ROYAL SOCIETY OF CHEMISTRY

ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2021, 57, 6316

Received 16th April 2021,
Accepted 26th May 2021

DOI: 10.1039/d1cc02040d

rsc.li/chemcomm

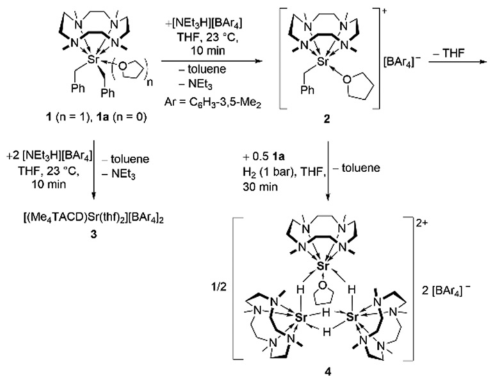
Cationic strontium hydride complexes supported by an NNNN-type macrocycle†

Thomas Höllerhage,[a] Ambre Carpentier,[b] Thomas P. Spaniol,[a] Laurent Maron,[b] Ulli Englert[a] and Jun Okuda*[a]

A trinuclear strontium hydride $[(Me_4TACD)_3Sr_3(\mu_2\text{-}H)_4(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ (Me_4TACD = 1,4,7,10-tetramethyltetraazacyclododecane) and a mixed calcium strontium hydride $[(Me_4TACD)_2CaSr(\mu\text{-}H)_2(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ were isolated by hydrogenolysis of cationic benzyl precursors. A solution of $[(Me_4TACD)_2CaSr(\mu\text{-}H)_2(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ shows hydride ligand exchange between calcium and strontium centers and higher affinity of the hydride ligand toward calcium.

Currently there is considerable interest in utilizing inexpensive and relatively abundant heavy alkaline earth metal complexes as homogeneous catalysts for hydrogenation and hydrofunctionalization of unsaturated substrates. Hydride species of the type $[(L)_l(X)_xMH]^{(1-x)+}$ (L = two-electron ligand, l = 0–4; X = one-electron ligand, x = 0, 1) are proposed as catalytically active species in these catalytic cycles.[1–4] Recently, Harder *et al.* proposed alkaline earth metal hydride aggregates to be catalytically active in the hydrogenation for alkenes and imines by alkaline earth metal amides.[5–8] While in general, activity and substrate scope appear to increase in the series Ca < Sr < Ba, the substantial increase in ionic radius down the group results in a coordination sphere more difficult to control, more labile ligands, and ultimately in the formation of larger clusters and aggregates.[9–11] Conclusively, the application of sterically demanding ancillary ligands is often required to stabilize molecular heavy alkaline earth metal hydrides.[12–15] Few strontium hydride complexes have been isolated since the first example in 2017 and compared to the lighter homologs, isolated strontium hydride complexes remain still rare.[10,11,13,15–17] In the context of understanding the chemical properties of homologous elements within group 2 of the periodic table, a comparison between calcium and strontium appears relevant. Cationic calcium hydride complexes of $[CaH]^+$ supported by the macrocyclic ligand Me_4TACD have previously been reported as catalysts for olefin hydrogenation and hydrosilylation.[18,19] Here, we describe the synthesis, structural characterization and reactivity of strontium hydrides derived from $[SrH]^+$ and elaborate on the difference to the lighter homolog $[CaH]^+$.

Cationic calcium hydride complexes with varying ligand sizes from the nine-membered Me_3TACN (Me_3TACN = 1,4,7-trimethyltriazacyclononane) to fifteen-membered Me_5PACP (Me_5PACP = 1,4,7,10,13-pentaazacyclopentadecane) have been isolated starting from the corresponding cationic benzyl precursors.[18–21] Following this established method for calcium, we investigated strontium benzyl complexes as a precursor for cationic strontium hydride complexes. Addition of Me_4TACD to a concentrated solution of $[Sr(CH_2Ph)_2(thf)]$[22] in THF led to the precipitation of light orange dibenzyl complex $[(Me_4TACD)Sr(CH_2Ph)_2(thf)]$ (**1**) (Scheme 1). In contrast to the six-coordinate calcium homolog, the crystal structure of **1** revealed a seven-coordinate metal center with two η^1-coordinated benzyl ligands and an additional THF ligand.[18] **1** is poorly soluble in common organic solvents which precluded NMR spectroscopic analysis.



