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

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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 \( \equiv \text{C} \) bonds of the trop ligand. This reaction is chemoselective and converts \( \equiv \text{C} \) bonds to a bridging carbene and an olefinic ligand in the first and the second semihydrogenation steps, respectively. Stabilization by a bridging diphenosphosphate ligand allows characterization of a Rh hydride species by advanced NMR techniques and may provide insight into possible elementary steps of \( \text{H}_2 \) activation by interfacial sites of heterogeneous Rh/C catalysts.

Introduction

Bimetallic transition metal complexes have been investigated since the 1970s,1 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.2 These and more recent bimetallic systems typically outperform monometallic alternatives in terms of activity and selectivity, functional group tolerance, and catalyst loading.3–5 The interest in homobimetallic catalysts has recently seen a renaissance.6 Selected catalytic applications include diazo-free cyclopropanation,7 small molecule activation,8 hydroformylation11 and C–C coupling reactions.12 Notably, heterobimetallic complexes serve as models of the transmetallation step for the latter process.13–17 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.18 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.19 Group (ii) relies on symmetric bridging ligands, often leading to an apolar bimetallic interaction.20 Complexes of the group (ii) have been of particular interest for the understanding of reactivity of small clusters.21–23

Rhodium nanoparticles on support materials are widely used in heterogeneous catalysis and various industrial processes especially for hydrogenation–dehydrogenation reactions.24 But the mode of interaction between the supported rhodium sites and \( \text{H}_2 \) is not fully understood.25 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.26 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.19 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 \( \text{H}_2 \) are scarce.27 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.\textsuperscript{38} Again, experimental evidence for such a dihedral dihydride species is still lacking, although disymmetric complexes with a dihromium core containing chloride ligands in place of the hydrides were reported.\textsuperscript{29} A symmetric dihedral dihydride complex, which forms an intermetallic bond, was characterized by NMR and IR (Scheme 1c).\textsuperscript{39}

In contrast to the exploitation of complexes with symmetric ligands, the advantages of disymmetric ligands to control the reactivity of two adjacent Rh centers are underutilized.\textsuperscript{31} The dissymmetry of the electronic environment imposed by the ligand could not only enable otherwise inaccessible reactivity manifolds,\textsuperscript{19,32} but also allows modelling the environment and complexity of heterogeneous 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 tropPPh\(_2\) (trop = 5H-dibenzo[a,d]cyclohepten-5-yl) ligand featuring both a σ-donor (Ph\(_3\)P group) and a σ-accepting binding site (C≡Ctrop) enables a strong binding\textsuperscript{13} to several transition metal centers including Pd,\textsuperscript{34} Rh,\textsuperscript{35,36} and Ir.\textsuperscript{36,37} In order to synthesize a homobimetalllic low valent dirhodium complex, we developed a tailored (TMS)\(_2\)tropPPh\(_2\) ligand with a second binding site created by two alkylene moieties \textit{vide infra}. This framework supports a Rh\(_2\)(I) complex with labile trflate ligands \textit{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 alkylene units of the (TMS)\(_2\)tropPPh\(_2\) ligand. We performed in depth NMR studies, including the use of the parahydrogen-induced polarization (PHIP) technique,\textsuperscript{38–42} to elucidate the structure and transformations of these Rh hydride intermediates that convert the trop ligand into a carbene-like motif \textit{via} semi-hydrogenation of the first C≡C bond. Remarkably, the semi-hydrogenation of the second C≡C bond proceeds with a different chemoselectivity forming a \textit{cis}-olefinic ligand. Tuning the Rh coordination sphere by exchanging one trflate for a bis(diphenylphosphino)methane (dpmm) ligand inhibits the semi-hydrogenation steps and allows to characterize the intermediate rhodium hydride species by NMR. Overall, reactivity of Rh\(_2\) complexes in a carbon-rich ligand environment offers mechanistic insight on the net \(\text{H}_2\) 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-dibenzo[a,d]cyclohepten-5-diphenylphosphine and its Rh\(_2\) complexes**

The tropketone \textsuperscript{14} was converted to the polydentate trop ligand in 5 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 [(C\(_5\)H\(_4\))\(_2\)RhCl]\(_2\) leads to the chloro bridged dimer \textbf{6} having two adjacent rhodium centers per trop ligand (83% yield). The abstraction of the chloride ligands in \textbf{6} with silver triflate gives the monomeric homobimetalllic complex \textbf{7} in 82% yield. According to single crystal X-ray diffraction of \textbf{7}, two trflate ligands bridge between the two rhodium centers. The addition of one equivalent of diphenylphosphinomethane (dpmm) displaces one trflate ligand to form the dpmm adduct \textbf{8} (83% yield, Fig. 1, bottom panel).

