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Computational insights into three-centre four-electron bridging hydride bond in boryl type PBP-M dihydride complexes☆ ☆

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ABSTRACT

Metal hydrides serve as crucial intermediates in many chemical processes, facilitating the utilization of hydrogen resources. Traditionally, three-centre metal hydrides have been viewed as less reactive due to their multi-stabilization effects. However, recent discoveries show the "three-centre four-electron" (**3c-4e**) bridging hydride bond exhibits significant activity in boryl transition metal systems. This research employs computational techniques to explore the factors that influence the formation of the **3c-4e** bridging hydride, focusing on boryl 3d non-noble transition metals ranging from chromium (Cr) to nickel (Ni). By analyzing bond distances and bond orders, the study sheds light on the electronic and structural characteristics of the B-H-M bridging hydride. It reveals a clear link between the metal centre's redox properties and the emergence of bridging hydrides. Specifically, metal centres like Cr and Co, which have lower oxidation states and electronegativity, are more inclined to form active **3c-4e** bridging hydrides. These insights, derived from computational analyses, offer valuable guidelines for the development of active **3c-4e** bridging metal hydrides, thereby contributing to the advancement of new hydrogen transformation catalysts.

Metal hydride complexes have attracted widespread attention for their wide participation in various chemical processes such as hydrogen storage and catalysis [1]. Interest in metal hydride complexes is due to the potential for chemical reactivity, where the composition of a metal hydride complex and its metal/ligand combination affects reactivity significantly, like C(sp^3)-H functionalization [2], carbon dioxide conversion [3] and transfer hydrogenation [4].

The study of transition metal hydrides dates to the 1930s, initiated by seminal works from Heiber *et al.* [5–7]. Scheme 1a provides a proposed concept of the transition metal (TM) hydride, mapping key milestones against the increasing volume of research in this area. By the 1950s, there was a noticeable surge in research activity, coinciding with the determination of organometallic complex structures like $HRe(C_5H_5)_2$ (Scheme 1b) [8,9]. The 1960s further expanded the scope of this field, introducing innovative structures – ternary TM hydride – discovered by Ginsberg *et al.* (Scheme 1c) [10] and the concept of 'M-H-M Bridging Hydrides' in 1975 (Scheme 1d) [11]. The conventional metal hydride is characterized by a single metal centre and an anion of hydrogen (H^-), with the terminal hydride bonds on the classical metal hydride exhibiting the "two-centre two-electron" (**2c-2e**) bonding feature [12]. While the classical terminal hydride bonds have promising applications in catalysis, bridging hydride bonds, with their multi-centre systems, could have a distinct characteristic in catalyst development [13–15]. A typical bridging bond, the "three-centre two-electron" **3c-2e** bridging hydride bond can be traced back to the literature in many transition metal complexes, such as $[CpNi(\mu\text{-}H)]_2$ [16,17] (Scheme 1e).

However, our latest research marked a transformative phase, with the exploration of boryl-TM hydrides, elucidating a totally new type 'B-H-M bridging hydride', in which the hydride exhibits an extraordinarily high activity for the hydrogenation reaction due to the unique "three-centre four-electron" (**3c-4e**) electronic structure for the bridging hydride bond (Scheme 1f) [18]. With the recent development of the novel Lewis acid–transition metal (Boryl-TM) complexes, a different type of bridging hydride has been observed in the Boryl-TM hydride complexes (Schemes 2a and b) [19–21]. The interaction between the Lewis acid boryl centre and the transition metal centre with the metal hydride forms a new three-

☆ ☆This paper is dedicated to the Memory and 90th Birthday of Prof. Keiji Morokuma.

