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Low-valent homobimetallic Rh complexes: influence of ligands on the structure and the intramolecular reactivity of Rh–H intermediates

Pascal Jurt, Oleg G. Salnikov, Thomas L. Gianetti, Nikita V. Chukanov, Matthew G. Baker, Grégoire Le Corre, Jaap E. Borger, Rene Verel, Sébastien Gauthier, Olaf Fuhr, Kirill V. Kovtunov, Alexey Fedorov, Dieter Fenske, Igor V. Koptyug and Hansjörg Grützmacher

Supporting two metal binding sites by a tailored polydentate trop-based (trop = 5H-dibenzo[a,d]cyclohepten-5-yl) ligand yields highly unsymmetric homobimetallic rhodium(i) complexes. Their reaction with hydrogen rapidly forms Rh hydrides that undergo an intramolecular semihydrogenation of two C≡C bonds of the trop ligand. This reaction is chemoselective and converts C≡C bonds to a bridging carbene and an olefinic ligand in the first and the second semihydrogenation steps, respectively. Stabilization by a bridging diphosphine ligand allows characterization of a Rh hydride species by advanced NMR techniques and may provide insight into possible elementary steps of H₂ activation by interfacial sites of heterogeneous Rh/C catalysts.

Introduction

Bimetallic transition metal complexes have been investigated since the 1970s, however despite numerous reports, only a few complexes are widely used in catalytic applications. The most prominent is a rhodium(ii) acetate dimer and its derivatives exploited for carbene transfer reactions. These and more recent bimetallic systems typically outperform monometallic alternatives in terms of activity and selectivity, functional group tolerance, and catalyst loading. The interest in homobimetallic catalysts has recently seen a renaissance. Selected catalytic applications include diazo-free cyclopropanation, small molecule activation, hydrogenation, hydroformylation and C–C coupling reactions. Notably, heterobimetallic complexes serve as models of the transmetallation step for the latter process. Most of these bimetallic species fall into two groups: (i) heterobimetallic early-late transition metal complexes, or (ii) symmetric bimetallic complexes with a core consisting of two mid-to-late transition metals. Group (i) typically relies on ligands that combine in close proximity both soft and hard moieties, and feature a highly polar dative interaction from the late to the early transition metal. Group (ii) relies on symmetric bridging ligands, often leading to an apolar bimetallic interaction. Complexes of the group (ii) have been of particular interest for the understanding of reactivity of small clusters.

Rhodium nanoparticles on support materials are widely used in heterogeneous catalysis and various industrial processes especially for hydrogenation–dehydrogenation reactions. But the mode of interaction between the supported rhodium sites and H₂ is not fully understood. A recent DFT study reported that hydrogen activation by small rhodium clusters on a carbon support features a bridging hydride species and a hydride ligand (Scheme 1a) that could be transferred to the carbon support. However, such intermediates have not been observed experimentally to date. Low valent homobimetallic rhodium complexes serve as molecular models for supported Rh sites towards understanding the hydrogen activation on such materials. While representation of supported heterogeneous catalysts by a bimetallic model significantly reduces their complexity, this approach allows for a reliable identification of reaction products and is therefore insightful, despite the apparent oversimplification of the intrinsic complexity of heterogeneous catalysts. That said, examples of well-defined bimetallic Rh(i)-Rh(i) systems capable of activating H₂ are scarce. Scheme 1b presents a rare dirhodium(i) complex that,
according to DFT calculations, activates dihydrogen leading to one bridging and one terminal hydride ligand, in a similar fashion as mentioned above for the supported rhodium centers. This mode of the hydrogen activation dissymmetrizes the dihedral bond while simultaneously forming a stabilizing Rh–Rh bond.28 Again, experimental evidence for such a disdimer dihydride species is still lacking, although dissymmetric complexes with a dirhodium(i) core containing chloride ligands in place of the hydrides were reported.29 A symmetric dirhodium dihydride complex, which forms an intermetallic bond, was characterized by NMR and IR (Scheme 1c).30

