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A low-valent dinuclear ruthenium diazadiene complex catalyzes the oxidation of dihydrogen and reversible hydrogenation of quinones†

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The dinuclear ruthenium complex \([\text{Ru}_2\text{H}(\mu-\text{H})(\text{Me}_2\text{dad})(\text{dcbct})_2]\) contains a 1,4-dimethyl-diazabuta-1,3-diene (Me2dad) as a non-innocent bridging ligand between the metal centers to give a \([\text{Ru}_2(\text{Me}_2\text{dad})]\) core. In addition, each ruthenium is bound to one dibenzo[α,ε]cyclooctatetraene (dcbct) ligand. This Ru dimer converts \(\text{H}_2\) to protons and electrons. It also catalyzes reversibly under mild conditions the selective hydrogenation of vitamins \(K_2\) and \(K_3\) to their corresponding hydroquinone equivalents without affecting the \(\text{C}==\text{C}\) double bonds. Mechanistic studies suggest that the \([\text{Ru}_2(\text{Me}_2\text{dad})]\) moiety, like hydrogenases, reacts with \(\text{H}_2\) and releases electrons and protons stepwise.

Hydrogenase enzymes are the most efficient biological catalysts for the mutual interconversion of hydrogen to protons and electrons, \(\text{H}_2 \rightleftharpoons \text{H}^+ + \text{H}^-\).\(^{1,4}\) A detailed understanding of the mechanisms of these reactions is necessary for the development of efficient artificial catalytic systems for the use of \(\text{H}_2\) as a renewable energy source.\(^3\) Currently, there are three classes of hydrogenases known which either contain a binuclear core, \([\text{Fe},\text{Fe}]\) or \([\text{Fe},\text{Ni}]\), or a single Fe center as active sites.\(^4\) Intensive spectroscopic investigations, including the determination of the structures of several hydrogenases by single-crystal X-ray diffraction methods,\(^6\) allowed extraction of the essential features needed for activity: (i) redox active metal centers; (ii) an electron reservoir; (iii) a cooperating ligand\(^9\)–\(^11\) participating reversibly in the heterolytic cleavage/formation of \(\text{H}_2\); and (iv) a free coordination site for substrate binding (see a simplified sketch of the active \([\text{Fe},\text{Fe}]\) core at the top of Fig. 1).

All hydrogenases contain CO and some CN as archetypical \(\sigma\)-donor/\(\pi\)-acceptor ligands that keep iron in a low spin state and link these enzymes to classical organometallic chemistry. Consequently, the synthesis of hydrogenase model complexes is an intensively investigated topic of organometallic chemistry and some recent relevant examples A–G are shown in Fig. 1. Complexes A and B employ redox non-innocent ligands like bipyridine\(^{12}\) or phosphole\(^{13}\) in order to mimic \(\text{Fe}_4\text{S}_4\) ferredoxines as ubiquitous electron reservoirs in enzymes.\(^{14,15}\) Both complexes, A and B, are active electrocatalysts for the production of \(\text{H}_2\) from acidic media. To date, the closest model to natural \([\text{Fe},\text{Fe}]\) hydrogenases is complex C, which can catalyze the oxidation of \(\text{H}_2\) to \(\text{H}^+\) in the presence of an oxidant and a base.\(^{16}\) The discovery that basic sites in a cheating diphosphane ligand greatly enhance the efficiency of heterolytic \(\text{H}_2\) splitting and the electrochemical oxidation of \(\text{H}_2\)\(^{17,18}\) has led to the development of iron or nickel complexes like D as functional hydrogenase models which achieve truly impressive turnover frequencies (TOFs) of up to 100 000 s\(^{-1}\) for the electrocatalytic production of \(\text{H}_2\)\(^{19,20}\). When tethered to conducting support materials, derivatives of D allow fabrication of membrane-electrode assemblies at which \(\text{H}_2\) is produced at a very low overpotential.\(^{18}\) The structural and functional model E for [Ni,Fe] hydrogenase was reported, which likewise generates \(\text{H}_2\) from mildly acidic solutions with high rates.\(^{24}\) The mononuclear iron model complex F in combination with an apoenzyme was used to prepare an [Fe] hydrogenase model.\(^{25}\) Remarkably, this semiartificial enzyme, like its natural counterpart, is able to reversibly hydrogenate methylene tetrahydromethanopterin. Due to the enhanced stability of Ru hydrides, the replacement of Fe with Ru in artificial enzymes has also been investigated.\(^{26–29}\) Several dinuclear ruthenium complexes were proposed as hydrogenase mimics.\(^{30–34}\) For example, Rauchfuss et al. achieved the photochemical addition of \(\text{H}_2\) across the Ru–Ru bond in complex G and moreover could demonstrate that the terminal hydride ligand in the resulting diruthenium dihydride complex is more easily protonated than the bridging hydride.\(^{30}\)

