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Stoichiometric and Catalytic Solid–Gas Reactivity of Rhodium Bis-phosphine Complexes

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Supporting Information

ABSTRACT: The complexes \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)\text{L}_2][\text{BAr}_4]\) \((\text{L}_2 = \text{C}_4\text{H}_6, (\text{C}_2\text{H}_4)_2, (\text{CO})_2; \text{Ar}_4 = 3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2\) have been synthesized by solid–gas reactivity via ligand exchange reactions with, in some cases, crystallinity retained through single-crystal to single-crystal transformations. The solid-state structures of these complexes have been determined, but in only one case \((\text{L}_2 = (\text{NH}_3)_2\) is the cation ordered sufficiently to enable its structural metrics to be determined by single-crystal X-ray diffraction. The onward solid-state reactivity of some of these complexes has been probed. The bis-ammonia complex \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)(\text{NH}_3)_2][\text{BAr}_4]\) undergoes H/D exchange at bound NH3 when exposed to D2. The bis-ethene complex \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)(\text{C}_2\text{H}_4)_2][\text{BAr}_4]\) undergoes a slow dehydrogenative coupling reaction to produce a material containing a 1:1 mixture of the butadiene complex and a postulated mono-ethene complex. The mechanisms of these processes have been probed by DFT calculations on the isolated Rh cations. All the solid materials were tested as heterogeneous catalysts for the hydrogenation of ethene. Complexes with weakly bound ligands (e.g., \(\text{L}_2 = (\text{C}_6\text{H}_6)_2\)) are more active catalysts than those with stronger bound ligands (e.g., \(\text{L} = (\text{CO})_2\)). Surface-passivated crystals, formed through partial reaction with CO, allow for active sites to be probed, either on the surface or the interior of the single crystal.

1. INTRODUCTION

While the study of organometallic complexes in the solution phase is widely explored, 1 investigation of their solid-state reactivity is less well-developed. 2–7 Potential advantages of reactivity in the solid-state lead from the constrained local environment that may influence selectivity and the lack of possibly deleterious solvent interactions. Indeed, for the isolation of highly reactive organometallic species, the solid state might be considered as the “perfect solvent” in that it offers a potentially noncoordinating environment. Demonstrating these advantages, we have recently reported the synthesis of σ-alkane complexes by a solid–gas route, e.g., \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)(\text{NBA})][\text{BAr}_4]\) \((\text{L}_2 = (\text{NH}_3)_2\) in which a saturated norbornane (NBA) fragment coordinates with the metal center through two 3-center 2-electron interactions. 8,9 Complex 2 was generated in situ in a single-crystal to single-crystal (SC–SC) transformation by simple addition of H2 to a crystalline norbornadiene (NBD) precursor, \([\text{Rh}(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)(\text{NBD})][\text{BAr}_4]\) \((\text{L}_2 = (\text{NH}_3)_2\) Scheme 1. Solid–Gas Reaction to Form a σ-Alkane Complex, and the Eventual, Anion-Bound, Thermodynamic Product (S.S. = Solid-State; SC–SC = Single-Crystal to Single-Crystal)

4% change in unit-cell volume, although some examples report larger changes.19–21

For the transformation of complex 1 to 2, that retains crystallinity and only has a 1.5% change in unit-cell volume, we postulated that packing in the lattice is dominated by bulky \([\text{BAr}_4]\) anions which also form a defined octahedral cavity around 1 that is retained almost exactly in 2. The anions thus have a dual role to play by defining the lattice and also allowing for structural change in the organometallic cation (i.e., NBD to NBA). Complex 2 is unstable at room temperature in the solid state, eventually forming the zwitterion \([\text{Rh}-

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ligands butadiene, ethene, CO, and NH3 to form the contribution, we detail such reactivity with the exogenous comparison to the \( \text{1H NMR} \) signals of free 1,3-C\(_4\)H\(_6\) (depling) and catalysis (hydrogenation of ethene) in these well-defined solid materials.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Butadiene and Bis-ethene Complexes. The addition of 1,3-butadiene gas (\( \sim 4 \text{ atm} \)) to freshly prepared crystalline 2 results in the rapid (\( \sim 1 \text{ min} \)) formation of the dark-red/purple butadiene complex \([\text{Rh}-(\text{BuPCH}_2\text{CH}_2\text{PBu}_2)(\eta^6-\text{C}_6\text{H}_4\text{F}_2)][\text{BAr}_6^\text{F}_4] \), 4, with the concomitant release of one equivalent of NBA (Scheme 2) as measured by \(^1\text{H} \) NMR spectroscopy in CH\(_2\)Cl\(_2\) solution. Complex 4 also forms as an amorphous solid, i.e., this process is not a SC–SC transformation but can be conveniently recrystallized from 1,2-C\(_6\)H\(_4\)F\(_2\)/pentane, affording analytically pure material. Complex 4 can also be formed directly by solution routes by the addition of 1,3-butadiene gas to a 1,2-C\(_6\)H\(_4\)F\(_2\) solution of \([\text{Rh}-(\text{BuPCH}_2\text{CH}_2\text{PBu}_2)(\eta^6-1,2-\text{C}_6\text{H}_4\text{F}_2)][\text{BAr}_6^\text{F}_4] \), 5. The solution \(^1\text{H} \) NMR spectrum (CD\(_2\)Cl\(_2\)) of 4 prepared by either route reveals three peaks of equal integration (\( \delta 2.85, 4.27 \) and 5.44; 2H each) attributed to the diene, which occur upfield in comparison to the \(^1\text{H} \) NMR signals of free 1,3-C\(_6\)H\(_4\) (\( \delta \) (CCl\(_4\)) 5.03, 5.14, and 6.27), \(^2\) consistent with coordination to a metal center. The solution \(^{31}\text{P} \)\(^1\text{H} \) NMR spectrum shows a doublet (\( \delta 54.6 \), \( J_{\text{RhP}} = 170 \text{ Hz} \)). These data are similar to those reported for the closely related analogue \([\text{Rh}-(\text{PrPCH}_2\text{CH}_2\text{CH}_2\text{PPr}_2)(\eta^5-\text{C}_6\text{H}_4\text{H}_2)][\text{CF}_3\text{SO}_3] \). The solid-state \(^{31}\text{P} \)\(^1\text{H} \) NMR spectrum shows a number of environments (i.e., more than 2), consistent with a disordered cation (vide infra and Supporting Information).

