nature reviews chemistry

https://doi.org/10.1038/s41570-023-00501-1

Review article

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Cyclopentadienyl ring activation in organometallic chemistry and catalysis

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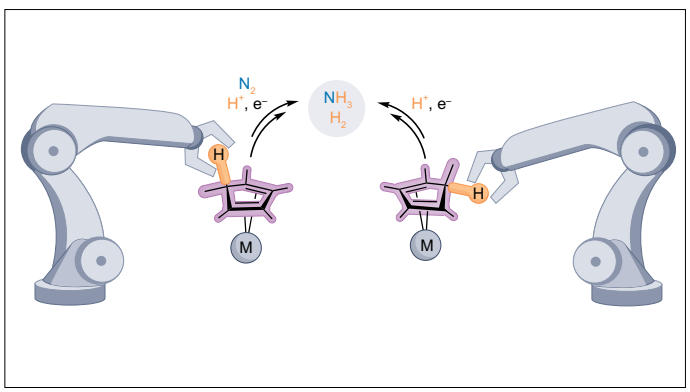
Abstract

The cyclopentadienyl (Cp) ligand is a cornerstone of modern organometallic chemistry. Since the discovery of ferrocene, the Cp ligand and its various derivatives have become foundational motifs in catalysis, medicine and materials science. Although largely considered an ancillary ligand for altering the stereoelectronic properties of transition metal centres, there is mounting evidence that the core Cp ring structure also serves as a reservoir for reactive protons (H^+), hydrides (H^-) or radical hydrogen ($H^•$) atoms. This Review chronicles the field of Cp ring activation, highlighting the pivotal role that Cp ligands can have in electrocatalytic H_2 production, N_2 reduction, hydride transfer reactions and proton-coupled electron transfer.



Sections

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Introduction

Ligand design has played a central role in expanding the toolbox of available transition metal complexes, with cyclopentadienyl (Cp) becoming a privileged ligand class in homogeneous catalyst development throughout the past several decades[1–5]. The unsubstituted Cp and its well-known electron-rich analogue pentamethylcyclopentadienyl (Cp*) can modify the stereoelectronic properties of transition metals, usually serving as 'innocent' ancillary ligands that modulate reactivity at the metal centre without directly participating in bond-making and bond-breaking processes (Fig. 1). Although there are numerous literature examples showcasing the ancillary prowess of Cp and Cp* ligands, there is an established precedent that Cp and Cp* ligands have an active role in C–X bond activation in the presence of nucleophiles (Nu^-), electrophiles (E^+) or radicals ($R^•$). In all the three cases, addition reactions to coordinatively saturated complexes containing Cp ligands disrupt the contiguous η^5-binding mode to generate stable and isolable η^4-cyclopentadiene frameworks, with *exo*-substitution being preferred in most cases.

Understanding the movement of protons and electrons by means of H^+, $H^•$ and H^- transfer is fundamentally important for synthetic chemistry, biology, materials science and energy-related processes. The reactivity of transition metal hydride complexes (M–H) has garnered sustained interest over the past several decades, and much has been discovered about their homolytic and heterolytic M–H bond strengths to deliver reactive $H^+/H^•/H^-$ moieties for applications in catalysis[6–8]. For example, generating reactive (weak) M–H bonds has enabled electrocatalytic H_2 production and oxidation[9], organoradical cyclization[10,11], epoxide hydrogenation[12] and hydrogenation of CO_2 to formate (HCO_2^-)[13–15]. By contrast, using C–H bonds within chelating ligands such as Cp and η^4-cyclopentadiene (Fig. 1) to deliver reactive $H^+/H^•/H^-$ moieties for applications in chemical fuel synthesis and electrocatalysis remains quite rare. In this Review, we show that reactivity of the Cp manifold has long been a curiosity in organometallic chemistry by first presenting literature accounts of Cp ligand functionalization, chronologically highlighting selected examples and classifying these instances by the type of addition agent used (Nu^-, E^+ or $R^•$). Then, we demonstrate how since 2016 this reactivity manifold has been used for applications in chemical energy conversion such as H_2 production, N_2 reduction, proton-coupled electron transfer (PCET) and hydride transfer reactions.

Early examples of Cp ring activation

Shortly after the discovery of ferrocene, there was a surge of interest in understanding its reactivity, preparing other metallocene derivatives and exploring the coordination chemistry of the Cp ligand in combination with other ligand types[16]. Although modification of the substituents surrounding the core Cp ring had become standard practice in synthetic chemistry laboratories, it was relatively uncommon to isolate, characterize and study the reactivity of η^4-cyclopentadiene complexes. Herein, we focus on some early accounts of reacting Cp with nucleophiles, electrophiles and organic radicals to generate stable (and often isolable) complexes containing η^4-cyclopentadiene ligands coordinated to transition metals.

Nucleophilic additions to Cp rings

Some of the earliest examples of Cp derivatization use nucleophilic reagents that attack the electrophilic Cp ring of coordinatively saturated metallocenes. The formal oxidation state of the metal decreases by 2, which is favoured by group 8 and 9 transition metals that readily undergo $d^6 \rightarrow d^8$ electronic reconfigurations. In 1959, seminal work by Green et al.[17] reported the reactions of cobaltocenium or rhodocenium salts with hydride transfer agents to isolate (η^4-C_5H_6)MCp (M = Co, Rh; **1**), which were characterized by infrared (IR) and ^{1}H NMR spectroscopy (Fig. 2). In 1961, Fischer and Herberich[18] first reported the nucleophilic addition of phenyllithium to $[Cp_2Co][ClO_4]$, generating neutral (η^4-C_5H_5Ph)CoCp (**2**). On the basis of IR spectroscopic data, this product was assigned as the *endo*-η^4-C_5H_5Ph adduct; however, complex **2** was verified as the *exo* isomer by X-ray crystallography in 1964 upon combining [Cp2Co][I] with phenyllithium[19]. Many years later, additional spectral data for **2**, other alkyl derivatives, alkoxides, amides and phopshides indicated that *exo*-substitution occured in practically all cases[20]. In 1961, Wilkinson and co-workers[21] extended their work to piano-stool (that is, half-sandwich) iron complexes, in which $[CpFe(CO)_2PPh_3]^+$ was treated with sodium borohydride to generate (η^4-C_5H_6)Fe(CO)$_2$PPh$_3$ (**3**) and characterized by IR and ^{1}H NMR spectroscopy. The rhodium variant, (*exo*-η^4-C_5H_4Ph)RhCp, was reported 2 years later[22]. In 1978, these nucleophilic addition patterns were framed in a broader context as part of the Davies–Green–Mingos rules for nucleophilic addition to unsaturated hydrocarbon ligands[23]. Decades later, the electrophilic character of the cobaltocenium cation was 'rediscovered' to generate other *exo*-substituted η^4-C_5H_4R derivatives[24–26]. For example, the complex (*exo*-η^4-$C_5H_5C{\equiv}C(SiMe_3)$)CoCp (**4**) was prepared by Tang and co-workers by reacting $[Cp_2Co][PF_6]$ with lithium trimethylsilylacetylide. Complex **4** was then used as a building block to prepare monomers via azide-alkyne 'click' chemistry to make metallopolymers (**5**), which was later extended to rhodocenes[27]. Shortly afterwards, Bildstein and co-workers independently published a very similar pathway to prepare complex **4** as a synthon for the preparation of cobaltocenium carboxylic acid[28]. Very recently, Cp* ring activation with an Ir^{III} cation was found to be strongly dependent on the identity of the carbon-based nucleophile[29]. In summary, the *exo*-addition of nucleophiles to Cp and Cp* has been firmly established; however, the release of H^- (that is, the reverse reaction) has only been applied in recent years for the reduction of small molecules such as NAD^+ and CO_2.

