate, although kinetically accessible, is found highly endergonic, mainly due to the low kinetic stability of CS. The possibility of having the bimetallic sulfido complex as transient species for subsequent CS$_2$ addition was found unlikely, mainly because the formation of thiocarbonate is endergonic.

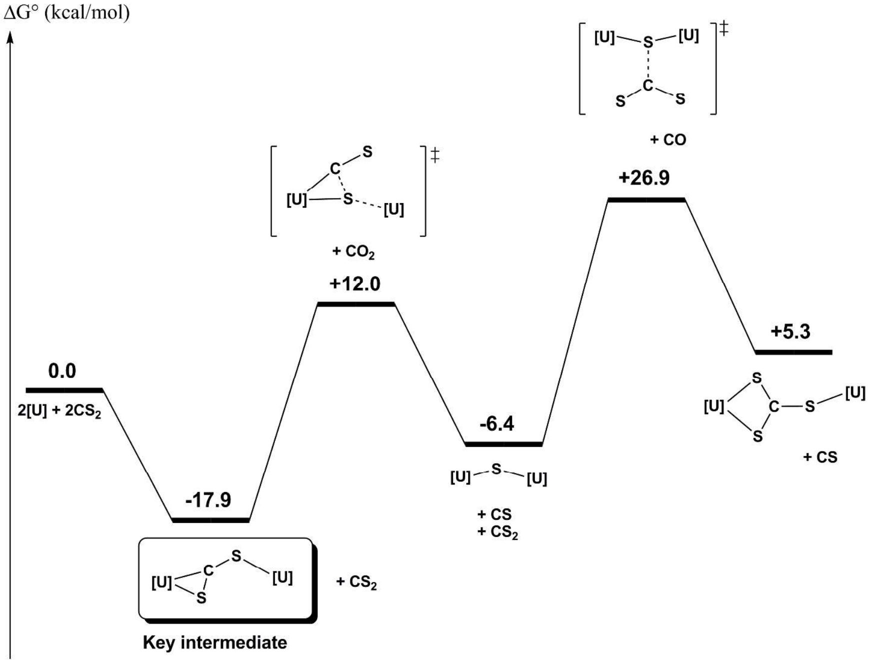


Figure 4. Gibbs free energy profile for the possible reaction between CS_2 and $Cp^*{}_3U$ (noted [U] in the figure).

A similar reaction in diethylether at room temperature with COS leads to the formation of a different product, namely the bimetallic sulfido complex [$Cp^*{}_3$U-S-U$Cp^*{}_3$]. The reaction mechanism is proposed to involve the formation of the key intermediate, as in the case of CS_2, [$Cp^*{}_3$U-COS-U$Cp^*{}_3$] that undergoes facile release of CO (Figure 5).

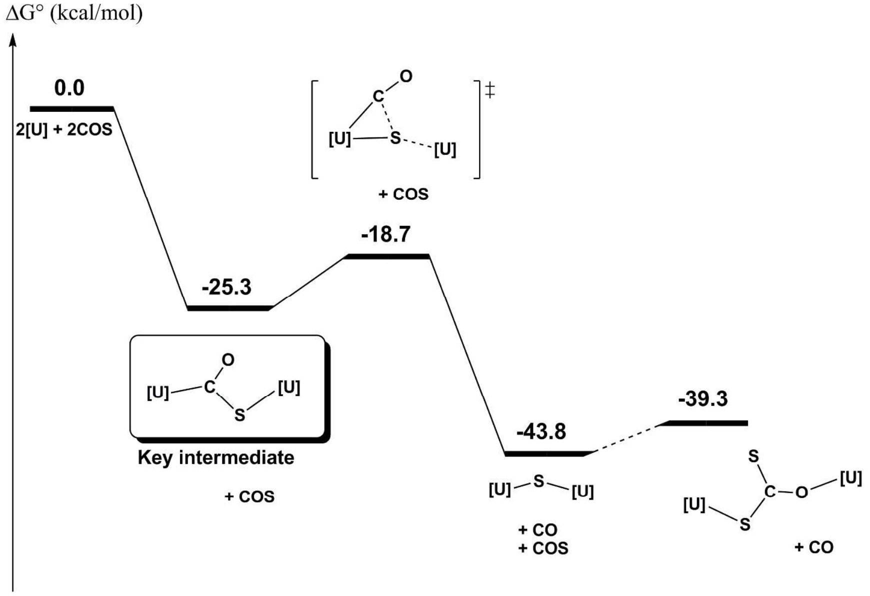


Figure 5. Gibbs free energy profile for the possible reaction between COS and Cp*$_3$U (noted [U] in the figure).

