## Chemical Science

### EDGE ARTICLE

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Cite this: Chem. Sci., 2024, 15, 20582

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 1st July 2024 Accepted 12th November 2024

DOI: 10.1039/d4sc04345f

rsc.li/chemical-science

#### Introduction

Carbon dioxide  $(CO_2)$  is an appealing primary source of carbon atoms for the development of new sustainable synthetic procedures of both carbon-based commodity chemicals and fuels.1-6 Although inexpensive, relatively abundant and non-toxic, CO<sub>2</sub> suffers from severe thermodynamic and kinetic limitations that significantly restrict its use as a routine reagent. Transition metal-based complexes have commonly been employed to overcome this inherent kinetic reluctance.7-9 They have been demonstrated to be highly effective catalysts for the conversion of CO<sub>2</sub> into a range of hydrogenated C<sub>1</sub> products (HCOOH, CH<sub>3</sub>OH and CH<sub>4</sub>), either through electro-assisted approaches or via traditional catalytic hydrogenation. In the majority of such processes, the formation of a metal formate species through CO<sub>2</sub> insertion into metal hydride bonds represents a fundamental step in catalytic cycles.<sup>10</sup> Consequently, a substantial focus has been directed toward elucidating thermodynamic11-13 and kinetic14-18 aspects of this reaction.

Although rare, alternative reactivities of metal hydrides have also been reported (Fig. 1). The group of Parkin described C–O bond cleavage upon exposure of  $[Cp*Mo(PMe_3)_3H]$  to a CO<sub>2</sub>

# Reactivity of metal hydrides with CO<sub>2</sub>: going beyond formate with a high-valent cationic pentahydride Mo(vi) complex<sup>†</sup>

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The cationic molybdenum pentahydride complex  $[MoH_5(depe)_2]^+$  (depe = 1,2-bis(diethylphosphino) ethane) is shown to undergo two consecutive reactions with carbon dioxide. In the initial, room-temperature process, classical insertion of CO<sub>2</sub> into a metal–hydride bond is observed, resulting in the formation of the expected formate complex,  $[MoH_2(HCOO)(depe)_2]^+$ . Further reactivity is triggered at temperature above 100 °C. Complete conversion into two new complexes is indeed observed, resulting from the formal cleavage of a C–O bond of carbon dioxide,  $[MoH(CO)_2(depe)_2]^+$  and  $[MoO(HCOO)(depe)_2]^+$ . Unprecedented in the absence of ligand assistance, such metal hydride reactivity has been comprehensively studied by a combination of experimental and computational means with the aim of elucidating the underlying mechanism that governs this process.

atmosphere, resulting in the formation of a carbonyl complex together with trimethyl phosphine oxide.<sup>19</sup> In the same vein, the group of Milstein investigated the reductive cleavage of CO<sub>2</sub> by hydride complexes of group 9 metals (Rh, Ir) supported by PNP pincer ligands.<sup>20,21</sup> This reactivity, triggered by metal–ligand cooperation, again gave access to carbonyl derivatives – the second oxygen atom being released as a water molecule.

+ CO<sub>2</sub> Me<sub>3</sub>P<sup>1</sup>, Mo...<sub>H</sub> + OPMe<sub>3</sub> OC PMe<sub>3</sub>

Parkin, 2002



Fig. 1 Examples of C-O bond cleavages in the  $CO_2$  molecule mediated by transition metal hydride complexes.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Detailed experimental procedures, computational details, NMR and FTIR spectra and crystallographic data. CCDC 2365476–2365478 and 2365557. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4sc04345f

Interestingly, a diisocyanato/dioxo dititanium complex was obtained from the stepwise, double reductive cleavage of  $CO_2$  by a dihydride dititanium complex, through the concomitant activation of a dinitrogen ligand.<sup>22</sup> On-metal C–O bond activation by metal hydride complexes can also be facilitated by the assistance of exogenous main-group Lewis acids (LA).<sup>23</sup> Ultimately, such assistance is capable to promote a cooperative reductive cleavage of  $CO_2$ , as recently reported by the group of Camp with a strongly polarized heterobimetallic Ir–Al complex.<sup>24</sup> In most of those cases, the transfer of an oxo group to a particularly oxophilic exogenous – or remote – partner thus appears to be an important thermodynamic lever that drives the C–O cleavage reaction.