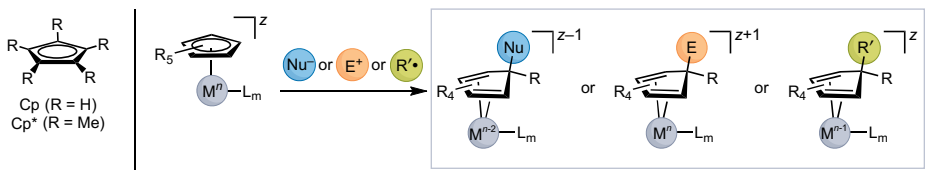

Fig. 1 | The active role of Cp ligands in transition metal complexes. Possible reaction outcomes via activation of cyclopentadiene ligands using nucleophiles (Nu^-), electrophiles (E^+) or radicals ($R'•$), which are the focus of this Review. R_5 represents cyclopentadienyl (Cp), Cp* and other substituted Cp analogues. L_m, coordinating ligand (ligands); M, transition metal; *n*, oxidation state; *Z*, overall charge.

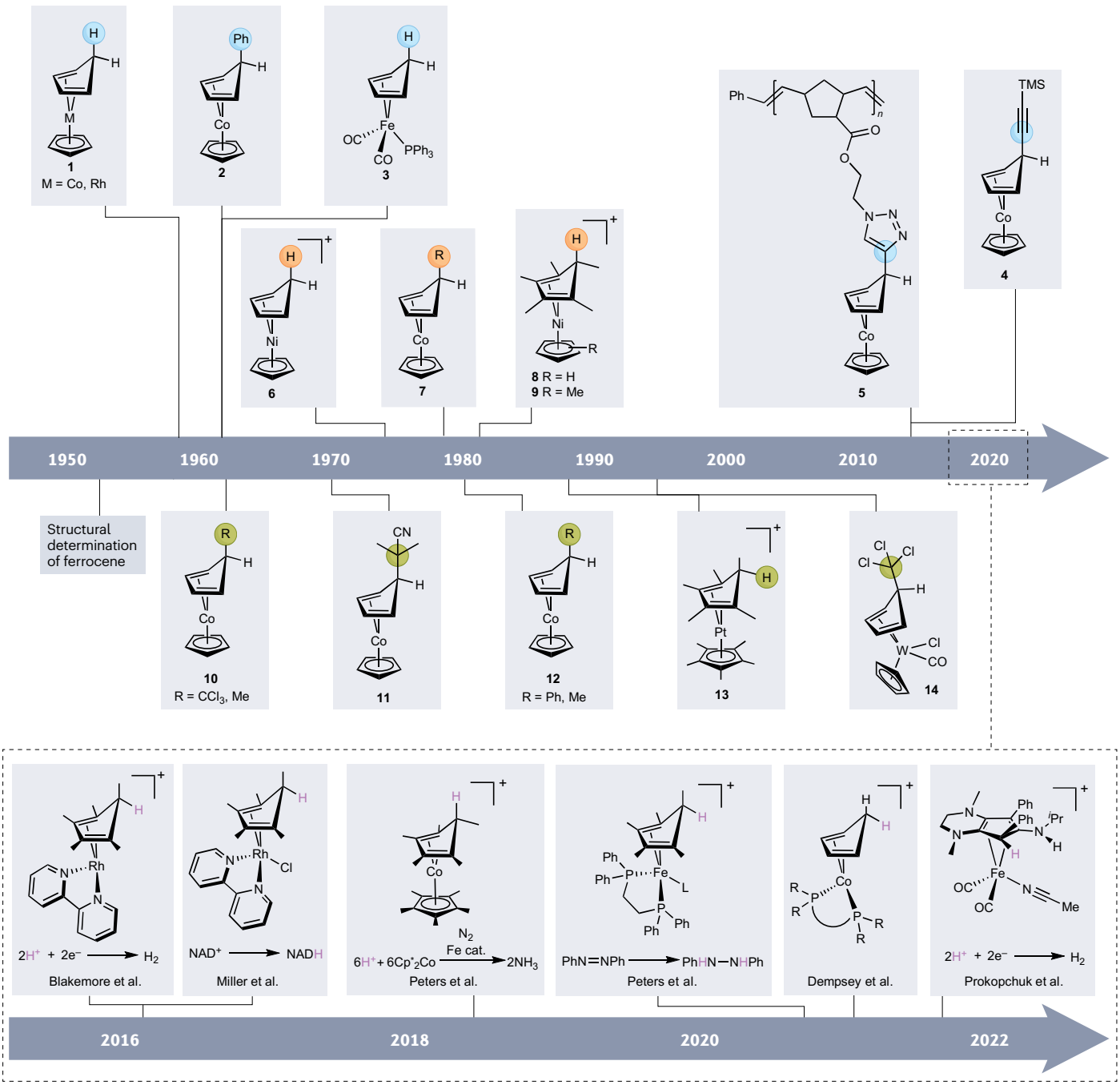

Fig. 2 | Discovery timeline of selected ring-activated cyclopentadiene complexes. The top section shows selected ring activation examples before 2016, in which the η^5-cyclopentadienyl ring is attacked by nucleophiles, electrophiles or radicals. Complexes **1**–**5** were synthesized via nucleophilic addition (blue)[17–28], complexes **6**–**9** were synthesized via electrophilic addition (orange)[34–38,89], and complexes **10**–**14** were synthesized via radical addition (yellow)[17,37,39–47]. The lower box shows the resurgence of interest in cyclopentadienyl ring activation from 2016 onwards, which involves the net transfer of H^+, $H^\cdot$ or H^- to/from small molecules[91,95–97,107,122–124,129,132,134]. TMS, trimethylsilyl.

Electrophilic additions to Cp rings

The discovery of electrophilic substitution reactions with ferrocene opened new vistas of organometallic chemistry in the twentieth century[30–32]. It is widely accepted that Cp ring activation by the incoming electrophile (E^+) occurs before loss of H^+, generating a transient $[(\eta^4\text{-}C_5H_4E)FeCp]^+$ intermediate[31,33]. In later years, electrophilic addition products were reported with electron-rich metallocenes that formally have 20 valence electrons, which make the Cp ligands more susceptible

to electrophilic attack. In 1974, the protonation of nickelocene was achieved by treating it with anhydrous HF, which allowed for the spectroscopic detection of $[(\eta^4\text{-}C_5H_6)NiCp]^+$ (**6**) by ^1H NMR spectroscopy with a proposed F^- or $[FHF]^-$ counterion[34] (Fig. 2). However, attempts to isolate this complex with a $[BF_4]^-$ counterion led to diene loss and the formation of $[CpNi][BF_4]$. In 1975 and 1976, reports of the electrogenerated anion $[Cp_2Co]^-$ reacting with carbon-based electrophiles RX (R = CH_2Ph, CHClPh, CCl_3, CH_2Br) to furnish the neutral (*exo*-η^4-C_5H_5R)CoCp (**7**) in high yield were published[35,36]. Interestingly, CO_2 also reacts with $[Cp_2Co]^-$ to generate a proposed (unstable) ring-activated carboxylate anion $[(exo\text{-}\eta^4\text{-}C_5H_5CO_2)CoCp]^-$ that is converted to the isolable ester (*exo*-η^4-$C_5H_5CO_2Me$)CoCp by reaction with methyl iodide. In 1980, the synthesis of $[(exo\text{-}\eta^4\text{-}C_5Me_5R)NiCp^*][BF_4]$ (**9**) from nickelocene was reported using several different alkyl and aryl electrophiles, which were suggested to be *exo*-products owing to the similar chemical shifts for all the *endo*-methyl resonances via ^1H NMR spectroscopy[37]. In the same year, it was shown that HBF_4 selectively protonates the electron-rich Cp* ligand of Cp^*_2Ni and Cp*NiCp to yield the stable $[(\eta^4\text{-}C_5Me_5H)NiCp][BF_4]$ and $[(\eta^4\text{-}C_5Me_5H)NiCp^*][BF_4]$ (**8**); however, *exo*-protonation versus *endo*-protonation was structurally ambiguous[38]. As described in the sections covering N_2 reduction and stoichiometric PCET, protonation of a paramagnetic metallocene yields an isolable ring-activated product that releases $H^\bullet$, whereas Cp protonation of diamagnetic piano-stool complexes precedes ligand-to-metal proton migration reactions. These types of electrophilic addition reactions are relevant to (electro)catalytic NH_3 formation and H_2 production, respectively, under reducing conditions.