Recently, diazadiene olefin complexes \([\text{M}(\text{trop}_2\text{dad})]\)\(^{9}\) with low-valent iron or ruthenium centers became accessible
In these complexes, the trop2dad ligand combines the well-established chemical and redox non-innocence of diazadienes (dads) and related ligands with the σ-donor/π-acceptor properties of olefins. Some of these low-valent metal complexes have remarkable properties. For example, [Ru0(trop2dad)] was found to be an efficient catalyst for the clean conversion of aqueous basic methanol or formaldehyde solutions into H2 and carbonate. Herein we report the synthesis of the dinuclear complex [Ru2(Me2dad)(dbcot)2](3) which under 1 bar of H2 is converted to [Ru2H(m-H)(Me2dad)(dbcot)2](3(m-H)H) as a fully artificial but functional [Fe,Fe] hydrogenase model (Fig. 2). This complex catalyzes the oxidation of hydrogen to protons and electrons as well as the reversible and selective hydrogenation of vitamin K3 (VK3) or vitamin K2 (VK2) forming dihydrovitamin K3 (VK3H2) or VK2 hydroquinone (VK2H2) without affecting the C=C double bonds of these vitamins.

Refluxing dbcot with ruthenium(III) chloride trihydrate in ethanol and THF quantitatively produces the brown coordination polymer [RuCl2(dbcot)]1, which reacts further with N,N'-dimethylaminomethane (Me2en) in THF and forms the mononuclear complex [RuCl2(Me2en)(dbcot)]2 in 92% yield (Fig. 2). The deprotonation of 2 by 2.05 eq. of KOtBu produced a tetranuclear complex, [K][Ru4(m-H)(Me2dad)2(dbcot)4][K][32(m-H)]2, in 40% yield as the major species (for detailed spectroscopic data of all isolated complexes reported in this work see the ESI†). Reducing the tetranuclear [K][32(m-H)]2 with 3.4 equivalents of KC8 generates the dianionic dinuclear [K]2[Ru2(Me2dad)(dbcot)2](3) in 85% yield. The 2 : 1 ratio of dbcot to Me2dad and lack of hydride signals in the 1H NMR spectrum suggests the presence of a Ru dimer complex with no hydrides. The low-frequency shift of the Me2dad and olefinic protons in [K][3][3] compared to [K][32(m-H)]2 is consistent with a more electron rich complex (see ESI Table 2†). The oxidation of [K][3][3] with 2 eq. of [Fe][PF6] gives a neutral dinuclear complex Ru2(Me2dad)(dbcot)2(3) in 77% yield. The 1H NMR spectra of 3 show sharp resonances at 0 °C, indicating the structure shown in Fig. 2, in which one Ru center is coordinated in a κ2,N,N fashion, and the other in an η4 fashion by the bridging Me2dad ligand. But broad signals for the aromatic and olefinic protons are observed at room temperature, indicating molecular dynamics phenomena. Various NMR experiments show that two dynamic processes occur: (i) exchange of the κ2,N,N/η4
coordination mode of the Me₂dad ligand between the two Ru centers and (ii) rotation of the dbcot ligands (see ESI Fig. 3 for details). Finally, exposure of 3 to 1 bar of H₂ quickly forms a dinuclear dihydride complex, [Ru₂H₂(Me₂dad)(dbcot)₂] (3(μ-H)H), in quantitative yield. The two Ru–H resonances at −0.74 ppm and −2.74 ppm in THF-d₈ show a coupling of 2JHH = 8.7 Hz, which suggests that both hydrides coordinate to the same Ru atom. The NOESY spectrum allows us to propose the structure of 3(μ-H)H as shown in Fig. 2 with a bridging hydride (δ = −0.74 ppm) and a terminal hydride (δ = −2.74 ppm) (see ESI Fig. 5†).