Addition of ethene gas to crystalline 2 forms a red, oily product assigned to the bis-ethene adduct \([\text{Rh}-(\text{BuPCH}_2\text{CH}_2\text{PBu}_2)(\eta^5-\text{C}_6\text{H}_4\text{H}_2)][\text{BAr}_6^\text{F}_4] \), 6, and free NBA as measured by solution NMR spectroscopy (Scheme 3). Analytically pure 6 can be generated by recrystallization from CH\(_2\)Cl\(_2\)/pentane while under 1 atm of ethene. Complex 6 is not stable at room temperature in solution in the absence of an ethene atmosphere. For example, in CH\(_2\)Cl\(_2\) solution, decomposition to 3 occurs, whereas in 1,2-C\(_6\)H\(_4\)F\(_2\) complex 5 forms, making solution-based routes less than ideal. By contrast, solid 6 does not lose ethene even when placed under a vacuum, as indicated by elemental microanalysis of a crystalline sample. That 6 is stable to vacuum in the solid-state suggests that ethene loss might proceed via an associative mechanism within the crystal and not by loss of ethene followed by coordination of an exogenous ligand. Similar observations have been made previously for the substitution of a dinitrogen ligand at a \( \langle \text{Ir}(\text{POCOP}) \rangle \) fragment in the solid-state \([\text{POCOP} = 2,6\text{-bis(di-tert-butylphosphinoo})\text{benzene}] \). The \(^1\text{H} \) NMR spectrum of complex 6 at 240 K in CD\(_2\)Cl\(_2\) reveals a sharp signal assigned to coordinated ethene (\( \delta 3.98, \) \( f_{\text{whm}} = 7 \text{ Hz} \), relative integral 8 H), \(^3\) while the \(^{31}\text{P} \)\(^1\text{H} \) NMR spectrum at 240 K shows a doublet signal (\( \delta 54.7, \) \( J_{\text{RhP}} = 144 \text{ Hz} \)). At room temperature under four atmospheres of ethene, the \(^1\text{H} \) NMR spectrum shows a broad signal assigned to free ethene (\( \delta 5.31, \) \( f_{\text{whm}} = 49 \text{ Hz} \)), with no separate peak observed for coordinated ethene, suggesting rapid exchange between coordinated and free ethene in solution. The \(^{31}\text{P} \)\(^1\text{H} \) NMR spectrum displays a singlet (vide infra).

2.2. Synthesis of a Bis-carbonyl Complex by a Gas–Solid Reaction. Complexes such as 4 and 6 present ideal opportunities for solid-state reactivity, as the alkene ligands are likely to be relatively labile. Reaction with hydrogen in the solid state rapidly (less than 1 min) releases butane/ethane (observed by \(^1\text{H} \) gas-phase NMR spectroscopy, see Supporting Information) with the concomitant formation of amorphous 3 as determined by \(^{31}\text{P} \)\(^1\text{H} \) SSNMR spectroscopy, Scheme 4.

Presumably, the first formed alkane is lost from the metal center to result in \([\text{Rh}(\text{BuPCH}_2\text{CH}_2\text{PBu}_2)]^+\) coordinated with the \([\text{BAr}_6^\text{F}_4]^-\) anion, with the associated large structural change leading to the loss of crystallinity. By contrast, addition of CO gas (1 atm) to solid 4 or 6 forms bright yellow \([\text{Rh}(\text{BuPCH}_2\text{CH}_2\text{PBu}_2)(\text{CO})_2][\text{BAr}_6^\text{F}_4] \), 7, with release of 1,3-butadiene or ethene into the head-space of the reaction vessel (a sealed NMR tube) and no loss of crystallinity (Figure 1). Complex 7 can also be produced by addition of CO gas to 5 in solution (1,2-C\(_6\)H\(_4\)F\(_2\)). The solution \(^{31}\text{P} \)\(^1\text{H} \) NMR spectrum of 7 shows a single resonance (\( \delta 56.1, \) \( J_{\text{RhP}} = 116 \text{ Hz} \)). The \(^{31}\text{P} \)\(^1\text{H} \) SSNMR spectrum also shows one environment, which is consistent with its solid-state structure (vide infra). The CO stretching frequencies in the IR spectra of 7 shows the anticipated two CO stretching bands (CH\(_2\)Cl\(_2\), 2093.4 and 2049.1 cm\(^{-1}\); ATR InfraRed, 2099.0 and 2065.9 cm\(^{-1}\)). These data are similar to closely related cationic Rh bis-