Recently, our group reported on the isolation of a cationic molybdenum(vi) pentahydride complex supported with a bis(phosphine) ligand,<sup>25</sup>  $[MoH_5(depe)_2]^+$  (1<sup>+</sup>, depe = 1,2-bis(diethylphosphino)ethane). Related group 6 pentahydride derivatives were previously postulated, observed or isolated by the groups of Wilkinson,<sup>26</sup> Semenenko,<sup>27,28</sup> Ito,<sup>29</sup> Henderson,<sup>30</sup> Cundari/Yousufuddin<sup>31</sup> and Chirik.<sup>32</sup> Their reactivity towards carbon dioxide remains, however, largely uncharted. In this article, we explore the stoichiometric reactivity of pentahydride complex 1<sup>+</sup> towards CO<sub>2</sub> and its nitrogen- and sulphur-based analogues (N,N'-diisopropylcarbodiimide – DIC – and CS<sub>2</sub>). We demonstrate that complex  $\mathbf{1}^+$  readily loses  $H_2$  in those processes to generate unsaturated derivatives capable of quick reaction with the considered heterocumulenes. In all cases, insertion of the substrates into a metal-hydride bond occurs. Interestingly, further reactivity is observed for CO2 upon thermal activation. A rare example of unassisted, on-metal C-O bond cleavage is evidenced, with the formation of both  $Mo(\pi)$ carbonyl and Mo(IV)-oxo cationic complexes. Comprehensive computational investigations have been conducted to assess the overall mechanism of this intriguing process.

#### **Results and discussion**

We have recently reported the protonation behaviour of the neutral Mo(rv) tetrahydride complex 2 towards a variety of proton sources, highlighting the importance of the nature of the conjugate base of the acid used to warrant protonation-only processes.<sup>25</sup> Based on these previous findings, we selected trie-thylammonium tetraphenylborate [HNEt<sub>3</sub>][BPh<sub>4</sub>] – that combines both weakly coordinating counter-anion and conjugate base – to serve as the proton purveyor.

Treating a solution of 2 with 1 equiv. of  $[HNEt_3][BPh_4]$  at room temperature resulted in the immediate formation of the



Scheme 1 Protonation of 2 employing  $[HNEt_3][BPh_4]$  as the proton source affords  $1 \cdot BPh_4$ .

expected pentahydride complex  $[MoH_5(depe)_2][BPh_4]$ , **1**·**BPh\_4** (Scheme 1). A diagnostic signal appears as a quintet at -5.0 ppm in the hydride region of the <sup>1</sup>H NMR spectrum. This complex can be isolated in good yields (80–90%) as a pale-yellow powder.

Single crystals suitable for X-ray diffraction analysis were obtained upon low temperature storage (-40 °C) of THF-pentane solution of the complex. The resulting structure is almost identical to the one we previously reported, should the nature of the counterion be excluded (see ESI†).<sup>25</sup>

When a solution of  $1 \cdot BPh_4$  in THF was exposed to CO<sub>2</sub> (3 bar) at room temperature, the solution rapidly turned red. The newly formed complex 3 · BPh<sub>4</sub> shows a new signal in the hydride region of the <sup>1</sup>H NMR spectrum (in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>), emerging as a pseudo-quintet at -7.94 ppm with an apparent  ${}^{2}J_{(P-H)}$ coupling of 42.0 Hz. Another notable, new resonance is observed at 7.77 ppm in the form of a singlet that splits into a doublet  $({}^{1}J_{(C-H)} = 209.3 \text{ Hz})$  when  ${}^{13}C$ -labelled CO<sub>2</sub> was used. We assigned this new signal to a formato ligand generated by CO<sub>2</sub> insertion into a Mo-H bond of **1** · BPh<sub>4</sub>. This NMR data is in good agreement with previously reported formato ligands.33-37 This was further supported by the appearance of a quintet  ${}^{3}I_{(C-1)}$  $P_{P} = 3.5$  Hz) at 176.1 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $3 \cdot BPh_4$ . The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum features two singlets at 43.9 and 78.3 ppm that expanded into triplets  ${}^{2}J_{(P-H)} = 36.0$  and 41.9 Hz, respectively) upon selective <sup>1</sup>H-decoupling centred at 1.5 ppm. Collectively, these results point towards the formula- $[MoH_2(HCOO-\kappa^2 O)(depe)_2][BPh_4]$ tion of  $3 \cdot BPh_4$ as (Scheme 2).38