The main difference with CS_2 is that CO is kinetically much more stable than CS. Finally, the subsequent addition of COS to the sulfide complex is found to be endergonic. Brennan and Andersen also reported reactivity of isoelectronic heteroallenes such as PhN_3 and PhNCO.[56] The former leads to the formation of the monometallic U(V) complex, Cp*$_3$UNPh, whereas the latter only forms the key intermediate [Cp*$_3$U-PhNCO-UCp*$_3$]. Castro et *al.* reported that in both cases the reactivity involves the formation of the key intermediate. In the case of PhN_3 (Figure 6), the key intermediate [Cp*$_3$U-PhN$_3$-UCp*$_3$] is easily formed and readily releases Cp*$_3$U-N$_2$, yielding Cp*$_3$U-NPh.

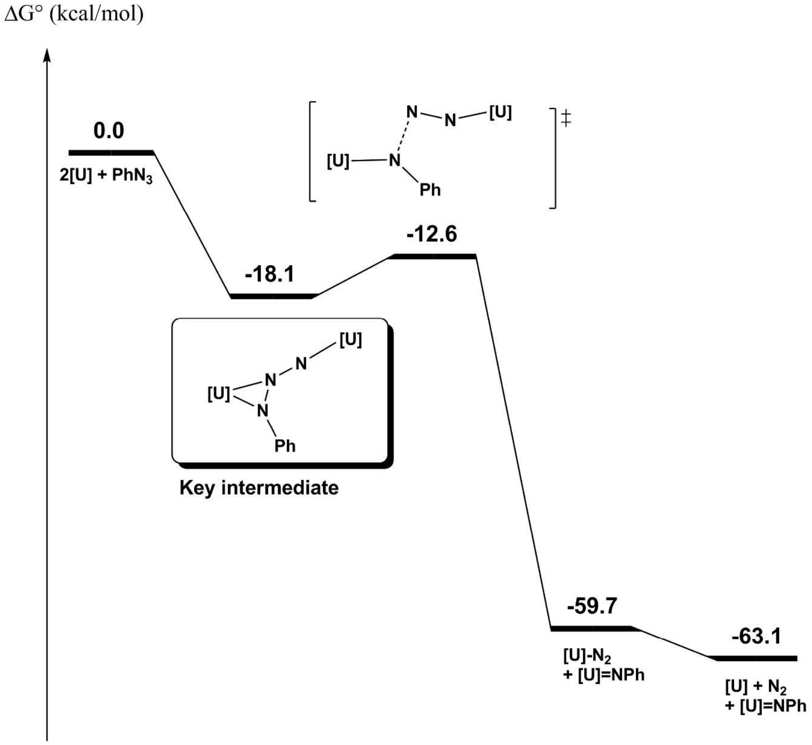


Figure 6. Gibbs free energy profile for the reaction of PhN_3 with Cp*$_3$U (noted [U] in the figure).

In the case of PhNCO, the formation of the key intermediate is found to be thermodynamically favorable. Any subsequent release of CO is predicted to be kinetically difficult and highly endergonic (Figure 7).