Scheme 1 Synthesis of a molecular strontium hydride stabilized by Me_4TACD.

---

[a] *Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany. E-mail: jun.okuda@ac.rwth-aachen.de*

[b] *CNRS, INSA, UPS, UMR 5215, LPCNO, Université de Toulouse 135 avenue de Rangueil, 31077 Toulouse, France. E-mail: laurent.maron@irsamc.ups-tlse.fr*

† Electronic supplementary information (ESI) available: General experimental procedures, analytical/spectroscopic data, crystallographic and calculation data. CCDC 2078067–2078070. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1cc02040d

Hydrogenolysis of the dibenzyl with H_2 (1 bar) in THF-d_8 gave a reaction mixture of which the ^1H NMR spectrum showed in addition to signals for toluene and free Me_4TACD ligand, a broad resonance at δ 5.67 ppm tentatively assigned to oligomeric $[SrH_2]_n$ in the expected ratio. The absence of proto-THF in the mixture indicates that the THF ligand in **1** is labile and can be removed *in vacuo* to give $[(Me_4TACD)Sr(CH_2Ph)_2]$ (**1a**). **1a** reacts with one equivalent of the Brønsted acid $[NEt_3H][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ in THF to give the cationic benzyl complex $[(Me_4TACD)Sr(CH_2Ph)(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ (**2**), which was isolated by precipitation with *n*-pentane as light orange powder in good yields. The ^1H NMR of **2** showed a coordinated THF molecule that could not be removed *in vacuo* and a very broad resonance for the methylene groups of the Me_4TACD ligand, indicating conformational flexibility of Me_4TACD in solution. The resonances of the benzyl ligand appear in the same region and ratio as those of the calcium homolog $[(Me_4TACD)Ca(CH_2Ph)(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ (**2-Ca**), indicating a similar η^1-coordination of the benzyl ligand in solution. In contrast to **2-Ca**, which reacted with the methyl group of the borate anion, **2** appears to be inert towards the borate anion and no zwitterionic borate species was observed by NMR.[18] Attempts to grow single crystals of **2** from THF/*n*-pentane were unsuccessful but when the protonolysis of **1a** was carried out in the more weakly coordinating solvent THP, single crystals of $[(Me_4TACD)Sr(CH_2Ph)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ (**2a**) without any coordinated solvent molecule grew from the reaction mixture. X-Ray diffraction of **2a** shows the atomic connectivity within the molecule and the coordinated benzyl ligand (see ESI†). The calcium homolog and its isostructural cationic ytterbium analog both show η^6-coordination of the benzyl ligand.[23,24] The use of THP allowed the synthesis and structural analysis of **2a** but proved disadvantageous for the isolation of the cationic strontium benzyl precursor on a larger scale due to low yield and lower purity. Thus complex **2** was used for further reactivity studies. The protonolysis of **1** with two equivalents of $[NEt_3H][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ gave the dicationic complex $[(Me_4TACD)Sr(thf)_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ (**3**) that was used for further reactivity studies (see below). The calcium homolog $[(Me_4TACD)Ca(thf)_2][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ (**3-Ca**) was prepared analogously from $[(Me_4TACD)Ca(CH_2Ph)_2]$ and $[NEt_3H][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$.