In contrast to the exploitation of complexes with symmetric ligands, the advantages of dissymmetric ligands to control the reactivity of two adjacent Rh centers are underutilized.31 The disymmetry of the electronic environment imposed by the ligand could not only enable otherwise inaccessible reactivity manifolds,19,32 but also allows modelling the environment and complexity of heterogenous catalysts (metal-support interface, surface defects, etc.). In particular, a non-innocent ligand with multiple unsaturated C–C bonds could provide insights in the reactivity of Rh/C interfacial sites of metallic Rh nanoclusters or nanoparticles on carbon-based supports.

Previous work by the Grützmacher group showed that the bidentate concavely shaped tropPPh2 (trop = 5H-dibenz[a,d]cyclohepten-5-yl) ligand featuring both a σ-donor (Ph3P group) and a π-accepting binding site (C=Ctrop) enables a strong binding33 to several transition metal centers including Pd,34 Rh35,36 and Ir.36,37 In order to synthesize a homobimetalllic low valent dirhodium complex, we developed a tailored [(TMSP)2tropPPh2 ligand with a second binding site created by two alkyl moieties (vide infra). This framework supports a Rh2(I) complex with labile triolate ligands cis to the polarized intermetallic Rh–Rh bond and demonstrates cooperativity of two metal sites in the hydrogen activation. However, resulting hydrides react intra-molecularly by adding hydrogen to the alkyl units of the [(TMSP)C=C]2tropPPh2 ligand. We performed in depth NMR studies, including the use of the parahydrogen-induced polarization (PHIP) technique,38–42 to elucidate the structure and transformations of these Rh hydride intermediates that convert the trop ligand into a carbene-like motif via semihydrogenation of the first C=C bond. Remarkably, the semihydrogenation of the second C=C bond proceeds with a different chemoselectivity forming a cis-olefinic ligand. Tuning the Rh coordination sphere by exchanging one triolate for a bis(diphenylphosphino)methane (dppm) ligand inhibits the semihydrogenation steps and allows to characterize the intermediate rhodium hydride species by NMR. Overall, reactivity of Rh2 complexes in a carbon-rich ligand environment offers mechanistic insight on the net H2 activation across a Rh–Rh bond and interaction of Rh–H species with a carbon support in Rh/C heterogeneous catalysts.

Results and discussion

Synthesis and characterization of 10,11-di-(trimethylsilyl) acetylene-5H-dibenz[a,d]cyclohepten-5-diphenylphosphate and its Rh2 complexes

The tropketone 143 was converted to the polydentate trop ligand 5 in four steps with an overall yield of 34%, utilizing a Sonogashira protocol and conventional functional group transformation reactions (Fig. 1, top panel). Mixing 5 with one equivalent of [(C5H4)2RhCl]2 leads to the chloro bridged dimer 6 having two adjacent rhodium centers per trop ligand (83% yield). The abstraction of the chloride ligands in 6 with silver triflate gives the monomeric homobimetallic complex 7 in 82% yield. According to single crystal X-ray diffraction of 7, two triflate ligands bridge between the two rhodium centers. The addition of one equivalent of diphenylphosphinomethane (dppm) displaces one triflate ligand to form the dppm adduct 8 (83% yield, Fig. 1, bottom panel).