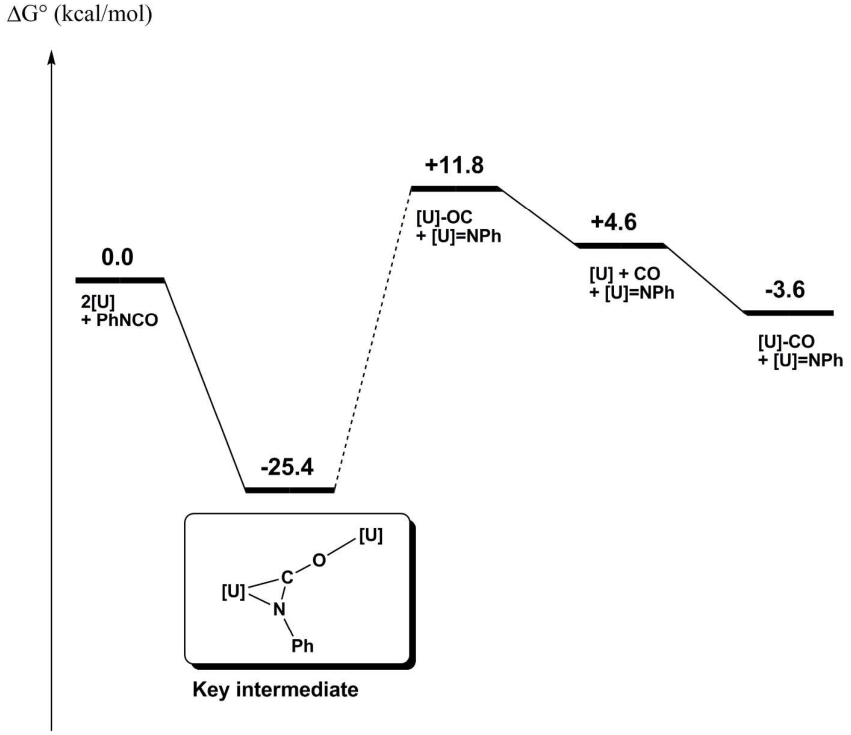


Figure 7. Gibbs free energy profile for the reaction of PhNCO with $Cp*_3U$ (noted [U] in the figure).

Thus, DFT approaches were found in excellent agreement with experiment and were able to explain the reactivity of heteroallenes other than CO_2.

Reduction of alkynes

The concept of SET reactivity was extended to the addition of terminal mono- or bis-alkynes to $^{N}U^{III}$(DME) complexes (where N stands for N-anchored tris-aryloxides ligands).[57]The DFT derived mechanism can be summarized as a two-step pathway with SET and subsequent formation of the activated binuclear alkynyl complex, followed by a C-C coupling reaction with a second terminal alkyne yielding the first vinyl bridged binuclear uranium(IV) complex (Figure 8). The same mechanism was found to operate for terminal bis-alkynes, resulting in the *cyclo*-products through C-C coupling cyclization step.