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**Scheme 3. Formation of Complex 6 in the Solid-State and the Decomposition Reactions That Occur in Solution When Excess Ethene Is Not Present**

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**Scheme 4. Addition of H\(_2\) to Complexes 4 or 6**

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**Scheme 2. Synthesis of Complex 4 by Solid-State and Solution Routes**

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2.3. Synthesis of a Bis-ammonia Complex. Addition of ammonia gas to freshly prepared 4, in the solid state, results in the formation of bis-ammonia complex [Rh-(Bu₂PCH₂CH₂PBu₂)(NH₃)][BARF₄], 8, alongside free NBA (Scheme 5). Crystallinity is lost in this reaction. Complex 8 can be recrystallized from 1,2-C₆H₄F₆/pentane solutions to afford crystals that were suitable for X-ray diffraction. To avoid traces of 3 in the final product, the direct addition of a mixture of NH₃ and H₂ to crystalline 1 was found to be the most effective way of synthesizing 8. Ammonia complexes similar to 8 have been previously reported, in particular the closely related [Rh(dppe)(NH₃)]⁺ [28]. Solution methods using 1,2-C₆H₄F₆ solvent were unsuccessful for the synthesis of 8 with decomposition to unidentified species occurring, even though complex 8 is stable in 1,2-C₆H₄F₆ solvent once formed by the solid-state route. Complex 8 can also be synthesized by the relatively rapid reaction (1 h) of solid 4 with NH₃ gas (with release of butadiene gas). Neither of these routes are SC reactions, with the product forming as an amorphous solid, in contrast to the analogous reaction of 4 with CO. The 3¹P{¹H} NMR spectrum of 8 solvated in 1,2-C₆H₄F₆ displays a doublet (δ 65.5, Jₚ=177 Hz), similar to [Rh(dppe)(NH₃)]⁺ [28]. The ¹H NMR spectrum of 8 contains a sharp peak at δ 1.93 (relative integral 6 H) assigned to the coordinated ammine ligands. The proton chemical shift of ammine ligands is dependent upon hydrogen-bonding interactions with solvent or anion, and in the case of 8 with a weakly coordinating anion in the weakly coordinating 1,2-C₆H₄F₆ solvent, the chemical shift observed is upfield of other reported values in similar complexes. Complex 8 does not react with ethene in the solid state but does react with D₂, undergoing H/D exchange at the NH₃ ligand (Section 2.5).

2.4. Solid-State Structures. Single crystals of 4, 6, 7, and 8 were prepared by solution recrystallization (see Supporting Information). For complexes 4, 6, and 7, all three structures show significant disorder of the cation, which sits within an octahedral environment described by six, well-refined, [BARF₄]⁻ anions. The cations in these structures were refined by use of similarity restraints to model the disorder components. In the case of complex 6, the cation is disordered over two positions (~2:1 occupancy ratio) in which the corresponding two RhP₃ planes lie approximately perpendicular to each other (angle between planes 81°), and only the heavy atom positions (Rh and P) could be reliably resolved. The cation of 7 is also disordered over two positions (1:1 occupancy ratio), adopting a structure in which one cation is inverted relative to the other, and the RhP₃ planes are again perpendicular to each other. Each cation straddles a crystallographic mirror plane, and so the CO ligands in each cation are crystallographically equivalent. Figures 2A and B show this in detail. For 4, refinement reveals four cation positions overlaid, with one rotated, one inverted, and one rotated and inverted relative to the original. These structures demonstrate the impact of rigid bulky anions upon relatively small cations: the anions dominate the packing structure and the cations may lie in a variety of thermodynamically advantageous conformations.
often between N–H and an oxygen atom, and N⋯O distances vary from 2.84 to 3.19 Å (H⋯O, 2.00–2.37 Å). The change in anion packing structure to accommodate N–H⋯F hydrogen bonds could also cause the loss of crystallinity upon transition from 4 to 8. These hydrogen bonds also result in a cation that is not disordered, in contrast to, for example, 6, in which the ethene ligands cannot engage in such interactions.

2.5. H/D Exchange in Complex 8. Microcrystalline samples of 8 react with D₂ in the solid state (48 h), or in 1,2-C₆H₄F₂ solution (24 h), to form d₄-8 with H/D exchange occurring exclusively at the ammine ligands (Scheme 6). When dissolved in 1,2-C₆H₄F₂, the ¹H NMR spectrum of d₄-8 reveals that the proto ammine signal observed for 8 (δ 1.93) is absent, while the ²H NMR spectra contains a signal corresponding to the ND₃ ligands (δ 1.94). No signals indicating H/D exchange at the phosphine ligands were observed. No degradation of the crystal was observed during this process, as confirmed by X-ray crystallography. H/D exchange of bound ammonia has been previously reported in solution and, most recently, within frozen argon matrices using Ir(Cp*)₂H₂(NH₃)₄⁺ cation, with added H₂. The most accessible computed pathway is outlined in Figure 4, which shows free energies computed both in vacuo and corrected for 1,2-C₆H₄Cl₂ solvent (this being used in the absence of data for 1,2-C₆H₄F₂). Initial H₂ oxidative addition in solution proceeds with a computed barrier of 18.7 kcal/mol to give a RhIII dihydride, B (Gᵦₕ = +3.3 kcal/mol). The NH₃ ligand trans to hydride in B is labilized by X-ray crystallography and so readily dissociates with a barrier of only 13.0 kcal/mol to give an isomer C (Gᵦₕ = +9.8 kcal/mol) in which it now H-bonds to the remaining ammine ligand. Rh–H/N–H exchange then proceeds through TS(C–D) at +22.8 kcal/mol, in which the outer-sphere NH₃ deprotonates the axial hydride (Rh–H¹ = 2.31 Å; N²–H¹ = 1.08 Å) while simultaneously transferring a proton onto the equatorial hydride (H²–H¹ = 1.54 Å; N²–H¹ = 1.08 Å).