Radical additions to Cp rings

Radical-based addition reactions of haloalkanes to Cp-containing complexes have been primarily investigated with cobaltocene (Cp_2Co), a paramagnetic metallocene that formally possesses 19 valence electrons. In 1956, Wilkinson et al.[39] observed that Cp_2Co reacts with bromoethane to generate the diamagnetic cobaltocenium bromide, however the fate of the alkyl moiety was unclear. Subsequently, reactions with other haloalkanes were reported (MeI, CCl_4), and Cp_2Co disproportionates to afford (*exo*-η^4-C_5H_5R)Co^{I}Cp (**10**) (Fig. 2) and an equivalent of $[Cp_2Co^{III}][X]$ (X = I, Cl), as evidenced by IR and ^1H NMR spectroscopy[17,40]. Starting in 1969, a series of papers were published that discovered a radical addition mechanism to form such *exo*-alkylation products. Kinetic studies showed that the rate of Cp_2Co alkylation expectedly increases with better leaving group halogen (Cl > Br > I) and rates increase when the halomethyl group has one, two or three halogen atoms, respectively[41]. In 1970, the reaction of Cp_2Co with the radical initiator azaisobutyronitrile afforded nearly quantitative amounts of (*exo*-η^4-$C_5H_5(C(CH_3)_2CN)$)CoCp (**11**), demonstrating that Cp_2Co is an effective radical trap[42]. Follow-up kinetic studies further supported these claims, showing that an initial electron transfer step to generate $[Cp_2Co^{III}]^+$ and $R^\bullet$ is rate-limiting[43,44]. The electron-rich Cp^*_2Co reacts similarly with CH_3I and C_6H_5I to generate diamagnetic (*exo*-η^4-C_5Me_5R)CoCp* (**15**) and $[Cp^*_2Co][I]$[37]. In 1994, the platinum adduct $[(endo\text{-}\eta^4\text{-}C_5Me_5H)PtCp^*][BF_4]$ (**13**) was reported to undergo oxidation via controlled potential electrolysis to produce the Pt^{IV} metallocene dication $[Cp^*_2Pt]^{2+}$; however, the fate of released $H^\bullet$ remained unclear[45]. Controlled potential electrolysis of the resultant $[Cp^*_2Pt]^{2+}$ under reducing conditions regenerates $[(\eta^4\text{-}C_5Me_5H)PtCp^*]^+$, with solvent or decomposition product (products) possibly acting as $H^\bullet$ sources[46]. In 1996, the isolation and structural characterization of (*exo*-η^4-$C_5H_4CCl_3$)WCp(Cl)(CO) (**14**) was achieved by reaction of $Cp_2W(CO)$ with a large excess of CCl_4, and it was proposed that initial *exo*-attack of a trichloromethyl radical on the Cp ring was followed by chloride addition to the metal centre[47]. In recent years, addition reactions using organoradicals have garnered much less attention, but the release of $H^\bullet$ from η^4-CpH ligands has become important, as described in the sections below on N_2 reduction and stoichiometric PCET.

Other instances of Cp ring activation

Other reports of Cp ring activation do not cleanly fit into one of the aforementioned reactivity classes. For instance, other hapticity changes (that is, ring slippage to η^3-Cp or η^1-Cp) can accompany ring activation; this subject has been reviewed elsewhere[48]. In some cases, ring-activated molecules are isolated as unexpected by-products and/or characterized to varying degrees[49–53], whereas in other cases, the exact reaction conditions that lead to ring activation are unclear[54–57]. Ring-activated complexes can also be isolated as products of intramolecular insertion reactions, in which a coordinatively saturated metal complex bears a ligand capable of inserting into the Cp–M bond, driven to form an η^4-C_5H_4R moiety in the presence of excess ligand and UV[58] or visible[59] light. Electronic effects at the metal centre[60–62] or the influence of cluster ligands[63–67] can also lead to cases in which η^4-coordination is preferred over η^5-coordination. Ring-activated complexes have also been proposed as transient reaction intermediates involving *f*-block metallocenes[68] and to explain deuterium incorporation into the Cp ligand[69–71]. Notably, the reactivity of alkyl substituents on Cp ligands to generate fulvenes[72–74] and of η^6-C_6Me_6 ligands on CpFe sandwich complexes[75] are beyond the scope of this Review.

Implications in synthesis and catalysis

The remainder of this Review focuses on the resurgence of Cp ring activation chemistry from 2016 onwards, where perturbation of the aromatic ring structure to form η^4-CpH moieties becomes essential to mediate the delivery of H^+, H^- or $H^\bullet$ to produce H_2, NH_3 and reduced organic molecules (Fig. 2, bottom). In particular, H_2 and NH_3 are essential commodity chemicals for the agriculture enterprise to support our current global population, and their sustainable production will have a central role in minimizing global CO_2 emissions[76]. Furthermore, understanding the kinetic and thermochemical requirements for rapidly and efficiently moving hydrogen using the η^4-Cp ring system has broad implications in developing new catalysts that mediate PCET reactions[77].

H_2 production

The sustainable and economical production of H_2 is an essential component of converting solar energy into chemical fuels[78]. Many groups have taken inspiration from hydrogenases[79,80], placing amine bases capable of shuttling protons to the metal in the secondary coordination sphere to increase the efficacy of hydrogen production catalysis[9,81]. Complexes with the general formula $[Cp^*Rh^{III}L(bpy)]^{2+}$ (bpy = 2,2′-bipyridine, L = H_2O or MeCN) are well-known precatalysts for various reactions such as reduction of NAD^+ (refs. 82–84), oxidation of formate[85,86] and the reduction of $2H^+$ to H_2 (refs. 87,88). The hydrogen production reactions were believed to proceed through a well-accepted mechanism that first involves $2e^-$ reduction of $[Cp^*Rh^{III}(NCMe)(bpy)]^{2+}$ (**20**) to furnish the electron-rich $Cp^*Rh^{I}(bpy)$ (**15**), followed by protonation to give hydride complex $Cp^*Rh^{III}H(bpy)$ (**18**), followed by electrophilic attack of Rh-H moiety with a second proton to generate H_2 (ref. 87) (Fig. 3). Evidence in support of this mechanism first included ^1H NMR spectroscopic observation of complex **15** (ref. 89), followed by the synthesis and crystallographic characterization of complex **15** in high yield[90].