Single crystals of [K][3(μ-H)H] and [K₂][3] were obtained from a THF/DME/hexane mixture in the presence of 18-crown-6. Crystals of 3(μ-H)H were grown by slow evaporation of a saturated benzene solution. All structures were investigated by X-ray diffraction methods and plots are shown in Fig. 3. [K][3(μ-H)H] is a tetranuclear complex which contains two bimetallic ruthenium moieties bridged by a hydride. The complex [K][3] is best described as an ion pair [K⁺][K[3]−] in which the [K[3]−] anion consists of a sandwich complex with a (dbcot)RuN₂C₂ unit as the central deck to which a Ru(dbcot) fragment binds in an η₁-fashion to one side and a K(18-crown-6) fragment to the other side. The dinuclear dihydride 3(μ-H)H contains a bridging and a terminal hydride located on a plane of symmetry including also the two Ru centers, similar to the complex Ru₂(S₂C₃H₆)(μ-H)(H)(CO)₂(PCy₃)₂ G reported by Rauchfuss et al. Note that in the Ru₂ complex fragments, the κ²N,Nη₁ coordination mode of the diazadiene ligand centers is retained in all complexes. This structural motif is known for related dimeric [Ru₂(CO)₅(R₂dad)] complexes.

The Ru–Ru distances in [K][3(μ-H)H], [K₂][3] and 3(μ-H)H are 2.6947(5), 2.8239(8) and 2.7300(3) Å, respectively, similar to the ones observed in the Ru₄ complex (2.632–2.937 Å), suggesting the presence of Ru–Ru bonds. The longer Ru–Ru distance in [K₂][3] (2.8239(8) Å) reflects the highly reduced state of this species. Also, the olefinic bonds in [K][3] (average of 1.450(3) Å) are longer than the ones in [K][3(μ-H)H] (average of 1.433(3) Å) and 3(μ-H)H (average of 1.424(3) Å), indicating strong back donation from the Ru–Ru unit into the π*-orbitals of the coordinated C=Cdbcot bonds. This effect increases with increasing anionic charge of the complex (in free dbcot, the average olefin bond length is 1.321 Å). Note that the C=Cdbcot bond lengths coordinated to Ru2 are longer than those bound to Ru1, indicating a higher electron density at Ru2. Of special interest are the C–N and C–C bond lengths of the diazadiene ligand because they reflect the oxidation state of the ligand and consequently also of the metal. The neutral diimine form, RN=CH=CH=NR, binds to a low-valent metal center, M⁰, and is characterized by short C–N bonds (≈ 1.29 Å) and a long C–C bond (≈ 1.46 Å). With increasing shift of electron density from the metal center to the ligand, the C–N bonds are lengthened while the C–C bond shortens: in the diazadiene radical anion [RN=CH=CH=NR]− coordinated to M⁰⁺, C–N = 1.33 Å and C–C = 1.39 Å; in the diazadiene bisamido olefin form [RN=CH=CH=NR]− coordinated to M⁰⁺⁺, C–N = 1.38 Å and C–C = 1.35 Å. The C–N and C–C bonds of the Me₂dad ligand in [K][3(μ-H)H], [K₂][3] and 3(μ-H)H are approx. 1.38 Å and 1.39 Å, respectively, indicating a reduced form of the ligand. Consequently, the oxidation states at the Ru centers vary between 0 and +1. These data illustrate the redox non-innocent behavior of the Me₂dad ligand in these complexes. The bridging coordination modes of 2e⁻ reduced dad and the closely related pyridine-diimine ligands have been reported before.

