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ARTICLE

Can the pentamethylcyclopentadienyl ligand act as a proton-relay in *f*-element chemistry? Insights from a joint experimental/theoretical study.

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Isomerisation of buta-1,2-diene to but-2-yne by $(\text{Me}_5\text{C}_5)_2\text{Yb}$ is a thermodynamically favourable reaction, with the $\Delta_r G^\circ$ estimated from experimental data at 298 K to be $-3.0 \text{ kcal mol}^{-1}$. It proceeds in hydrocarbon solvents with a pseudo first-order rate constant of $6.4 \cdot 10^{-6} \text{ s}^{-1}$ and $7.4 \cdot 10^{-5} \text{ s}^{-1}$ in C_6D_{12} and C_6D_6 , respectively, at 20°C . This 1,3-hydrogen shift is formally forbidden by symmetry and has to occur by an alternative pathway. The proposed mechanism for buta-1,2-diene to but-2-yne isomerisation by $(\text{Me}_5\text{C}_5)_2\text{Yb}$ involves: coordination of methylallene (buta-1,2-diene) to $(\text{Me}_5\text{C}_5)_2\text{Yb}$, deprotonation of methylallene by one of the Me_5C_5 ligands followed by protonation of the terminal methylallenyl carbon to yield the known coordination compound $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$. Computationally, this mechanism is not initiated by a single electron transfer step and the ytterbium retains its oxidation state (II) throughout the reactivity. Experimentally, the influence of the metal centre is discussed by comparison with the reaction of $(\text{Me}_5\text{C}_5)_2\text{Ca}$ towards buta-1,2-diene, and $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with ethylene. The mechanism by which the Me_5C_5 acts as a proton-relay within the coordination sphere of a metal also rationalises the reactivity of (i) $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{OEt}_2)$ with phenylacetylene, (ii) $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ with phenylphosphine and (iii) $(\text{Me}_5\text{C}_5)_2\text{U}(\text{NPh})_2$ with H_2 to yield $(\text{Me}_5\text{C}_5)_2\text{U}(\text{HNPh})_2$. In the latter case, the computed mechanism is the heterolytic activation of H_2 by $(\text{Me}_5\text{C}_5)_2\text{U}(\text{NPh})_2$ to yield $(\text{Me}_5\text{C}_5)_2\text{U}(\text{H})(\text{HNPh})(\text{NPh})$, followed by a hydrogen transfer from uranium back to the imido nitrogen atom using one Me_5C_5 ligand as a proton-relay. The overall mechanism by which hydrogen shifts using a pentamethylcyclopentadienyl ligand as a proton-relay is named *Carambole* in reference to carom billiards.

Introduction

It is well-established that significant development in homogeneous organometallic chemistry is associated with the use of cyclopentadienyl ligands. Their propensity to act as excellent electron donors, due to their electron rich π system, in combination with their low electron acceptor abilities, made them crucial for stabilising electron-deficient metal centres in organometallic complexes. Their coordination often involves three metal orbitals and thus allows the stabilisation of reactive species, as well as the completion of catalytic cycles. In text books, this family of ligands is commonly presented as spectator ancillary ligands that stabilise high oxidation states of various metals, ranging from early *d*-transition metal to *f*-element based complexes.¹ It has been shown, that in various organometallic systems the amount of electron density

transferred from a cyclopentadienyl motif to the metal can be adjusted by haptotropic shift, also named as ring slippage, and results in different bonding modes.²

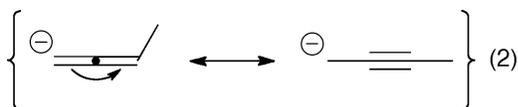
In *d*⁰- or *f*-element complexes, their inertness is relative, since metallation by deprotonation of the methyl substituents in pentamethylcyclopentadienyl (Me_5C_5 or Cp^*) ligands has been observed and well characterised both experimentally and computationally (the so-called “tucked-in” compounds).³ This metallation reaction is important since, for example, it has been used for the (1,2,4-*t*-Bu₃C₅H₂) ligand to generate a key precursor complex in the chemistry of Ce.⁴ This ligand is suggested to act as a hydrogen relay in metal hydride complexes in few cases.⁵ In a seminal study, Jones et al. proposed the involvement of the Cp ligand as a proton carrier, generating a transient η^4 -cyclopentadiene complex.⁶ From a computational point of view and to the best of our knowledge, only Eisenstein's and Bühl's

groups have considered this type of mechanism.^{7a,7b} Nevertheless, for this particular reaction, the authors concluded that this mechanism was not operative. Reactivity of Cp* ligand was also reported in scandium chemistry by Evans et al.⁸ but in this case, the reactive Cp* displays at η^1 -coordination mode even in the solid-state structure. To the best of our knowledge, there is no precedent in the literature for reactions that involve f -elements in which the reactivity is explicitly mediated by cyclopentadienyl (Cp-type) ligands.

The unexpected isomerisation of buta-1,2-diene (methylallene) to but-2-yne (dimethylacetylene) catalysed by decamethylterbocene, (Me₅C₅)₂Yb, lead us to explore the inertness of the Me₅C₅ ligand using DFT calculations. Indeed, this apparently very simple organic transformation is a forbidden reaction and requires a catalyst to proceed. However, the isomerisation of buta-1,2-diene to but-2-yne (eq. 1) is an exergonic process with $\Delta_r G^\circ$ (estimated from measured $\Delta_r H^\circ$ at 25°C) being of 3.0 kcal mol⁻¹.^{9a}



Similarly, the rearrangement of methylallene to either ethylacetylene or buta-1,3-diene is also an exergonic reaction, with estimated $\Delta_r G^\circ$'s of 0.9 and 11 kcal mol⁻¹ at 25°C, respectively.^{9a} Even though these rearrangements are exergonic, they do not occur in presence of (Me₅C₅)₂Yb due to kinetic limitation. For instance, the suprafacial 1,3-sigmatropic shift is thermally forbidden in a concerted process, according to Woodward-Hoffmann rules.¹⁰ The unimolecular rate for the rearrangement of allene to propyne has been estimated from shock tube experiments in the temperature range of 750 to 1500°C. It proceeds with activation energies ranging from 93 to 61 kcal mol⁻¹, in line with symmetry forbidden reaction. It is also well-known that symmetry rules can be bypassed by catalysing the reaction using, for example, metal complexes.¹¹ In that sense, various heterogeneous catalysts such as TiO₂ or ZnO can catalyse the allene to alkyne at low temperature.¹² The reaction using ZnO as a catalyst has been extensively studied, and it is thought to proceed by abstraction of a proton from zinc oxide as a base. The resulting carbanion, [CH₂=C=CH]⁻, rearranges to [CH₂-C≡CH]⁻ followed by reprotonation by the [ZnOH]⁺.^{12c} This mechanism is analogous to the one proposed for the base catalysed rearrangement in solution,^{9b} in which it is thought to involve a deprotonation by a base, B, to give a carbanion, symbolised by the resonance structures (eq. 2), and the conjugated acid BH⁺.



In the specific case of the rearrangement of 1,3,3-triphenyl-3-deutero-prop-1-yne to 1,3,3-triphenyl-1-deutero-propa-1,2-diene, inter- and intra-molecular processes have been observed depending on the nature of the base.¹³ An intramolecular 1,3-shift mechanism is envisioned as being formed by hydrogen-bonding between B-H⁺ and subsequent protonation of the

propargylic carbanion. This would formally allow the formation of the 1,3-suprafacial sigmatropic shift product. It should be noted that this mechanism finds support in the ion-molecule rearrangement of allene and methylacetylene in the presence of the alcohol/alkoxide couple reported in gas phase.¹⁴

