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Modulation of $\sigma$-Alkane Interactions in [Rh(L$_2$(alkane))]$^+$ Solid-State Molecular Organometallic (SMOM) Systems by Variation of the Chelating Phosphine and Alkane: Access to $\eta^2,\eta^2$-$\sigma$-Alkane Rh(I), $\eta^1$-$\sigma$-Alkane Rh(III) Complexes, and Alkane Encapsulation

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Supporting Information

ABSTRACT: Solid/gas single-crystal to single-crystal (SC–SC) hydrogenation of appropriate diene precursors forms the corresponding $\sigma$-alkane complexes $[\text{Rh}(\text{Cy}_2\text{P}($CH)$_2$PCy$_3$)($L$)⁻$][\text{BAr}_4]$ ($n = 3, 4$) and $[\text{RhH}($Cy$_2\text{P}($CH)$_2$($CH$)$_2$PCy$_3$)($L$)$_2$]$[\text{BAr}_4]$ ($n = 5, L =$ norbornane, NBA; cyclooctane, COA). Their structures, as determined by single-crystal X-ray diffraction, have cations exhibiting Rh–H–C $\sigma$-interactions which are modulated by both the chelating ligand and the identity of the alkane, while all sit in an octahedral anion microenvironment. These range from chelating $\eta^1\eta^2$ Rh–H–C (e.g., $[\text{Rh}($Cy$_2\text{P}($CH)$_2$PCy$_3$)(1,3(CH)$_2$PCy$_3$)($\eta^1\eta^2$-NBA)]$[\text{BAr}_4]$, $n = 3$ and 4), through to more weakly bound $\eta^1$ Rh–H–C in which C–H activation of the chelate backbone has also occurred (e.g., $[\text{RhH}($Cy$_2\text{P}($CH)$_2$($CH$)$_2$PCy$_3$)(1,3(CH)$_2$PCy$_3$)($\eta^1$-COA)]$[\text{BAr}_4]$ and ultimately to systems where the alkane is not ligated with the metal center, but sits encapsulated in the supporting anion microenvironment, $[\text{Rh}($Cy$_2\text{P}($CH)$_2$PCy$_3$)]($\text{COACBAr}_4$)$_2$, in which the metal center instead forms two intramolecular agostic $\eta^1$ Rh–H–C interactions with the phosphine cyclohexyl groups. CH$_2$Cl$_2$ adducts formed by displacement of the $\eta^1$-alkanes in solution ($n = 5; L =$ NBA, COA), $[\text{Rh}($Cy$_2\text{P}($CH)$_2$($CH$)$_2$PCy$_3$)(3,4-(Cl)$_2$($CH$)$_2$Cl)]$[\text{BAr}_4]$, are characterized crystallographically. Analyses via periodic DFT, QTAIM, NBO, and NCI calculations, alongside variable temperature solid-state NMR spectroscopy, provide snapshots marking the onset of Rh–alkane interactions along a C–H activation trajectory. These are negligible in $[\text{Rh}($Cy$_2\text{P}($CH)$_2$PCy$_3$)]$[\text{COACBAr}_4]$; in $[\text{RhH}($Cy$_2\text{P}($CH)$_2$($CH$)$_2$PCy$_3$)($\eta^1$-COA)]$[\text{BAr}_4]$, $\sigma_{C-H} \rightarrow$ Rh $\sigma$-donation is supported by Rh $\rightarrow$ $\sigma^*_{C-H}$ "pregostic" donation, and in $[\text{Rh}($Cy$_2\text{P}($CH)$_2$PCy$_3$)($\eta^1\eta^2$-NBA)]$[\text{BAr}_4]$ ($n = 3$–4), $\sigma$-donation dominates, supported by classical Rh(dx$^z$) $\rightarrow$ $\sigma^*_{C-H}$ $\pi$-back-donation. Dispersive interactions with the $[\text{BAr}_4]$ anions and Cy substituents further stabilize the alkane within the binding pocket.

1. INTRODUCTION

The ability to tune the local environment around a metal center by variation of supporting ligands is an important concept widely used in homogeneous organometallic synthesis and catalysis. A well-documented example of this comes from bidentate phosphine ML$_2$-type complexes, as by altering the L–M–L bite-angle and substitution at phosphine the resulting sterics (e.g., the solid-cone angle, $\Theta^*$), or electronic (e.g., oxidation state or degree of bond activation), changes ultimately can provide the ability to control structure, speciation, and, through the energetics of elementary reaction steps in catalysis, activity and selectivity. Figure 1A.