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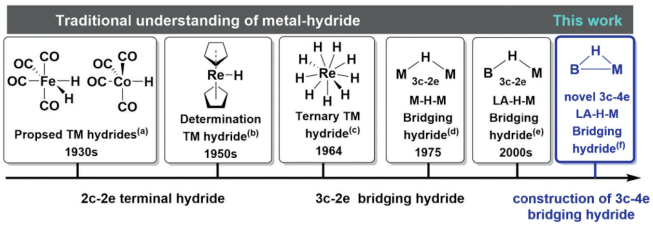
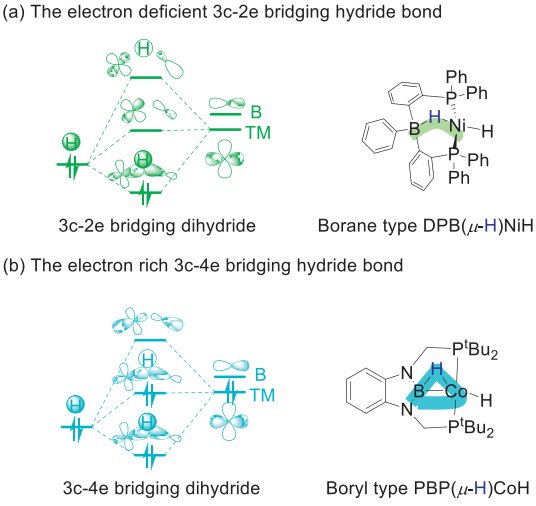


Scheme 1. The timeline of key dates for important metal hydrides from publications (top).



Scheme 2. Detailed molecular orbital around bridging hydride bond with (a) electron deficient **3c-2e** bridging hydride and (b) electron rich **3c-4e** bridging hydride. (c) Potential factors that affect the formation of **3c-2e** and **3c-4e** dihydride.

centre bridging bond. Various boryl-TM hydride complexes have been identified with the unique **3c-4e** bridging hydride, such as DPB(μ-H)Ni(H), PBP(H)CoH, and BIM(H)PtH [21–25]. These novel Boryl-TM metal hydride complexes have found extensive use in various catalytic reactions, including but not limited to hydrogenation, hydrosilylation, and borohydride [26,27].

Boron-TM systems generally include two primary bridging hydrides: the borane-type bridging hydride and the boryl-type bridging hydride. The interaction between the borane-type bridging hydride and metal hydride is facilitated by the Z-type ligand, specifically through the boron's empty orbital, without implying sp^3 hybridization. In contrast, the boryl-type bridging hydride comes from the X-type ligand, establishing an interaction with the metal hydride through the metal-boron bond. In the previous study, a systematic analysis was conducted on the electronic structure of two bridging hydrides in DPB-Ni and PBP-Co systems [18]. The sp^3 Lewis acid borane ligand in the Ni-borane system helps stabilize the bridging hydride, forming a **3c-4e** bridging bond. Conversely, in the boryl-Co system, due to X-type Co-B coordination, two additional electrons are placed in the antibonding orbital of the three-centre bridging bond, forming a **3c-4e** bridging hydride bond. Mechanistic analyses associated with the olefin hydrogenation reaction have demonstrated that the **3c-4e** bridging hydride exhibits a higher nucleophilic character than the **3c-2e** bridging hydride due to the highly lying hydride orbital. Consequently, the bridging hydride in boryl-type metal hydride complexes could exhibit enhanced reactivity compared to those in the borane-type hydride system.

Although the electronic structure and nucleophilicity of a metal hydride are significant factors, the formation of a **3c-4e** bridging hydride bond cannot be predicted solely based on the type of ligand involved. The metal centres are crucial in the formulation of bridging hydrides [28]. Particularly for boryl-type ligands, various hydride complexes exist with different metal centres, including those like PBP-Ru, PBP-Rh, PBP-Ir, PBP-Ni, and more [29–32]. These transition metal centres, with varied electronic structures and redox capacities, might cause the bridging hydrides within these PBP-M complexes to have a range of electronic structures and nucleophilic properties. However, questions remain regarding the electronic structure of bridging hydrides with different metal centres and how we can alter the bridging hydrides for enhanced reactivity (Scheme 2c). Hence, this paper presents a thorough examination of transition metal centres in boryl-type bridging hydride *via* the computational method, focusing on the outer shell electron effects using theoretical calculations. This investigation aims to provide valuable guidance for both the design of catalysts and the study of reaction mechanisms.