The use of (Me₅C₅)₂Yb to affect this transformation could be imagined since it is known that this species forms coordination compounds with potential proton donor ligands, such as NH₃^{15a} or phenylacetylene.^{15b} The pKa of the latter ligands are in the same order of magnitude or even greater than that of Me₅C₅H; the pKa of which in dimethylsulfoxide is 26.¹⁷ When the pKa of the proton donor ligand is less than that of Me₅C₅H, proton transfer occurs with loss of Me₅C₅H.^{15b} Although the pKa has not been determined for methylallene, gas phase acidities of allene and propyne are almost identical within the measurement uncertainty of ± 3 kcal mol⁻¹.¹⁴ As a consequence, the pKa of an allene should be close to that of Me₅C₅H. In this case, the determination of a plausible reaction mechanism could be more complicated than in the examples previously described, since in addition to the possible acid-base mechanisms highlighted above, low-valent lanthanide(II) complexes are often postulated to induce reactivity by Single Electron Transfer (SET).¹⁸ In the allene reaction, SET would yield a radical (or a carbanion) of the substrate that would isomerise to acetylenic radicals (or carbanions). The electron transfer back to the ytterbium(III) centre is then an issue since this might be endoergic. However, for the special case of dimethylacetylene, the back electron-transfer might be exoergic, since the electron affinity of the substrate is -3.4 eV.¹⁹ On the other hand, trivalent ytterbium which possesses a 4f¹³ electronic configuration,²⁰ is more stable than divalent ytterbium in aqueous acid solution by +1.1 V relative to NHE.^{21a} Moreover, in acetonitrile, the reduction potential of (Me₅C₅)₂Yb⁺ is -1.4 V,^{21b} while in tetrahydrofuran (THF) the reduction potential of Cp₃Yb is -1.5 V.^{21c} Hence, oxidation of (Me₅C₅)₂Yb is thermodynamically favourable, and several examples of its electron transfer behaviour have been described.²² Among others, the bonding situation resulting from a single electron transfer has been particularly well studied in the case of bipyridine and phenanthroline adducts of (Me₅C₅)₂Yb.²³ Interestingly, the reduction potential of methylallene has never been measured, even though a value of -2.1 V is estimated for the two-electron reduction of tetraphenylallene.²⁰ A more relevant quantity could be the electron affinity of allene, which is -1.9 \pm 0.1V.²⁴ These approximate values suggest that electron transfer from (Me₅C₅)₂Yb to methylallene is not a preposterous idea. Thus, the key element in the electron-transfer cycle is the difference between the estimated electron affinities of methylallene and dimethylacetylene. In addition, as suggested in the polymerisation of ethylene catalysed by (Me₅C₅)₂Yb,^{25b} initiation by a single electron transfer from Yb(II) to ethylene is not absurd.

Hereafter, we report the isomerisation reaction of buta-1,2-diene into but-2-yne catalysed by (Me₅C₅)₂Yb. The reaction mechanism has been explored by DFT calculations and appears

not to involve SET but rather a Cp^* -assisted hydrogen transfer. This new mechanism is proposed to operate in other reactions that involve different divalent lanthanide and uranium(VI) complexes.

Results and Discussion

Isomerisation of but-1,2-diene to but-2-yne.

Addition of an equimolar amount of buta-1,2-diene to an orange solution of $(Me_5C_5)_2Yb$ in pentane results in darkening of the colour of the solution until a deep red colour is apparent after ca. 1 hour. Red crystals of $(Me_5C_5)_2Yb(\eta^2-MeC\equiv CMe)$ may be isolated in 72% yield on cooling. The acetylene complex is identical to that prepared from $(Me_5C_5)_2Yb$ and but-2-yne and characterised by X-ray crystallography.^{25a} Hence the ytterbium metallocene isomerises methylallene to dimethylacetylene (eq. 1).

The synthesis reaction is stoichiometric since one molar equivalent of buta-1,2-diene gives one molar equivalent of $(Me_5C_5)_2Yb(\eta^2-MeC\equiv CMe)$,^{25a} though the isomerisation reaction is catalytic as shown by the following experiment. Addition of ca. 10-fold excess of buta-1,2-diene to $(Me_5C_5)_2Yb$ in C_6D_6 in an NMR tube and monitoring the reaction by 1H NMR spectroscopy shows that the resonances due to buta-1,2-diene disappear and the resonances due to but-2-yne appear. The starting materials and products are diamagnetic. The time evolution of the 1H NMR spectrum is shown in Figure 1.

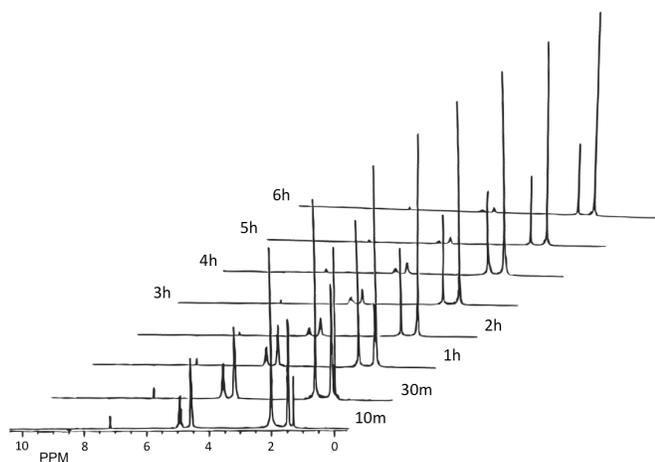


Fig. 1 Time evolution of the 1H NMR spectrum for the reaction $(Me_5C_5)_2Yb$ with buta-1,2-diene in C_6D_6 at $20^\circ C$.

Initially, the ratio of methylallene to $(Me_5C_5)_2Yb$ is 10.7 to 1. Within 10 minutes, the resonance of $MeC\equiv CMe$ appears, the chemical shift of which is the average between $(Me_5C_5)_2Yb(\eta^2-MeC\equiv CMe)$ and free $MeC\equiv CMe$. After 6 hours, the ratio of methylallene to $(Me_5C_5)_2Yb$ is 2.8 to 1, while that of but-2-yne to $(Me_5C_5)_2Yb$ is 7.4 to 1. After 3 days, all the resonances due to methylallene are gone. The isomerisation is catalytic since the area of the resonance due to the $(Me_5C_5)_2Yb$ protons does not change relative to those of the residual protons in C_6D_6 over six hours. The methyl resonance of but-2-yne initially appears at the value of the coordination complex; as more alkyne forms,

the coordinated and free ligands exchange and the methyl resonance moves towards that of the free ligand whose protons are deshielded. The exchange between free and coordinated but-2-yne is rapid at $20^\circ C$ and the chemical shift is the weighted average. The exchange is still rapid on the 1H NMR time scale at $-75^\circ C$.^{25a} The time evolution in cyclohexane- d_{12} follows a pattern similar to that in C_6D_6 except that it is slower in the former solvent.

The pseudo-first order rate constant for the isomerisation can be determined from a plot of $\ln([buta-1,2-diene])$ as a function of time over ca. three half-lives. In C_6D_{12} , with $(Me_5C_5)_2Yb$ concentration of $0.16\ mol\ L^{-1}$ and the initial concentration of buta-1,2-diene of $2.6\ mol\ L^{-1}$ at $20^\circ C$, the rate constant is $6.4\ 10^{-6}\ s^{-1}$. The half-life is 30 h. In C_6D_6 , with the concentration of $(Me_5C_5)_2Yb$ of $0.19\ mol\ L^{-1}$ and the initial concentration of buta-1,2-diene of $2.0\ mol\ L^{-1}$ at $20^\circ C$, the rate constant is $7.4\ 10^{-5}\ s^{-1}$ and the half-life is 160 min. These plots are available as supplementary material (see Figures S1 and S2).

It is difficult to learn more about the isomerisation reaction mechanism since the product, $(Me_5C_5)_2Yb(\eta^2-MeC\equiv CMe)$, is exchanging with free but-2-yne in the solution, and the 1H NMR spectrum gives an averaged chemical shift. Further, we assume that buta-1,2-diene is coordinated to $(Me_5C_5)_2Yb$ as was shown in $(Me_5C_5)_2Yb(\mu, \eta^2-C_2H_4)Pt(PPh_3)_2$ case,^{25b} and that the coordinated buta-1,2-diene is exchanging with free buta-1,2-diene and but-2-yne since a single averaged chemical shift is observed for the $(Me_5C_5)_2Yb$ protons. This exchange prevents us from determining the order of the reaction in allene since the 1H NMR spectrum is an averaged one and the chemical shift of the $(Me_5C_5)_2Yb$ protons as a function of methylallene concentration is very small as these compounds are diamagnetic. The small chemical shift change would give values of questionable validity. The chemical exchange averaged spectra renders meaningless crossover experiments between labelled and unlabelled compounds so that we cannot demonstrate the molecularity of the reaction. Hence all we can measure is the pseudo-first order rate constant and show that the reaction is catalytic.