This ion pair crystallised from a THF-pentane solution, and the single-crystal X-ray diffraction (sc-XRD) analysis confirmed the  $\kappa^2 O$  bidentate coordination of the formate anion, with Mo-O bond lengths of ca. 2.26 Å (Fig. 4). If we restrict to the first coordination sphere, the Mo centre is found in a C<sub>2v</sub>-symmetric environment. The phosphorus nuclei lie in twos above or under the symmetry plane, in good agreement with the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showing two resonances. Although the hydrido ligands could not be unambiguously located in the final Fourier difference map, their most likely positions can be estimated from the presence of a large open site located below a mean plane formed by the phosphorus atoms, trans to the formato ligand. It is reasonable to propose that the two hydrides should be staggered relative to the formato ligand, so that d orbital destabilization is minimized in an overall dodecahedral geometry, common for 8-coordination.39



Scheme 2 Formation of Mo( $\nu$ )-formato complex  $3 \cdot BPh_4$  from  $1 \cdot BPh_4$  under CO<sub>2</sub> atmosphere.

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To gain more insight into the reactivity of complex 1<sup>+</sup> toward CO<sub>2</sub>, we carried out Density Functional Theory (DFT) calculations. We initially performed geometry optimizations at B3LYP-D3(BJ)/SDD+f(Mo), 6-31G\*\* (other atoms) level of theory. Further energy refinement through single point calculations was carried out at PCM(THF)-M06-L-D3/def2-TZVPP level of theory considering solvent effects by means of the Polarizable Continuum Model (PCM) method (see ESI<sup>†</sup>). Optimization of 3<sup>+</sup> was first performed in order to validate the reliability of our selected computational level of theory. We found an excellent agreement between the X-ray and DFT geometries, with a relative error between experimental and calculated structures consistently below 1.5% (Table S1<sup>†</sup>). We then turned our attention to the mechanistic pathway followed by the reaction of  $1^+$  with CO<sub>2</sub>. As illustrated in the reaction profile (Fig. 2), a reductive elimination of H<sub>2</sub> was found to initiate the overall process with a low energy transition state (TS1,  $\Delta G^{\#} = 4.0$  kcal $mol^{-1}$ ) yielding the  $\sigma$ -complex **INT1**. This is followed by a barrierless dissociation of H<sub>2</sub> to afford **INT1**' (Fig. S1<sup>†</sup>). Further  $\kappa O^1$ coordination of CO<sub>2</sub> to the metal centre then occurs through **TS2** ( $\Delta G^{\#} = 22.0 \text{ kcal mol}^{-1}$ ). Formation of the resulting **INT2** is slightly endergonic from INT1' ( $\Delta G = 5.5 \text{ kcal mol}^{-1}$ ). Interestingly, kinetic measurements performed under two different pressures of  $CO_2$  (1.5 vs. 3 bar) showed no influence of the latter (see ESI<sup>†</sup>). This agrees with the computed energy profile where H<sub>2</sub> release is energetically more demanding than CO<sub>2</sub> addition. Then, a rapid hydride transfer from the Mo centre to the coordinated CO<sub>2</sub> was found to occur (**TS3**,  $\Delta G^{\#} = 0.9$  kcal mol<sup>-1</sup> from INT2), granting further stabilization. We also considered that the hydride transfer process could occur via an outer-sphere mechanism, but the corresponding TS was found to be