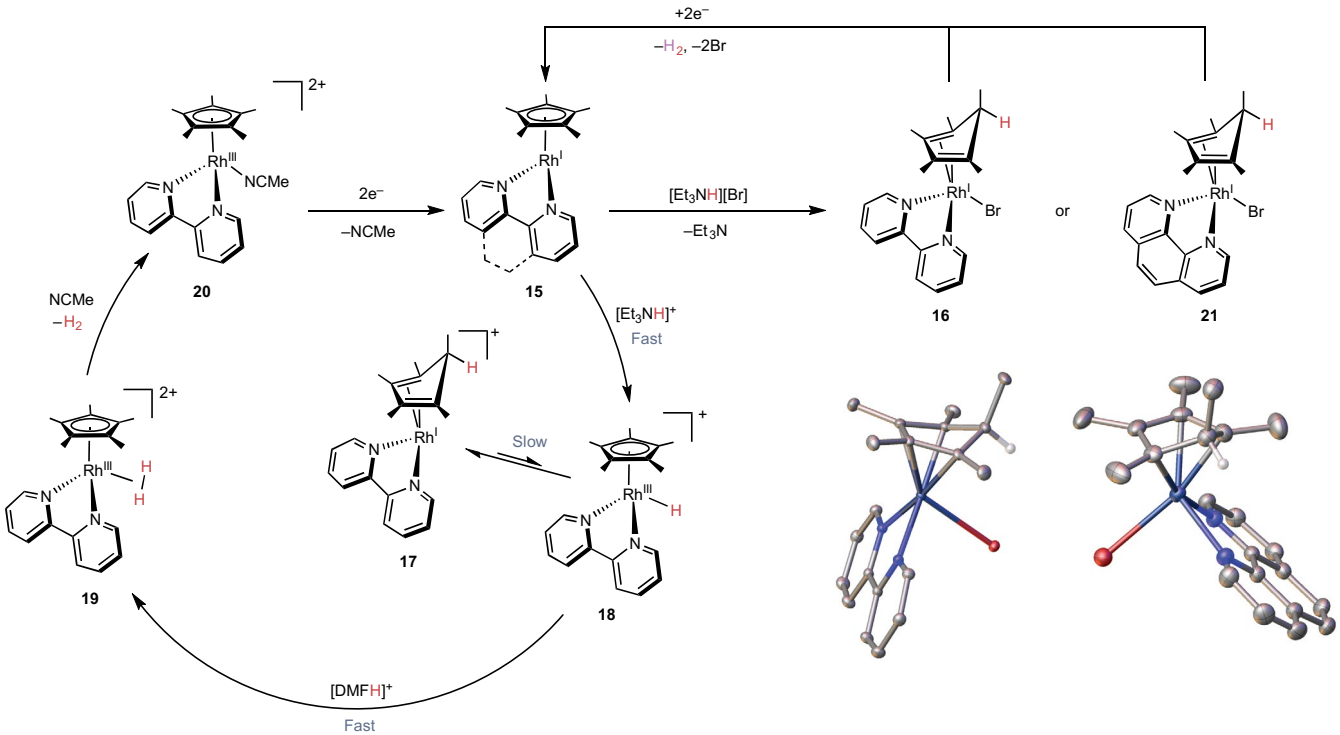

Fig. 3 | Cyclopentadiene ring activation in H_2 production using $[Cp^*Rh^{III}(NCMe)(bpy)]^{2+}$ catalysts. The $2e^-$ reduction of complex **20** enables ligand protonation by $[Et_3NH][Br]$, generating ring-activated complexes **16** or **21** (phenanthroline derivative), which have been characterized by single-crystal X-ray diffraction (CCDC 1424707 (**16**) and 1546016 (**21**))[91,96]. Using $[Et_3NH]^+$ with a weakly coordinating anion generates off-cycle complex **17** via transient metal hydride intermediate **18** (refs. 91,95). Reacting **17**/**18** with strong acids such as $[DMFH]^+$ results in H_2 evolution and regeneration of **20**. bpy, 2,2′-bipyridine; Cp*, pentamethylcyclopentadienyl; $[DMFH]^+$, *N*,*N*′-dimethylformamidinium.

In 2016, Blakemore et al. reported that $Cp^*Rh^I(bpy)$ (**15**) behaves as a chemically non-innocent Cp* ligand coordinated to Rh, forming an η^4-Cp*H intermediate that might have a role in catalytic H_2 evolution[91] (Fig. 3). Established conditions for catalytic H_2 production using complex **15** require strongly acidic conditions[87,88], and exposure of complex **15** to excess *N*,*N*-dimethylformamidinium trifluoromethanesulfonate ([DMFH][OTf]; $pK_a^{MeCN} = 6.1$)[92] releases a stochiometric amount of H_2, as measured by gas chromatography. Switching to weaker acids not only lowered the driving force for H_2 evolution[93] but also offered the possibility of isolating catalytically relevant intermediates if the acid is strong enough to react with the electron-rich catalyst but too weak to generate H_2. When $Cp^*Rh^I(bpy)$ is exposed to $[Et_3NH][Br]$ ($pK_a^{MeCN} = 18.8$)[94], a colour change is observed but no H_2 is released. This crucial reaction enabled the isolation and X-ray crystallographic characterization of (*endo*-η^4-C_5Me_5H)$Rh^IBr(bpy)$ (**16**), in which the proton is located *endo*-orientation relative to the metal centre (Fig. 3, right). The bromide-free salt [(*endo*-η^4-C_5Me_5H)$Rh^I(bpy)$][OTf] (**17**) was characterized via NMR spectroscopy by instead using $[Et_3NH][OTf]$ as the acid source. Importantly, exposure of these *endo*-η^4-C_5Me_5H complexes to excess [DMFH][OTf] cleanly releases H_2 and produces $[Cp^*Rh^{III}(L)(bpy)]^+$ (**20**), in which L is the coordinated solvent (MeCN) or conjugate base (DMF).

The protonation behaviour of $Cp^*Rh^I(bpy)$ was probed by ground-state density functional theory (DFT) studies[91,95]. When complex **15** reacts with a weaker acid, $Et_3NH,^+$ the metal is first protonated to give complex **18**, which then isomerizes to give the more stable complex **17**. These results are all consistent with the observation of exclusive *endo*-selectivity in the presence of Et_3NH^+. The lowest computed energy pathway requires tautomerization from the ligand to the metal before protonation of complex **18** to generate transient dihydrogen-bound complex **19**. In summary, these computational findings showed that [(*endo*-η^4-C_5Me_5H)$Rh^I(bpy)$]$^+$ (**17**) is an off-cycle thermodynamic sink during H_2 production, which can be avoided in the presence of strong acids owing to the kinetically favourable sequential protonation of the Rh^I metal centre and Rh^{III}–H intermediate[95].

Conjugated N-donor ligands beyond 2,2′-bipyridine can also be used for stoichiometric and electrocatalytic H_2 production[96,97]. The structurally authenticated complex (*endo*-η^4-C_5Me_5H)$Rh^IBr(phen)$ (phen = phenanthroline; **21**) was synthesized, and its electrochemical behaviour was interrogated[96] (Fig. 3, right). Controlled potential electrolysis experiments with complex **21** (or isostructural complex **16**) produced 1 equiv. H_2, underscoring that H_2 evolution is feasible in the absence of exogenous acid. Electronic modifications at the 4,4′ positions of the bipyridine ligand (bpy^R where R = ^{t}Bu, H or CF_3) were conducted and compared with the reactivity of **15** (ref. 97). Controlled potential electrolysis verified that H_2 is produced in catalytic amounts, with a maximum turnover number of 4.4. Post-electrolysis solutions using $[Cp^*Rh^{III}Br(bpy^{CF3})]^+$ reveal a large build-up of the protonated solvent adduct [(*endo*-η^4-C_5Me_5H)$Rh^I(NCMe)(bpy^{CF3})$]$^+$, implying that it is a plausible (off-cycle) resting state during electrocatalysis. Collectively, these observations suggest that electronic modifications to the ancillary ligand environment do not enhance catalytic

performance and cast further doubt on the relevance of Cp* ring activation with these Rh-based systems.

The sluggish catalytic activity reactivity of the precious metal complexes described above indicates that they are economically and environmentally impractical to meet demands for sustainable H_2 on a scale suitable for chemical energy production[98]. Iron is the most abundant transition metal in the upper crust of the Earth and represents an ideal alternative; however, the library of synthetically tractable CpFe-based H_2 production or H_2 oxidation electrocatalysts remains limited[99–104] and none rival the efficiency and speed of [FeFe]-hydrogenase (less than 0.1 V overpotential and turnover frequency of 6,000–9,000 s^{-1} for H_2 production)[80,105,106]. Thus, there is still great interest in designing Earth-abundant H_2 production catalysts, particularly with systems that incorporate biomimetic primary or secondary coordination sphere modifications to facilitate proton shuttling to/from the metal centre[9,79,105]. In 2021, Prokopchuk and co-workers reported tri-amine-functionalized piano-stool Fe complexes $[^{en}Cp^{R}Fe(NCMe)(CO)_2]^+$ (en = *N*,*N*′-dimethylethylenediamine, R = NH^{i}Pr, Pyrr, NBn) as proton reduction electrocatalysts to form H_2, with the ^{i}Pr variant $[^{en}Cp^{NHiPr}Fe(NCMe)(CO)_2]^+$ (**22**)[107] shown in Fig. 4. All three solvent adducts catalyse the production of H_2 in acetonitrile using Tos_2NH as the proton source with maximum H_2 production catalytic rates of 29–45 s^{-1}.