Complexes 6–8 were characterized by single crystal X-ray diffraction methods. All complexes possess a distorted square planar geometry around Rh1 and a nearly ideal square planar environment around Rh2 (trans = 0.29, 0.46 and 0.37, and trans = 0.06, 0.01 and 0.03 for 6, 7 and 8 respectively).44 The Rh–Rh contact in monomeric 7 is 2.6297(2) Å, that is 0.21 Å shorter than in dimeric 6 (2.8464(3) Å, Table 1). This shortening of the Rh–Rh distances is accompanied by an elongation of the P–Rh bond from 2.1829(3) Å in the chloro bridged dimer 6 to 2.2115(5) Å in the monomeric triflate complex 7, indicating that the Rh–Rh interaction in 7 is stronger. However, the bond lengths of the coordinated C–C multiple bonds as well as the respective C–Rh distances do not differ much between 6 and 7 (Table 1). Dppm adduct 8 has a Rh–Rh bond of 2.7691(7) Å, an intermediate value between those of 6 and 7. Additional significant changes are observed in the alkene/alkyne bonds trans to P2 and P3, which are elongated in 8 (Rh1-ct(C5–C6) 1.981(7) Å and Rh2-ct(C1–C2) 2.232(7) Å in 8 compared to Rh1-ct(C5–C6) 1.913(2) Å and Rh2-ct(C1–C2) 2.062(2) Å in 7, explained by the higher trans influence of the phosphine ligand.45

The 13C NMR olefinic chemical shifts for the chloro bridged dimer 6 and the monomeric triflate complex 7 are similar (δ13C
¼

37.9 vs. 37.0 ppm for 6 and 7, respectively). However, a strong shielding is observed for both triple bonds in the trflate complex (δ^{13}C = 99.4 to 86.6 ppm for TMS-CCC and δ^{13}C = 74.0 to 65.3 for TMS-CCC for 6 and 7, respectively) suggesting that Rh2 site in 7 is more electron-rich than in 6. Likely, the Rh–Rh bond can be best described as a dative bond where electron donation from Rh2 into the antibonding orbital of the Rh1–P bond occurs, similar to the bonding in early-late bimetallic transition metal complexes. For complex 8, this is supported by calculations, as the HOMO/C0 and HOMO/C0 orbitals show a clear overlap between the two metal centers, with a larger orbital contribution of Rh2 (Fig. S1†).

Reactivity of [Rh2(TMS)C=C]_2tropPPh_2 complexes with H2

Adding hydrogen (1–2 bar) to the headspace of a J. Young NMR tube with monomeric trflate complex 7 dissolved in CD_3CN and following the reaction progress by NMR allows observing a stepwise hydrogenation of the two triple bonds of the supporting (TMS)C=C ligand. The first alkene semihydrogenation step proceeds quantitatively within 15 min and, strikingly, yields carbene species 9 (Scheme 2). Such chemo-selective hydrogenation is uncommon and was only previously observed for alkynes bound to d^8 metal centers with a Pt(II)–(m-H)_3–Pt(II) core. The semihydrogenation of the remaining triple bond leads to a coordinated alkene 10 (Scheme 2) and proceeds with a slower rate requiring ca. 20 h at 2 bar of H_2 for quantitative conversion. The carbene complex 9 and the carbene alkene complex 10 display characteristic signals in ^{13}C NMR spectra assigned to the bridging carbene at δ^{13}C = 171.1 and

Table 1 Selected bond lengths (Å) and angles (°) for complexes 6 to 8, ct: center of coordinated multiple bond

| Bond length or angle | 6           | 7           | 8           |
|---------------------|-------------|-------------|-------------|
| Rh1–Rh2             | 2.8464(3)   | 2.6297(2)   | 2.7691(7)   |
| Rh1–P               | 2.1829(3)   | 2.2115(5)   | 2.2385(17)  |
| C1–C2               | 1.242(3)    | 1.246(3)    | 1.235(10)   |
| C3–C4               | 1.247(4)    | 1.248(3)    | 1.230(9)    |
| C5–C6               | 1.499(3)    | 1.495(3)    | 1.475(10)   |
| ct(C1–C2)–Rh2       | 2.077(2)    | 2.062(2)    | 2.232(7)    |
| ct(C3–C4)–Rh2       | 2.054(3)    | 2.057(2)    | 2.051(6)    |
| ct(C5–C6)–Rh1       | 1.962(2)    | 1.913(2)    | 1.981(7)    |
| P1–Rh1–Rh2          | 162.708(19) | 168.488(16) | 164.92(5)   |
| Rh1–Rh2–ct(C1–C2)   | 87.83(7)    | 87.48(6)    | 80.82(19)   |
| Rh1–Rh2–ct(C3–C4)   | 81.01(7)    | 83.07(6)    | 80.93(19)   |
| ct(C1–C2)–Rh2–ct(C3–C4) | 89.67(10) | 82.19(6)    | 85.9(2)     |
| P1–Rh1–ct(C5–C6)    | 91.43(7)    | 90.56(8)    | 91.4(2)     |