PBP-M pincer complexes were selected to study active **3c-4e** bridging hydride formation. These complexes feature sp^2 hybridized boron centres with X-type B-M bonds. We chose various 3d metals (Cr(0), Mn(I), Fe(0), Co(I), Ni(0)) to explore the metal's impact on TM-H-B bridging hydrides. Additional metals in different oxidation states (Cr(II), Mn(III), Fe(II), Co(III), Ni(II)) were also examined, and all optimization performed at the M06-L [33] or uM06-L/def2-SVP [34] level of theory, and single point energy performed with a higher basis set – def2-TZVP [35] and incorporated with SMD model with solvent of benzene. The stability of these metal complexes hinges on their multiplicity (singlet, triplet, or quintet), as shown in Fig. 1. Quintet states, characterized by four unpaired electrons, are especially stable for Cr(0), Cr(III), Mn(I), Mn(III), and Fe(II) due to half-filled or nearly half-filled d-orbitals. Half-filled configurations such as d^4 or d^6 optimize exchange stabilization energy, significantly favouring higher spin states by reducing electron repulsion and enhancing exchange energy. Fe(0) and Co(III), with their d^8 and d^6 configurations, respectively, exhibit maximum stability in triplet states, as these configurations balance electron pairing energy and exchange stabilization. In contrast, Co(I), Ni(0), and Ni(II) adopt singlet states owing to their closed-shell or nearly closed-shell configurations, where full electron pairing minimizes repulsion, stabilizing low-spin states. Cr-Hy and Mn-Hy complexes show high stability in quintet states, with energy levels between −29.8 kcal/mol to −59.1 kcal/mol. Fe-Hy and Co-Hy's stability varies with the metal's oxidation state, with Fe(0)-Hy, Fe(II)-Hy, Co(I)-Hy, and Co(III)-Hy being most stable in triplet, quintet, singlet, and triplet states respectively. Ni-Hy prefers a singlet state due to its closed-shell stability. For metal centres in high oxidation states with fewer D-electrons, there is a tendency to adopt a high-spin state. For instance, Cr(III) and Mn(III) in their quintet states possess four unpaired D-electrons, making the formation of **3c-2e** bridge bonds challenging. Conversely, metal centres in low oxidation states with more D-electrons tend to adopt a low-spin state. For example, Co(I), in its singlet state, has four pairs of D-electrons, which can more easily form **3c-4e** bridge bonds. Fig. S1 (Supporting information) reveals that elements like Mn(I)

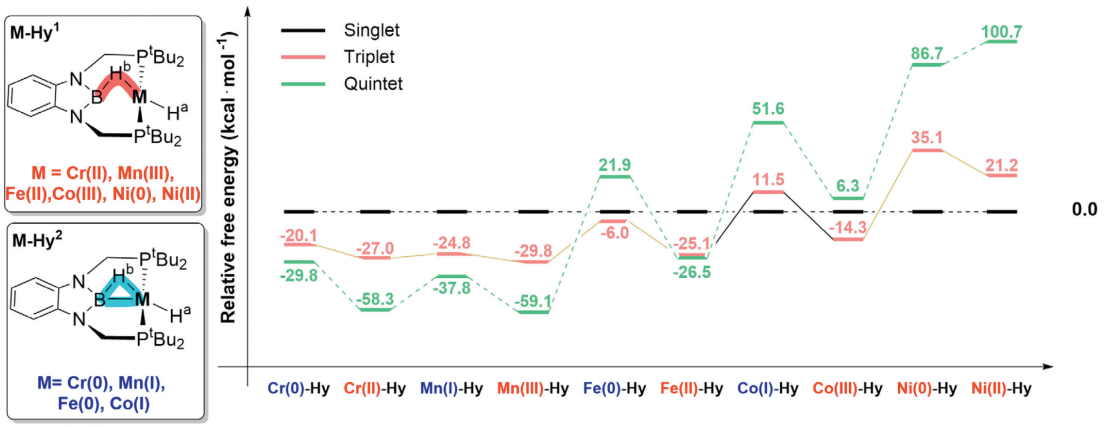


Fig. 1. Comparative relative free energies of M-Hy[1] and M-Hy[2] complexes optimized under singlet, triplet, and quintet states, with the free energy of singlet as reference.

and Ni(0) with higher atomic numbers are more thermodynamically stable upon hydrogen activation, aligning with periodic trends of d-orbital filling. The stability decreases with the metal's oxidation state, as shown by Co(I) and Co(III)'s varying energy values, highlighting how electron correlation and oxidation states influence stability during hydrogen activation.