Two distinct structural motifs have been found for cationic hydride complexes of calcium with Me_4TACD as a stabilizing ligand. The isolated hydride structures comprise of two calcium centers bridged by either two or three hydride ligands. The dihydride can be seen as the dimer of cationic $[(Me_4TACD)CaH]^+$ and has been crystallized with and without an additional THF ligand coordinated to one of the calcium centers.[18,19] The trihydride has been isolated from both triphenylsilyl and benzyl precursors and can be interpreted as the adduct of neutral $[(Me_4TACD)CaH_2]$ and $[(Me_4TACD)CaH]^+$.[18,25] When the preparation of the analogous strontium hydride complexes $[(Me_4TACD)_2Sr_2(\mu\text{-}H)_2]^{2+}$ by hydrogenolysis of **2** and $[(Me_4TACD)_2Sr_2(\mu\text{-}H)_3]^+$ by hydrogenolysis of **2** in the presence of **1a** was attempted, the ^1H NMR spectrum of the reaction mixture showed one major hydride peak at δ 5.98 ppm along with several minor hydride peaks in the expected hydride region from δ 4.48 to 6.64 ppm.[10,13,15–17] When **1a** was hydrogenated in the presence of two equivalents of **2** a more selective reaction was observed and hydride complex $[(Me_4TACD)_3Sr_3(thf)(\mu_2\text{-}H)_4][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ (**4**) isolated in good yields as colorless crystals by crystallization from THF/*n*-pentane at −40 °C. The crystal structure of **4** revealed two nearly identical crystallographically independent trinuclear clusters containing a $[Sr_3(thf)(\mu_2\text{-}H)_4]^{2+}$ core with three seven-coordinate strontium centers bridged by four hydride ligands (Fig. 1). The Sr–H distances range from 2.427(17) Å to 2.458(18) Å and compare well to Sr–H distances reported in the literature.[10,11,13,15–17] **4** shows two long Sr···Sr distances (Sr1···Sr2: 4.4248(6) Å, Sr1···Sr3: 4.5701(6) Å) and a shorter Sr2···Sr3 distance (3.9555(6) Å). The Sr···Sr distances are longer than those reported in the trinuclear strontium hydride $[(Me_3TACD)_3Sr(\mu_3\text{-}H)_2][SiPh_3]$ ($(Me_3TACD)H$ = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) (3.5689(6) Å to 3.5790(6) Å). **4** can be regarded as the adduct of two neutral $[(Me_4TACD)SrH_2]$ fragments stabilized by dicationic $[(Me_4TACD)Sr(thf)]^{2+}$. It resembles the cationic zinc hydride cluster $[(IMes)_3Zn_3(\mu\text{-}H)_4(thf)][BPh_4]_2$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) that comprises of a similar trinuclear core with three tetrahedrally coordinated zinc centers bridged by four hydride ligands.[26] With the exception of polymeric $[(Me_4TACD)Cs(SiPh_3)]_\infty$, Me_4TACD commonly forms mono- and dinuclear complexes.[27]

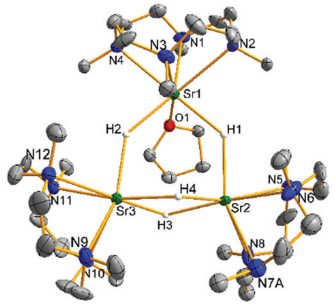


Fig. 1 Molecular structure of the cationic trinuclear core in **4** in solid state. Displacement parameters are set at the 30% probability level; hydrogen atoms except of the hydride ligands are omitted for clarity.

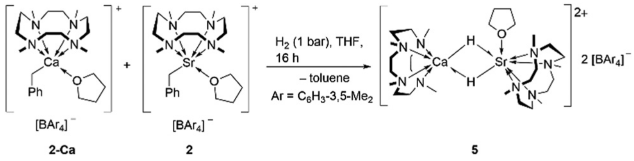
In order to obtain insights into the bonding situation in complex **4**, DFT calculations (B3PW91) including dispersion corrections were carried out. The optimized geometry is in good agreement with the experimental one with the Sr–H distances in the 2.37–2.47 Å range (see ESI†). At the Natural Bonding Orbital (NBO) level, four Sr–H bonds were found which are strongly polarized toward H (85–87%). However, at the second-order donor acceptor level, these four Sr–H bonds are found to be strongly delocalized toward the adjacent Sr centers, in line with the formation of 3 center–2 electron (3c–2e) bonds. This is in line with the fact that the Sr–H Wiberg Bond Indexes (WBI) are all equivalent (0.3). Scrutinizing the Molecular Orbital (MO), it appears that the HOMO to HOMO-3 describe the Sr–H interactions (see ESI†).

The ^1H NMR spectrum of isolated 4 in THF-d_8 shows the hydride resonance at δ 5.98 ppm. The two different hydride environments observed in the solid state are indistinguishable by ^1H NMR spectroscopy even at −60 °C, probably due to fast exchange on the NMR time scale. In the ligand region a sharp singlet for the methyl groups of Me_4TACD corresponding to 24 protons as well as broad resonance corresponding to 12 methyl protons are observed in agreement with two different strontium environments in a 2 : 1 ratio. The methylene protons gave a very broad resonance, indicating a conformational fluxionality of the macrocycle. **4** reacts with D_2 to undergo complete deuteration within 30 min which is faster than for the calcium homologs (8 h).[18] In this reaction the isotopomers of **4** were not observed by ^1H NMR spectroscopy in contrast to the deuteration of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_3]^+$.[18,25] The deuteride peak of **4-*d*$_4$** appears at δ 6.08 ppm in the ^2H NMR spectrum.