Experimentally, we cannot prove or disapprove the supposition that $(Me_5C_5)_2Yb$ is an electron-transfer catalyst, though we can provide some supporting evidence of a negative kind. For instance, the bis-pentamethylcyclopentadienyl calcium complex, $(Me_5C_5)_2Ca$, is unlikely to act as an electron source since the third ionisation potential of calcium is 50.9 eV, being almost two times higher than that of ytterbocene (25.0 eV). This is the reason for the inaccessibility of oxidation state +III for the calcium atom. Both metallocenes have a bent structure in the gas phase with averaged Ca-C and Yb-C distances of 2.609(6) Å and 2.622(6) Å, respectively,²⁶ showing that the size of the two metal centres is quite similar. Further, $(Me_5C_5)_2Ca$ reacts with but-2-yne to give the colourless coordination compound $(Me_5C_5)_2Ca(\eta^2-MeC\equiv CMe)$, which probably has the same structure as that determined for $(Me_5C_5)_2Yb(\eta^2-MeC\equiv CMe)$ ^{25a} since their physical properties are very close. In addition, both compounds crystallise from

pentane, have melting points within 20°C, and similar infrared spectra. In both cases we cannot assign the triple bond stretching frequency, since the MeC≡C angle is nearly linear and the stretch is not allowed in the infrared spectrum. The solution properties are similar also; the ¹H NMR resonances are averaged due to the equilibrium shown in eq. 3, which we have not been able to stop by lowering the temperature, as found for the ytterbium system.



The reported X-ray crystal structure of $(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)$ shows that diacetylenes can coordinate to $(\text{Me}_5\text{C}_5)_2\text{Ca}$.²⁷ This supports our deductions about the coordination of dimethylacetylene. Hence, $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $(\text{Me}_5\text{C}_5)_2\text{Ca}$ are forming similar coordination compounds with dimethylacetylene. Although $(\text{Me}_5\text{C}_5)_2\text{Ca}$ does indeed isomerise buta-1,2-diene to $(\text{Me}_5\text{C}_5)_2\text{Ca}(\eta^2\text{-MeC}\equiv\text{CMe})$, the rate of isomerisation in cyclohexane at 20°C is much slower than that observed in the ytterbium system; the half-life of which is greater than 4 days. Possible explanation for this can be due to the difference in polarisability between the two metals, being higher for calcium atom.

Ethylene Polymerisation.

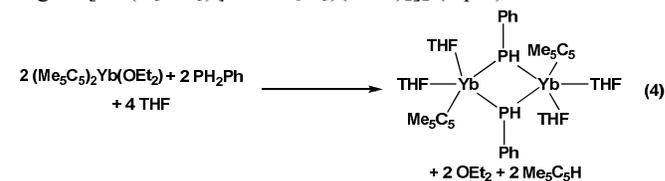
As noted earlier, ethylene can be polymerised to polyethylene by $(\text{Me}_5\text{C}_5)_2\text{Yb}$, a perplexing observation since it is not obvious how the reaction is initiated.^{25b} Thus, addition of ethylene (total pressure of 12 atm.) to an orange solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in hexane instantaneously gives a green solution which becomes turbid and a white precipitate of polyethylene forms; 0.1 g of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ gives 2-3 g of polyethylene in a time of 1-2 hours. When the ethylene pressure is released, the green solution turns orange again. We interpret the green colour as being due to an ethylene coordination complex since coordination compounds of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with classical Lewis bases are green.²⁸ We are not aware of the precise stoichiometry of this hypothetical ethylene complex, though evidence has been presented some time ago for the existence of an ethylene complex of $(\text{Me}_5\text{C}_5)_2\text{Eu}$ in cyclohexane,^{29a} and of $(\text{C}_2\text{H}_4)_n\text{Eu}$ complexes using europium atoms in cryogenic matrices.^{29b} Neither $(\text{Me}_5\text{C}_5)_2\text{Ca}$ nor $(\text{Me}_5\text{C}_5)_2\text{Eu}$ polymerise ethylene under similar conditions (12 atm. in hexane for 1 day), but $(\text{Me}_5\text{C}_5)_2\text{Sm}$ does polymerise ethylene quickly. As suggested earlier, generation of $[(\text{Me}_5\text{C}_5)_2\text{Eu}^{\text{III}}]^+$ is difficult, its reduction potential being -0.56 V,^{21b} whereas $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $(\text{Me}_5\text{C}_5)_2\text{Sm}$ are very good to excellent reducing agent with reduction potentials of -1.12 V and -1.7 V, with respect to NHE respectively.^{21b}

In addition, the green crystalline diethyl ether complex of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in hexane does not polymerise ethylene even when the olefin is in large excess. An orange hexane solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ was saturated with methane to a pressure of 7 atm., no colour change was apparent. Ethylene was added to a total pressure of 14 atm. and no polymer formed over six hours. Removal of both gases followed by adding ethylene to a pressure of 14 atm. gives polyethylene instantaneously. Further,

xenon behaves similarly to methane: it inhibits polymerisation. The colour of the solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in hexane is not visually affected by xenon. A red-orange toluene solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ does not prevent polymerisation of ethylene though the rate is markedly slower than that in hexane.

Reaction of phenylphosphine with $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$.

The reaction of phenylphosphine with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ in toluene produces a dark red powder which redissolves in THF to give $[\text{Yb}(\text{C}_5\text{Me}_5)(\mu\text{-PhC}_6\text{H}_5)(\text{THF})_2]_2$ (eq. 4).



The presence of only one C_5Me_5 ring per ytterbium is readily established by proton and phosphorus NMR. The proton NMR spectrum indicates that the complex is diamagnetic. The ratio of C_5Me_5 to phenyl protons of 15:5 immediately suggests a monoring ytterbium(II)-phosphide formulation. The presence of a phenylphosphide unit is confirmed by the observation of a doublet ($^1J_{\text{P-H}}$ 185 Hz) at -89.7 ppm in the proton-coupled phosphorus NMR spectrum. The phosphorus resonance appears at 33 ppm downfield of the signal for free phenylphosphine as a result of the strong electron withdrawing effect of the Yb(II) centre. The P-H coupling constant only decreases by ca. 12 Hz going from free phenylphosphine to complexed phenylphosphide. Unfortunately ^{31}P - ^{171}Yb ($I = 1/2$, 14.3 % natural abundance) coupling is not observed, despite the fact that the phosphorus resonance is less than 5 Hz wide at half peak height. The infrared spectrum shows a single P-H stretch at 2259 cm^{-1} , consistent with a coordinated RPH⁻ ligand.

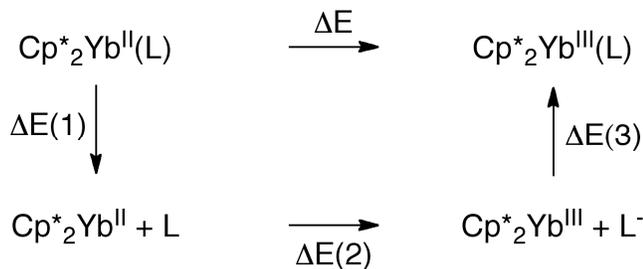
An ORTEP diagram is shown in Figure S3 along with selected bond distances and angles, as tabulated in Table S1. The structure consists of a dimer in which two ytterbium centres are bridged by two phenylphosphide ligands. A crystallographic inversion centre, located at the midpoint of the Yb-Yb vector, renders both ytterbium atoms equivalent. There is no plane of symmetry in this molecule. Each ytterbium atom is surrounded by one C_5Me_5 ring, two bridging phenylphosphides and two THF molecules: the metal centre is formally seven-coordinate and divalent. The Yb-O bond lengths of 2.445(7) and 2.497(7) Å are slightly longer than the value of 2.412(5) Å found in $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{THF})$.^{28a} The two unique Yb-P distances in **4** are 2.957(2) and 3.066(2) Å.

Mechanistic Exploration

Single electron transfer in $(\text{Me}_5\text{C}_5)_2\text{Yb}$ alkene, allenes, dienes and alkyne adducts.