All PBP-M complexes form square structures with P^1-M-P^2-B angles nearly 180°, as shown in Fig. S2 (Supporting information). Higher oxidation state M-Cat complexes exhibit longer B-TM distances compared to those with lower oxidation states, attributed to stronger B=M double bonds from d electron back-donation in low oxidation state metals. M-Cat complexes transition to M-Hy dihydride complexes through hydrogen activation, featuring both terminal and bridging hydrides with bond distances ranging from 1.479 Å to 2.095 Å, as shown in Fig. 2. Bridging hydrides are closer to boron, especially in high oxidation state metals like Cr(II), Mn(III), Fe(II), and Co(III), compared to their lower state counterparts. Dihydride complexes show variation in dihedral angles, indicating two types of bridging hydrides in different planes. B-H hydride types, preferred by high oxidation metals, align with B-N^1-N^2 planes, while M-H hydride types, chosen by low oxidation metals, feature H^b out of these planes, suggesting a significant metal centre impact on hydride positioning. The orbital component of metal centres for those with d_{xy} orbitals is from 24.4% to 70.8%, and H^b is merely from 3.0% to 5.2%.

In order to have a further understanding of the difference between the **3c-4e** and **3c-2e** bridging hydrides M-H-B bridging hydride type, the molecular orbitals are discussed by the localized molecular orbital (LMO) analysis. The two types of bridging hydrides in the PBP-M systems can be revealed by LMO analyses. For Cr(0), Mn(I), Fe(0), and Co(I) metal centres, the molecular orbitals of the B-H^b-M bridging bonds are mainly constituted by the filled sp^2 orbital of the boron atom, the d orbital of metal, and the 1s orbital of the hydride. There is an additional paired electrons located in the no-bonding orbital, which derived from the metal d orbital. The bridging hydrides form **3c-4e** bonds in those complexes. Therefore, the positioning of a hydrogen atom either inside or outside the N^1-N^2-B plane can be used to deduce the complexes are **3c-2e** or **3c-4e** bridging hydrides, and Cr(0), Mn(I), Fe(0), Co(I), and Ni(0) are likely to form **3c-4e** bridging hydride where Cr(II), Fe(II), Co(III), and Ni(II) are forming **3c-2e** bridging hydride, as depicted in Fig. 3. However, due to the strong electronegativity of nickel, the Ni(0) will form **3c-2e** instead of **3c-4e**, as depicted in Fig. 3.

To elucidate the influence of metal centres on the formation of bridging hydrides, a bond order analysis of metal hydride complexes was conducted. This analysis revealed that the bond orders

Table 1
Fuzzy bond order, bond order contribution (BOC) and orbital energy in M-Hy transition metal hydride complexes.

M-Hy	Fuzzy bond order		BOC			Orbital energy (eV)		
	M-H^a	B-H^b	M-H^b	Hydride	d_{xy}	M-H^a	M-H^b	d_{xy}
Cr(0)-Hy	0.466	0.273	0.145	0.127	−0.066	−4.0	−7.3	−0.9
Cr(II)-Hy	0.887	0.305	0.266	0.085	N/A	−7.7	−15.5	−6.1
Mn(I)-Hy	0.451	0.274	0.181	0.192	−0.070	−6.6	−9.5	−2.7
Mn(III)-Hy	0.388	0.318	0.116	0.076	N/A	−11.7	−14.3	−9.7
Fe(0)-Hy	0.414	0.261	0.185	0.188	−0.066	−3.8	−7.5	−1.5
Fe(II)-Hy	0.438	0.344	0.104	0.052	N/A	−7.8	−15.3	−6.4
Co(I)-Hy	0.407	0.202	0.247	0.293	−0.078	−6.1	−12.9	−4.1
Co(III)-Hy	0.379	0.250	0.182	0.113	N/A	−10.2	−14.6	−8.2
Ni(0)-Hy	0.793	0.543	0.349	0.149	N/A	−4.4	−7.6	−1.5
Ni(II)-Hy	0.813	0.239	0.389	0.217	N/A	−8.7	−13.0	−8.7