When **4** was reacted with the strontium dication **3**, an additional hydride resonance at δ 5.92 ppm appeared in the ^1H NMR spectrum of the reaction mixture. While we were unable to isolate this hydride complex, it is likely that this resonance corresponds to the dihydride dication $[(Me_4TACD)_2Sr_2(\mu\text{-}H)_2(thf)_x]^{2+}$. The same species was also observed as the second major resonance in the hydrogenolysis of **2**. It is noteworthy that **4** was the only isolable strontium hydride complex and was also isolated from the reaction of **2** with hydrogen, albeit in poor yield. Compound **4** is unstable in solution and the formation of several new hydride resonances is observed in the ^1H NMR spectrum within 48 h. H_2 formation was not observed in the ^1H NMR spectrum, ruling out the possibility of Me_4TACD ligand deprotonation.

The difficulties to isolate a dinuclear strontium hydride stabilized by Me_4TACD prompted us to evaluate the possibility of a dinuclear multimetallic alkaline earth metal hydride. When the strontium monobenzyl cation **2** was hydrogenated in the presence of the calcium monobenzyl cation **2-Ca**, colorless crystals of the heterobimetallic calcium strontium hydride $[(Me_4TACD)_2CaSr(\mu\text{-}H)_2(thf)][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$ (**5**) crystallized in 85% yield within 16 h (Scheme 2). The crystal structure of **5** shows a dinuclear hydride complex that resembles that of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2(thf)]^{2+}$.[19] Both contain one six-coordinate calcium atom and one seven-coordinate metal atom with an additional THF ligand (Fig. 2). According to the result of the X-ray diffraction, the solid state of **5** also incorporates traces of the dinuclear hydride dicalcium complex leading to a non-stoichiometric composition (see ESI†). In the heterobimetallic compound **5**, which also shows a slightly longer metal–metal distance of 3.7095(5) Å than the dicalcium hydride with a Ca· · ·Ca distance of 3.6306(11) Å, the THF ligand coordinates preferentially to the strontium center.[19]

A bonding analysis was carried out on complex **5** at the same level of theory as that used for complex **4**. The geometry is again well-reproduced computationally with the two Sr–H bond distances of 2.39–2.43 Å (2.40(3) Å and 2.42(3) Å experimentally) and the two Ca–H distances of 2.20–2.21 Å (2.22(3) and 2.24(3) Å experimentally). At the NBO level, two Sr–H bonds are found, which are strongly polarized toward H(86%). Once again, at the second order, these two bonds appear to be delocalized to calcium in line with the formation of 3c–2e bonds. This is in line with the Sr–H WBI of 0.37 and the Ca–H of 0.30. These 3c–2e bonds are reflected in the HOMO and HOMO−1 of complex **5**.



Scheme 2 Synthesis of mixed calcium strontium hydride stabilized by Me_4TACD.

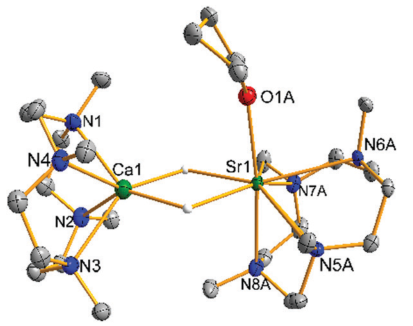


Fig. 2 Molecular structure of the dication in **5** in solid state. Displacement parameters are set at the 30% probability level; hydrogen atoms except of the hydride ligands are omitted for clarity.

While mixed heterobimetallic hydride complexes containing group 1 and group 2 metals are well known, heterobimetallic hydride species containing two different alkaline earth metals are rare.[28] To the best of our knowledge the only other example is $[(BDI)_2Mg_2Ca(\mu\text{-}H)_3(C_6D_6)][Al\{OC(CF_3)_3\}_4]$ (BDI = $CH\{C(CH_3)NDipp\}_2$, Dipp = 2,6-diisopropylphenyl) reported by Hill *et al.* in 2019.[29]