The ability to split H₂ into protons and electrons like that of hydrogenases was investigated using the “Rauchfuss test”. In the presence of ten equivalents of PPh₃ and [Fe][PF₆]₃, 3(μ-H)H catalytically splits hydrogen into protons and electrons under 1 bar H₂ at 40 ºC, forming protonated triphenylphosphine [Ph₃P][PF₆] and Cp₂Fe in THF within 1.5 hours (Fig. 4a). More compellingly, 3(μ-H)H is able to catalyze reversibly the hydrogenation of the biologically relevant vitamins VK₃ and VK₂ (Fig. 4b). Hydrogenation of VK₃ was investigated under 1 bar or 15 bar H₂ pressure, at 40 ºC or 70 ºC (ESI Table 3, entries 1–37). With 1 bar H₂, a TON of 252 was achieved. Remarkably, 3(μ-H)H remained active even after 2 months. At 70 ºC and 15 bar H₂, 0.13 mol% 3(μ-H)H converts 65% of VK₃ to VK₃H₂ to give a TON of 220. Under 15 bar H₂, the TOF values at 40 ºC and
70 °C are 2.2 and 10 h⁻¹, respectively. VK₂ is a more delicate substrate because it tautomterizes. At room temperature, the hydrogenation of VK₂ is more selectively achieved (ESI Table 3, entry 4†). In addition, the C=C double bonds of VK₂ remain intact and the hydrogenation occurs selectively at the quinone moiety of the substrate. These catalytic reactions can be reversed. The dehydrogenation of VK₃H₂ and VK₂H₂ was tested at 40 °C under Ar (ESI Table 3, entries 5–7†). The TON values of VK₃H₂ and VK₂H₂ are 70 (in 48 h) and 24 (in 40 h), respectively. The TOFs for hydrogenation and dehydrogenation reactions are comparable. A kinetic isotope effect of k_d/k_0 = 1.9(2) was measured experimentally for the hydrogenation of VK₃ by measuring k_d and k_0 in separate experiments (ESI, part 7.1†).

Stoichiometric reactions were performed and monitored by NMR spectroscopy in order to gain some insights into possible reaction mechanisms. 3[µ-H]H can be rapidly and quantitatively oxidized at room temperature by ferrocenium salts, [Fe][X] (X = PF₆ or OTf), to give the complex [Ru₂(µ-H)(Me₂dad)(dbcot)₂][PF₆]⁻ or [Ru₂(µ-H)(OTf)(Me₂dad)(dbcot)₂] with a bridging hydride (Fig. 5a) in good yield. The complex [Ru₂(µ-H)(Me₂dad)(dbcot)₂][PF₆] [3[µ-H]][PF₆] (Ru-H, δ = −10.34 ppm) was characterized by NMR in THF-d₈, while [Ru₂(µ-H)(OTf)(Me₂dad)(dbcot)₂] [3[µ-H][OTf]] was isolated in crystalline form. Characterization of this complex by single crystal X-ray diffraction reveals the presence of a structure closely related to 3[µ-H]H with a trflate anion bound to Ru₁ instead of the terminal hydride (see Fig. 2 and ESI Fig. 2†). In THF solution, partial dissociation occurs to give [3[µ-H][OTf]] (Ru-H, δ = −10.34 ppm) and [3[µ-H][OTf]] (Ru-H, δ = −10.18 ppm) in a 1:9 ratio. These results indicate that the radical cation salt [3[µ-H][H]⁺[X]⁻ as a primary oxidation product rapidly loses hydrogen to give [3[µ-H]][X] (Fig. 6). The cyclic voltammogram of 3[µ-H]H shows only one irreversible oxidation peak in THF (ESI Fig. 14†). Our attempts to characterize [3[µ-H][H]⁺[X]⁻ by EPR spectroscopy failed so far and oxidation of 3[µ-H]H with [Fe][OTf] or reduction of [3[µ-H][OTf]] with Cp₂Co at 20 K in Me₂THF glass afforded only very weak EPR signals characteristic of (a mixture of) metal-centered radical species with g-values in the range of 2.6–1.8 and 2.5–1.7, respectively, which are unlikely to stem from any of the paramagnetic on-cycle catalytic intermediates (such as [3[µ-H][H]⁺ or [3[µ-H]]); vide infra). Note that
complex [3(μ-H)(OTf)] is catalytically active in both reactions (a) and (b) shown in Fig. 4.