energetically prohibitive at 44.9 kcal mol<sup>-1</sup> (Scheme S1<sup>†</sup>). Interestingly, the resulting intermediate **INT3**, featuring a formato ligand, is nearly isoenergetic with **INT1**', suggesting that  $CO_2$  insertion-deinsertion processes are easily accessible. Rotation around the C–O bond, allowing the expected  $\kappa^2 O$  coordination of the formato ligand, finally affords complex 3<sup>+</sup> in a global exergonic process ( $\Delta G$ : –3.0 kcal mol<sup>-1</sup>). Overall, this mechanism is in good agreement with the concerted  $CO_2$  insertion pathway, previously reported by Hazari for group 9 and 10 metal hydride complexes.<sup>10</sup>

An *o*-dichlorobenzene solution of the  $3 \cdot BPh_4$  complex was heated at 100 °C for 24 hours under an atmosphere of CO<sub>2</sub>, resulting in a complex mixture of compounds. Large, unresolved signals were notably observed in the <sup>1</sup>H NMR spectrum, suggesting the formation of a paramagnetic molybdenum species identified as [Mo(depe)<sub>2</sub>Cl<sub>2</sub>] (see ESI<sup>†</sup>). Simultaneously, the appearance of new resonances in the aromatic domain is also noted. We tentatively assigned those new signals to the formation of biphenyl (see ESI<sup>†</sup>), arising from the radical-driven reductive rearrangements of the tetraphenylborate anion.<sup>40,41</sup> Slight chemical shift deviations are, however, noted in comparison with an authentic biphenyl sample, which we attribute to the influence of [Mo(depe)<sub>2</sub>Cl<sub>2</sub>] paramagnetism. We thus decided to opt for the  $HB(C_6F_5)_3^-$  anion, that displays increased redox stability. 3 · HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> could easily be prepared by the reaction of 2 with  $[HP^{t}Bu_{3}][HB(C_{6}F_{5})_{3}]^{25}$  followed by room temperature reaction with CO2. Under similar conditions (reaction time increased to 36 h),  $3 \cdot HB(C_6F_5)_3$  indeed granted access to a much cleaner reactivity. More specifically, two new complexes  $4 \cdot HB(C_6F_5)_3$  and  $5 \cdot HB(C_6F_5)_3$  are formed in an approximate 36:64 ratio (Scheme 3, top), together with  $H_2$ 



Fig. 2 Computed profile for the reaction of complex  $1^+$  with CO<sub>2</sub>. Free energy values ( $\Delta G$ ) and distances are given in kcal mol<sup>-1</sup> and Å, respectively. All data have been computed at the PCM(THF)-M06-L-D3/def2-TZVPP//B3LYP-D3(BJ)/SDD+f(Mo), 6-31G\*\* (other atoms) level of theory.

evolution. The positively charged part of the minor species was identified as  $[MoH(CO)_2(depe)_2]^+$ , 4<sup>+</sup>. This monohydride cationic complex bearing two carbonyl ligands in a trans configuration was independently prepared from the reaction of 1<sup>+</sup> with CO (Scheme 3, bottom, and Fig. 4). The second complex that formed, 5<sup>+</sup>, features a singlet at 46.0 ppm in the  ${}^{31}P{}^{1}H{}$ NMR spectrum. The latter unresolvedly broadens upon selective decoupling of the aliphatic protons, suggesting the absence of hydrido ligands. This is further confirmed by the <sup>1</sup>H NMR spectrum, which is devoid of any new hydride signals. Interestingly, a new proton signal resonating at 7.31 ppm was observed, which correlates with a singlet at 163.8 ppm in the <sup>13</sup>C  ${^{1}H}$  NMR spectrum. This signal splits upon  ${^{13}C}$ -labeling  ${^{1}J}_{(C-H)}$ = 204.3 Hz), indicating the formation of a new formato derivative. High-resolution mass spectrometry was used to gain further insight into the nature of compound  $5^+$ . The isotopic pattern of the resulting signal strongly suggests the presence of