The reaction mechanism was rationalized via state-of-the-art DFT approaches[108] using $[^{en}Cp^{NHiPr}Fe(NCMe)(CO)_2]^+$ (**22**)[107] (Fig. 4). The delivery of $2H^+$ and $2e^-$ to complex **22** can occur in several different permutations before H_2 evolution, which include protonation at many possible sites as highlighted in blue for the structure of complex **22**. The most thermochemically reasonable pathway after $1e^-$ reduction was found to be *endo*-selective protonation at the Cp ring (**23**) based on its computed acidity (pK_a^{MeCN} = 15.7) relative to exogenous acid Tos_2NH (pK_a^{MeCN} = 11.97)[109], whereas protonation at the NH^{i}Pr moiety (**25**) was deemed unlikely on thermochemical grounds (pK_a^{MeCN} = 8.9). Steric arguments presumably make *exo*-protonation at the $^{en}Cp^{NHiPr}$ ring significantly less favourable (pK_a^{MeCN} = 5.4), and direct protonation of the metal centre (**24**) is also implausible owing to the higher computed acidity of the resultant Fe^{III}-H intermediate (pK_a^{MeCN} = 9.6). Reduction of the solvent-coordinated intermediate $[(endo\text{-}\eta^4\text{-}^{en}CpH)Fe(NCMe)(CO)_2]^+$ ($E°$ = −1.01 V) followed by solvent dissociation and ligand-to-metal proton migration was proposed to yield a stable $Fe^{II}H$ complex (**26**). Finally, complex **26** was proposed to undergo direct protonation by exogenous acid to yield complex **27**, followed by H_2 release. Overall, these data indicated that the amines were chemically innocent during electrocatalysis, and ligand-to-metal proton migration was essential for electrocatalytic H_2 evolution, contrasting with the inhibitory tautomerization behaviour of the Cp^*Rh^I(bpy) complexes described earlier. Therefore, amine-functionalized Cp ligands coordinated to Earth-abundant metals exhibit unique chemically non-innocent reactivity patterns under electrochemical bias, and the kinetic details for these elementary reaction steps warrant deeper investigation.

N_2 reduction

There have been widespread efforts to develop homogeneous and heterogeneous catalysts for the efficient conversion of N_2 to NH_3 (ref. 110), particularly in processes that minimize the use of fossil fuel feedstocks to circumvent the need for centralized Haber–Bosch production facilities[76]. To date, no molecular catalysts have been reported that directly convert gaseous H_2 and N_2 into NH_3; therefore, powerful reductants ($E° \leq -1.3$ V versus $Fc^{+/0}$) and strong acids ($pK_a^{THF} \leq 8$) dissolved in organic solvent are commonly used in molecular catalysis to achieve catalytic turnovers in the N_2 reduction reaction (N_2RR), with particular attention focused on minimizing H_2 evolution by metering the amount of available H^+/e^- in solution[111–115]. In recent years, researchers have made progress towards increasing molecular N_2RR efficiency by surveying PCET reagents that minimize the thermochemical driving force for this $6H^+/6e^-$ reaction[77,116–118]. In 2017, Peters and co-workers recognized that some of the most active molecular N_2RR catalysts use Cp_2Co or Cp^*_2Co as $1e^-$ reductants in the presence of strong acid to generate NH_3 and/or N_2H_4 (refs. 111,112,119–121) and postulated that metallocenes might play a chemically non-innocent role[122]. Compelling DFT calculations

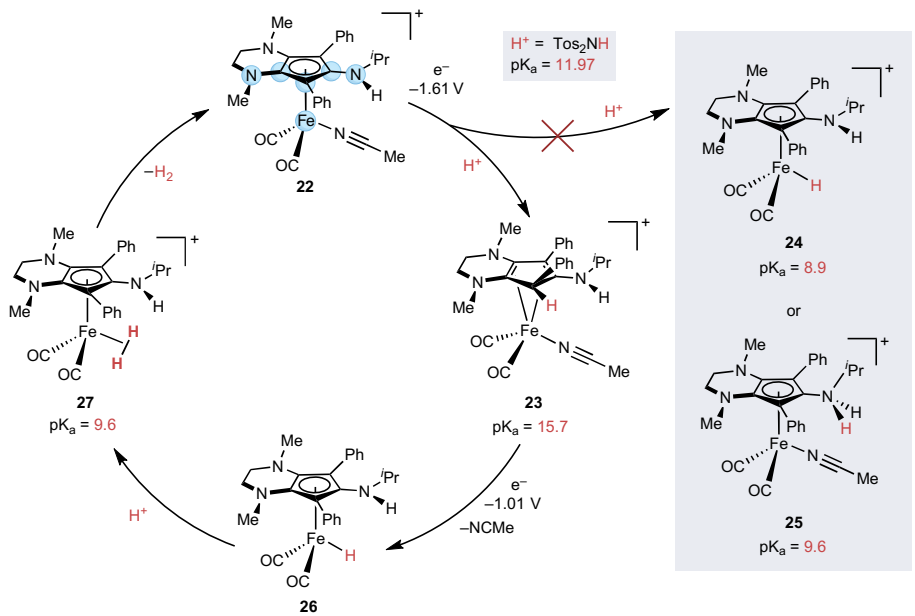

Fig. 4 | Proposed *endo*-selective protonation and ligand-to-metal proton migration during H_2 production using $[^{en}Cp^{NHiPr}Fe(NCMe)(CO)_2]^+$ catalysts[107]. The $1e^-$ reduction of complex **22** is followed by stereoselective protonation at the *endo*-Cp site to give compound **23**, based on density functional theory calculations (other considered protonation sites for this step are highlighted in blue in complex **22**). The *endo*-protonated complex **23** then undergoes ligand-to-metal proton migration after a second reduction event, which enables H_2 evolution via direct protonation of intermediate **26**. Complexes **24** and **25** are inaccessible on the basis of computed pK_a measurements. All redox potentials are referenced to the $Cp_2Fe^{+/0}$ redox couple. Cp, cyclopentadienyl; Tos, toluenesulfonyl.