Fig. 1 [a] NaBH_4, MeOH, 98%. [b] TMS=CH, 5 mol% [Pd(PPh_3)_4], CuI, toluene, Et_3N, 76%. [c] SOC_3, DCM, 0 °C, 80%. [d] LiPPh_3, toluene, 63%. [e] [(C_2H_4)RhCl]_2, benzene, 82%. [f] AgOTf, DCM, 83%. [g] Ph_2PCH_2PPh_2, DCM/hexane, 80%. The representation of ligand 5 is simplified in structures 6–8 for clarity. The crystal structures of bimetallic complexes 6–8 are given below the respective chemical structures and have the solvent molecules and non-coordinated trflate anions omitted for clarity.
the chemical shift of ligand 5 (Scheme 1) was simplified for clarity.

Table 2 Selected NMR data of complexes 7, 9, and 10

| Nucleus | Position | \( \delta \) (ppm) | \( J \) (Hz) | \( \delta \) (ppm) | \( J \) (Hz) | \( \delta \) (ppm) | \( J \) (Hz) |
|---------|----------|-----------------|-------------|-----------------|-------------|-----------------|-------------|
| \( ^{13}C \) | C1 | 75.4 | \( J_{\text{CC}} = 11.9 \) | | 59.7 | \( J_{\text{CC}} = 11.6 \) | | 67.0 | \( J_{\text{CC}} = 8.1 \) |
| | C2 | 97.0 | \( J_{\text{CC}} = 7.7 \) | | 76.9 | \( J_{\text{CC}} = 7.6 \) | | 81.5 | \( J_{\text{CC}} = 7.1 \) |
| | C3 | 75.5 | \( J_{\text{CC}} = 11.0 \) | | 98.8 | \( J_{\text{CC}} = 11.0 \) | | 100.0 | \( J_{\text{CC}} = 10.8 \) |
| | C4 | 97.0 | \( J_{\text{CC}} = 7.7 \) | | 43.3 | \( J_{\text{CC}} = 7.1 \) | | 62.9 | \( J_{\text{CC}} = 8.1 \) |
| | C5 | 38.1 | \( J_{\text{CC}} = 14.9 \) | | 2.38, 3.18 | \( J_{\text{CC}} = 18.3 \) | | 1.99, 3.03 | \( J_{\text{CC}} = 13.1 \) |
| | C6 | 38.1 | \( J_{\text{CC}} = 14.9 \) | | 59.7 | \( J_{\text{CC}} = 12.1 \) | | 67.0 | \( J_{\text{CC}} = 13.1 \) |
| \( ^{31}P \) | C1H2 | 104.6 | \( J_{\text{HH}} = 185.6 \) | | 2.38, 3.18 | \( J_{\text{HH}} = 18.4 \) | | 1.99, 3.03 | \( J_{\text{HH}} = 13.1 \) |
| \( ^{103}Rh \) | P–Rh1–Rh2 | −6852 | \( J_{\text{HH}} = 186 \) | | −7184 | \( J_{\text{HH}} = 126 \) | | −7163 | \( J_{\text{HH}} = 136 \) |

* No proton showed a significant coupling to Rh2 in the \( ^{1}H–^{103}Rh \) HMQC spectrum.
Analysis of the $^{103}$Rh NMR data reveals that Rh1 is significantly shifted upfield when comparing 7 with 9 and 10 ($\delta^{103}$Rh = $-6852$, $-7184$, and $-7163$ ppm for 7, 9 and 10, respectively) further supporting a more electron rich Rh core. Comparing 9 and 10 using the $^{103}$Rh NMR shift of Rh2 suggests that the Rh2 site in 10 is more electron rich than in 9 ($\delta^{103}$Rh = $-6733$, $-7066$ ppm for 9 and 10, respectively), which is consistent with a change in the ligand sphere from an alkyne to a weaker $\pi$-accepting alkene. These results indicate that the bimetallic core becomes more electron rich with each hydrogenation step.