The ^1H NMR spectrum of the heterobimetallic dimer **5** shows one major hydride resonance at δ 5.10 ppm, upfield shifted compared to the hydride resonance of the strontium hydride **4** and downfield shifted compared to the hydride resonances of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ (δ 4.45 ppm) and $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_3]^+$ (δ 4.72 ppm). In addition, the ^1H NMR spectrum of **5** shows resonances of dicalcium hydrides $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ and $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_3]^+$ as well as broad resonances at δ 5.98, 5.92, 5.84, and 5.29 ppm in the region expected for strontium hydrides. These resonances are tentatively assigned to **4** (δ 5.98), $[(Me_4TACD)_2Sr_2(\mu\text{-}H)_2(thf)_x]^{2+}$ (δ 5.92), and other unidentified strontium hydride species. As shown previously, the monomer–dimer equilibrium plays an important role for the solution properties and catalytic activity for $[(L)_2Ca_2(\mu\text{-}H)_2]^{2+}$ (L = Me_4TACD or Me_5PACP).[21] In the case of **5** a dissociative equilibrium would form $[(Me_4TACD)CaH_2]$, $[(Me_4TACD)CaH]^+$, $[(Me_4TACD)SrH]^+$ and $[(Me_4TACD)SrH_2]$ fragments. The association of these fragments result in the formation of the observed hydride species. We note that the *in situ* ^1H NMR spectra of the hydrogenolysis of **2** in the presence of **2-Ca** and of **1a** in the presence of **3-Ca** gave the same reaction mixture as pure **5** in the same ratio of hydride species, corroborating that an equilibrium mixture is formed. ^1H–^1H EXSY experiments of **5** show the exchange of hydride ligands between the mixed hydride species and the aforementioned homometallic calcium hydride and strontium hydride species. To investigate the hydride ligand exchange between the metal centers, we reacted **5** with the dicationic complexes **3** and **3-Ca**. The ^1H NMR of a 1 : 1 mixture of **5** and **3-Ca** showed the formation of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ and

3 with no resonances of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_3]^+$ or residual **5**. This can be explained by a complete hydride transfer from the strontium ions to the calcium ions added to the mixture. In contrast, when an excess of **3** was added to **5**, resonances of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ and $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_3]^+$ were still observed in the ^1H NMR spectrum. The main hydride resonance in this reaction corresponds to the mixed hydride species. The homometallic strontium hydride $[(Me_4TACD)_2Sr_2(\mu\text{-}H)_2(thf)_x]^{2+}$ was observed only in traces. These observations indicate the higher affinity of the nucleophilic hydride ligand for the more Lewis acidic/electrophilic calcium ion.

Complexes **4** and **5** were tested as catalysts in the hydrogenation of unactivated alkenes and compared to the catalytic activity of $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ under the conditions reported previously (60 °C, 1 bar H_2, details given in the ESI†).[18] Whereas **4** showed a slightly shortened reaction time of 12 h as opposed to 24 h for $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ in the hydrogenation of 1-octene, **5** did not show an increased activity compared to the monometallic analog. The improved catalytic activity of **4** compared to the calcium homolog is in line with the results for hydrogenation catalysis with alkaline earth metal hydrides reported previously.[6,13] However, a quantitative comparison of **4** and $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$ is difficult as **4** is unstable at 60 °C in solution. The internal double bond of 1,4-hexadiene was not hydrogenated by either **4** or **5**.

In conclusion, using the macrocyclic ligand Me_4TACD allowed the isolation of two cationic strontium hydride complexes by hydrogenolysis of benzyl precursors. In contrast to the smaller magnesium and calcium ion, $[SrH]^+$ could not be isolated as a stable dimer (ionic radii for c.n. = 6: 0.86 Å for Mg, 1.14 Å for Ca, 1.32 Å for Sr). $[SrH]^+$ was found as part of homometallic strontium hydride complex $[(Me_4TACD)_3Sr_3(\mu_2\text{-}H)_4(thf)]^{2+}$ (**4**) which can also be regarded as the adduct of two neutral $[(Me_4TACD)SrH_2]$ fragments stabilized by dicationic $[(Me_4TACD)Sr(thf)]^{2+}$. Hydrogenolysis of the cationic strontium benzyl in the presence of the homologous calcium benzyl gave the heterobimetallic calcium strontium hydride complex $[(Me_4TACD)_2CaSr(\mu\text{-}H)_2]^{2+}$ (**5**) isostructural with the dicalcium complex. Hydride ligand exchange between the metal centers in solution showed a higher affinity of the hydride ligand for calcium, in line with the higher electrophilicity of Ca and more polarized/nucleophilic Sr–H bonds (electronegativity Ca: 1.00, Sr: 0.95), thus rationalizing the increased reactivity of strontium hydride complexes compared to those of the lighter homologs.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Harder, *Chem. Commun.*, 2012, **48**, 11165–11177.