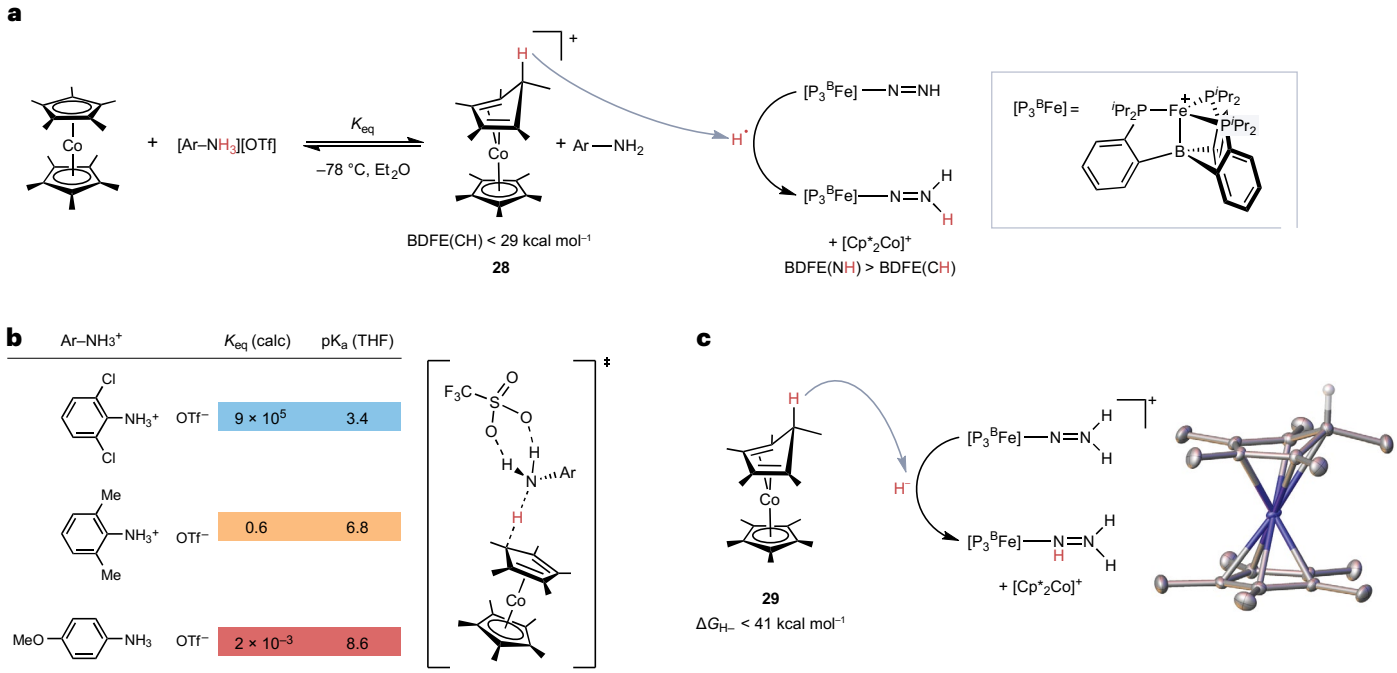

Fig. 5 | The role of cyclopentadiene ring activation of decamethylcobaltocene in N_2 reduction catalysis. a, Ring protonation of Cp^*_2Co gives complex **28**, which has a C–H bond dissociation free energy (BDFE) of 29 kcal mol^{-1}, enabling proton-coupled electron transfer reactivity during N_2 reduction catalysis using the boratrane complex [$\mathbf{P_3^BFe}$] (ref. 122). **b**, pK_a dependence on the formation of *exo*-$Cp^*Co(\eta^4\text{-}C_5Me_5H)^+$ (**28**). Increased concentrations of complex **28** in solution enhance N_2 to NH_3 reduction yields with complex [$\mathbf{P_3^BFe}$] (refs. 122,124). **c**, The hydricity (ΔG_{H^-}) of complex **29** was determined to be 41 kcal mol^{-1}, suggesting that complex **29** (CCDC 1902775) is capable of hydride transfer to a diazenido ligand during N_2 reduction with catalyst [$\mathbf{P_3^BFe}$] (ref. 123). Ar, substituted aryl group; Cp*, pentamethylcyclopentadienyl; Tf, trifluoromethylsulfonate; THF, tetrahydrofuran.

and electron paramagnetic resonance (EPR) experiments revealed that the Cp* ring of Cp^*_2Co is protonated in the *exo*-position to generate $[(exo\text{-}\eta^4\text{-}C_5Me_5H)CoCp^*]^+$ (**28**), priming it to deliver $H^\bullet$ via PCET during N_2 reduction catalysed by iron boratrane complex [$\mathbf{P_3^BFe}$][122] (Fig. 5a). The proclivity for C–H bond scission in complex **28** is rationalized by its low bond dissociation free energy (BDFE(CH) < 29 kcal mol^{-1})[123], driven by re-aromatization of the ring system to the $\eta^5\text{-}C_5Me_5$ state and subsequent generation of the diamagnetic $[Cp^*_2Co]^+$. DFT calculations further support this hypothesis by revealing that the calculated N–H bond dissociation enthalpy for an early-stage N_2 reduction intermediate is higher (47 kcal mol^{-1})[122] than the measured C–H bond dissociation enthalpy of complex **28** (< 29 kcal mol^{-1})[123]. Thus, Cp* ring protonation was proposed to be an essential component of delivering reactive $H^\bullet$ moieties during N_2RR.

In a separate report, thorough catalytic studies were undertaken using Cp^*_2Co, demonstrating a strong correlation between N_2RR activity, acidity of the exogenous cationic acid and its counteranion[124]. Freeze-quench Mössbauer spectra containing stoichiometric amounts of the acid 2,6-dichloroanilinium trifluoromethanesulfonate ($[^{2,6\text{-}Cl}PhNH_3][OTf]$) with the early-stage N_2-fixed intermediate [$\mathbf{P_3^BFe\text{-}N{\equiv}N}$]$^-$ did not furnish the known protonation product [$\mathbf{P_3^BFe\text{-}NNH_2}$]$^+$ (ref. 125), suggesting that Cp^*_2Co and acid must react with one another before productive N_2RR can occur. DFT calculations revealed a correlation between the equilibrium constant (K_{eq}) for the formation of complex **28** and the pK_a of the exogenous acid used[124] (Fig. 4b). In all the three instances, protonation is kinetically facile but stronger acids increase the concentration of available $[(exo\text{-}\eta^4\text{-}C_5Me_5H)CoCp^*]^+$ (**28**) in solution through a computed transition state involving hydrogen-bonded $[OTf]^-$. Therefore, the observed pK_a effects on catalytic activity largely arise from the differences in concentration of protonated metallocene relative to Fe catalyst, with higher concentrations of complex **28** enhancing the rate of N_2RR. To further show the critical role of metallocene-mediated N_2RR, cyclic voltammetry (CV) studies with [$\mathbf{P_3^BFe}$], exogenous acid and $[Cp^*_2Co]^+$ revealed a current enhancement in comparison to CVs without added metallocene. Controlled potential electrolysis experiments with added metallocene also showed a modest increase in overall NH_3 yield, verifying that [$\mathbf{P_3^BFe}$] is a bona fide molecular electrocatalyst for the reduction of N_2 to NH_3 in the presence of exogenous acid and a Cp^*_2Co PCET mediator.

Unequivocal spectroscopic evidence for the formation of complex **28** was later reported, in which both the *endo*-isomers and *exo*-isomers were thoroughly characterized using pulse EPR spectroscopic techniques[123]. Protonating Cp^*_2Co with a sterically unencumbered strong acid such as HOTf at low temperature generated a 10:1 mixture of *endo*-isomers and *exo*-isomers, with computations revealing the latter being more thermochemically stable by approximately 2 kcal mol^{-1}. By choosing a bulkier acid, the *endo*/*exo* ratio can become 3:10, as measured by X-band EPR spectroscopy. On the basis of steric arguments, the *exo*-isomer is the only one considered to be active for PCET. Although the X-ray structure of $[(exo\text{-}\eta^4\text{-}C_5Me_5H)CoCp^*]^+$ (**28**) remains elusive, the reduction product ($exo\text{-}\eta^4\text{-}C_5Me_5H)CoCp^*$ (**29**) can be isolated and structurally characterized (Fig. 4c). By using thermochemical free energy relationships, the C–H BDFE and hydride donor ability (hydricity) of complexes **28** and **29** were experimentally determined,

respectively, validating the exceptionally weak C–H BDFE of the radical cation (<29 kcal mol^{-1}) and potent hydride donor ability of the neutral adduct (<41 kcal mol^{-1}). Therefore, it was posited that complex **29** may also serve as a hydride donor during catalytic N_2RR, delivering a hydride equivalent to the proximal N atom of a coordinated diazenido ligand.

Although the unique reactivity of Cp^*_2Co has been thoroughly demonstrated through the vignette of N_2RR catalysed by [$\mathbf{P_3^BFe}$], it is not a general-purpose PCET/hydride donor for N_2RR. An isostructural silatrane ligand that uses an Si anchor in place of boron is inactive for N_2RR catalysis under otherwise identical reaction conditions[122]. Recently, Peters and co-workers[126] reported a more generally compatible class of amine-functionalized Cp_2Co mediators that deliver H$^\bullet$ via N–H bond cleavage for electrocatalytic N_2RR. In summary, redox-active metallocene mediators have proven to be successful at delivering potent H$^\bullet$ to inert substrates such as N_2 via C–H or N–H bond activation pathways.

Stoichiometric hydrogen atom and hydride transfer reactions

The Fe^{III} hydride complex [Cp*Fe(dppe)H]$^+$ (**30**; 1,2-bis(diphenylphosphino)ethane (dppe)) was isolated in 1992 via oxidation of the neutral 18e$^-$ complex Cp*Fe(dppe)H using Fc$^+$ (ref. 127) (Fig. 6). After X-ray structural characterization and analysis via EPR and ^{57}Fe Mössbauer spectroscopies, a follow-up report reacted complex **30** with CO, which was proposed to generate the formally 19e$^-$ intermediate [Cp*FeH(dppe)(CO)]$^+$ (ref. 128). Reduction of '[Cp*FeH(dppe)(CO)]$^+$' with Cp_2Co furnishes the stable 18e$^-$ complex (*endo*-η^4-C_5Me_5H)Fe(dppe)CO (**31**), which was further characterized by ^{1}H and ^{31}P NMR spectroscopy. Re-examination of the X-band EPR spectra of the putative [Cp*FeH(dppe)(CO)]$^+$, including additional pulse EPR spectroscopic data, determined that the ^{1}H and ^{31}P hyperfine parameters differ significantly from terminal transition metal hydrides and the complex is actually [(*endo*-η^4-C_5Me_5H)Fe^I(dppe)CO]$^+$ (ref. 129) (**32**) (Fig. 6). This structural assignment was also confirmed by X-ray crystallography. Notably, warming a sample of complex **32** to room temperature under a CO atmosphere yields the complex [Cp*Fe(dppe)CO]$^+$ (**33**) and releases 0.5 equivalents of H_2 in nearly quantitative yield, suggesting that the C–H BDFE of this paramagnetic ring-activated species is lower than the driving force for homolytic H_2 formation ($\Delta G°$(1/2 H_2 → H•) = 52 kcal mol^{-1})[130]. Consistent with this interpretation, thermochemical analysis of complex **32** indicates that the C–H BDFE is less than 36 kcal mol^{-1}. Interestingly, complex **31** is able to transfer a hydride to CO_2, indicating that its hydricity must be less than the hydricity of the formate anion ($HCOO^-$; approximately 44 kcal mol^{-1} in acetonitrile)[13,131].