Among the adducts described above, the only adduct that is characterised by X-ray crystallography is $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$. In the solid state, the structure of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$ ^{25a} displays nearly linear Me-C≡C angles of $177.4 \pm 0.7^\circ$. Optimisations of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$ complex using *f*-in-core relativistic effective core potentials (RECP's)

designed for either the +II or the +III ytterbium oxidation states lead to angles of 176.8° of 145.6°, respectively. Experimentally, no signature for the presence of paramagnetic compounds is seen by NMR spectroscopy during the reaction between buta-1,2-diene and $(\text{Me}_5\text{C}_5)_2\text{Yb}$, nor in solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$ in the presence of excess but-2-yne.^{25a} In the same conditions, it has been shown that bounded and free but-2-yne undergo fast exchange on the NMR time scale, when this exchange remains fast at -75°C.^{25a} The bond dissociation energy computed between $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and but-2-yne is around 2 kcal mol⁻¹ using both large core Yb(II) RECP or small core RECP (singlet spin state for the latter). At the DFT level using a small core RECPs, $(\text{Me}_5\text{C}_5)_2\text{Yb}^{\text{III}}(\eta^2\text{-MeC}\equiv\text{CMe})$ is less stable than $(\text{Me}_5\text{C}_5)_2\text{Yb}^{\text{III}}$ and free $\text{MeC}\equiv\text{CMe}$ by 23.3 kcal mol⁻¹. At the CAS-SCF level, $(\text{Me}_5\text{C}_5)_2\text{Yb}^{\text{III}}[(\eta^2\text{-Me-C}\equiv\text{C-Me})^*]$ turns out to be more stable by -24.4 kcal mol⁻¹ with respect to the same separated reactants. For this particular case, these two calculations give contradictory results about stabilities of the putative Yb(III) adducts and more importantly fail to account for the experimentally characterised fast exchange between $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $\text{MeC}\equiv\text{CMe}$. Indeed, for a Yb(III) adduct of but-2-yne, DFT does not account for the formation of the adduct, whereas CAS-SCF over stabilises the relative energy of the adduct preventing any fast exchange at low temperature. As a result, binding of $\text{MeC}\equiv\text{CMe}$ to an Yb(II) centre is not clarified in either computation. Similarity, the fast exchange that is observed between buta-1,2-diene and $(\text{Me}_5\text{C}_5)_2\text{Yb}$ rules out mechanisms that rely on a SET initiation mechanism. This is further supported by the computed SET energies for the $(\text{Me}_5\text{C}_5)_2\text{Yb}^{\text{II}}$ adducts according to the thermodynamic cycle defined in Scheme 1. It should be noted, that this computational strategy has been successfully applied for the indirect estimation of the relative SET energies in lanthanide and actinide chemistry.^{18,30}



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

In particular, the $\Delta E(1)$ and $\Delta E(3)$ in this Hess cycle correspond to the dissociation and binding energy of L and L⁻

to $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $[(\text{Me}_5\text{C}_5)_2\text{Yb}]^+$, respectively. These values are computed at the DFT level, including the ZPE correction using large core RECPs. $\Delta E(2)$ is the energy difference of the electron affinity between L and $(\text{Me}_5\text{C}_5)_2\text{Yb}$; the contribution from ytterbocene has not been computed but is constant for all ligands, namely buta-1,2-diene, but-2-yne and ethylene. The electron affinity of the ligands L have been computed at the WIU level (see Supporting Information for further details).³¹ Single Electron Transfer from Yb(II) to buta-1,2-diene is less favourable by 3.5 kcal mol⁻¹ compared to the but-2-yne. This is consistent with the reactivity occurring at a Yb(II) centre.

Interestingly, the SET from Yb(II) to ethylene is computed to be less than a kcal mol⁻¹ more favourable than for but-2-yne. As the polymerisation of ethylene is most likely induced by SET the formation of the $(\text{Me}_5\text{C}_5)_2\text{Yb}^{\text{III}}[(\text{C}_2\text{H}_4)^*]$ is favourable. This correlates with the fact that initiation of ethylene polymerisation is inhibited by weak ligand such as CH₄ and Xe, and suggests that the different behaviour of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with respect to ethylene and buta-1,2-diene originates experimentally from small differences between the reduction potentials (electron affinities) of the ligands. This point was previously addressed for weak adducts of divalent lanthanocenes.³²

Mechanistic aspects for the catalytic isomerisation reaction of buta-1,2-diene to but-2-yne using $(\text{Me}_5\text{C}_5)_2\text{Yb}$.

In a plausible mechanism, Me_5C_5 is the only base in the reaction media that could mediate the 1,3-shift by deprotonation of C³-H of methylallene followed by protonation at C¹H₂ to yield but-2-yne (see Figure 2 for label definitions). This mechanism, the so called *carambole*, by which hydrogen shifts from C³ to C¹ using one Me_5C_5 ligand as a proton-relay has been computed for Yb, Eu, Sm, Tm and Ca. The energy profile for the Yb case is given in Figure 2, and can also be considered as a general profile for these set of metallocenes.

The reaction begins with the formation of the allene adduct **A** that undergoes deprotonation of C³-H (**TS_{A-I}**). The latter transition state yields intermediate **I** in which Yb binds a pentamethylcyclopentadiene, a methylallenyl and the remaining Me_5C_5 ligand. This intermediate **I** evolves *via* transition state **TS_{I-P}** to the final but-2-yne adduct **P**. **TS_{I-P}** corresponds to the protonation of the propargylic C¹ carbon atom from the protonated Me_5C_5 ligand. The associated thermodynamic and kinetic data of **A**, **TS_{A-I}**, **I**, **TS_{I-P}**, and **P** is given in Table 1 for the different metal centres, with the values corresponding to enthalpies.

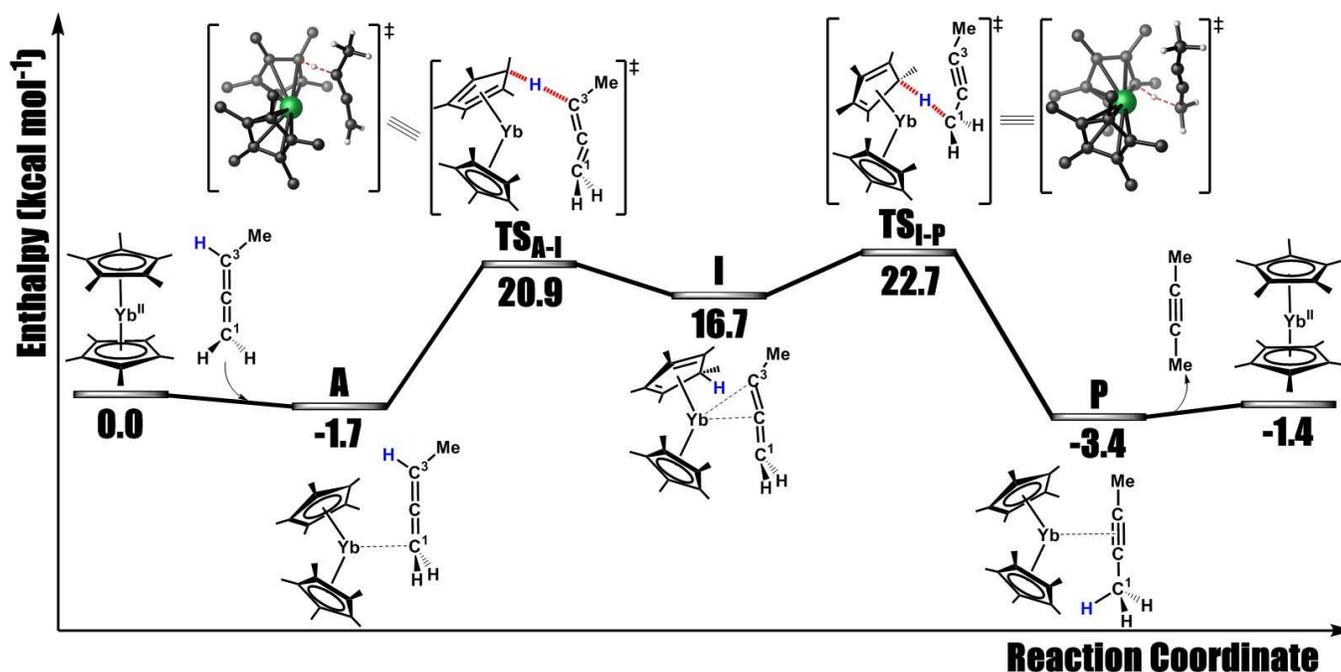


Fig. 2 B3PW91 enthalpy profile in kcal mol⁻¹ for the 1,3-shift reaction mechanism in (Me₅C₅)₂Yb(buta-1,2-diene) to (Me₅C₅)₂Yb(MeCCMe).