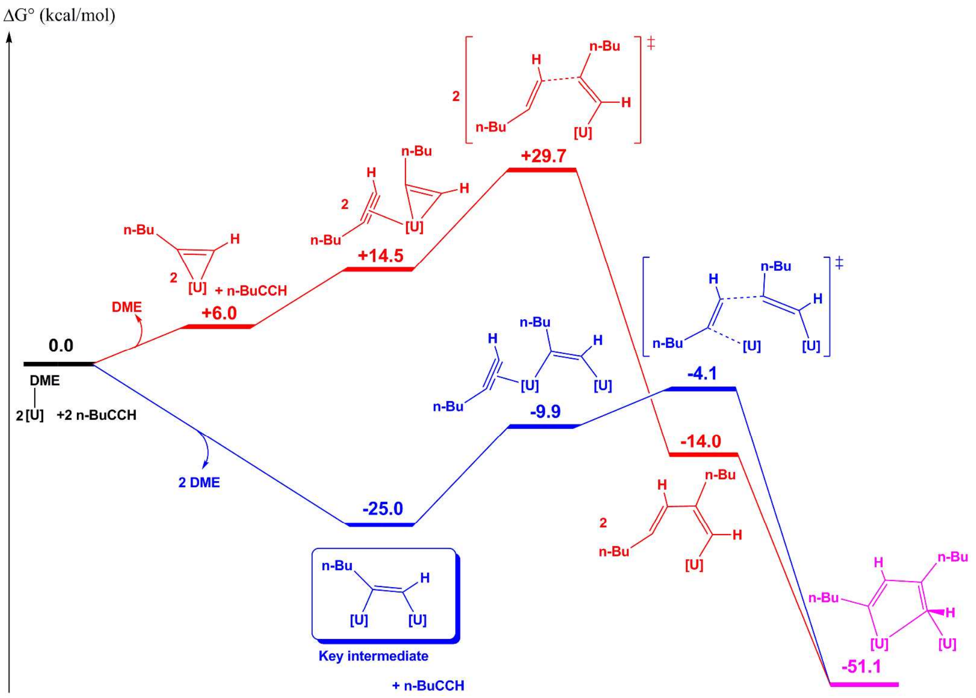


Figure 8. Gibbs free energy profiles of the reactions of $[((^{Me}ArO)_3N)U]$(noted as [U] in the figure) withn-BuCCH.

Reduction of CO

An additional theoretical study of importance concerning U(III) redox reactivity is the reaction of $[U^{III}(C_8H_6\{Si^{i}Pr_3\text{-}1,4\}_2)(Cp^*)]$ with CO.[58] Experimentally, the reaction leads to the formation of the deltate(and/or squarate)product $[U^{IV}(C_8H_6\{Si^{i}Pr_3\text{-}1,4\}_2)(Cp^*)]_2\text{-}(\mu\text{-}C_nO_n^{2-})$ (n = 3, 4) but if the stoichiometry is carefully controlled, a linear ynediolate-bridged $[U^{IV}(C_8H_6\{Si^{i}Pr_3\text{-}1,4\}_2)(Cp^*)]_2\text{-}(\mu\text{-}C_2O_2^{2-})$ can be obtained.[59,60]McKay *et al.* reported two different mechanisms leading to the respective formations of both products.[58]The ynediolate-bridged complex is found to result from a very facile C-C coupling (+2.0 kcal mol^{-1}) of two monometallic adducts $[U^{IV}(C_8H_6\{Si^{i}Pr_3\text{-}1,4\}_2)(Cp^*)(CO^{-})]$, where CO is coordinated to U by the carbon atom. Interestingly, the formation of the deltate complex involves a completely different pathway with the formation of $[U^{IV}]\text{-}(\eta^2\text{:}\eta^2\text{-}CO)\text{-}[U^{IV}]$ complex, that through the addition of a second CO readily forms a bimetallic ketene complex (the $C_2O_2^{2-}$moiety lies between both U^{IV} centers). The side-on complex has not yet been identified experimentally, however the complex is isoelectronic with known dinitrogen-bridged diuranium species[61]. A summary of both pathways is reported in Figure 9.