In the next experiment, 3(μ-H)H was oxidized with one equivalent of [Fc][PF6] in the presence of one equivalent of PPh₃. Exclusively, [Ru₂(μ-H)(Me₂dad)(dbcot)](PPh₃)[PF₆], [3(μ-H)(PPh₃)][PF₆], ³¹P NMR: δ = 32.8 ppm, was obtained and no phosphonium salt, [Ph₃PH][PF₆], was formed (Fig. 5b and ESI, Fig. 6†). The compound [3(μ-H)(PPh₃)]⁺ was also obtained from the reaction of [3(μ-H)(OTf)] and PPh₃. Furthermore, the PPh₃ ligand in [3(μ-H)(PPh₃)]⁺ can be replaced by a stronger ligand such as P(OEt)₃ (ESI, Fig. 7). When 3(μ-H)H was exposed to 1 bar of D₂, either at room temperature or under catalytic conditions, the complex [Ru₂(μ-H)(Me₂dad)(dbcot)] was observed (ESI, Fig. 8 and 9†), along with deuterium incorporation into the substrate, VK₃D₂, when present (ESI, Fig. 9†). In combination, these experiments show that (i) only the terminal hydride in 3(μ-H)H participates in the reactions, and that (ii) the ligand at the terminal site of Ru1 can be exchanged. When experiments were performed under 1 bar of H₂ in the absence of an oxidant, no reaction took place and 3(μ-H)H remained intact. When 3(μ-H)H was reacted in the presence of a large excess of PPh₃ (10 equivalents) but only 1 equivalent of [Fc][PF₆] under 1 bar of H₂, the cationic PPh₃ complex [3(μ-H)(PPh₃)]⁺ was observed but no [Ph₃PH]⁺ (Fig. 5b and ESI, Fig. 10†). However, the formation of [PPh₃H⁺] from a mixture of [3(μ-H)(PPh₃)]⁺, PPh₃, and H₂ was observed in the presence of 1 equiv. of Fc⁺ (Fig. 5c and ESI, Fig. 11†). These experiments suggest that two equivalents of ferrocene are needed to observe turnover with 3(μ-H)H as the catalyst, and that the second equivalent is needed to rapidly convert 3(μ-H)H into [3(μ-H)]⁺ in order to prevent the reaction between the [Ph₃PH]⁺ and the hydric complex 3(μ-H)H, according to [Ph₃PH]⁺ + 3(μ-H)H → [3(μ-H)]⁺ + H₂, which was experimentally found to be exergonic (see ESI Fig. 12†).

Taken together, these results support the proposed catalytic cycle A shown in Fig. 6. 3(μ-H)H is first oxidized with loss of one electron to give the radical cation [3(μ-H)H]⁺, which rapidly loses half an equivalent of H₂ to yield [3(μ-H)]⁺. This complex with a labile coordination site at Ru1 is intercepted by PPh₃ to give [3(μ-H)(PPh₃)]⁺ which is the resting state within the catalytic cycle. The complex [3(μ-H)(PPh₃)]⁺ is in equilibrium with [3(μ-H)]⁺ (likely as a solvated adduct [3(μ-H)(solv)]⁻ and present at low concentration), which may coordinate with H₂ to give [3(μ-H)(H₂)]⁻. Deprotonation of [3(μ-H)(H₂)]⁻ by PPh₃ (vide infra) gives the phosphonium salt [Ph₃PH]⁺ and regenerates 3(μ-H)H. A second equivalent of oxidant is needed to turn over the catalytic cycle to give back [3(μ-H)(PPh₃)]⁺ as the resting state via the reaction sequence given above.

A slightly different reaction path was observed for the reaction of 3(μ-H)H with quinones. The reaction between 3(μ-H)H and VK₃ in the absence of H₂ formed a thick suspension, which prevents further characterization by NMR spectroscopy. However, upon addition of a large excess of NaOTf, a signal attributed to complex [3(μ-H)(OTf)] was detected by ¹H NMR spectroscopy. No reaction between NaOTf and 3(μ-H)H was observed in the absence of VK₃. These data suggest that the terminal hydride of 3(μ-H)H was transferred to VK₃, which then formed a protonated semiquinone oxygen bound species [3(μ-H)VK₃H] (see the proposed structure based on DFT calculations in Fig. 8), and that VK₃H⁺ is labile enough to be partially displaced by OTf⁻. When followed by EPR spectroscopy at room temperature, the reaction between 3(μ-H)H and VK₃ led to the formation of one organic radical species, which is detected by EPR spectroscopy at room temperature when 3(μ-H)H is reacted with VK₃. The signal disappears with time resulting in the formation of the EPR silent and sparsely soluble [3(μ-H)(VK₃H)] as the only product. With the symmetrical benzoquinone 2,5-di-tert-butyl-p-benzoquinone as the model substrate, in situ monitoring of the reaction with 3(μ-H)H afforded immediately the paramagnetic HSQ⁻ (protonated semi-quinine) species (doublet, giso = 2.005, Aiso = 10.0 Hz; see ESI part 7.4†).