Extending such concepts to heterogeneous systems is difficult given the resulting challenges associated with precisely defining single-site active centers and their extended coordination environments. While chelating phosphine complexes supported by metal–organic frameworks, porous coordination polymers, nanoparticles, mesoporous hosts, and silica surfaces have...
been reported, the role of the chelating ligand in determining structure and reactivity is less well-developed. Nevertheless, precise control of well-defined, and reactive, metal centers in heterogeneous systems could lead to enhanced activity and selectivity in catalysis, as frequently demonstrated in homogeneous processes.1,4

We have recently shown that single-crystal to single-crystal (SC–SC) solid/gas reactions between H2 and the appropriate [RhL2(diene)]+ precursors form well-defined but reactive σ-alkanes14–16 complexes directly in the solid-state, e.g., [Rh(Cy2P(CH2)4PCy2)2(n2η2-NBA)][BArF4], [1-NBA][BArF4] (NBA = norbornane, Ar+ = 3,5-(CF3)2C6H3, Figure 1B).17–20 Such σ-complexes contain 3-center 2-electron (3c-2e) Rh···H–C bonds21,22 and are of general interest from the fundamental challenges presented by their synthesis and characterization,4,15 as well as their central role as intermediates in C–H activation processes.23–26 When prepared in this way, these σ-alkane complexes show remarkable relative stability compared with species prepared by solution routes; the latter are generally characterized in situ using NMR spectroscopy, on a small scale (2–20 mg) at very low temperature, and have limited lifetimes even under these relatively constrained conditions.27–31

This stability in the solid-state originates from the [BArF4]− anions providing a robust, octahedral, crystalline microenvironment32 that allows for isolation, characterization, and onward reactivity of the encapsulated organometallic cation to be studied in detail (Figure 1C).26,33 These so-called33 solid-state molecular organometallic (SMOM) systems are related to supported organometallic catalysts (SSHC),13 single-site heterogeneous catalysts (SSHC),13 and MOF-functionalized organometallics9,35–37 but, in contrast to these, are not supported by a platform material. Moreover, SMOM systems have the desirable properties of being readily studied at the molecular-level by single-crystal X-ray diffraction, solid-state NMR (SSNMR) spectroscopy, and computational techniques such as periodic DFT.

We now report that systematic variation of the P−Rh−P bite angle with the identity of the diene in SMOM systems based upon precursors [Rh(Cy2P(CH2)nPCy2)(diene)][BArF4] (n = 3 to 5, diene = norbornadiene, NBD, or 1,5-cyclooctadiene, COD, Scheme 1) results in significant changes in structure and reactivity on addition of H2 in SC–SC reactions. This results in crystallographically characterized σ-alkane complexes that show markedly different degrees of Rh···H–C interaction in response to the changes in both phosphine and the precursor diene, while they are stabilized in the microenvironment provided by the octahedral arrangement of [BArF4]− anions: these range from

![Figure 1. (A) Control of local environment in {ML2} complexes: bite-angle = β. (B) Synthesis of the σ-alkane complex [1-NBA][BArF4]; NBD = norbornadiene. (C) The SMOM concept.](image)
surrounding the organometallic cations, as observed for [1-NBA][BF₄] and related complexes. The Supporting Information details their structures. For the NBD precursors, this homologous series allows for the bite-angle (β) of the various diphosphines in this environment to be compared. Unsurprisingly, β becomes progressively larger with an increasing number of methylene units in the chelate backbone (Scheme 2B). The same trend, albeit interestingly with slightly smaller β-angles, is apparent for the COD precursors. With these complexes in hand a systematic study of solid/gas hydrogenation was undertaken.

2.2 Hydrogenation of (Rh(Cy₂P(CH₂)₃PCy₂))⁺/COD. As previously reported, hydrogenation of [1-NBD][BF₄] gives [1-NBA][BF₄] in a rapid (less than 10 min) SC–SC transformation (see Figure 1B). Here, use of [1-COD][BF₄] results in a slower¹⁰,⁴¹ reaction with H₂ (3 h) and loss of crystallinity. Dissolving the resulting solid in CD₂Cl₂ afforded the previously reported zwitterion [Rh(Cy₂P(CH₂)₃PCy₂)(η−C₂H₄(CF₃)₂)][BF₄], [1-BAR₄]+, and free COA.¹⁸