Figure 4 shows the overall computed barrier for H/H exchange between cation A and H₂ is 22.8 kcal/mol, and it is apparent that the solvent correction reduces the barrier compared to the result in vacuo (ΔG° vac = 26.5 kcal/mol). This suggests increased charge separation in TS(A–D) compared to A, consistent with the involvement of a near-intact NH₄⁺ cation in the former. Experimentally, H/D exchange occurs more rapidly in solution than in the solid state. While we have not attempted to model the solid-state environment here, the proximity of several fluorinated anions may produce a similar environment to that in solution, with a resultant reduction in barrier height. Alternative mechanisms for H/D exchange were also considered, including those based on initial oxidative addition of ammonia or heterolytic.

Scheme 6. H/D Exchange upon Ammine Ligands in Solution or the Solid State

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cleavage of H₂ over a Rh–NH₃ bond. These were both disfavored, however, the former entailing a barrier of 27.6 kcal/mol, while for the latter no intermediate incorporating an NH₄⁺ cation could be located. Full details of these alternative pathways are given in the Supporting Information (see Figures S14–S17).

2.6. Solid–State Ethene Dehydrocoupling. Over a number of weeks at 298 K, orange/red single crystals of freshly prepared 6 change to a darker red/purple, becoming similar in color to freshly prepared complex 4. When this material is dissolved in 1,2-C₆H₄F₂ solvent complex 4 is indeed observed in the ³¹P{¹H} NMR spectrum, alongside the difluorobenzene adduct 5 (confirmed by ESI-MS). Complex 5 forms on dissolving 6 in 1,2-C₆H₄F₂ solvent (vide supra) and is thus a marker for this unstable bis-ethene complex or closely related complexes (Scheme 7). The transformation of 6 to 4 is formally a dehydrocoupling of ethene. This transformation in the solid state was initially monitored over time by periodic sampling via dissolution in 1,2-C₆H₄F₂ of a solid sample kept at 298 K. This showed a gradual increase in the proportion of complex 4 present and a decrease in 5, with 40% conversion after 7 weeks (Figure 5). A sample kept for four months revealed ~50% conversion to 4, this likely representing an upper limit for conversion. Interestingly, crystallinity is retained during this process, which further suggests the sacrificial 6 does not lose ethene completely, as the resulting 12-electron fragment would likely form amorphous-3 (Section 2.1). We suggest the formation of a 14-electron, 3-coordinate species [Rh-(iBu₂PCH₂CH₂PiBu₂)(η₂-C₂H₄)][BArF₄], 9, in which only one ethene ligand is retained (Scheme 7) to account for the production of ethane. This species could be stabilized by an agostic interaction from the iPr groups, or by an interaction with the CF₃ groups from proximate anions in the lattice, and would likely form 5 on dissolution in 1,2-C₆H₄F₂. Budzelaar and co-workers have previously reported a related three-coordinate rhodium complex with a bidentate β-dimine ligand and one alkene ligand. Evidence for the formation of complex 9 comes from solvation (at 200 K, CD₂Cl₂) of a solid-sample sample of 6 that has been aged for two months. The ³¹P{¹H} NMR spectrum recorded at this temperature reveals 4 to be the major product but less than 50% of the total integral, alongside signals for starting material 6 and its solution decomposition product 3. Two new signals are also observed, liberating one equivalent of hydrogen, which would then react with unreacted 6 to produce ethane gas (i.e., Scheme 4). It thus appears 6 converts to 4, accompanied by sacrificial hydrogenation of one equivalent of ethene from a second molecule of 6, also accounting for the apparent 50% maximum reaction conversion. Interestingly, crystallinity is retained during this process, which further suggests the sacrificial 6 does not lose ethene completely, as the resulting 12-electron fragment would likely form amorphous-3 (Section 2.1). We suggest the formation of a 14-electron, 3-coordinate species [Rh-(iBu₂PCH₂CH₂PiBu₂)(η₂-C₂H₄)][BArF₄], 9, in which only one ethene ligand is retained (Scheme 7) to account for the production of ethane. This species could be stabilized by an agostic interaction from the iPr groups, or by an interaction with the CF₃ groups from proximate anions in the lattice, and would likely form 5 on dissolution in 1,2-C₆H₄F₂. Budzelaar and co-workers have previously reported a related three-coordinate rhodium complex with a bidentate β-dimine ligand and one alkene ligand. Evidence for the formation of complex 9 comes from solvation (at 200 K, CD₂Cl₂) of a solid-sample sample of 6 that has been aged for two months. The ³¹P{¹H} NMR spectrum recorded at this temperature reveals 4 to be the major product but less than 50% of the total integral, alongside signals for starting material 6 and its solution decomposition product 3. Two new signals are also observed,
which are assigned to complex 9, which couple to each other ($^{31}$P--$^{31}$P COSY experiment at 200 K), at δ 47.0 ($J_{RhP} = 162$ Hz, $J_{PP} = 28$ Hz); δ 71.4 ($J_{RhP} = 186$ Hz, $J_{PP} = 28$ Hz), Figure 6.