These observations support the catalytic cycle B shown in red in Fig. 6, in which the neutral semiquinone radical VKn⁻ and the neutral organometallic Ru₂ radical [3(μ-H)]⁺ were formed. It
Fig. 6 Proposed mechanisms of H2 splitting by 3[μ-H]H using PPh3 and [Fc][PF6] as the proton and electron acceptors (Cycle A, left), and hydrogenation of vitamin Kₙ (n = 2 or 3) to their hydroquinone analogs by 3[μ-H]H (Cycle B, right).

Fig. 7 DFT calculation for the activation of H2 from [3[μ-H]]⁺ in the presence of PPh3. The transition state for the deprotonation of the H2 complex by PPh3 was not found; however, the direct reaction path from [3[μ-H][H2]]⁺ (−3.5 kcal mol⁻¹) to 3[μ-H]H + [Ph3PH]⁺ (−11.3 kcal mol⁻¹) cannot be excluded.
is still unclear if these radical species are formed via direct hydrogen transfer from $3\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\mu\m
analogue of archetypical cyclopentadienyl ligands, a structural feature known for dinuclear Ru2(dad) complexes. However, the Ru3(dad) complexes reported in the literature carry CO as additional ligands and are likely too unstable to serve as efficient catalysts. In this study, the very rigid and concave shaped dibenzocyclooctatriene, dbcot, was used as a neutral four electron \( \pi \)-donor and \( \pi^* \)-acceptor ligand, which stabilizes all complexes. A Ru–Ru interaction of about 2.7 Å is observed in all complexes, structurally characterized by single crystal X-ray diffraction methods, which is remarkably invariant. Furthermore, the C=C→C=C=O bound units to the Ru centers do not differ much in length (by 0.05 Å between [K3][3] (longest) and [3(m-H)] [PF6] (shortest)), indicating that the electron densities at the Ru centers in the various complexes are rather similar. Small structural and electronic variances at the metal centers are also a feature of [Fe,Fe] and [Ni,Fe] hydrogenases.\(^{1,2,4,51-58}\) The complex 3[3](m-H)\( \pi \) is a catalyst that splits \( \text{H}_2 \) into protons and electrons in the presence of \( \text{PPH}_3 \) and [FC][PF6], forming \( \text{PH}_3 \text{PH} \) [PF6] and \( \text{Cp}_2 \text{Fe} \) (Rauchfuss test for hydrogenase activity), and reversibly and selectively hydrogenates vitamins VK3 or VK2, which are natural substrates for the enzyme hydrogen:quinone oxidoreductase. Spectroscopic data strongly suggest that like in hydrogenases, multiple coupled electron and proton transfer steps might be involved in these reactions. Clearly, the observed activities and efficiencies must be significantly improved. But this investigation demonstrates that redox and chemically non-innocent ligands may be key components and their variation may allow further improvements and uncovering of new bearings in synthesizing small molecular hydrogenase mimics.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