2.3. (Rh(Cy₂P(CH₂)₃PCy₂))⁺/NBA: An η⁶-C⁶–σ-Alkane Complex. Addition of H₂ (1 bar, 298 K) to single-crystals of [Rh(Cy₂P(CH₂)₃PCy₂)(NBD)][BF₄], [2-NBD][BF₄], resulted in the rapid (~5 min) formation of the σ-alkane complex [Rh(Cy₂P(CH₂)₃PCy₂)(η⁶-C⁶-NBA)][BF₄], [2-NBA][BAR₄], in an SC–SC transformation, as shown by single-crystal X-ray diffraction (Figure 2) and ¹³P{¹H}/¹³C{¹H} SSNMR spectroscopies. The octahedral arrangement of [BAR₄]+ anions is retained in [2-NBA][BAR₄] while the central cation is pseudo-square-planar, with the (RhL₄)⁺ fragment bound to the alkane NBA through two endo Rh···H–C σ interactions showing relatively short Rh···C distances [Rh···C (2.408(2)–2.402(2) Å] and rather acute ㄥRhHC, e.g., Rh₁–H₁A–C₁ 105.1(2)°. These H atoms were located and freely refined. These data suggest an η⁶-C⁶ chelating Rh···H–C motif¹⁴,⁴², as corroborated by computational studies (see later). Despite the P–Rh–P bite-angle increasing compared with [1-NBA][BAR₄] (e.g., Scheme 2B), the Rh···C distances are not different within error [cf. 2.389(3)/2.400(3) Å] and the structures are very similar, suggesting that the NBA ligand fits comfortably into the ligand pocket defined by the Cy groups. This similarity is not strongly influenced by the anion microenvironment as evidenced by calculations on isolated cations (Section 2.7 and Supporting Information). In the solid-state, there are a number of weak C–H···F interactions between the NBA ligand and the [BAR₄]+ anion, Figure S73.

The ¹³P{¹H} SSNMR spectrum of [2-NBA][BAR₄] shows two relatively sharp environments at δ = 50.6, 51.6 [J(RhP) = ~170 Hz], while the ¹³C{¹H} NMR spectrum is featureless between δ 110 and 50, demonstrating hydrogenation of the NBD. A ¹¹/¹³C frequency switched Lee–Goldburg (FSLG) HETCOR experiment at 298 K, which has been used to characterize early–H–M interactions in the solid-state (E = Si, C),¹⁸,²⁶,⁴³ shows two strong correlations between ¹³C(ºC) ≈ 26 and ¹³δ(ºH) = −2 which are consistent with the crystallographically inequivalent Rh···H–C interactions observed in the solid-state (Figure S13). An additional correlation [¹³δ(¹³C) 42/δ(ºH) = −0.6]¹⁴ is assigned to the CH₃ bridge on the norbornane, which is affected by [BAR₄]+ ring-current effects as described for [1-NBA][BAR₄] and related complexes.¹⁸,¹⁹,²⁶

Dissolving crystalline material of [2-NBA][BAR₄] in CD₂Cl₂ at 183 K results in free NBA being observed by ¹H NMR spectroscopy and a ¹³P{¹H} NMR spectrum that is suggestive of a solvent-coordinated complex, [Rh(Cy₂P(CH₂)₃PCy₂)-(ClCH₂Cl)]-[BAR₄], δ 47.4 [J(RhP) = 198 Hz], similar to that reported for [Rh₂(PC(CH₃)₃)₃]⁻[Cl(CH₂Cl₂)]-[BAR₄].²⁶ On warming decomposition occurs via C–Cl activation to give a mixture of partially soluble chloride-bridged hydride dimers, e.g., [Rh(Cy₂P(CH₂)₃PCy₂)(μ-Cl)][BAR₄] that precipitate from solution and are best identified by ESI-MS. The formation of the [BAR₄⁺]-coordinated zwitterion was not observed,⁴⁵ in contrast to [1-NBA][BAR₄] that forms [1-BAR₄⁺] in CD₂Cl₂.¹⁸ We suggest this is a consequence of the increased steric profile of the chelating phosphine Cy₂P(CH₂)₃PCy₂ versus Cy₂P(CH₂)₃PCy₂, disfavoring coordination of the, local to the metal center, planar and bulky [BAR₄⁺] anion, coupled with the wider bite-angle phosphines encouraging oxidative addition at Rh(I).⁶

2.4. (Rh(Cy₂P(CH₂)₃PCy₂))⁺/COA: A 12-Electron Rh(I) Complex Supported by Agostic Interactions with an Encapsulated Nonbonding Alkane. Exposing single crystals of [2-COD][BAR₄] to H₂ for 3 h results in, slower,⁴¹¹ SC–SC hydrogenation and expulsion of cyclooctane (COA) from the metal center to form formally 12-electron "naked"⁴⁷ [Rh(Cy₂P(CH₂)₃PCy₂)][COACBAR₄], [2][COACBAR₄], Scheme 3.

SSNMR spectroscopies. The octahedral arrangement of [BAR₄⁺] anions is retained in [2-NBA][BAR₄] while the central cation is pseudo-square-planar, with the (RhL₄)⁺ fragment bound to the alkane NBA through two endo Rh···H–C σ interactions showing relatively short Rh···C distances [Rh···C 2.408(2)/2.402(2) Å] and rather acute ㄥRhHC, e.g., Rh₁–H₁A–C₁ 105.1(2)°. These H atoms were located and freely refined. These data suggest an η⁶-C⁶ chelating Rh···H–C motif, as corroborated by computational studies (see later). Despite the P–Rh–P bite-angle increasing compared with [1-NBA][BAR₄] (e.g., Scheme 2B), the Rh···C distances are not different within error [cf. 2.389(3)/2.400(3) Å] and the structures are very similar, suggesting that the NBA ligand fits comfortably into the ligand pocket defined by the Cy groups. This similarity is not strongly influenced by the anion microenvironment as evidenced by calculations on isolated cations (Section 2.7 and Supporting Information). In the solid-state, there are a number of weak C–H···F interactions between the NBA ligand and the [BAR₄⁺] anion, Figure S73.