Table 1 Thermodynamic and kinetic in kcal mol⁻¹ data for the buta-1,2-diene to but-2-yne isomerisation mediated by (Me₅C₅)₂M, M = Yb, Eu, Sm, Tm and Ca.^{9b}

Metal	$\Delta H(\text{A})$	$\Delta H(\text{TS}_{\text{A-I}})$	$\Delta H(\text{I})$	$\Delta H(\text{TS}_{\text{I-P}})$	$\Delta_r H^\circ$
Yb(II)	-1.7	20.9	16.7	22.7	-3.4
Yb ^b	-1.0	21.4	18.1	22.9	-3.2
Eu(II)	-1.6	20.9	16.0	22.4	-4.0
Sm(II)	-1.2	21.5	16.4	23.1	-3.5
Tm(II)	-2.3	20.4	16.0	22.1	-4.1
Ca(II)	0.6	25.1	21.2	26.8	-0.5

For Yb(II), the initial deprotonation of the C³-H of buta-1,2-diene involves a barrier of 20.9 kcal mol⁻¹ to yield intermediate **I** that lies 16.7 kcal mol⁻¹ above the separated reactants. This intermediate can evolve either backward, towards allene adduct, or forward, towards alkyne adduct, with activation energy of 4.2 (TS_{A-I}) and 6.0 (TS_{I-P}) kcal mol⁻¹, respectively. Protonation at C¹ directly affords the final adduct (Me₅C₅)₂Yb(η²-MeCCMe) (**P**) with an overall exothermicity of 3.4 kcal mol⁻¹. The highest energy point of the mechanism corresponds to the reprotonation of the substrate (22.7 kcal mol⁻¹ with respect to the entrance channel).

We assessed the selectivity of the deprotonation reaction by computing analogous mechanisms that begins by the deprotonation of the methyl group or the terminal methylene of buta-1,2-diene. Deprotonation of the methyl group of buta-1,2-

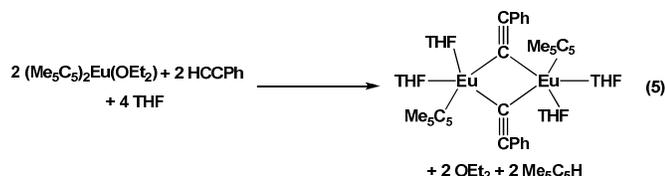
diene by the Me₅C₅ ligand is kinetically prevented by an energy barrier of 31.5 kcal mol⁻¹ with respect to separated methylallene and (Me₅C₅)₂Yb reactants. On the other hand, deprotonation of the terminal C¹H₂ group proceeds with an energy barrier of 21.5 kcal mol⁻¹ that is similar to the one computed for the activation of C³-H. However, in this case, the ensuing intermediate leads to a dead end, since the activation barrier of the second transition state (protonation at C³) lays at 30.9 kcal mol⁻¹ above the separated reactants. Energy profiles for to these pathways are given as a supporting material (Figure S4). All our attempts to search for alternative mechanisms based on an Yb(II) metal centre failed. Any transition state that involves a direct shift or stepwise shift within the coordinated buta-1,2-diene is higher than 50 kcal mol⁻¹ above starting adduct. For Yb, the most favourable energy profile has been recomputed by taking into account explicitly the 4f electrons. This leads to variations of less than a kcal mol⁻¹ compared to the enthalpies computed using the large core RECPs (see the first 2 entries in Table 1).

The same energy profile discussed above has been computed for the hypothetical (Me₅C₅)₂M (M = Eu(II), Sm(II), Tm(II)), and the (Me₅C₅)₂Ca complexes (Figure 2 and Table 1). For all lanthanides, the enthalpies of both transition states and intermediate complexes are almost identical to those computed for Yb(II), so that the reaction seems independent of the lanthanide. Since the molecularity of this reaction is zero, computed thermodynamics can fit with the experimental $\Delta_r G^\circ$ value of -3 kcal mol⁻¹ at 298 K in hydrocarbon solvents. In the case of calcium, the enthalpies of transition states and of the intermediates are raised by almost 4 kcal mol⁻¹, with the global thermodynamic balance picture being more neutral. Assuming a first order kinetic law, the difference in half-times between

$(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $(\text{Me}_5\text{C}_5)_2\text{Ca}$ determined in C_6D_{12} leads to a difference in the corresponding activation barriers of less than a kcal mol^{-1} . Finally, the computed energy difference of almost 4 kcal mol^{-1} leads to a fair agreement with the experimental observations, further supporting the authenticity of the proposed mechanism.

Mechanistic aspects for the reaction of PhCCH with $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{OEt}_2)$.

In the same spirit, we were interested in a related reactivity that concerns the reaction of $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{OEt}_2)$ with $\text{PhC}\equiv\text{CH}$ in the presence of tetrahydrofuran (eq. 5).³³



The outcome of this reaction shares some common features with the concept of the *carambole* mechanism, as previously described. Indeed, a common element with respect to the allene isomerisation is that the formal oxidation state of the europium remains unchanged during the course of the reaction, being the lowest one (+II). The latter observation was recently confirmed theoretically by our group using the SOMO-LUMO gap methodology.^{18a} In particular, inspection of the frontier orbitals of $\text{Cp}^*_2\text{Eu}(\text{PhCCH})$ adduct revealed the absence of a single electron transfer from Yb centre to the unsaturated substrate. On the other hand, the major difference with the allene isomerisation reaction is the fact that the $\text{Me}_5\text{C}_5\text{H}$ now

dissociates, and is replaced by two THF molecules forming a dimer with bridging phenylacetylide groups. This particular reactivity is mainly due to the incapability of the newly formed phenylacetylide to undergo an isomerisation process, through the protonation of its β -carbon. Hence, we were interested in finding a plausible mechanism for the protonation of the cyclopentadienyl group. In this respect, the most reasonable mechanistic scenario is to consider an acid-base reactivity, with the phenylacetylene playing the role of the acid and the pentamethylcyclopentadienyl the role of the base (Figure 3). The reaction sequence starts most likely through an exchange of the ether by the phenylacetylene ligand, the latter being weakly coordinated to the metal centre. The energetic cost of passing from the transition state TS_{2-3} that corresponds to the proton transfer is relatively low ($\Delta H^\ddagger = 18.8 \text{ kcal mol}^{-1}$) with respect to the reactants. The product of this step is the transient intermediate **3**, which upon dimerisation and rearrangement will afford the relative stable intermediate **4**. Notably, the geometry of this intermediate is very similar to that of the final experimental product, **5**. In particular, the phenylacetylides are bridging the two europium centres with the protonated cyclopentadienyls being loosely bonded to the metals. Hence, in the presence of a stronger base such as THF, the two $\text{Me}_5\text{C}_5\text{H}$ ligands will be replaced by two molecules per Yb. This induces relatively large stabilisation energy, with the exothermicity of this process being $19.1 \text{ kcal mol}^{-1}$, and serving as the driving force of the whole reactivity. It is worth to note that the corresponding computed geometry for dimer **5** is in perfect agreement with the known X-ray structure.³³

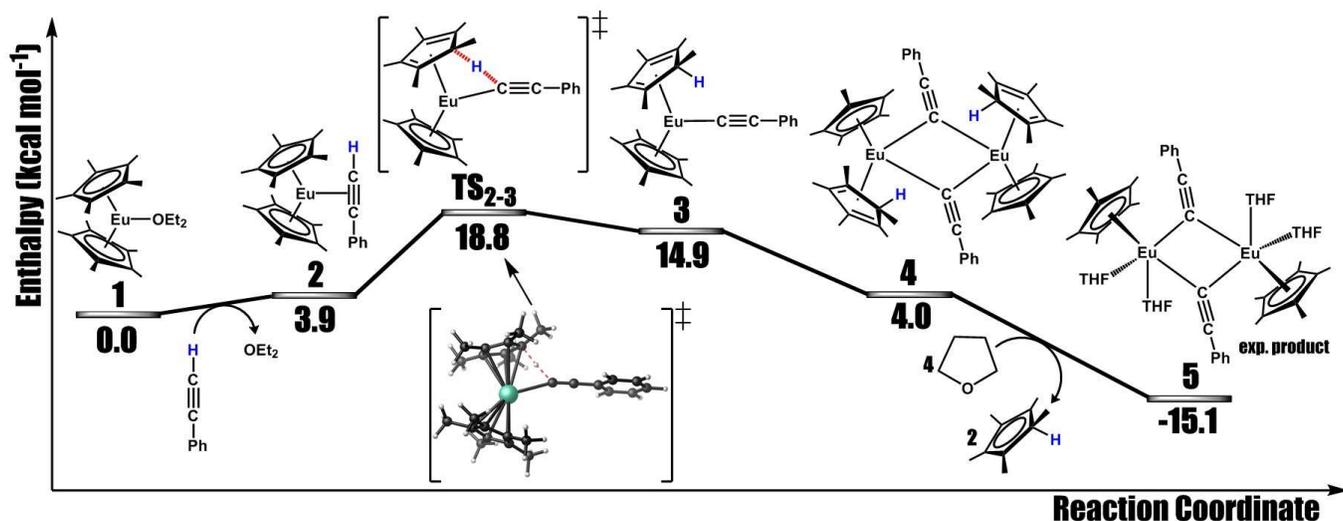


Fig. 3 B3PW91 enthalpy profile for the reaction mechanism of phenylacetylene with $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{OEt}_2)$ in THF.