for bridging hydrides M-H^b are lower than terminal hydrides M-H^a, as shown in Table 1. Specifically, bond orders for M-H^b range from 0.145 to 0.247 in Cr(0), Mn(I), Fe(0), and Co(I) systems, indicating characteristics of metal hydride bonds. Conversely, in Cr(II), Fe(II), Co(III), Ni(0), and Ni(II) centres, M-H^b bond orders vary between 0.104 to 0.389. Furthermore, B-H^b bond orders in the latter systems varied from 0.250 to 0.543, highlighting the pronounced characteristics of B-H bonds. These variations suggest that bridging hydrides exhibit either metal hydride or B-H bond characteristics, depending on the specific metal centre involved. A comprehensive orbital occupancy-perturbed Mayer bond order analysis provided further insight, indicating that the d orbitals of the metals occupy non-bonding orbitals of the bridging hydrides, detrimentally affecting the bond order of the hydride bonds. Bridging hydrides' bond orders are primarily influenced by hydride orbitals, with the bond order contribution (BOC) ranging from 0.052 to 0.293 (Table 1). The BOC of the metal orbitals is −0.078 to −0.066. While for the Cr(0), Mn(I), Fe(0), and Co(I) metal centres, the B-H-M bridging hydride bonds are influenced by the d orbitals of metal centres. The orbital component analysis further confirms the attribution. The metal's d_{xy} orbital weakens the bond order suggesting the electrons filled on the non-bonding orbital of **3c-4e** bridging hydride (Cr(0), Mn(I), Fe(0) and Co(I)), where other metal centres (Cr(II), Mn(III), Fe(II), Co(III) and Ni(0)/(II)) do not have d_{xy} orbital weakens the bonding.

As shown in Table 1, the bond orbital energy of the d_{xy} orbitals ranges from −9.7 eV to −0.9 eV, which is higher than the M-H^a orbitals (−11.7 eV∼−3.8 eV). Those **3c-4e** bridging hydrides show more reactivity than the **3c-2e** terminal hydrides. However, for the Cr(II), Mn(III), Fe(II), Co(III), Ni(0) and Ni(II) metal centres, the B-H-TM bridging orbitals are constituted by the empty sp^2 orbital of the