Figure 6. Low temperature $^{31}$P{[H]} NMR spectrum (CD$_2$Cl$_2$, 200 K) of a solid sample of 6 that has been aged for 2 months.

One signal has a considerably larger $J_{RhP}$ coupling constant, suggesting a weakly-bound trans-ligand (solvent or agostic interaction). On warming to 250 K, complex 3 grows in at the expense of complex 9.

SSNMR spectroscopy was also used to follow the solid-state transformation of 6 in situ. The $^{13}$C{[H]} and $^{31}$P{[H]} SSNMR spectra of freshly prepared complexes 4 and 6 were initially collected, and in keeping with their highly disordered solid-state structures, these spectra revealed multiple peaks for the signals related to the cation. For example, the $^{31}$P{[H]} SSNMR spectrum of 4 shows a variety of closely spaced broad peaks, while that of 6 displays at least three broad phosphorus environments in the solid state, Figure 7. The $^{13}$C{[H]} SSNMR spectra of 4 and 6 also show multiple peaks for the butadiene and ethene environments in their respective spectra, between 60–100 ppm. Monitoring a sample of 6 over the course of 6 weeks revealed the formation of complex 4 in both the $^{31}$P{[H]} and $^{13}$C{[H]} NMR spectra. In addition, a new signal (δ 82.4) slightly downfield to the ethene resonances in 6 was also observed in the $^{13}$C{[H]} NMR spectrum, while the $^{31}$P{[H]} SSNMR spectra show additional broad signals centered at δ 77 (Figure 7D). These signals are assigned to [Rh–]

Figure 7. SSNMR spectra ($^{13}$C{[H]} left, $^{31}$P{[H]} right) displaying the transformation of 6 over time (A–D) followed by the reaction of the products with ethene gas (E) at 298 K and a comparison with a pure sample of 6 (F).

The dehydrocoupling of ethene at rhodium centers has been previously observed and mechanisms based on initial oxidative coupling or C–H bond activation have been proposed. Such processes are also related to alkene oligomerization reactions. Interestingly, the complex RhTp*($C_2H_4$)$_2$ [Tp* = tris(3,5-dimethyl-1-pyrazol-1-yl)hydroborate] undergoes dehydrocoupling to give a butadiene complex in solution (with the concomitant release of ethene), but in the solid state, a hydrido-allyl species is formed.

DFT calculations on isolated cations were again used to assess these different mechanistic possibilities and our favored pathway is outlined in Figure 8A. Starting from E,

Figure 8. Free energy profiles (kcal/mol) for (A) the dehydrocoupling of ethene in [($Bu_2$P$CH_2$CH$_2$P$Bu_2$)($C_2H_4$)$_2$][Tp*][BArF$_4$], E, and (B) hydrogenation of E. Several processes involve more than one step and these are indicated with a double arrow, and only the energy of the highest lying transition state between the two key minima is indicated. Full details of these and alternative mechanisms are available in the Supporting Information (see Figure S18–S24).

[($Bu_2$P$CH_2$CH$_2$P$Bu_2$)Rh($C_2H_4$)$_2$]$^+$ (i.e., the cation of 6), oxidative coupling of ethene occurs with a barrier of 22.9 kcal/mol to give intermediate F (+10.8 kcal/mol). F exhibits a seesaw structure for which there are precedents with isoelectronic d$^8$ Ru(II) and Ir(III) centers. Further β-H transfer then generates G from which facile C–H reductive coupling yields 1-butene complex H (~8.1 kcal/mol). Rearrangement and γ-H transfer then leads to hydrido-methylallyl intermediate...
I at −11.6 kcal/mol. It features a weak Rh⋯H⋯C agostic interaction and so could undergo H-transfer to form a trans dihydride intermediate (an isomer of J, see below, and Supporting Information, Figure S20). Instead a lower energy process involving facile rearrangement of the methylallyl ligand places the agostic cis to the hydride in isomer I’ (−6.2 kcal/mol) from which H-transfer then gives J with cis hydrides and a cis η⁶-C₄H₆ ligand. Dehydrocoupling is then completed via reductive elimination of H₂ to give K (the cation of 4) at −3.7 kcal/mol.

Figure 8A shows the formation of I is thermodynamically favored over K, and so the facile, exergonic hydrogenation of E to N (modeling the cation of species 9 postulated experimentally) is required to drive the dehydrocoupling to completion (see Figure 8B: overall barrier = 13.8 kcal/mol; ΔG = −16.0 kcal/mol). The optimized structure of N features an agostic interaction between the Rh center and one of the ‘Bu methyl groups (see Supporting Information, Figure S11). The barrier energy span of the dehydrocoupling profile (corresponding to I to TS(M-N)) is 25.4 kcal/mol, a value that is consistent with a slow dehydrocoupling process. The intermediacy of H is also consistent with the observation of 2-butene formed (after isomerization) in the presence of excess ethene.

Alternative dehydrocoupling mechanisms based on initial C–H activation to hydrido-alkenyl intermediates were also assessed. The C–H activation step (ΔG° = 24.1 kcal/mol; ΔG = +19.3 kcal/mol) proved only slightly less accessible than the oxidative coupling; however, the onward reaction, either via ethene insertion into the Rh–alkenyl bond or insertion into the Rh–H bond involved transition states at 31.7 or 31.0 kcal/mol. Thus, these pathways have considerably higher barriers than the process based on oxidative coupling in Figure 8A. Full details of all alternative pathways are provided in the Supporting Information.