Mechanistic aspects of the reaction of $\text{C}_6\text{H}_5\text{PH}_2$ with $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$.

We have now investigated the reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ with monophenyl substituted phosphine, in presence of THF (eq. 4). Since the dimeric product,

$[(\text{Me}_5\text{C}_5)(\text{THF})_2\text{Yb}^{\text{III}}(\mu\text{-PPh})_2]_2$, is very similar to that for the europium acetylide compound discussed above, we subsequently considered computationally a similar type of mechanism as shown in Figure 4. The reaction begins with the replacement of the diethylether by the incoming phosphine, followed by a proton transfer from the phosphine to the closest

sp^2 carbon atom of one of the Cp^* ligands. The activation barrier is again relatively low ($19.9 \text{ kcal mol}^{-1}$ with respect to the reactants) and similar to that found for the europium reaction. The product of this process corresponds to the fleeting phosphide intermediate, **8**, in which a pentamethylcyclopentadiene ligand is now present. The latter

monometallic intermediate will thus likely dimerise to yield the more energetically stable intermediate **9**. The two pentamethylcyclopentadiene ligands of dimer **9** can be easily displaced by four THF molecules to afford the experimentally characterised complex **10**, contributing hence significantly to the overall energetics of the reaction mechanism.

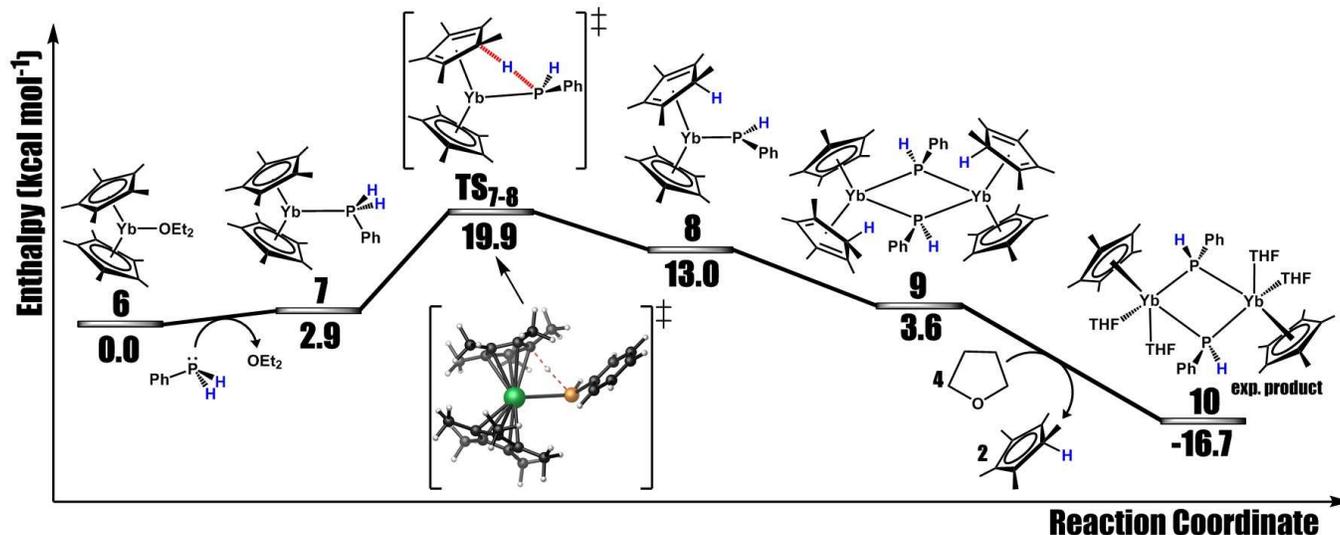
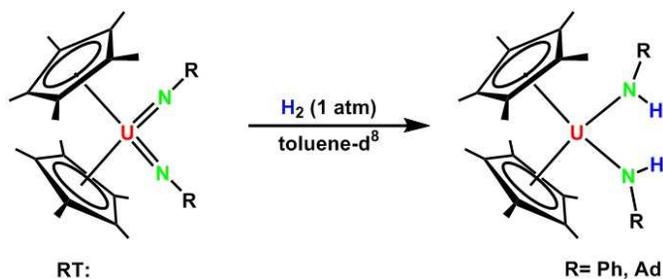


Fig. 4 B3PW91 enthalpy profile for the reaction mechanism of $C_6H_5PH_2$ with $(Me_5C_5)_2Yb(OEt_2)$ in THF.

Mechanistic aspects for the reaction of H_2 with $(Me_5C_5)_2U(NPh)_2$.

Finally, due to the lack of an obvious reaction mechanism, we became interested in the mechanism of the reaction shown in Scheme 2, reported by the group of Burns in Los Alamos.³⁴ This reaction is described as a formal reductive addition of H_2 to the bis-imido U(VI) complex.



Scheme 2 Experimental net reaction of H_2 with $(Me_5C_5)_2U(NR)_2$, with $R = \text{phenyl}$ or adamantyl.

DFT calculations on the direct reductive addition of H_2 lead to a very high activation barrier of $64.9 \text{ kcal mol}^{-1}$, ruling out this type of mechanism. Based on previous studies on the addition of H_2 to $Cp^*_2Ce(\eta^2\text{-OCH})$ complex,³⁵ the possibility of a heterolytic cleavage of H_2 yielding an intermediate hydride complex is investigated. The computed energy profile is shown in Figure 5.

Since the net reaction involves reduction of the uranium centre from +VI to +IV, the heterolytic cleavage of H_2 is investigated either on the singlet Potential Energy Surface (PES), in line with a +VI formal oxidation state, or on the triplet PES, in line with +IV formal oxidation state. It should be noted that because of the change in spin state during the course of the reaction, the small core RECP for the uranium atom is used. The barrier obtained for the singlet spin state is much lower than the one obtained in the triplet spin state (22.8 vs. $34.7 \text{ kcal mol}^{-1}$) indicating that the reduction does not occur at this stage. The barrier is found to be easily accessible at room temperature in line with the experiment. Following the reaction coordinate, it yields intermediate **2X**, an imido-amido-hydride complex that appears to be relatively unstable. Then, two scenarios can be envisioned. In a direct reaction, the hydride may undergo a reductive migratory insertion onto the U-imido bond, yielding directly the desired product. However, this would involve a reaction between two formal anions, the imido and the hydride, unless the uranium centre is reduced. Despite our efforts, it has not been possible to locate such a transition state, since all attempts converged on the migration of H to the Cp^* , that is the second scenario. Indeed, as already shown earlier for the divalent lanthanides, the *carambole* mechanism can be imagined where the cyclopentadienyl ligand serves as shuttle to transform the hydride into a proton that allows the migratory insertion onto the U-imido bond (Figure 5). The barrier for the hydrogen transfer to the Cp^* is very low ($0.5 \text{ kcal mol}^{-1}$ with respect to the hydride, $21.3 \text{ kcal mol}^{-1}$ with respect

to the entrance channel) in line with the low stability of the intermediate **2X**. This transition state yields the intermediate **3**, a characteristic feature of a *carambole* mechanism in which the protonated Cp* ligand remains attached to the metal centre. Formally, the uranium centre has to be reduced in complex **3** (one Cp*, one imido and amido ligand) so that the triplet spin state should be lower in energy than the singlet spin state. Computationally, it is possible to optimise the structure of complex **3** in both spin states and as expected the triplet spin state is much lower than the singlet one (of 14.4 kcal mol⁻¹), in line with a formal reduction of the metal centre. Finally, the HCp* ligand back-transfers the hydrogen atom to the imido

ligand with a very low activation barrier (2.5 kcal mol⁻¹ from complex **3t**, 0.4 kcal mol⁻¹ with respect to the entrance channel) yielding the very stable bis-amido complex **4t**.