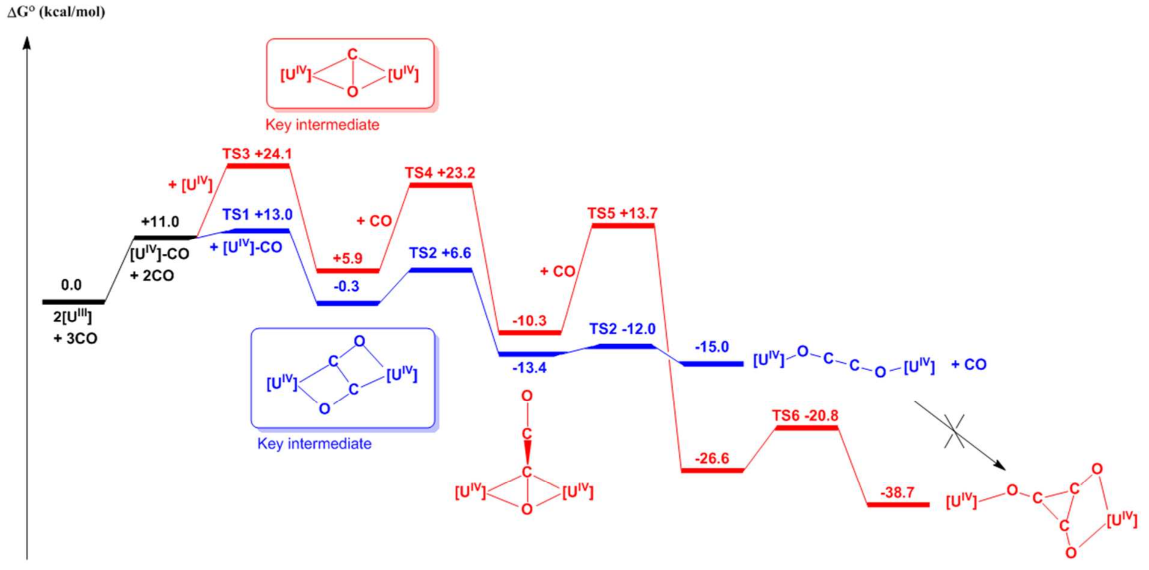


Figure 9. Summary of the theoretical investigation of the reactivity of $[U^{III}(C_8H_6\{Si^iPr_3\text{-}1,4\}_2)(Cp^*)]$ with CO. The complex is simplified as $[U^{III}]$. The numbers in parentheses are calculated Gibbs free energies. The values near the arrows are relative activation barriers while the values near the compounds are their free energies of formation.

Conclusions

Computational methods have proven their ability in dealing with f-element chemistry, even when single electron transfers (SET) are involved. By carefully defining a computational strategy and thanks to the use of Relativistic Effective Core Potentials, one can safely tackle important chemical problem such as CO_2 transformation mediated by low-valent lanthanide and actinide complexes. The use of f-in-core RECPs, both for 4f and 5f elements, allows proposing plausible reaction mechanism on chemical problem that involves bimetallic species. Thus, computational methods, even in the field of f-element chemistry, are able to help experimental chemist, and even sometimes to guide them.

The heteroallene reactivity mediated by divalent lanthanide or trivalent uranium is shown to first involve the formation of a complex with doubly reduced substrate sandwiched between two oxidized metal. This intermediate, called the key intermediate, is in general the precursor of all subsequent reactivity. This subsequent reactivity is finally easily explained by classical chemical concepts such as thermodynamic and kinetic stability of the formed small molecule, charge distribution at the transition state and steric hindrance.

Author Contributions

The manuscript was written through contributions of all authors.

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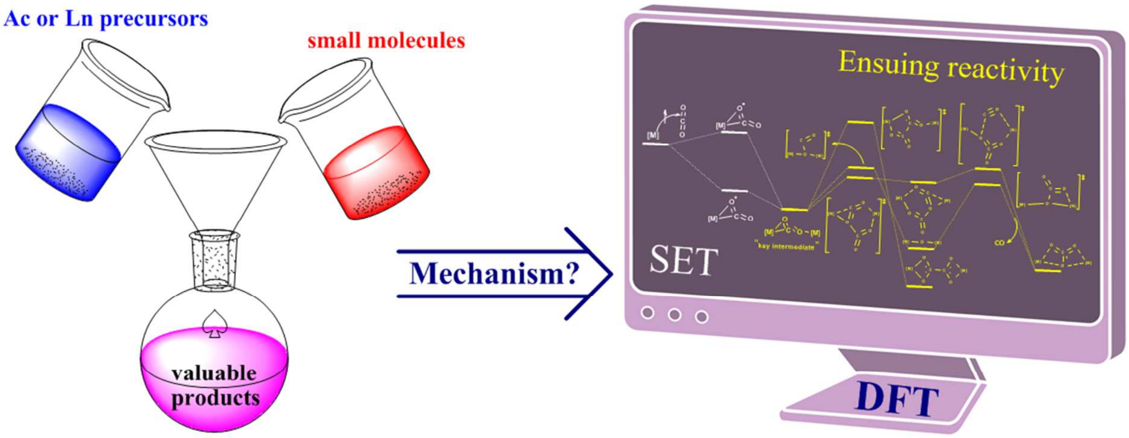

DFT calculations can provide useful insights on low-valent f-element single electron transfer reactivity.