2.7. Solid-State Catalysis: Hydrogenation of Ethene. The complexes 1–8 were tested as solid-state catalysts for the hydrogenation of ethene. Such solid–gas reactivity has been reported before for organometallic catalysts in the solid state. Gas-phase NMR spectroscopy was used to measure the hydrogenation of ethene in situ by the conversion of ethene to ethane. T₁ relaxation times for ethane and ethene in the gas phase were found to be similar for both species (ca. 0.6 s), as were their relative integrals with different acquisition delay times, suggesting that the relative integration of the two signals in to the gas-phase species is reliable. In a typical experiment, a high pressure NMR tube was loaded with (3 ± 0.3 mg) (e.g., 2.2 × 10⁻³ mmol for 1) of solid catalyst, and to this 1 atm (~0.08 mmol) of ethene was added followed by ~4 atm (~0.31 mmol) of H₂. The progress of the reaction was monitored directly by integration of the gas-phase ¹H NMR spectra at 298 K.

Under these conditions of excess hydrogen, precatalysts containing alkene ligands (1, 4, and 6) all catalyze the reaction rapidly; for example, 1 requires less than 2 min to effect complete conversion (Figure 9). At the end of catalysis, when the ethene is fully consumed and hydrogen is still in excess, complex 3 is observed to be formed as characterized by ³¹P{¹H} NMR spectra in CD₂Cl₂ solution, as there is no exogenous ligand to stabilize the metal center, consistent with the stoichiometric studies (section 2.1). This zwitterionic complex 3 is a very slow catalyst itself, only turning over ~5% after 25 min, suggesting that dissociation, or η⁶- to η⁷-ring slippage, of the anion to reveal a vacant site is a disfavored process in the solid state. This is a solid-state phenomenon, as in CH₂Cl₂ solution under an atmosphere of ethene 3 forms 6, and hydrogenation of the bound alkene is then rapid (upon mixing). This also suggests that the resting state during catalysis in the solid state when using precatalysts such as 1 is unlikely to be 3. Complex 7 is a very slow catalyst, showing essentially no turnover after 30 min, presumably as the carbonyl ligands are strongly bound. Complex 8 does show some activity (15% conversion after 30 min), perhaps suggesting that the ammine ligands are somewhat labile, consistent with the computational studies. In both of these cases, the organometallic species observed after completion of catalysis to the detection limit of solution ³¹P{¹H} NMR spectroscopy is the same as the starting material, i.e., unchanged 7 and 8. Interestingly, for precatalysts 2, 5, and 6, the rate of hydrogenation, which is at first rapid, drops after around 2 min. This similar slower rate for all may be indicative of transformation of any surface organometallic species into a common species (possibly related to 3) that turns over slowly. Also noteworthy is that this simple hydrogenation reaction occurs rapidly at ambient temperature (~5 atm total pressure), while previous reports of the catalytic hydrogenation of ethene using solid-state organometallic catalysts typically require longer time scales and/or higher temperatures (albeit with lower pressure reaction conditions). As the surface area of a solid catalyst is likely to be important for the rate of catalysis, microcrystalline 1 was ground and separated into different particle size fractions using microsieves to give the following particle size regimes: less than 50 μm, 50–71 μm, and 71–150 μm. These materials were then subjected to catalytic hydrogenation of ethene using the standard conditions previously defined (i.e., 3.0 ± 0.3 mg of catalyst). Figure 10 shows that all the different size particles rapidly hydrogenate ethene with broadly similar temporal profiles over the first 10 min, promoting between 75 and 90% conversion. After a much longer time (16 h), all reached 100% conversion but at a much slower rate. Interestingly, the smaller particle sized catalysts appear to operate slightly faster as an ensemble, suggesting that the surfaces of the crystals are particularly active compared to the interior, or that smaller particle sizes allow for more rapid hydrogenation of the precatalyst. An alternative explanation is that the larger particle sizes of catalyst become deactivated sooner as there are relatively fewer active sites. As it might well be that all these factors are operating, possibly with a different temporal dependence depending on crystal size, and
given the differences are relatively small, we are reluctant to speculate further with the current data.

2.8. Solid-State Catalysis: Passivation Studies. The data presented in the previous section suggest that catalysis might occur fastest upon the surface sites of the organometallic crystals. However, it is also likely that the metal centers located inside the interior of the crystal could be active by gas diffusion through the crystalline lattice. To probe this, we used CO-Passivated-4, an approach encouraged by the passivation techniques used by Brookhart and co-workers in studying alkene hydrogenation using [Ir(POCOP)(H)2] systems. As complex 7 essentially does not catalyze the hydrogenation of ethene, while 4 catalyzes the reaction rapidly (Figure 9), the CO-Passivated-4 probes the ability of these interior metal sites to take part in catalysis. However, as complex 4 reacts with H2 in the absence of ethene to, deleteriously, form 3, in order to maintain single crystallinity, and thus the surface passivation of CO-Passivated-4, ethene is kept in excess with H2 in the limiting substrate in previous to previously discussed catalysis in which hydrogen is in excess.