In this reaction, the highest barrier is found for the heterolytic cleavage of H₂ so that the *carambole* mechanism is found to be again a low energy process. This further demonstrates the ability of the Cp* ligand to be an efficient non-innocent ligand that plays an important role in the reaction mechanisms concerning divalent lanthanide and trivalent uranium chemistry, as it is shown in the two examples discussed in this paper.

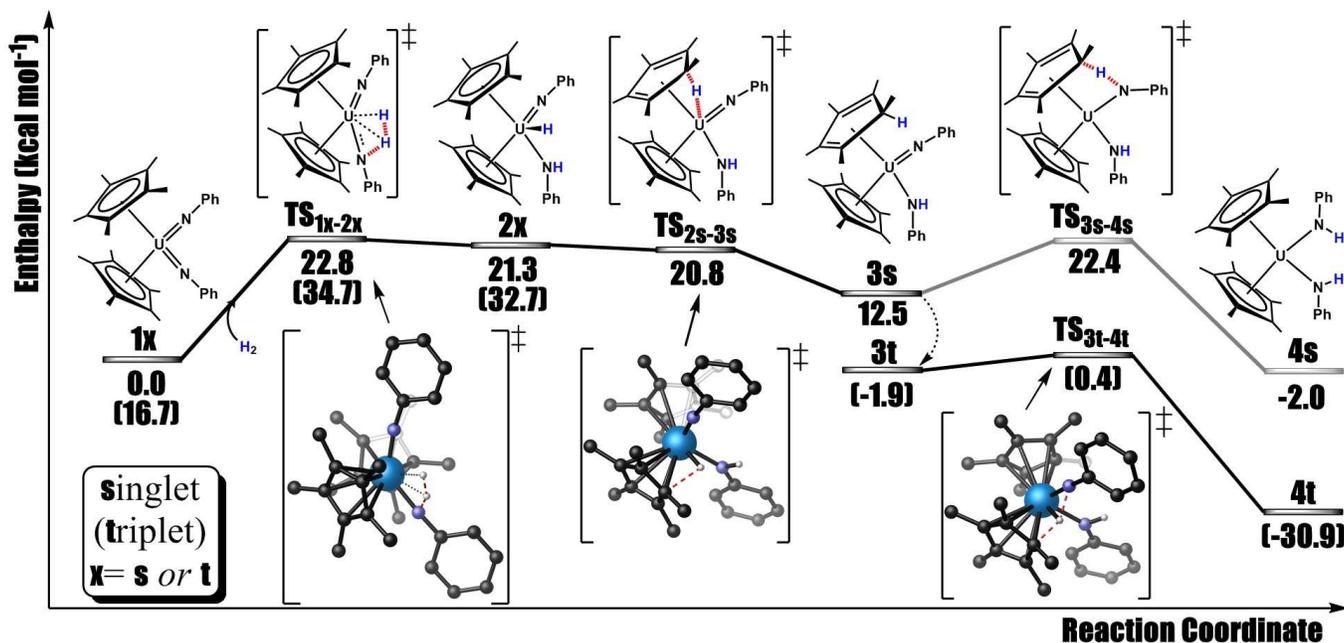


Fig. 5 B3PW91 enthalpy profile for the reaction of H₂ with (Me₅C₅)₂U(NPh)₂.

Conclusions

In this study, the ability of the often-called spectator or ancillary ligand Cp*, which implies that Cp* is only an observer of the chemistry occurring at the metal centre, to influence directly and become a participating actor in the chemistry of *f*-element complexes has been demonstrated in this joint theoretical-experimental study. It has been shown that in divalent lanthanide reactivity, which was initially assumed to involve a SET, the Cp* ligand can act as a proton-relay. This is an efficient way of promoting reactivity, especially when hydrogen transfer is involved. For instance, the spectacular facile catalytic isomerisation of methylallene onto dimethylacetylene catalysed by (Me₅C₅)₂Yb is proposed to take place through a Cp*-assisted hydrogen shuttle mechanism, named as a *carambole*, without any change in the oxidation state of the metal. Such a mechanism is also found to be effective enough to explain the reactivity of (Me₅C₅)₂Eu(OEt₂) with phenylacetylene or the reactivity of (Me₅C₅)₂Yb(OEt₂) with monophenylphosphine. In these last two examples, a

pentamethylcyclopentadiene molecule is released from the metallic fragment whereas this was not the case for the isomerisation reaction. Finally, the *carambole* mechanism was also proposed to explain the reductive addition of H₂ to the bis-imido-uranium(VI) complex. In this case, the rate-determining step is found to be the heterolytic cleavage of H₂, whereas the *carambole* type part of the mechanism is almost barrier less.

This type of mechanism, involving assistance of the Cp* ligand, seems to be general and should be considered as a plausible pathway in other hydrogen transfer reactions in organometallic chemistry as it was shown in a seminal work by Jones *et al.* in transition metal chemistry. However, to the best of our knowledge, it is the first time that the *carambole* accounts for an experimentally observed reactions whose mechanisms were unknown and, indeed, not obvious.

Experimental section

General procedures

All synthetic work was done under a nitrogen atmosphere. Spectroscopic and analytical studies were done as described previously.²⁵

Synthesis of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$. $(\text{Me}_5\text{C}_5)_2\text{Yb}$ (0.22 g, 0.50 mmol) dissolved in pentane (15 mL) was added to a solution of but-2-yne (0.50 mL, 0.35 g, 6.5 mmol) in pentane (5 mL). The solution colour changed immediately from orange to deep red. The volume of the solution was reduced to 5 mL, and the solution was cooled to -78°C for 12h, resulting in the formation of dark purple-red needles. When isolated and exposed to vacuum, the needles seemed to lose solvent, but did not crumble or change colour. The yield was 0.18 g (73%), m.p. $170\text{-}173^\circ\text{C}$. IR (nujol): 2722m, 1653vwbr, 1492s, 1444vs, 1152m, 1132vw, 1093m, 1063w, 1036sh, 1019s, 997w, 956wbr, 937wbr, 904vw, 876vw, 724w, 705mbr, 676sh, 668m, 622w, 588vw, 549vw, 528vw, 440brsh, 373mbr, 306sbr, 275vsbr cm^{-1} . Anal. calcd. for $\text{C}_{24}\text{H}_{36}\text{Yb}$: C, 57.9; H, 7.31; anal. found: C, 54.6; H, 7.33. ^1H NMR (C_6D_6 , 30°C): δ 1.99 (s, 30H), δ 1.27 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 30°C): δ 113.4 (C_5Me_5), δ 76.86 (CMe), δ 10.88 ($\text{C}_5(\text{CH}_3)_5$), δ 3.73 ($\text{C}(\text{CH}_3)$). ^1H NMR of but-2-yne (C_6D_6 , 30°C): δ 1.52 (s). ^{13}C NMR of but-2-yne (C_6D_6 , 30°C): δ 74.60 (s, CMe), δ 3.08 (q, $^1J_{\text{C-H}} = 124.7$ Hz, $\text{C}(\text{CH}_3)_3$). The crystal structure of this complex has been described.^{6a}

Synthesis of $(\text{Me}_5\text{C}_5)_2\text{Ca}(\eta^2\text{-MeC}\equiv\text{CMe})$. $(\text{Me}_5\text{C}_5)_2\text{Ca}^{15}$ (0.18 g, 0.58 mmol) was dissolved in pentane (15 mL) and was added to a degassed solution of but-2-yne (0.5 mL, 0.35g, 6.5 mmol) in pentane (5 mL). The solution remained colourless. The volume of this solution was reduced to 5 mL, and the solution was cooled to -78°C for 12h, resulting in the formation of white crystals. The yield was 0.14 g (66%), m.p. $192\text{-}195^\circ\text{C}$. IR (nujol): 2726m, 1665wbr, i613vw, 1492s, 1443vs, 1347m, 1318 vw, 1290w, 1237m, 1146m, 1090sh, 1093m, 1080vs, 1035sh, 1019s, 1006s, 973vw, 955wbr, 935s, 748sh, 735sh, 722w, 691vw, 642w, 628m, 619m, 599vw, 586vw, 553sh, 544w, 517w, 455s, 404shbr, 349vsbr, 327sh, 313shbr, 289mbr cm^{-1} . Anal. calcd. for $\text{C}_{24}\text{H}_{36}\text{Ca}$: C, 79.0; H, 9.97; anal. found: C, 77.7; H, 9.75. ^1H NMR (C_6D_6 , 25°C): δ 1.99 (s, 30H), δ 1.26 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 30°C): δ 113.4 (C_5Me_5), δ 76.86 (CMe), δ 10.88 ($\text{C}_5(\text{CH}_3)_5$), δ 3.73 ($\text{C}(\text{CH}_3)$). ^1H NMR of but-2-yne (C_6D_6 , 30°C): δ 1.52 (s). ^{13}C NMR of but-2-yne (C_6D_6 , 30°C): δ 74.60 (s, CMe), δ 3.08 (q, $^1J = 124.7$ Hz, $\text{C}(\text{CH}_3)_3$).

Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with buta-1,2-diene. $(\text{Me}_5\text{C}_5)_2\text{Yb}$ (0.31 g, 0.70 mmol) was dissolved in 20 mL of pentane. To this was added a pentane solution (5 mL) of buta-1,2-diene (ca. 0.4 mL) with stirring. The orange colour of the ytterbium complex in solution changed to dark green-brown. After stirring 1 h, the solution colour had changed again to deep red. The mixture was allowed to stir for another 2 h. The volume of the solution was then reduced to 5 mL, and the solution was cooled to -78°C , producing red crystals (0.25 g, 72%). The compound was identified as $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$ by examination of its IR spectrum, m.p., ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

Reaction of $(\text{Me}_5\text{C}_5)_2\text{M}$ with C_2H_4 (M = Ca, Eu, and Sm). In each case, 0.030-0.050 g of compound was dissolved in 30 mL of hexane and transferred to a thick-walled pressure bottle. The solutions were pressurised to 10 atm. with ethylene.

When M = Ca or Eu, there was no apparent change in the colour of the solution, and after 1 day stirring under ethylene, there was no appreciable formation of polyethylene. When M = Sm, polyethylene formed rapidly, but within minutes the solution changed colour from green to yellow, and polymerisation slowed. The polymer formed was isolated in the same manner as in the ytterbium reaction.

Polymerisation of Ethylene by $(\text{Me}_5\text{C}_5)_2\text{Yb}$. In a representative reaction, $(\text{Me}_5\text{C}_5)_2\text{Yb}$ (0.10 g, 0.23 mmol) was dissolved in ca. 25 mL of hexane (or toluene) and transferred to a thick-walled pressure bottle. Ethylene was admitted to the bottle, and the pressure released three times to flush the air space above the solution. Finally, ethylene was admitted to a pressure of 12 atm., producing an immediate colour change from orange (or red) to green, and the formation of cloudiness due to suspended polyethylene; the solution was stirred for 2-4 h. The pressure was then released, whereupon the colour reverted to orange (or red), and the bottle was opened to air. The solution was hydrolysed with dilute HCl, and the polymer formed was washed with acid, water, and acetone, and dried in the air. In polymerisation inhibition experiments, the inhibiting gas (Xe, or CH_4) was first admitted to a pressure of 7 atm., and then ethylene was added to bring the total pressure above the solution to 14 atm. Any colour changes were noted. In all cases, the ytterbium complex could be recovered by removing the solvent under reduced pressure. In polymerisation termination experiments, ethylene was first admitted to a pressure of 7 atm., and the polymerisation allowed to proceed for ca. 5 min. The inhibiting gas was then admitted to bring the total pressure above the solution to 14 atm. The reaction was then stirred for 6-8 h. After the pressure was released, the polymer was isolated as before.

Reaction of $(\text{Me}_5\text{C}_5)_2\text{M}$ with C_2H_4 (M = Ca, Eu, and Sm). In each case, 0.030-0.050 g of compound was dissolved in 30 mL of hexane and transferred to a thick-walled pressure bottle. The solutions were pressurised to 10 atm. with ethylene. When M = Ca or Eu, there was no apparent change in the colour of the solution, and after 1 day stirring under ethylene, there was no appreciable formation of polyethylene. When M = Sm, polyethylene formed rapidly, but within minutes the solution changed colour from green to yellow, and polymerisation slowed. The polymer formed was isolated in the same manner as in the ytterbium reaction.

Synthesis of $\text{C}_6\text{H}_5\text{PH}_2$. Phenylphosphine was prepared by reduction of $\text{C}_6\text{H}_5\text{PCl}_2$ with lithium aluminum hydride in diethyl ether according to a literature procedure.³⁶ The crude product was vacuum distilled (95°C , 50 Torr) and the distillate was stored over molecular sieves under nitrogen. ^1H NMR (C_6D_6 , 20°C): δ 7.40 (2H, m), 7.14 (3H, m), 3.98 (2H, d, $^1J_{\text{P-H}} = 197$ Hz). ^{31}P NMR: δ -122.7 ppm relative to external 85 % H_3PO_4 (t, $^1J_{\text{P-H}} = 197$ Hz).

Reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with $\text{C}_6\text{H}_5\text{PH}_2$. $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.02 g, 1.97 mmol) was dissolved in 50 mL of toluene. Phenylphosphine (0.40 mL, 3.6 mmol) was added to this solution by syringe with rapid stirring. The solution slowly changed colour (3-4 h) to brown with a dark red precipitate.

After stirring overnight, the suspension was allowed to settle and the colourless supernatant was filtered and discarded. The red residue was washed with 100 mL of hexane and dried under reduced pressure. Tetrahydrofuran (100 mL) was added to the red solid to produce a deep red solution. This solution was filtered and the filtrate was concentrated to 50 mL. Slow cooling to $-78\text{ }^{\circ}\text{C}$ produced red-orange crystals. Yield- 0.35 g (32 %). m.p., dec. $193 - 195\text{ }^{\circ}\text{C}$. IR (Nujol, CsI): 3060 (w), 2718 (w), 2259 (m), 1575 (m), 1180 (w), 1095 (w), 1069 (w), 1033 (s), 919 (w), 880 (s), 848 (sh w), 732 (s), 697 (m-s), 480 (w-m), 308 (w), 256 (br s) cm^{-1} . ^1H NMR ($\text{C}_6\text{D}_6\text{O}$, $21\text{ }^{\circ}\text{C}$): δ 7.21 (2H, dd), 6.85 (2H, t), 6.62 (1H, t), 1.97 (30H, s). The PH proton was not observed and may be obscured by the α -H of thf. ^{31}P NMR: δ -89.9 relative to external H_3PO_4 (d, $^1J_{\text{P-H}} = 185\text{ Hz}$).

Computational section

All the quantum chemical calculations were performed using Gaussian 09 suite software.³⁷ Unless specified, the B3PW91^{38,39} functional was considered in all the geometry optimisations without imposing any constraint and in the gas phase. Two different Stuttgart-Dresden effective core potentials were used for Yb atoms; the small core ECP in combination with its adapted basis set to study the change of oxidation state from +II to +III,⁴⁰ while the 4*f*-in-core ECP (augmented by a *f* polarisation function, $\alpha = 1.0$) for the mechanism exploration at in oxidation state +II.⁴¹ Also, the corresponding 4*f*-in-core ECP's (augmented by a *f* polarisation function, $\alpha = 1.0$) were used in the calculations involving Sm(II), Eu(II), and Tm(II) atoms.⁴¹ The relativistic energy-consistent small-core pseudopotential, from the Stuttgart-Köln ECP library, was used in combination with its adapted segmented basis set to study the reactivity in which a change in oxidation state of uranium atom is taking place (passing from +VI to +IV).⁴² Ca was represented by the 6-311+G(d) basis set.⁴³ P atoms were represented by the Stuttgart-Dresden effective core potential, and its associated basis set augmented by a *d*-polarisation function ($\alpha = 0.387$).⁴⁴ Carbon, nitrogen, oxygen and hydrogen atoms were represented by the 6-31G(d,p) basis set.⁴⁵ The nature of the optimised extrema (minimum or transition state) was confirmed with an analytical frequency calculation. The connectivity in the transition states was verified by following the Intrinsic Reaction Coordinates (IRC). The zero-point energy (ZPE) and entropic contribution were calculated within the harmonic potential approximation. Enthalpies were calculated at 298.15 K and 1 atm. Electron affinities have been computed according to the following the electron convention: $\Delta_f H^{\circ}(\text{e}^-, 0\text{ K}) = 0\text{ kcal mol}^{-1}$. Calculated values correspond to the electronic values at 0 K corrected by the zero-point vibrational energy (ZPVE) in gas phase.⁴⁶ Electron affinities have been computed at the CBS-QB3⁴⁷ and WIU31 levels.

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Electronic Supplementary Information (ESI) available: Kinetic plots, crystallographic, and computational data.

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ToC Entry

a Cp*-assisted "proton-rely" mechanism