Complexes \textbf{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 (\(r_{\text{Rh1}} = 0.29, 0.46\) and 0.37, and \(r_{\text{Rh2}} = 0.06, 0.01\) and 0.03 for \textbf{6, 7} and \textbf{8} respectively).\textsuperscript{44} The Rh–Rh contact in monomeric \textbf{7} is 2.6297(2) Å, that is 0.21 Å shorter than in dimeric \textbf{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 \textbf{6} to 2.2115(5) Å in the monomeric trflate complex \textbf{7}, indicating that the Rh–Rh interaction in \textbf{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 \textbf{6} and \textbf{7} (Table 1). Dpmm adduct \textbf{8} has a Rh–Rh bond of 2.7691(7) Å, an intermediate value between those of \textbf{6} and \textbf{7}. Additional significant changes are observed in the alkene/alkyne bonds \textit{trans} to P2 and P3, which are elongated in \textbf{8} (Rh1-ct(C5–C6) 1.981(7) Å and Rh2-ct(C1–C2) 2.232(7) Å in \textbf{8} compared to Rh1-ct(C5–C6) 1.913(2) Å and Rh2-ct(C1–C2) 2.062(2) Å in \textbf{7}), explained by the higher \textit{trans} influence of the phosphine ligand.\textsuperscript{45}

The \(^{13}\text{C}\) NMR olefinic chemical shifts for the chloro bridged dimer \textbf{6} and the monomeric trflate complex \textbf{7} are similar (\(\delta^{13}\text{C}\)...
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 (δ13C = 99.4 to 86.6 ppm for TMS–C≡C and δ13C = 74.0 to 65.3 for TMS–C=C 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}tropPPh2] complexes with H2**

Adding hydrogen (1–2 bar) to the headspace of a J. Young NMR tube with monomeric trflate complex 7 dissolved in CD3CN and following the reaction progress by NMR allows observing a stepwise hydrogenation of the two triple bonds of the supporting {(TMS)C≡C}tropPPh2 ligand. The first alkyne semihydrogenation step proceeds quantitatively within 15 min and, strikingly, yields carbene species 9 (Scheme 2). Such chemoselective hydrogenation is uncommon and was only previously observed for alkynes bound to d8 metal centers with a Pt(II)–(µ-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 H2 for quantitative conversion. The carbene complex 9 and the carbene alkene complex 10 display characteristic signals in 13C NMR spectra assigned to the bridging carbene at δ13C = 171.1 and
166.3 ppm and the methylene carbon at $\delta^{13}$C = 35.5 and 36.7 ppm, respectively. The methylene group formed is identified by the two diastereotopic proton signals in the $^1$H NMR spectrum at $\delta^1$H = 2.38, 3.18 and 1.99, 3.03 ppm for 9 and 10, respectively, showing a geminal $J_{\text{HH}}$ coupling of 12.1 and 13.1 Hz. 2D NMR experiments (COSY, HSQC and HMBC) support the structural assignment of complexes 9 and 10; this data is presented in the ESI (Fig. S2–S7†). The bridging nature of the carbene ligand is further characterized by two rather different $J_{\text{CRh}}$ coupling constants for 9 ($J_{\text{CRh}} = 33.9, 11.1$ Hz) and for 10 ($J_{\text{CRh}} = 35.7, 11.2$ Hz), which suggests that the Rh2 center has a closer contact to the carbene carbon than Rh1 (Scheme 2). Results of a single crystal X-ray analysis of 10 are consistent with the proposed structure, although the quality of data for 10 is rather poor (Fig. S6†). The observed $J_{\text{CRh}}$ coupling constants of 33.9 and 35.7 Hz are similar to the earlier reported values for dinuclear rhodium(I) complexes with bridging carbon (Table 2, numbering in the trop ligand is according to Scheme 1). A similar bonding motif was reported with a dinickel(I) core in the solid state. To summarize, complexes 9 and 10 contain a carbene carbon in conjugation with the central double bond of the trop ligand and this allyl-type ensemble is bridging to the Rh(i)-Rh(i) fragment. The ligand sphere of Rh2 in 9 and 10 in solution is likely stabilized by CD$_3$CN.