1. M. Senger, K. Laun, F. Wittkamp, J. Duan, M. Haumann, T. Happe, M. Winkler, U.-P. Apfel and S. T. Stripp, *Angew. Chem., Int. Ed.*, 2017, 56, 16503–16506.
2. M. Winkler, M. Senger, J. Duan, J. Esselborn, F. Wittkamp, E. Hofmann, U.-P. Apfel, S. T. Stripp and T. Happe, *Nat. Commun.*, 2017, 8, 16115.
3. W. Lubitz, H. Ogata, O. Rudiger and E. Reijerse, *Chem. Rev.*, 2014, 114, 4081–4148.
4. C. Tard and C. J. Pickett, *Chem. Rev.*, 2009, 109, 2245–2274.
5. R. Cammack, M. Frey and R. Robson, *Hydrogen as a fuel: Learning from nature*, CRC Press, London and New York, 2002.
6. A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *Nature*, 1995, 373, 580–587.
7. J. W. Peters, W. N. Lanzilotta, B. J. Lemon and L. C. Seeffeldt, *Science*, 1998, 282, 1853–1858.
8. S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer and U. Ermel, *Science*, 2008, 321, 572–575.
9. J. C. Fontecilla-Camps, A. Volbeda, C. Cavazza and Y. Nicolet, *Chem. Rev.*, 2007, 107, 4273–4303.
10. O. R. Luca and R. H. Crabtree, *Chem. Soc. Rev.*, 2013, 42, 1440–1459.
11. M. Trincado and H. Grützmacher, *Cooperative Catalysis: Designing Efficient Catalysts for Synthesis*, Wiley-VCH Verlag GmbH & Co., Weinheim, 2015, ch. 3, pp. 67–105.
12. S. Roy, T. L. Groy and A. K. Jones, *Dalton Trans.*, 2013, 42, 3843–3853.
13. R. Becker, S. Amirjalayer, P. Li, S. Woutersen and J. N. H. Reck, *Sci. Adv.*, 2016, 2, e1501014.
14. R. Lill, *Nature*, 2009, 460, 831–838.
15. S. C. Lee, W. Lo and R. H. Holm, *Chem. Rev.*, 2014, 114, 3579–3600.
16. J. M. Camara and T. B. Rauchfuss, *Nat. Chem.*, 2012, 4, 26–30.
17. C. J. Curtis, A. Miedaner, R. Ciancanelli, W. W. Ellis, B. C. Noll, M. Rakowski DuBois and D. L. DuBois, *Inorg. Chem.*, 2003, 42, 216–227.
18. A. Le Goff, V. Arttero, B. Jousselme, P. D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacín and M. Fontecave, *Science*, 2009, 326, 1384–1387.
19. T. B. Liu, D. L. DuBois and R. M. Bullock, *Nat. Chem.*, 2013, 5, 228–233.
20. M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois and D. L. DuBois, *Science*, 2011, 333, 863–866.
21. S. E. Smith, J. Y. Yang, D. L. DuBois and R. M. Bullock, *Angew. Chem., Int. Ed.*, 2012, 51, 3152–3155.
22. A. Dutta, D. L. DuBois, J. A. S. Roberts and W. J. Shaw, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, 111, 16286–16291.
23. N. Priyadarshani, A. Dutta, B. Ginovska, G. W. Buchko, M. O’Hagan, S. Raugei and W. J. Shaw, *ACS Catal.*, 2016, 6, 6037–6049.
24. D. Brazzolotto, M. Gennari, N. Querbyaia, T. R. Simmons, J. Pecaut, S. Demeshko, F. Meyer, M. Orii, V. Arttero and C. Duboc, *Nat. Chem.*, 2016, 8, 1054–1060.
25. S. Shima, D. F. Chen, T. Xu, M. D. Wodrich, T. Fuji shiro, K. M. Schultz, J. Kahnt, K. Ataka and X. L. Hu, *Nat. Chem.*, 2015, 7, 995–1002.
26. T. Liu, M. R. DuBois, D. L. DuBois and R. M. Bullock, *Energy Environ. Sci.*, 2014, 7, 3630–3639.
27. G. Gezer, S. Verbeek, M. A. Siegler and E. Bouwman, *Dalton Trans.*, 2017, 46, 13590–13596.
28. T. Matsumoto, Y. Nakaya, N. Itakura and K. Tatsumi, *J. Am. Chem. Soc.*, 2008, 130, 2458–2459.
29. G. M. Chambers, R. Angamuthu, D. L. Gray and T. B. Rauchfuss, *Organometallics*, 2013, 32, 6324–6329.