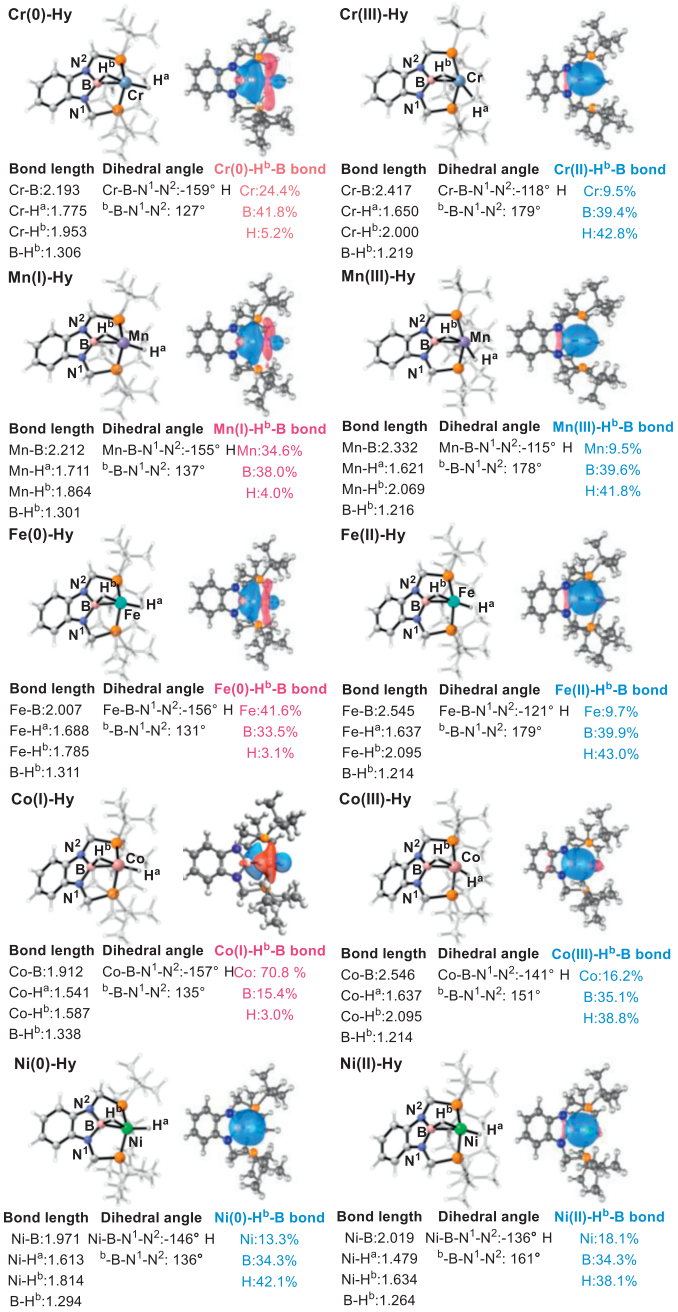


Fig. 2. Key structures and orbitals for BORYL-TM hydride complexes, with TM for Cr(0), Mn(I), Fe(0), Co(I), Ni(0), and their high oxidation states ions, Cr(II), Mn(III), Fe(II), Co(III) and Ni(II), respectively. The d orbitals and bridging hydride bonds of bond compositions within Metal-H^b-B bonds in green and pink, respectively.

boron atom, the empty d orbital of metal, and the 1s orbital of the hydride. These bridging hydrides are located as **3c-2e** bonds, which show less nucleophilic due to the two Lewis acid centres. The energy of the M-H^b-B orbitals is −15.5 eV to −7.3 eV, which is lower than the M-H^a orbitals' energy (−11.7 eV ∼ −3.8 eV). The **3c-2e** bridging hydrides show less reactivity than the terminal hydrides. In addition, the difference between M-H^a and M-H^b in M-Hy is shown in Fig. 4a, which exhibits the similarity of the two metal hydride bonds. For the Cr(0), Mn(I), Fe(0), and Co(I) metal centres, the bridging hydrides, exhibiting more metal hydride features, have similar bond distances with the terminal hydrides (ΔH^a–H^b from −0.05 Å to −0.18 Å). While for the Cr(II), Mn(III), Fe(II), Co(III), Ni(0) and Ni(II) metal centres, the bridging hydrides show fewer metal hydride features (ΔH^a-H^b from −0.01 Å to −0.458 Å). The

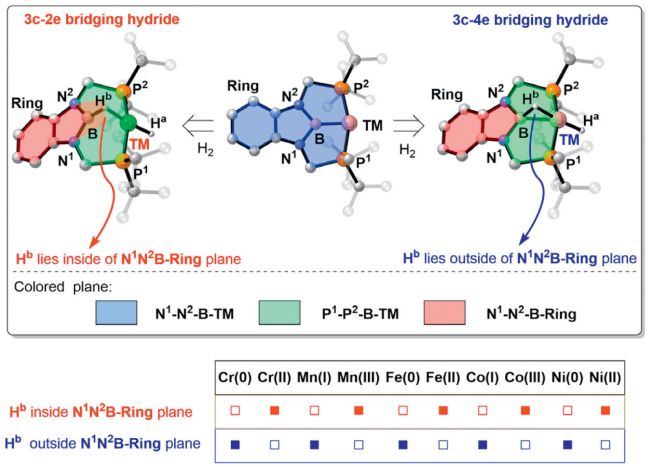


Fig. 3. Comparison of **3c-2e** and **3c-4e** bridging hydrides: spatial orientation and coordination in B-TM PBP complexes.