![Fig. 2](image_url) Proposed activation of hydrogen by complex 8 (L is one acetonitrile ligand) and relevant spectroscopic data: (a) reaction of 8 with hydrogen, as proposed on the basis of NMR experiments, (b) J-resolved $^1H(^{31}P)$ spectrum, (c) $^1H-^{103}$Rh HMQC spectrum, (d) PHIP $^1H$ spectrum (blue) with simulation (red), of hydride $H_a$, (e) PHIP $^1H(^{31}P)$ spectrum (blue) with simulation (red) of hydride $H_b$. The representation of ligand 5 was simplified in structures 8, 11 and 12 for clarity.

![Scheme 3](image_url) DFT calculations (Gaussian09, wB97X-D/def2-SVP) for the hydrogen activation pathways from 8-SM to 8a-HHox and 11-HHox. L is one acetonitrile ligand. The transition states were confirmed to connect the two respective energy minima by IRC calculations (see ESI†).
CD3CN, \{(TMS)C\} at the Rh2 fragment, indicating irreversible ligand deuterium is only incorporated at the double bond (blue sphere of H2 and subsequently placed under an atmosphere of CH2 protons of carbene complex). Instead, a mixture of a Rh dihydride complex of H2 for the hydrogenation of monomeric tri-2,5,8-naphthalene diacetylene. Conversion and selectivities are reported after 8.5 hours of the reaction.

| Entry | Catalyst | Conv. (%) | Sel. A (%) | Sel. B (%) | kobs (10⁻² h⁻¹) |
|-------|----------|-----------|------------|------------|-----------------|
| 1     | 7        | 39        | 90         | 10         | 5.9             |
| 2     | 8        | 79        | 97         | 3          | 23              |
| 3     | 9        | 39        | 97         | 3          | 6.7             |
| 4     | 12       | 16        | >99        | —          | 0.95            |

We have also performed the semihydrogenation of the ligand in a stepwise manner, where the carbene complex 9 was formed first under H2, followed by deuteration to the carbene alkene complex 10 under a D2 atmosphere. In this case, deuterium is only incorporated at the double bond (blue hydrogens atoms in Scheme 2) indicating irreversible ligand hydrogenation. This observation is consistent with the results of an experiment where 10 was formed in situ under an atmosphere of D2 and subsequently placed under an atmosphere of D2. In this case no deuterium incorporation is observed within 14 h, indicating that both hydrogenation steps are irreversible (Fig. S7 and S8†).

To gain further insight on how the H2 molecule is activated for the hydrogenation of monomeric trflate complex 7, resulting in no detectable hyperpolarized Rh hydride intermediates. Interestingly, the only PHIP hyperpolarized signals observed in the 1H NMR spectra are assigned to the methane CH2 protons of carbene complex 9 (Fig. S10 and S11†), which establishes a pairwise hydrogen addition to the triple bond of the trop ligand when forming the bridging carbene complex 9.

Table 3 Results of the catalytic semihydrogenation of phenylacetylene. Conversion and selectivities are reported after 8.5 hours of the reaction.

Fig. 3 Catalytic semihydrogenation of phenylacetylene by bimetallic catalysts 7–9 and the benchmark monometallic catalyst 12 (Ln is CD3CN, (TMS)C\n at the Rh2 fragment, indicating irreversible ligand deuterium is only incorporated at the double bond (blue sphere of H2 and subsequently placed under an atmosphere of CH2 protons of carbene complex). Instead, a mixture of a Rh dihydride complex of H2 for the hydrogenation of monomeric tri-2,5,8-naphthalene diacetylene. Conversion and selectivities are reported after 8.5 hours of the reaction.