To baseline studies, complexes 4 and 7 were subjected to these conditions of catalysis in which hydrogen is the limiting substrate. A high pressure NMR tube containing (3 ± 0.3) mg of crystalline catalyst 7 was evacuated and refilled with ~1 atm of ethene and ~0.3 atm of H2. As expected, single crystals of complex 7 are very poor catalysts for the hydrogenation of ethene under these conditions and only 3% conversion occurs within 1 h and little further progress is observed over the next 24 h (Figure 11). By contrast, single crystals of 4 hydrogenate ethene, until all hydrogen is consumed, in only ~9 min (i.e., 29% of ethene hydrogenated). These crystals retain their crystallinity and their ability to rotate polarized light. A second amount of hydrogen added at 1 atm (Figure 11). After catalysis, the crystals appear intact and in good condition without significant cracking or change. A small trace of butane was observed in the gas phase 3H NMR spectrum (~1% relative to the ethene signal), suggesting that a small proportion of the interior sites of 4 have been hydrogenated. A second amount of hydrogen can be subsequently added, and catalysis restarts. Low temperature 31P{1H} NMR spectroscopic analysis (220 K, CD2Cl2) of these crystals postcatalysis resolved only 4 and 7 to be present. This much slower rate of catalysis suggests that catalysis is mainly a surface process in these systems. However, that catalysis still does occur suggests that there is some penetration of ethene and hydrogen to access active interior sites of a crystal. These sites must be particularly active as no significant spectroscopic markers for their formation, i.e., 6 or 3 are observed. We cannot discount the possibility of crystal microcracking occurring (due to reaction with hydrogen and formation of 3), which may expose the interior of the crystals. Unfortunately, the remarkable selective hydrogenation of ethene in the presence of propene, demonstrated by Brookhart and co-workers using passivated single crystals, was not able to be reproduced with crystals of CO-Passivated-4. Using a mixture of ethene, butene, and hydrogen (approximate 2:2:1 ratio), an approximately equal ratio of butane and ethene was produced in each case with crystalline catalysts of 4, CO-Passivated-4, and 7, although the reaction rates varied dramatically as expected (4 > CO-Passivated-4 > 7).

3. CONCLUSIONS

A number of solid-state reactions of well-defined organometallic complexes with gases are reported based upon the fragment [Rh(Bu3PCH2CH2PPh3)2][BAR4]. In particular, we have shown that the σ-alkane complex 2 is a useful synthon for such solid-state synthesis, acting via a labile alkane ligand. This allows for the addition of gases such as ammonia and ethene to form the corresponding adducts, some of which, for example with ethene or NH3, are not readily accessible via solution techniques. The corresponding butadiene complex, 4, acts in a similar way by loss of alkene. Crystallinity may be maintained during some of these solid–gas ligand exchange reactions, when the crystal packing geometry remains similar in the starting materials and products (e.g., the displacement of ethene or butadiene ligands by CO). The crystal packing environments, which incorporate large [BAR4]− anions that compared with the 10 min for 4 (Figure 11).
provide a pseudo octahedral cavity in which the cations reside, can thus allow for subtle rearrangements in the solid state without disruption of the crystallinity or onward reactivity with the metal cation, as we have noted previously. In the solid state, these complexes can be used as precatalysts for the hydrogenation of ethene, show H/D exchange at bound NH2 ligands, and promote ethene dehydrocoupling. Mechanisms for these last two processes are proposed on the basis of DFT calculations using molecular model systems, and modeling such reactivity in the solid state is the focus of current work. For catalysis, particle size and surface passivation experiments suggest that species on the surface act as the most active sites for catalysis rather than within the crystal. These observations encourage the use of solid-state organometallic chemistry in both synthesis and catalysis. Of course, in the latter, the identification of the actual active species/sites will likely be challenging as these might only represent a relatively small proportion of the bulk crystal.

4. EXPERIMENTAL SECTION

4.1. General Details. All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk-line and glovebox techniques. Glassware was oven-dried at 403 K and flushed and flamed under vacuum prior to use. CH2Cl2, Et2O, and pentane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. CDCl3 and 1,2-C6H4F2 were distilled under vacuum and upon warming a color change to a dark-red/purple solution from CaH2 and stored over 3 Å molecular sieves. Complexes referencing is with respect to external neat tetramethylsilane for 13C values). SSNMR spectra were recorded on a Bruker Avance 3HD (EPSRC National SSNMR Service, Durham University), using the delay 1-2 s, with Spinal 64 or TPPM decoupling. A magic-angle spinning rate of 5 kHz was used. The decoupled proton spectra were recorded using a Bruker MicroTof, with iD3 ATR and iD1 transparency attachments. Electrospray ionization mass spectrometry was recorded using a Bruker MicroTOF QUltra mass spectrometer.

4.2. Synthesis of [Rh(iBu2PCH2CH2PiBu2)(NH3)2][BArF4] (6). First, 26 mg (0.019 mmol) of solid [Rh(iBu2PCH2CH2PiBu2)(η4-C6H4)][BArF4] (1) was placed in a crystallization tube with a Young tap and exposed to hydrogen (1 atm) for 10 min to form [Rh(iBu2PCH2CH2PiBu2)(η4-C6H4)][BArF4] (2). Then the flask was evacuated, and ethene (1 atm) was immediately added. With the flask under a pressure of ethene, CH2Cl2 was added by syringe to form a layer over the CH2Cl2, and the flask was sealed under 1 atm of ethene. Orange/red crystals formed over 48 h, which could be isolated and appear vacuum stable (25% yield). The complex is not stable in solution (or when suspended in pentane) at room temperature in the absence of an ethene atmosphere, as decomposition to 3 occurs. Anal. Calc. for C64H34BF24P2Rh: C, 48.38; H, 4.51. 1H NMR (500 MHz CD2Cl2 240 K): δ 0.86 [δ (iBu CH3), 12H], 1.03 [δ (Bu CH3), 12H], 1.5-2.0 [δ (Bu CH2, CH2, and CH3]), 16H], 7.29 [δ (C6H4), 16H], 7.73 [δ (CH3), 4H], 17.1 [δ (BArF4), 4C]. 31P{1H} NMR (202 MHz CD2Cl2 101 MHz): δ 22.7-36.2 [δ (Bu CH3), CH2, and PCH2CH2P), 16H], 3.98 [δ (C2H4), 8H], 7.53 [δ (BArF4), 8C], 124.6 [δ (BArF4), 8C], 130.3 [δ (BArF4), 8C], 133.6-134.6 [δ (BArF4), 4C], 163.8 [δ (BArF4), 4C]. See Supporting Information for crystallographic studies.