Furthermore, a characteristic shielding is observed in the $^{31}$P NMR spectra when comparing the trop phosphorus signal at $\delta^{31}$P = 104.6 ppm in the monomeric trflate complex 7 with the respective signals at $\delta^{31}$P = 59.7 and 67.0 ppm in the carbene complex 9 and the carbene alkene complex 10. This change is accompanied by a shift to a smaller $J_{\text{RHP}}$ coupling constant in 9 and 10 ($J_{\text{RHP}} = 127.2$ and 136.0 Hz) as compared to that in 7 ($J_{\text{RHP}} = 183.6$ Hz), indicating a higher trans influence of the Rh2 center in 9 and 10 compared to 7. This suggests weakening of the P-Rh bond that is offset by strengthening of the Rh-Rh bond, attributed to the interaction with the bridging carbene ligand. The latter could also be viewed as a distorted

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

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<th>Nucleus</th>
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<th>$\delta$ (ppm)</th>
<th>$J$ (Hz)</th>
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<td>171.1</td>
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<td>$J_{\text{RHP}} = 185.6$</td>
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<td>$J_{\text{RHP}} = 7.1$</td>
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* No proton showed a significant coupling to Rh2 in the $^1$H-$^{103}$Rh HMOC 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 π accepting alkene. These results indicate that the bimetallic core becomes more electron rich with each hydrogenation step.

Scheme 3  DFT calculations (Gaussian09, ωB97X-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†).
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, deuteration is only incorporated at the double bond (blue hydrogens 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 H₂ and subsequently placed under an atmosphere of D₂. In this case no deuteration 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 to gain access to 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 δ²H = −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 dpdm adduct 8 and the dihydride 11 cleanly reforms 8, indicating a fully reversible hydrogen activation (Fig. S12 and S13†). This is further supported by ESYX spectroscopy, variable temperature NMR and a partially negative line-shape (PNL) of the orthohydrogen 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 (δ¹⁰³Rh2 = −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). ¹H{¹³P} J-resolved 2D NMR spectroscopy reveals the J₁HH and J₂HH coupling constants (Fig. 2c). The two hydrides remain coupled in complex 11, revealed by the J₂HH = 15.4 Hz splitting in the indirect dimension. The hydride at δ²H = −16.2 ppm shows an additional J₁HH = 5.8 Hz coupling to another proton, assigned by COSY to one of the methane protons of the dpdm 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 dpdm adduct 8 activates hydrogen reversibly and is in equilibrium with the dihydride species 11. No semihydrogenation of the triple bond is observed in this case.

Recording the J-resolved spectrum with ³¹P decoupling allows extracting the J₁HH, coupling constants (Fig. 2c). While the hydride at δ²H = −16.3 ppm appears as a doublet of doublets (J₁HH = 20.4, 11.8 Hz), the hydride at δ²H = −20.2 ppm appears as a pseudo-triplet (J₁HH = 11.8 Hz). The observed J₁HH coupling of 15.4 Hz is larger than typically found in traditional cis hydrides formed via oxidative addition (J₁HH = 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 H₁ cis to the intermetallic bond is based on the observation of a remarkable long-range J₁HH coupling of H₄ to a CH₃ proton (J₁HH = 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 J₁HH couplings from both metal centers at once. Therefore, the J₁HH coupling constant could not be accessed with this approach. However, the ¹H–³¹P couplings constant 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 dpdm moiety. This allows distinguishing coupling constants between the hydrides and dpdm/trop phosphorous...
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 dpmp \(^{31}\)P center of \( j_{HH} = 13 \) and 6 Hz, indicating a cis \( j_{HH} \) coupling.\(^{26}\) The second hydrogen atom H\(_{R2}\) 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 dpmp 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\(_{A}\) as the terminal hydride, while H\(_{B}\) 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(n) → Rh(n) polarized bond, due to the bridging nature of H\(_{B}\). 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 dpmp 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.

Interestingly, a bridging hydride resembling that in 11 has been proposed and calculated in both rhodium-based homogeneous bimetallic\(^{26}\) and heterogeneous systems.\(^{26}\) This observation further underlines the utility of low valent homobimetallic complexes with ligands containing alkene and alkyne 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 dpmp 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 complex 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(n) d\(^{6}\) species\(^{28}\) formed by oxidative addition of dihydrogen. PHIP experiment performed under catalytic conditions with the dpmp 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 \((\text{TMS})\text{C}==\text{C})_2\text{tropPPh}_2\) molecule with one phosphine, one alkene, and two alkyne donor sites was designed to allow the synthesis of a new family of low-valent homobimetallic Rh(n)–Rh(n) 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 \((\text{TMS})\text{C}==\text{C})_2\text{tropPPh}_2\) 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 dpmp 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.

Acknowledgements

We gratefully acknowledge financial support of Swiss National Science Foundation. I. V. K. acknowledges the grant from the Russian Science Foundation (19-13-00172) for the support of hydrogenation experiments with parahydrogen. K. V. K thanks SB RAS integrated research program (# 0333-2018-0006/II.1.13) for parahydrogen activation studies and Ministry of Science and Higher Education of the RF (AAAA-A16-116121510087-5) for access to NMR equipment. A. F. thanks the Holcim Stiftung for the Habilitation fellowship.

Notes and references