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Next, we added 1–2 bar of H2 to the solution of dpmm adduct 8 in CD3CN in a J. Young NMR tube and observed no formation of the bridging carbene-like moiety. Instead, a mixture of 8 and a Rh dihydride complex 11 (Fig. 2a) is formed that is stable for several days at room temperature. Two characteristic hydride signals are observed at approximately δ1H = −16.2 and −20.5 ppm. Dihydride 11 was further characterized by low temperature NMR experiments as well as using the PHIP technique. The removal of the H2 (or the D2) atmosphere from a J. Young NMR tube containing a mixture of the dpmm adduct 8 and the dihydride 11 cleanly reforms 8, indicating a fully reversible hydrogen activation (Fig. S12 and S13†). This is further supported by EXSY spectroscopy, variable temperature NMR and a partially negative line-shape (PNL) of the ortho-hydrogen peak in PHIP NMR (Fig. S14–S17†). Since PNL does also occur in PHIP experiments with 7, the same mode of hydrogen activation is likely occurring with both species, 7 and 8. Upon formation of cis-dihydride 11, the Rh1 NMR resonance δ103Rh1 = −7758 ppm is significantly shifted to lower frequencies. This low-frequency shift exceeds even the ones observed for 9 (δ103Rh1 = −7184 ppm) and 10 (δ103Rh1 = −7163 ppm). The Rh2 nucleus (δ103Rh1 = −7630 ppm) shows likewise a strong shift to lower frequencies relative to the 103Rh2 nuclei in 9 and 10 (δ103Rh2 = −6733 and −7066 ppm, respectively), which is in agreement with the influence of strongly σ donating hydrides on both metal centers (Fig. 2b). 31H(31P) J-resolved 2D NMR spectroscopy reveals the JHH and JHH coupling constants (Fig. 2c). The two hydrides remain coupled in complex 11, revealed by the JHH = 15.4 Hz splitting in the indirect dimension. The hydride at δ1H = −16.2 ppm shows an additional JHH = 5.8 Hz coupling to another proton, assigned by COSY to one of the methylene protons of the dpmm ligand (red in Fig. 2a). The NMR characterization of 11 was also completed by 1H, 13C, 19F, 29Si and 31P spectra (Fig. S21–S27†). Altogether, this data confirmed that dpmm adduct 8 activates hydrogen reversibly and is in equilibrium with the dihydride species 11. No semihydrogenation of the triple bonds is observed in this case.

Recording the J-resolved spectrum with 31P decoupling allows extracting the JHH coupling constants (Fig. 2c). While the hydride at δ1H = −16.3 ppm appears as a doublet of doublets (JHH = 20.4, 11.8 Hz), the hydride at δ1H = −20.2 ppm appears as a pseudo-triplet (JHH = 11.8 Hz). The observed JHH coupling of 15.4 Hz is larger than typically found in traditional cis hydrides formed via oxidative addition (JHH = 7.2–9.5 Hz), suggesting another geometry since higher coupling constants indicate larger angles between the substituents. Overall, these results are consistent with a bridging geometry for the dihydride 11 (Fig. 2a). Assignment of 1H cis to the intermetallic bond is based on the observation of a remarkable long-range 4JHH coupling of H2 to a CH2 proton (JHH = 5.8 Hz, highlighted red in Fig. 2a and b). Unfortunately, recording a J-resolved spectrum with 103Rh decoupling was not successful due to the large difference in the chemical shift, and it was not possible to eliminate the JHH couplings from both metal centers at once. Therefore, the JHH coupling constant could not be accessed with this approach. However, the 1H–31P coupling constants could be extracted by fitting the observed PHIP signals (Fig. 2d and e). The PHIP spectrum in Fig. 2e was recorded with a 31P decoupling, which selectively eliminates only 31P couplings arising from the dpmm moiety. This allows distinguishing coupling constants between the hydrides and dpmm/trop phosphorus.
centers. In addition, PHIP experiments allowed to determine the sign of the $J_{HH}$ coupling constant between the two hydrides which is negative $J_{HH} = -15.4$ Hz.