2 M. S. Hill, D. J. Liptrot and C. Weetman, *Chem. Soc. Rev.*, 2016, **45**, 972–988.

3 Y. Sarazin and J.-F. Carpentier, *Chem. Rec.*, 2016, **16**, 2482–2505.

4 D. Mukherjee, D. Schuhknecht and J. Okuda, *Angew. Chem., Int. Ed.*, 2018, **57**, 9590–9602.

5 H. Bauer, M. Alonso, C. Färber, H. Elsen, J. Pahl, A. Causero, G. Ballmann, F. De Proft and S. Harder, *Nat. Catal.*, 2018, **1**, 40–47.

6 H. Bauer, M. Alonso, C. Fischer, B. Rösch, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2018, **57**, 15177–15182.

7 H. Bauer, K. Thum, M. Alonso, C. Fischer and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 4248–4253.

8 J. Martin, C. Knüpfer, J. Eyselein, C. Färber, S. Grams, J. Langer, K. Thum, M. Wiesinger and S. Harder, *Angew. Chem., Int. Ed.*, 2020, **59**, 9102–9112.

9 M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2017, **56**, 16654–16659.

10 B. Maitland, M. Wiesinger, J. Langer, G. Ballmann, J. Pahl, H. Elsen, C. Färber and S. Harder, *Angew. Chem., Int. Ed.*, 2017, **56**, 11880–11884.

11 J. Martin, J. Eyselein, J. Langer, H. Elsen and S. Harder, *Chem. Commun.*, 2020, **56**, 9178–9181.

12 X. Shi, C. Hou, C. Zhou, Y. Song and J. Cheng, *Angew. Chem., Int. Ed.*, 2017, **56**, 16650–16653.

13 X. Shi, G. Qin, Y. Wang, L. Zhao, Z. Liu and J. Cheng, *Angew. Chem., Int. Ed.*, 2019, **58**, 4356–4360.

14 X. Shi, C. Hou, L. Zhao, P. Deng and J. Cheng, *Chem. Commun.*, 2020, **56**, 5162–5165.

15 B. Rösch, T. X. Gentner, H. Elsen, C. A. Fischer, J. Langer, M. Wiesinger and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 5396–5401.

16 D. Mukherjee, T. Höllerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron and J. Okuda, *J. Am. Chem. Soc.*, 2018, **140**, 3403–3411.

17 C. N. de Bruin-Dickason, T. Sutcliffe, C. Alvarez Lamsfus, G. B. Deacon, L. Maron and C. Jones, *Chem. Commun.*, 2018, **54**, 786–789.

18 D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2017, **56**, 12367–12371.

19 D. Schuhknecht, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2020, **59**, 310–314.

20 D. Schuhknecht, T. P. Spaniol, I. Douair, L. Maron and J. Okuda, *Chem. Commun.*, 2019, **55**, 14837–14839.

21 T. Höllerhage, D. Schuhknecht, A. Mistry, T. P. Spaniol, Y. Yang, L. Maron and J. Okuda, *Chem. – Eur. J.*, 2021, **27**, 3002–3007.

22 K. Izod and P. G. Waddell, *Organometallics*, 2015, **34**, 2726–2730.

23 D. Schuhknecht, K.-N. Truong, T. P. Spaniol, L. Maron and J. Okuda, *Chem. Commun.*, 2018, **54**, 11280–11283.

24 D. Schuhknecht, PhD thesis, RWTH Aachen University, 2020.

25 V. Leich, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2016, **55**, 4794–4797.

26 A. Rit, A. Zanardi, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2014, **53**, 13273–13277.

27 D. Schuhknecht, V. Leich, T. P. Spaniol, I. Douair, L. Maron and J. Okuda, *Chem. – Eur. J.*, 2020, **26**, 2821–2825.

28 S. D. Robertson, M. Uzelac and R. E. Mulvey, *Chem. Rev.*, 2019, **119**, 8332–8405.

29 L. Garcia, M. F. Mahon and M. S. Hill, *Organometallics*, 2019, **38**, 3778–3785.