4.3. Synthesis of [Rh(iBu2PCH2CH2PiBu2)(NH3)2][BArF4] (6). Alternatively, addition of CO gas (1 atm) to a single crystalline solution route. A 3 mmol of solid [Rh(iBu2PCH2CH2PiBu2)(NH3)2][BArF4] (2) was degassed and placed under 1 atm NH3 gas. The flask was degassed and placed under 1 atm NH3 gas. The flask was then frozen in a liquid N2 bath and opened to 1 atm pressure of H2 while at low temperature.

4.4. Synthesis of [Rh(iBu2PCH2CH2PiBu2)(CO)][BArF4] (7). [Rh(iBu2PCH2CH2PiBu2)(η4-C6H4)][BArF4] (5) (30 mg, 0.022 mmol) was dissolved in CH2Cl2 and the solution frozen and placed under vacuum. CO gas was used to refill the flask, and upon warming, a slight color change from yellow/orange to bright-yellow occurred, and the flask was left sealed for 2 h. The solution was then degassed and crystallized by adding pentane (23 mg, 80% yield). Bright-yellow crystalline material formed. Anal. Calc. for C26H2OP2F8Rh: C, 46.59; H, 3.91. Found: C, 46.67; H, 3.82. ESI-MS [M+] calcd = 477.16, found [M+] m/z = 477.16. IR spectroscopy (CH2Cl2 solution): CO stretches 2093.4 and 2049.1 cm−1 (solid-state) CO stretches 2099.0 and 2056.9 cm−1. 1H NMR (300 MHz CD2Cl2): δ 0.12 [δ (Bu CH3), 12H], 1.16 [δ (Bu CH3), 12H], 1.89 [δ (Bu CH3), 4H], 1.96 [δ (Bu CH3), 4H], 2.10 [δ (PCH2CH2PiBu2), 18H], 5.77 [δ (BArF4), 4H], 7.72 [δ (BArF4), 8H]. 31P{1H} NMR (120 MHz CD2Cl2): δ 56.10 [δ (BArF4), 4C]. 31P{1H} SSNMR (161 MHz): δ 54.1 [δ (BArF4), 4C]. Alternatively, addition of CO gas (1 atm) to a single crystalline solution of complex 4 (~30 mg) resulted in slow conversion to yellow 7 as monitored by 31P SSNMR spectroscopy, with full conversion requiring 3-4 days depending on the crystal size. See Supporting Information for crystallographic studies on material produced via the solution route.

4.5. Synthesis of [Rh(iBu2PCH2CH2PiBu2)(NH3)2][BArF4] (8). Solid [Rh(iBu2PCH2CH2PiBu2)(η4-C6H4)][BArF4] (1) (50 mg, 0.036 mmol) was placed in a Young’s flask. The flask was degassed and placed under 1 atm NH3 gas. The flask was then frozen in a liquid N2 bath and opened to 1 atm pressure of H2 while at low temperature.
The flask was then sealed and warmed; this generated roughly 1 atm NH₃ and 3 atm H₂. The solid quickly turned a bright-yellow color. The flask was left for 3 h. The product was washed twice with pentane to remove NBA. Crystals were grown from 1,2-C₆H₄F₂/pentane; 35 mg (0.027 mmol) produced; 73% yield. Anal. Calc. for C₆H₆BPN₂F₂Rh: C, 45.54; H, 4.43; N, 2.12. Found: C, 45.69; H, 4.43; N, 1.95. "H NMR (500 MHz 1,2-C₆H₄F₂): δ 1.18 [d (Bu CH₃), J = 6 Hz, 12H], 1.33 [d (Bu CH₃), JHH = 6 Hz, 12H], 1.51 [d (CH₃CH₂P), JHH = 14 Hz, 4H], 1.57 [m (Bu CH₃), 8H], 1.91 [m (Bu CH₃), 4H], 1.93 [s, NH₃, 6H], 7.68 [s (BArF(fl), 4H), 8.32 [s (BArF(fl), 8H]. "¹³C NMR (125 MHz 1,2-C₆H₄F₂): 5 δ 65.45 [d, JHH = 175 Hz, 2P]. See Supporting Information for crystallographic details.

4.6. Synthesis of [Rh(bu₂PCH₂CH₂P)CHCH=CH(Me)(BF₄)][BF₄²⁻]

4.7. Catalysis: General Procedure.

4.8. Computational Details.

The authors declare no competing financial interest.

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(41) Exposure of a crystalline sample of 6 or 4 to 1-butene results in the isomerization to 2-butene, as measured by gas-phase $^1$H NMR spectroscopy. By IR spectroscopy, this is a mixture of cis- and trans-2-butene. See Supporting Information.