Scheme 3  $CO_2$  cleavage induced by thermal activation of the formato complex  $3 \cdot HB(C_6F_5)_3$  (top) and independent synthesis of the mono-hydrido bis(carbonyl) complex  $4 \cdot BPh_4$  (bottom).

an additional oxo ligand. Taken together, those results point towards  $5^+$  being formulated as  $[MoO(HCOO)(depe)_2]^+$ , a cationic Mo(IV) complex. Despite several attempts, independent synthesis of  $5^+$  was unsuccessful: it is, however, interesting to note that <sup>31</sup>P NMR features are in line with similar cationic d<sup>2</sup> molybdenum–oxo complexes.<sup>42</sup> Along these two main products, small amounts of free formate was also noticed, accounting for 8% of the non-gaseous compounds ultimately present in solution.

Interested in this unusual process - formally resulting from the cleavage of a CO<sub>2</sub> molecule C-O bond<sup>43</sup> - we again decided to investigate the mechanism of this transformation by the use of DFT calculations. We employed the PCM(o-dichlorobenzene)-6-31G\*\* M06-L-D3/def2-TZVPP//B3LYP-D3(BJ)/SDD+f(Mo), (other atoms) level of theory and corrected the free energies at 373.15 K using GoodVibes package.44 Two different pathways have been considered for the thermal evolution from complex  $3^+$  to complex  $5^+$ . As illustrated in Scheme 4, the first pathway (Pathway I) begins with the reductive elimination of H<sub>2</sub>, followed by the coordination of CO<sub>2</sub>. Then, the breaking of the C-O bond in the CO<sub>2</sub> ligand occurs, followed by the release of CO leading to the final compound  $5^+$ . The second pathway (Pathway II) involves as a first step a hydride transfer from the formato moiety to Mo centre-formally a de-insertion of CO<sub>2</sub>, the reverse of the final elementary step in the mechanism leading from  $\mathbf{1}^+$  to  $\mathbf{3}^+$ . H<sub>2</sub> is subsequently released, followed by the C-O bond cleavage in the CO<sub>2</sub> ligand. Finally, two routes were envisaged to achieve the formation of the final product 5<sup>+</sup>: either CO<sub>2</sub> can be added followed by the release of CO, or CO can be released first, followed by the addition of CO2. According to our DFT calculations, Pathway I can be safely ruled out due to several high energy barriers in the process (see the complete reaction profile in Fig. S2<sup> $\dagger$ </sup>). First, the release of H<sub>2</sub> from 3<sup> $\dagger$ </sup> is highly endergonic, with the complex INT4-I being 25.3 kcal mol<sup>-1</sup> higher in energy than 3<sup>+</sup>. Additionally, subsequent addition of CO2 requires an overall activation barrier of 45.1 kcal  $mol^{-1}$ , which cannot be reached under the reaction



Scheme 4 Plausible reaction pathways for the thermal evolution from 3<sup>+</sup> to 5<sup>+</sup>.



Fig. 3 Energy profile for the thermal evolution of complex  $3^+$  into complex  $5^+$  according to Pathway II (Scheme 4). All data have been computed at the PCM(o-dichlorobenzene)-M06-L-D3/def2-TZVPP//B3LYP-D3(BJ)/SDD+f(Mo), 6-31G\*\* (other atoms) level of theory. Free energies ( $\Delta G$ ) have been corrected at 373.15 K. All activation barriers are referred to  $3^+$ . Distances and energies are given in Å and kcal mol<sup>-1</sup>, respectively.