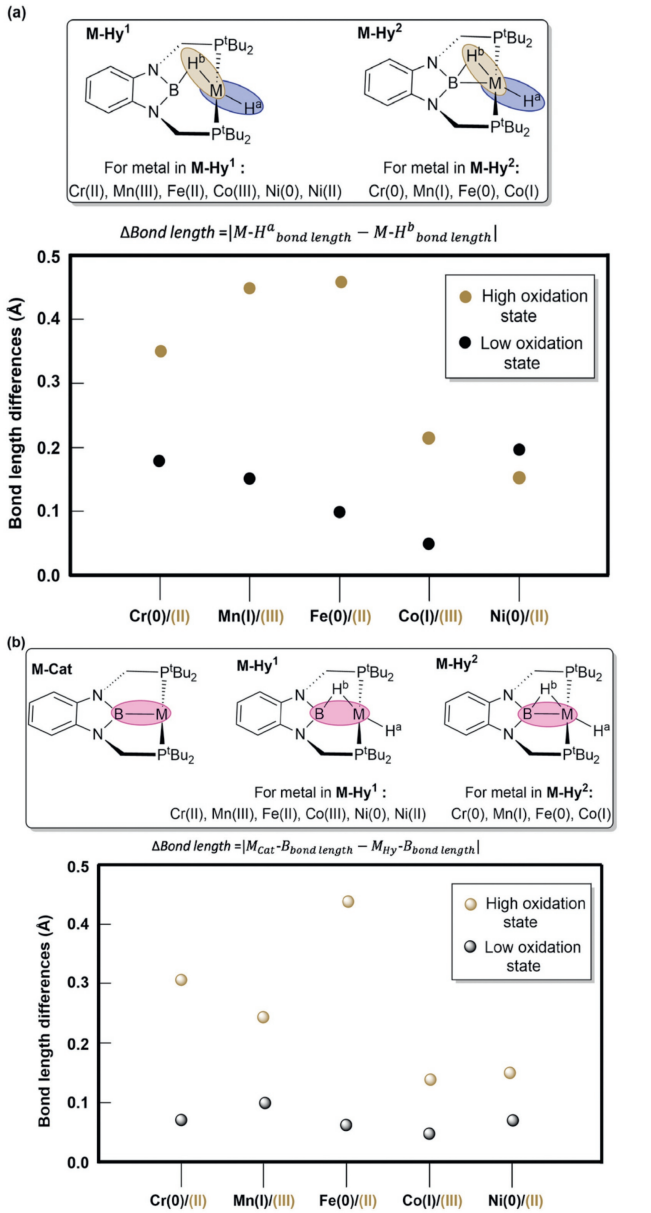


Fig. 4. (a) Bond length differences for M-H^a and M-H^b in M-Hy^1 and M-Hy^2 complexes. (b) Bond length differences for M-B between M-Cats to M-Hy^1 and M-Cats to M-Hy^2 complexes.

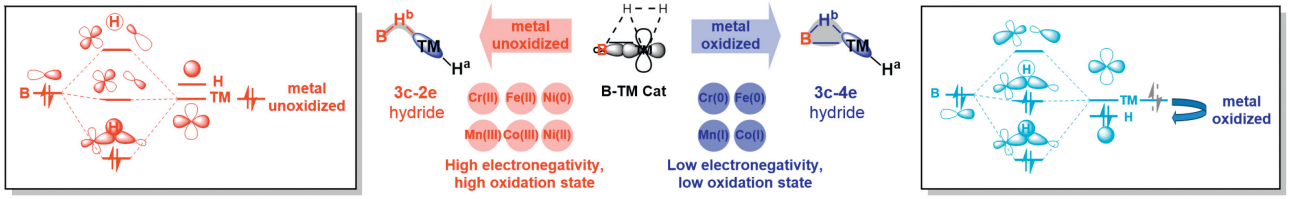


Fig. 5. Mechanism insights of **3c-2e** and **3c-4e** hydride formation from B-TM PBP catalysts.