The proton $H_2$ shows an $J_{HH}$ coupling to the dpmm $^3$P center of $J_{HH} = 13$ and 6 Hz, indicating a cis $J_{HH}$ coupling. The second hydrogen atom $H_2$ is likely close to the cis position of the trop phosphine center, as suggested by the couplings of $J_{HH} = 24$ and 18 Hz. The coupling to the second dpmm phosphorous center is substantially smaller ($J_{HH} = 4$ Hz). However, the large $J_{HH}$ coupling constant as well as the similar coupling constants to both Rh centers (resulting in the pseudo-triplet in Fig. 2b) are consistent with an interaction with the second Rh center. This assignment allows reporting a cis coupling constant of $J_{HH} = 11.8$ Hz. This indicates that the close Rh–Rh contact is preserved after the addition of dihydrogen. Having assigned $H_2$ as the terminal hydride, while $H_4$ interacts with the two Rh centers unsymmetrically, the Rh–Rh core can be described either as a Rh(II)–Rh(II) center or a Rh(II) → Rh(II) polarized bond, due to the bridging nature of $H_2$. Both descriptions imply a close Rh–Rh contact. We tested if this hydride reactivity could also be observed with other ligands and subjected tricyclohexylphosphine, diphenylphosphine oxide and triazabicyclodecene ligands to conditions of the in situ PHIP experiments demonstrating that only the dpmm ligand leads to the hydride species. However, all PHIP experiments with the added ligand except PHIP experiments with the H$_2$ molecule coordinated to Rh1 (Scheme 3) were consistent with an interaction with the second Rh center. This assignment allows reporting a cis coupling constant of $J_{HH} = 11.8$ Hz. This indicates that the close Rh–Rh contact is preserved after the addition of dihydrogen. Having assigned $H_4$ as the terminal hydride, while $H_2$ interacts with the two Rh centers unsymmetrically, the Rh–Rh core can be described either as a Rh(II)–Rh(II) center or a Rh(II) → Rh(II) polarized bond, due to the bridging nature of $H_2$. Both descriptions imply a close Rh–Rh contact. We tested if this hydride reactivity could also be observed with other ligands and subjected tricyclohexylphosphine, diphenylphosphine oxide and triazabicyclodecene ligands to conditions of the in situ PHIP experiments demonstrating that only the dpmm ligand leads to the hydride species. However, all PHIP experiments with the added ligand except triazabicyclodecene showed the hyperpolarized signals of methylene CH$_2$ protons with very similar chemical shifts and coupling constants as observed for $H_2$. In addition, a partially lineshape signal for the orthodihydrogen was observed for all ligands, suggesting that hydrogen activation is reversible (Fig. S31–S33).

DFT calculations (ωB97X-D/def2-SVP) support the proposed reversible hydrogen activation of the monomeric trflate complex 8 leading to the dihydride 11 (Scheme 3). From the computed 8–SM intermediate, two $H_2$ adducts can be formed: with the $H_2$ molecule coordinated cis (8–$H_2$) or trans (8a–$H_2$) to Rh1 (Scheme 3). Both complexes can undergo oxidative addition steps via activated complexes which are located at energetically low lying transition states ($[TS1]: \Delta G = 11.4$ kcal mol$^{-1}$; $[TS2]: \Delta G = 7.1$ kcal mol$^{-1}$), leading to dihydrides 8a–$H_2$ and 11–$H_2$, respectively. With the exception of 11–MeCN, all intermediates are relatively close in energy and are expected to be accessible from 8–SM at room temperature. Since 11–$H_2$ has an open coordination site to Rh1, binding of one acetonitrile ligand occurs giving a more stable species 11–MeCN ($\Delta G = -19.8$ kcal mol$^{-1}$) with a distorted octahedral coordination environment around Rh2, as expected for Rh(III) d$^6$ complexes. The energy of the coordinately saturated 11–MeCN is only slightly higher than that of 8–MeCN ($\Delta G = -12.3$ and $-16.8$ kcal mol$^{-1}$, respectively). These two complexes are therefore expected to slowly interconvert and be observable in solution, which is indeed supported by NMR spectroscopy. We note that $\Delta G$ values from DFT calculations and variable temperature NMR measurements obtained from a Van’t Hoff plot (Fig. S16†) are in reasonable agreement ($\Delta G = 4.5$ and 1.1 kcal mol$^{-1}$, respectively). It is of note that since the geometrical reorganization in going from $[TS2]$ to 11–$H_2$ is only minimal, the barrier for this step is very low and we attribute the small positive energy difference between 11–$H_2$ and $[TS2]$ to the numerical inaccuracy of the applied DFT method. In addition, we note that the bimetallic hydrogen activation pathway involving a four-membered M$_2$H$_2$ transition state was not considered because this reaction is symmetry forbidden.