conditions. The transition state for the next step (C-O bond cleavage in the CO<sub>2</sub> molecule) also has a prohibitive high energy at 43.9 kcal  $mol^{-1}$ . In the reaction profile corresponding to Pathway II (Fig. 3), the first step formally corresponds to the hydride transfer from the formato moiety to the Mo centre, which is the back-side reaction from  $3^+$  to INT2, previously described in Fig. 2. The reverse activation barrier of 21.9 kcal  $mol^{-1}$ , corrected with GoodVibes software to take the temperature into account, was found accessible at 100 °C. Then, the release of H<sub>2</sub> proceeds very easily through TS4, with a rather low barrier of 1.7 kcal mol<sup>-1</sup> from INT2, affording the  $\eta^2$ -CO<sub>2</sub>-Mo complex INT4.45 The subsequent C-O bond cleavage is energetically more costly, with a transition state, TS5, located at 31.3 kcal mol $^{-1}$  above 3<sup>+</sup>. Finally, DFT calculations suggest that CO is released (TS6) before addition of  $CO_2$  (TS7) to form the final product  $5^+$ . In this process, CO<sub>2</sub> plays the role of a hydride abstractor, generating a formato moiety, which finally coordinates on Mo in  $5^+$ . In Pathway II, the rate-determining step (RDS) corresponds to the addition of  $CO_2$  (TS7), with an overall activation barrier of 33.2 kcal mol<sup>-1</sup> from 3<sup>+</sup>, which is consistent with a high temperature for the reaction to occur. It is important to note that the released CO (TS6 in Pathway II) is necessary for the thermal evolution of complex  $3^+$  into complex  $4^+$  (Fig. S3<sup>+</sup>). Additionally, the CO<sub>2</sub> needed for the final step in Pathway II

(TS7) is derived from the reaction profile described in Fig. S3<sup> $\dagger$ </sup> (thermal evolution from 3<sup>+</sup> into 4<sup>+</sup>). Consequently, formation of 4<sup>+</sup> and 5<sup>+</sup> are intimately connected.

As an extension of our investigation on the activation of  $CO_2$ , we studied the reactivity of  $1 \cdot BPh_4$  with  $CS_2$  and DIC (Scheme 5). Upon treatment of complex  $1 \cdot BPh_4$  with 1 equiv. of  $CS_2$ , an immediate darkening of the THF solution is observed. The formation of complex  $6 \cdot BPh_4$  was characterized by the appearance of a new quintet at  $-6.09 \text{ ppm} (^2J_{(P-H)} = 44.0 \text{ Hz})$ and a singlet at 5.76 ppm in the <sup>1</sup>H NMR spectrum, as well as a <sup>31</sup>P{<sup>1</sup>H} resonance at 69.1 ppm. The latter splits into a doublet ( $^2J_{(P-H)} = 44.0 \text{ Hz}$ ) upon selective decoupling of the aliphatic protons. Unlike the behaviour observed in the presence of  $CO_2$ , these data support a 4e<sup>-</sup>-reduction of  $CS_2$  through double

![](_page_4_Figure_7.jpeg)

Scheme 5 Formation of  $6 \cdot BPh_4$  and  $7 \cdot BPh_4$  from  $1 \cdot BPh_4$ .

![](_page_5_Figure_2.jpeg)

Fig. 4 From left to right, molecular structures of compounds  $3 \cdot BPh_4$ ,  $4 \cdot BPh_4$  and  $7 \cdot BPh_4$  in the solid state. The  $BPh_4^-$  counter ions and the hydrogen atoms (except those on the reduced formato or amidinato ligand or bound to the metal centre) were omitted for clarity. Thermal ellipsoids are shown at the 25% level of probability. Compounds  $4 \cdot BPh_4$  and  $7 \cdot BPh_4$  crystallized with two molecules in the asymmetric unit (Z' = 2), only one is depicted for clarity.