The diamagnetic cation **33** was reacted with $LiHBEt_3$ to give the *exo*-isomer (*exo*-η^4-C_5Me_5H)Fe^I(dppe)CO (**34**), consistent with the selectivity observed for nucleophilic addition reactions on coordinatively saturated complexes described earlier (**1**–**5**) (Fig. 2). Oxidation of **34** with ferrocenium (Fc$^+$) generated the *exo*-substituted radical cation [(*exo*-η^4-C_5Me_5H)Fe^I(dppe)CO]$^+$ (**35**), whose low computed BDFE (25 kcal mol^{-1}) was also consistent with H_2 release upon warming (Fig. 6).

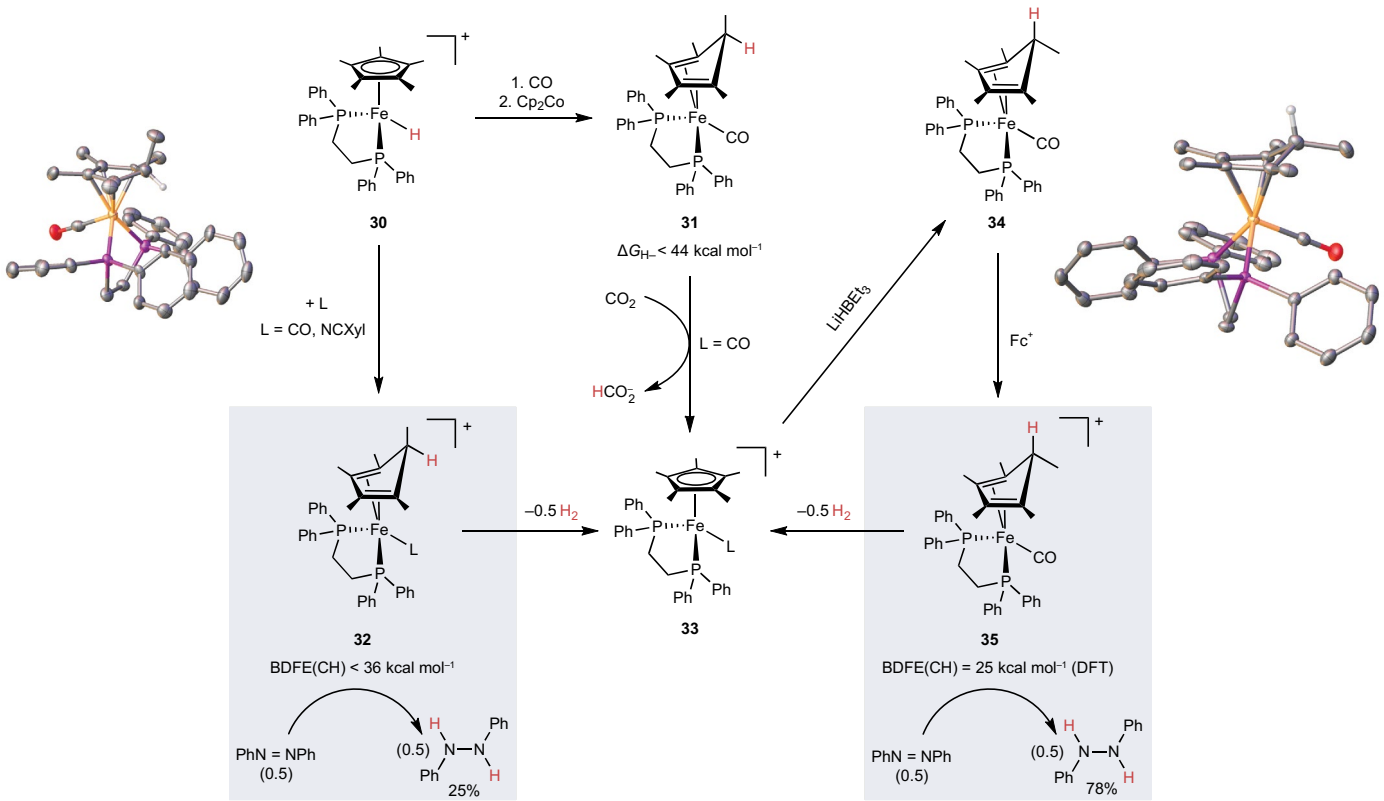

Fig. 6 | Metal-to-ligand proton migration for generating reactive PCET donors. Complex **32** (CCDC 1943148; left) releases 0.5 equivalents of H_2 after CO addition to complex **30**. Compound **31** was found to transfer hydride (H^-) in the presence of CO_2 to generate formate (HCO_2^-). The *exo*-isomer **34** (CCDC 2021151; right) can also be synthesized via hydride transfer from complex **33**, and 1e$^-$ oxidation yields complex **35**. Both **32** and **35** are capable of transferring hydrogen atoms to azobenzene to generate diphenylhydrazine[129]. BDFE, bond dissociation free energy; Cp, cyclopentadienyl; DFT, density functional theory; Fc$^+$, ferrocenium; PCET, proton-coupled electron transfer; Xyl, xylyl.

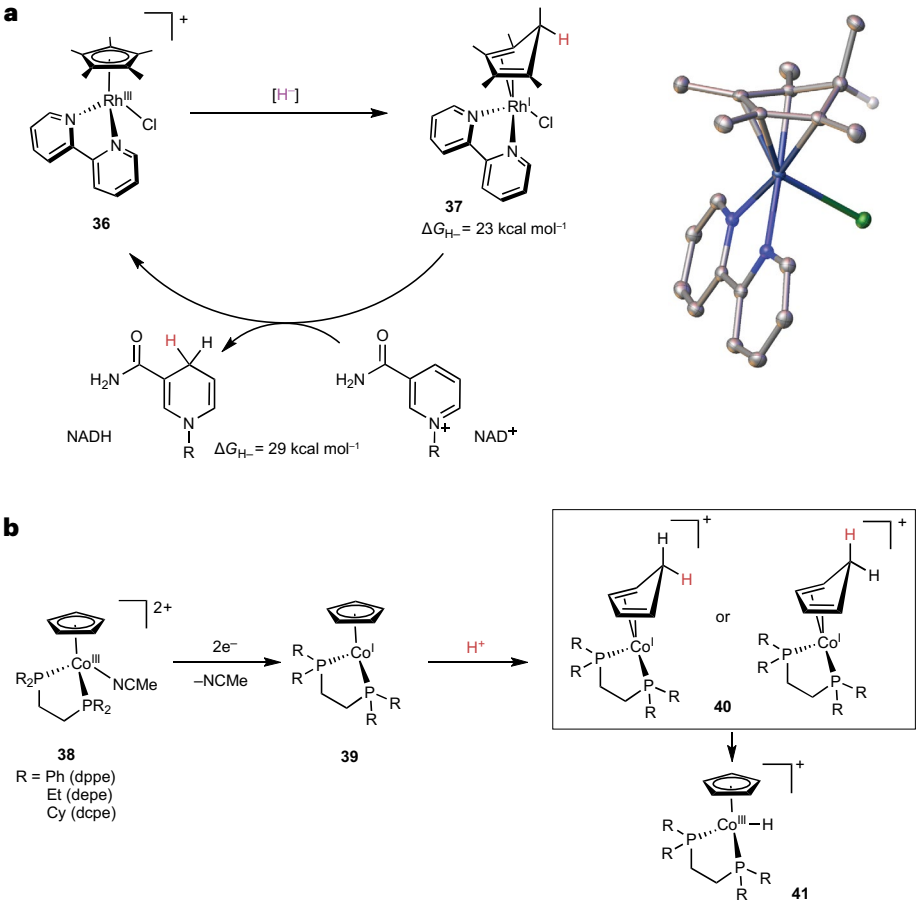

Fig. 7 | Ring-activated Cp*Rh and CpCo complexes for hydride and proton transfer. **a**, Equilibrium measurements determine the thermochemical hydricity (ΔG_H^-) of **37** (CCDC 1447440), which favourably transfers H^- to NAD^+ (ref. 132). **b**, Proposed mechanism involving electrochemical reduction and formation of Co-H complexes via Cp ring protonation of **39** (ref. 134). Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; dppe, 1,2-bis(diphenylphosphino)ethane.