Interestingly, a bridging hydride resembling that in 11 has been proposed and calculated in both rhodium-based homogeneous bimetallic and heterogeneous systems. This observation further underlines the utility of low valent homobimetallic complexes with ligands containing alkene and alkylene binding sites in understanding elementary steps in heterogeneous catalysts which are deposited on carbon support materials.

Bimetallic dirhodium complexes 7–9 and the monometallic catalyst 12 were then tested as catalysts for the semi-hydrogenation of phenylacetylene (5% catalyst loading, 25 °C, Fig. 3, for details see ESI†). No activation period was observed (Fig. S41†). The dpmm adduct 8 showed highest performance with a selectivity for styrene of 96% at 78% conversion and $k_{obs}$ around 3–5 times higher than those for monomeric trflate 7 and carbene complex 9 (Table 3, entries 1-3). The similar rates $k_{obs}$ observed with 7 and 9 indicate that the in situ hydrogenation of 7 to 9 takes place under the catalytic conditions and leads to the same active species, consistent with the presence of the hyperpolarized CH$_2$ signals characteristic for 9 in these catalytic reactions according to in situ PHIP NMR (Fig. S42†). Importantly, PHIP results also show that the dihydride species 11 form from 8 under catalytic conditions (Fig. S43†).

Remarkably, the monometallic catalyst 12 converts phenylacetylene significantly slower than all tested bimetallic complexes, with a rate of $k_{obs} = 9.5 \times 10^{-3}$ h$^{-1}$ (Table 3, entry 4). We speculate that the second metal serves as an electron reservoir which helps to avoid the formation of an inert trop-Rh(III) d$^6$ species formed by oxidative addition of dihydrogen. PHIP experiment performed under catalytic conditions with the dpmm adduct 8 indicates a pairwise hydrogen transfer to phenylacetylene forming styrene, i.e. hydrogen is activated by 8 to give dihydride 11, followed by the transfer of the two hydrides to the same substrate molecule (Fig. S43†).

Conclusions

The $([TMS]C≡C)_{2}$tropPPh$_2$ molecule with one phosphane, one alkene, and two alkylene donor sites was designed to allow the synthesis of a new family of low-valent homobimetallic Rh(II)–Rh(II) complexes. The reactivity of these complexes provides insight into possible metal–metal cooperation in hydrogen activation reactions. The unique ligand environment of the Rh2 site in $([TMS]C≡C)_{2}$tropPPh$_2$ complexes makes this ligand an interesting model for the interface between metal clusters and particles and a carbon support material as found in Rh/C heterogeneous catalysts. Two distinct modes of intramolecular hydrogenation of the ligand were identified leading to a bridging carbene or an olefin ligand. When stabilized by a dpmm ligand, an intermediate hydride species could be
characterized by advanced NMR methods which show that this species has a structure with a bridging and a terminal hydride ligand.

Conflicts of interest
The authors declare no conflicts of interest.

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