insertion into Mo-H bonds,46-49 resulting in a monohydride methanedithiolate derivative, [MoH(S2CH2)(depe)2][B(C6H5)4]  $(6 \cdot BPh_4$ , Scheme 5). Despite several attempts,  $6^+$  remained reluctant to crystallization and isolation of an analytically pure complex could not be reached (92% spectroscopic purity, see ESI<sup> $\dagger$ </sup>). Addition of 1 equiv. of DIC to  $1 \cdot BPh_4$  in THF led to the formation of the expected M-H insertion product 7. BPh4 (Scheme 5). In the <sup>1</sup>H NMR spectrum, loss of the hydride resonance of 1 · BPh<sub>4</sub> was observed along with the formation of two new diagnostic signals: a multi-lined hydride signal at -7.97 ppm and a singlet at 7.95 ppm assigned to the formamidinate methine proton. Typical of the methine carbon,<sup>50-53</sup> a signal at 159.4 ppm is observed in the  ${}^{13}C{}^{1}H$  NMR spectrum. The  ${}^{31}P{}^{1}H$  features two triplets at 71.0 and 41.5 ppm. Contrary to  $6 \cdot BPh_4$ , complex  $7 \cdot BPh_4$  easily crystallized from a THFpentane solution, as orange prisms ( $\eta = 54\%$ ). In the solid-state structure of  $7 \cdot BPh_4$  (Fig. 4), the formamidinate ligand is found in a  $\kappa^2 N$  coordination, with a N–Mo–N bite angle of 59.0°. As expected, this value and other relevant metrics are very similar to those determined in the molecular structure of 3. BPh4. Again, the exact location of the hydrido ligands could not be determined, although their most probable positions will similarly be found *trans* to the formamidinate ligand to fulfil the expected distorted dodecahedral coordination sphere.

#### Conclusions

In summary, we have thoroughly investigated the reactivity of a high-valent cationic pentahydride  $Mo(v_1)$  complex  $1 \cdot BPh_4$ towards  $CO_2$  and related heteroallenes ( $CS_2$ , DIC). The expected insertion of substrate molecules into Mo–H bonds was typically observed, resulting either in two-electron ( $CO_2$ , DIC) or fourelectron reduction of the substrate ( $CS_2$ ). Overall, and despite its high-valent character, complex  $1 \cdot BPh_4$  behaves as a potent reductant. Most of those reactivities is triggered by facile hydrogen release, suggesting  $1 \cdot BPh_4$  could be better described as a masked Mo(v) complex. Beyond this expected insertion chemistry, we have been able to evidence a rare example of C–O bond cleavage mediated by a metal hydride complex, that occurs without assistance of a ligand or another proximal reactive centre. Indeed, upon thermal activation, the formato complex 5<sup>+</sup> was shown to further evolve quantitatively towards a duet of complexes, namely Mo(n)-carbonyl and Mo(n)-oxo derivatives. This reaction was particularly scrutinized *via* a combination of experimental and theoretical tools. The intimate mechanism responsible for the formation of both carbonyl and oxo derivatives has been carefully deciphered and the importance of high temperature reversible  $CO_2$  hydrogenation–dehydrogenation process was evidenced. Ultimately, this reversibility – together with the high thermodynamic drivers associated with Mo–O bond formation and transient CO liberation – allows on-metal C–O bond cleavage to be accessed.

#### Data availability

The datasets supporting this article have been uploaded as part of the ESI.<sup>†</sup>

#### Author contributions

N. Q. and N. D. run the experiments and analysed the data. J. J. C.-T. performed DFT calculations. L. V. recorded single-crystal X-ray diffraction data and solved the structures. K. M. and A. S. obtained funding for the project, managed it and took part in the analysis of the data. N. Q. wrote the first draft of the manuscript. K. M. and J. J. C.-T. analysed the theoretical results and wrote the computational part of the manuscript. The manuscript was then further revised through contributions of all authors.

#### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

N. Q. and A. S. are indebted to the European Research Council for funding (ERC Starting Grant No. 757501). Mass

Spectrometry Service (N. Martins-Froment) of the Institute of Chemistry of Toulouse-UAR 2599 (Université de Toulouse, CNRS, Toulouse, France – https://www.ict.ups-tlse.fr) is acknowledged for technical assistance with ESI-HRMS experiments. J. J. C.-T. and K. M. would like to thank the Carnot ISI-FoR institute for its support and funding. The "Direction du Numérique" of the Université de Pau et des Pays de l'Adour and the Mésocentre de Calcul Intensif Aquitain (MCIA) are acknowledged for the support of computational facilities. This work was also granted access to the HPC resources of IDRIS under the allocation 2023-AD010800045R2 made by GENCI. All authors thank their respective institution for providing access to facilities.

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