30 A. K. Justice, R. C. Linck, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 2004, **126**, 13214–13215.
31 C. Sommer, C. P. Richers, W. Lubitz, T. B. Rauchfuss and E. J. Reijsje, *Angew. Chem., Int. Ed.*, 2018, **57**, 5429–5432.
32 M. Yuki, K. Sakata, Y. Hiroa, N. Nonoyama, K. Nakajima and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2015, **137**, 4173–4182.
33 C. Lichtenberg, L. Viciu, M. Vogt, R. E. Rodriguez-Lugo, M. Adelhardt, J. Sutter, M. M. Khusniyarov, K. Meyer, B. de Bruin, E. Bill and H. Grützmacher, *Chem. Commun.*, 2015, **51**, 13890–13893.
34 R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones and H. Grützmacher, *Nat. Chem.*, 2013, **5**, 342–347.
35 F. Richard Keene, *Coord. Chem. Rev.*, 1999, **187**, 121–149.
36 K. G. Caulton, *Eur. J. Inorg. Chem.*, 2012, 435–443.
37 D. L. J. Broere, R. Plessius and J. I. van der Vlugt, *Chem. Soc. Rev.*, 2015, **44**, 6886–6915.
38 M. Trincado, V. Sinha, R. E. Rodriguez-Lugo, B. Pribanic, B. de Bruin and H. Grützmacher, *Nat. Commun.*, 2017, **8**, 14990.
39 F. Wittkamp, M. Senger, S. T. Stripp and U. P. Apfel, *Chem. Commun.*, 2018, **54**, 5934–5942.
40 D. Schott, C. J. Sleigh, J. P. Lowe, S. B. Duckett, R. J. Mawby and M. G. Partridge, *Inorg. Chem.*, 2002, **41**, 2960–2970.
41 D. A. Vicic, T. J. Anderson, J. A. Cowan and A. J. Schultz, *J. Am. Chem. Soc.*, 2004, **126**, 8132–8133.
42 K. Vrieze, *J. Organomet. Chem.*, 1986, **300**, 307–326.
43 E. A. Seddon and K. R. Seddon, *The chemistry of ruthenium*, Elsevier, 1984.
44 A. Mederos, S. Domínguez, R. Hernández-Molina, J. n. Sanchiz and F. Brito, *Coord. Chem. Rev.*, 1999, **193–195**, 913–939.
45 C. Mealli, A. Ienco, A. D. Phillips and A. Galindo, *Eur. J. Inorg. Chem.*, 2007, **2007**, 2556–2568.
46 K. P. Butin, E. K. Beloglazkina and N. V. Zyk, *Russ. Chem. Rev.*, 2005, **74**, 531–553.
47 C. Tejel, M. A. Ciriano, M. P. del Rio, F. J. van den Bruele, D. G. H. Hetterscheid, N. Tsichlis i Spithas and B. de Bruin, *J. Am. Chem. Soc.*, 2008, **130**, 5844–5845.
48 G. V. Koten and K. Vrieze, in *Advances in Organometallic Chemistry*, ed. F. G. A. Stone and R. West, Academic Press, 1982, vol. 21, pp. 151–239.
49 S. Jiang, T. Y. Zhang, X. Zhang, G. H. Zhang and B. Li, *Dalton Trans.*, 2015, **44**, 16708–16712.
50 T. Matsumoto, H.-C. Chang, M. Wakizaka, S. Ueno, A. Kobayashi, A. Nakayama, T. Taketsugu and M. Kato, *J. Am. Chem. Soc.*, 2013, **135**, 8646–8654.
51 A. M. Swartz, M. Barra and D. Kuntz, *J. Org. Chem.*, 2004, **69**, 3198–3201.
52 Y. Higuchi, H. Ogata, K. Miki, N. Yasuoka and T. Yagi, *Structure*, 1999, 7, 549–556.
53 T. Krämer, M. Kampa, W. Lubitz, M. van Gastel and F. Neese, *ChemBioChem*, 2013, **14**, 1898–1905.
54 M.-E. Pandelia, H. Ogata and W. Lubitz, *ChemPhysChem*, 2010, **11**, 1127–1140.
55 P. Amara, A. Volbeda, J. C. Fontecilla-Camps and M. J. Field, *J. Am. Chem. Soc.*, 1999, **121**, 4468–4477.
56 Y. Nicolet, A. L. de Lacey, X. Vernède, V. M. Fernandez, E. C. Hatchikian and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 2001, **123**, 1596–1601.
57 S. Stripp, O. Sanganas, T. Happe and M. Haumann, *Biochemistry*, 2009, **48**, 5042–5049.
58 P. E. M. Siegbahn, J. W. Tye and M. B. Hall, *Chem. Rev.*, 2007, **107**, 4414–4435.