To demonstrate the utility of transferring reactive hydrogen atoms to other substrates, exposure of complexes **32** or **35** to azobenzene at −78 °C generated 1,2-diphenylhydrazine (BDFE(N–H)$_{avg}$ = 65 kcal mol^{-1}) in 25% and 78% yield, respectively (Fig. 6, bottom). The only observable by-products are H_2 and complex **33** and using ring-deuterated Fe analogues (η^4-C_5Me_5D) resulted in the formation of PhDN–NDPh. Although these systems suffer from thermal instability and deleterious H_2 formation, the incredibly weak C–H bonds of metalloradicals **32** and **35** demonstrated that PCET chemistry is possible with group 8 piano-stool complexes.

In contrast to using H^+ and $H^\cdot$ transfer for H_2 production and N_2 reduction described in the previous sections, organic and inorganic sources of hydride (H^-) can also have a key role in catalysis, chemical energy storage and chemical energy conversion[8]. Concurrent with the 2016 discovery that protonation of Cp*Rh^I(bpy) (**15**) generated (*endo*-η^4-C_5Me_5H)Rh^{I}Br(bpy) (**16**), Miller and co-workers[132] reported the preparation and structural elucidation of (*endo*-η^4-C_5Me_5H)Rh^{I}Cl(bpy) (**37**) via two different synthetic pathways starting from [Cp*Rh^{III}Cl(bpy)]$^+$ (**36**) (Fig. 7a). The aqueous hydricity of complex **37** was found to be 23 kcal mol^{-1}, enabling stoichiometric hydride transfer to the enzyme cofactor NAD^+ (ΔG_H^- = 29 kcal mol^{-1}), regenerating complex **36** and producing 1,4-NADH. Thus, direct hydride transfer from an *endo*-η^4-C_5Me_5H moiety is possible on thermochemical grounds in bio-organometallic 1,4-NADH regeneration catalysis. However, recent DFT calculations on hydride transfer from [*exo*-(η^4-C_5Me_5H)Rh^I(bpy)]$^+$ (**17**) (Fig. 3) to NAD^+ suggest that direct H^- transfer from the CpH ring is kinetically disfavoured over H^- transfer from the transition metal hydride complex (**18**)[133].

Stoichiometric proton-coupled electron transfer reactions

In general, transition metal hydride intermediates are frequently observed and/or proposed in chemical energy conversion reactions involving H_2 and CO_2. As demonstrated through piano-stool Fe complexes (Figs. 4,6), PCET processes containing Cp ligands can involve the interconversion of η^4-C_5Me_5H moieties and metal hydride intermediates. To better understand the relationship between the kinetics of Co-H formation and the strength of exogenous acid in [CpCo(dxpe)(NCMe)]$^{2+}$ (**38**; dxpe = dppe, depe, dcpe), Dempsey and co-workers investigated the proton transfer kinetics under an applied cathodic bias via CV[134] (Fig. 7b). The coordinated acetonitrile ligand dissociated after 2e$^-$ reduction and in the presence of acid, the CoH complex **41** is generated. To probe this mechanism further, the 2e$^-$ reduction product Co^{I}Cp(dppe) (**39**) was reacted with weak and strong deuterated acids, and deuterium incorporation is observed at both the Cp ring and CoH positions of complex **41**. Therefore, deuteration of the Cp ring likely occurs through *endo*-protonation or *exo*-protonation to generate complex **40** before formation of complex **41**. Ground-state computational data indicate that initial Cp ligand protonation followed by ligand-to-metal proton migration are exothermic ($\Delta G° \cong -20$ kcal mol^{-1}), strongly disfavouring metal–ligand

tautomerization equilibria. Thus, protonation may be indiscriminate to *exo* versus *endo* attack, which would support the observed CoD/CpD isotope distribution (Fig. 7b). These data also suggest that there is a substantially larger kinetic barrier for direct protonation of the metal centre, contrasting with the kinetically preferred direct metal protonation pathway for Rh complex **18** described earlier[95]. Nonetheless, a seemingly 'simple' PCET reaction with an Earth-abundant metal proceeds through a series of unexpected elementary reaction steps involving Cp ring activation.

Conclusions and future outlook

The Cp ligand is a ubiquitous ancillary ligand in transition metal chemistry. In certain cases, however, the contiguous carbon ring is susceptible to attack by nucleophiles, electrophiles or radicals. Addition of such functional groups can occur in the *exo*-position or *endo*-position relative to the metal centre and breaks the aromaticity of the η^5-Cp ring, generating an η^4-diene (η^4-CpH) ligand coordinated to a transition metal. Although largely considered a laboratory curiosity in the decades following the discovery of ferrocene, developments since 2016 have revealed that the chemically non-innocent character of Cp, Cp* and other Cp derivatives can be essential to the electrocatalytic reduction of H^+ to H_2, catalytic PCET of $H^•$ to N_2 and transfer of $H^•/H^-$ to organic substrates. Carbon–hydrogen bond strength analyses via experiment and/or computation have emerged as indispensable tools to rationalize H^+, $H^•$ and H^- movement with ring-activated complexes, enabling the measurement of C–H acidity, BDFE and hydricity, respectively. Thus, the phenomenon of Cp ring activation is more general than initially thought, and practitioners are encouraged to (re)consider pathways involving ring activation of Cp ligands, especially when proton, hydrogen atom or hydride transfer is invoked to rationalize reaction outcomes.

Ground-state thermochemical measurements have allowed researchers to rationally design Cp/CpH-mediated catalysts with a sufficient driving force for sustainable fuel-forming reactions; however, these results do not provide kinetic information for the making and breaking of ligand-based C–H bonds. It has been recently suggested that slow Cp ring protonation with Cp_2Co is governed by the high ligand reorganization energy associated with a change from sp^2 to sp^3 hybridization upon addition of H^+ (ref. 135). Although this may be true for Cp_2Co, a key challenge moving forward in this field will be to understand the requirements for promoting rapid $H^+/H^•/H^-$ transfer via Cp ring activation by exploring variations in metal centre (precious versus Earth abundant), overall spin state (paired versus unpaired electrons), ancillary ligand environment (metallocene versus piano-stool structure) and Cp ligand substitution pattern (Cp, Cp* and other derivatives). Another key challenge for expanding the vistas of ring-activated CpH complexes will be to avoid H_2 production via homolytic or heterolytic H–H bond formation pathways when the highly reactive $H^•/H^-$ moiety is intended for delivery to other substrates of interest. Overcoming these challenges, among others, will be achieved by surveying kinetic and thermodynamic landscapes for the myriad of other Cp-containing complexes awaiting deeper exploration.

Published online: 31 May 2023

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Acknowledgements

D.E.P. thanks Rutgers University — Newark and the National Science Foundation (2055097) for support. The authors thank M. Bullock and A. Hansen for constructive comments.

Author contributions

D.E.P. developed the conceptual framework for this manuscript. All authors contributed to writing and editing the manuscript. All authors reviewed and/or edited the manuscript before submission.

Competing interests

The authors declare no competing interests.

Additional information

Peer review information *Nature Reviews Chemistry* thanks the anonymous reviewers for their contribution to the peer review of this work.

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