B-H^b distances are 1.214 Å to 1.338 Å in those complexes, which show more B-H bond features. The results suggest that the metal centres would have a great influence on the metal hydride feature of the bridging hydride. From the M-B bond length differences for hydrogen activation, Mn's bond length difference increased from 0.098 Å in the low charge state to 0.246 Å in the high charge state. Fe(0) exhibited an even more pronounced change, from 0.067 Å to 0.441 Å. Co and Ni also displayed increases but were less dramatic, changing from 0.052 Å to 0.140 Å and 0.071 Å to 0.152 Å, respectively. Notably, the bond length differences for M-B in M-Cat and M-Hy, when plotted against metals' respective oxidation states, reveal those metals in a high oxidation state exhibit more significant bond length differences than those in a low oxidation state. This trend also suggests a potential correlation that high oxidation state metal centres (*i.e.*, Cr(II), Fe(II), Mn(III), Co(III) and Ni(II)) are likely to form **3c-2e** bridging hydride, and low oxidation metal centres (*i.e.*, Cr(0), Fe(0), Mn(I) and Co(I)) are likely to form **3c-4e** bridging hydride (Fig. 4b).

Drawing from our findings, we delineate two principal mechanisms in the genesis of bridging hydrides, as illustrated in Fig. 5. The **3c-4e** type emerges through the oxidation of metal centres, wherein the oxidized d electrons are instrumental in populating the *quasi*-non-bonding orbitals of the tri-centric B-H-M bond. Conversely, in the **3c-2e** type, the metal centres remain reduced, with a singular filled orbital allocated to the B-H-M bond. This dichotomy in bond formation is fundamentally a reflection of the metal centres' redox characteristics. Accordingly, metal centres such as Cr(0), Mn(I), Fe(0), and Co(I), which are in a reduced state, are inclined toward the formation of the more reactive **3c-4e** bridging hydrides. In contrast, centres like Cr(II), Mn(III), Fe(II), Co(III), Ni(0), and Ni(II), characterized by a heightened redox potential, are predisposed to form **3c-2e** bridging bonds. It is noteworthy that low oxidation state metal centres are more susceptible to oxidation, thereby favouring the establishment of the **3c-4e** bond over their high oxidation state counterparts. The transition metal centres are pivotal in the synthesis of highly active B-H-M bridging hydrides. This underscores a discernible trend: metal hydrides possessing high electronegativity and existing in high oxidation states are prone to form **3c-2e** hydrides, whereas those with low electronegativity and residing in low oxidation states are inclined to form **3c-4e** hydrides.

In summary, the factors influencing the formation of **3c-4e** or **3c-2e** bridging hydride bonds in boryl transition metal complexes were studied by DFT calculations. A series of 3d non-noble metal centres, including Cr, Mn, Fe, Co, and Ni, were systematically analyzed. The structure of the dihydride complexes indicates that **3c-4e** and **3c-2e** bridging hydrides are located in different planes of different complexes. The bond order of the bridging hydride is also affected by the metal centre. The BOC analysis further shows the orbital effect on the bond order of the bridging hydride. The orbital component and energy of the key orbital indicated the two-type bridging bond in those systems. For Cr(0), Mn(I), Fe(0), and Co(I) metal, the B-H-M prefer forming the more active **3c-4e** bridging hydride bond. While for Cr(II), Mn(III), Fe(II), Co(III), and Ni(0)/(II), the B-H-M prefers forming the **3c-2e** bridging hydride bond. The formation of different bridging hydrides is derived from the redox characteristic of the metal centre, as a lower oxidation state comes with lower electron negativity, which promotes hydrogen activation and fills the quasi-non-bonding orbital of the three-centre B-H-M bond. These results would serve as valuable guidance for the construction of highly active bridging hydrides for hydride transfer catalysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yubang Liu: Writing – original draft, Investigation, Formal analysis, Data curation. **Jiaxin Lin:** Formal analysis, Data curation. **Huayu Liang:** Formal analysis, Data curation. **Yinwu Li:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Zhuofeng Ke:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110291.

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