The ¹³P{¹H} SSNMR spectrum of [2-NBA][BAR₄] shows two relatively sharp environments at δ = 50.6, 51.6 [J(RhP) = ~170 Hz], while the ¹³C{¹H} NMR spectrum is featureless between δ 110 and 50, demonstrating hydrogenation of the NBD. A ¹¹/¹³C frequency switched Lee–Goldburg (FSLG) HETCOR experiment at 298 K, which has been used to characterize early–H–M interactions in the solid-state (E = Si, C),¹⁸,²⁶,⁴³ shows two strong correlations between ¹³C(ºC) ≈ 26 and ¹³δ(ºH) = −2 which are consistent with the crystallographically inequivalent Rh···H–C interactions observed in the solid-state (Figure S13). An additional correlation [¹³δ(¹³C) 42/δ(ºH) = −0.6]¹⁴ is assigned to the CH₃ bridge on the norbornane, which is affected by [BAR₄⁺] ring-current effects as described for [1-NBA][BAR₄] and related complexes.¹⁸,¹⁹,²⁶

The solid-state structure of the cation [2]⁺ (Figure 3A) shows two δ-agostic Rh···H–C interactions from the cyclohexyl rings [Rh···C 2.91(1) Å, Rh···C 2.87(1) Å] that form in response to the unsaturation now at the Rh(I) metal center. The Rh₁–P₁–C₁ angle reflects this, for example, being more acute [108.9(3)°] than Rh₁–P₁–C₁ 119.8(3)°. The Rh center also moves toward the C–H bonds involved in these agostic interactions, as shown by the angle between the planes ZRh₁P₂C₂5C₂7/Rh₁P₁P₂ = 42.6(2)° (Figure 3B).
It also retains the square planar geometry, although studies on related uranium complexes suggest that such distance reflects a nonbonding interaction.

In the 158 K $^{13}$P($^1$H) SSNMR spectrum of $[2]\text{[COACBa}^4]$ only two broad (fwhm ~400 Hz) environments are observed at $\delta$ 51.3 and $\delta$ 48.1 in an approximate 1:1 ratio. Coupling to $^{103}$Rh was not resolved. These do not vary significantly in chemical shift or relative intensity when measured at 298 K. The observation of only two signals suggests that the disorder observed in the cation could be static (with coincident signals) or dynamic (and fast) on the NMR time scale, but the observation that no change is observed on changing the temperature suggests the former.

$^{13}$C($^1$H) SSNMR spectrum shows a featureless region between $\delta$ 115 and 43, indicating that the COD has been hydrogenated to COA, which is observed as a sharp signal at $\delta$ 25.7. This assignment is supported by a nonquaternary suppression experiment (NQS) which, as well as detecting quaternary carbons, identifies CH groups that experience motion in a frequency range similar to, or greater than, the $^3$H–$^3$C dipolar coupling.

In the 158 K NQS spectrum a single prominent signal remains at $\delta$ 25.7 in the alkyl region, compared with the $^{13}$C($^1$H) SSNMR spectrum (Figure 4A). This peak remains at 298 K. These data are consistent with the encapsulated COA undergoing a low-energy site-exchange within the cavity (Figure 4B), suggested to be due to 1,2-jumps and/or exchange between the two disordered COA components. To calibrate our observations, a variable temperature NQS experiment on $[1\text{-NBA}]\text{[BAr}^4]$ showed an NBA fragment undergoing motion at 298 K which is halted at 158 K, fully consistent with previous variable temperature SSNMR studies (Figure S3).

The relatively long Rh–C distances, coupled with more open $\angle$RhHC angles, e.g., Rh–H9A–C9 147.9(6), albeit with the hydrogens placed in calculated positions, suggests an $\eta^1$ Rh–H–C bonding motif for the agostic interactions, a view supported by calculations (see Section 2.7). This movement of the metal center keeps the phosphine ligand in essentially the same environment in the anion cavity and maximizes the Rh–H–C agostic interactions, with two cyclohexyl groups also enfolding the metal center. It also retains the square planar geometry around Rh, with angles around the metal center = 360°. A minor, disordered, agostomeric component is also present (~10%) in which the Rh center swings up to interact with the chemically equivalent C15–H and C21–H bonds (Figure 3C). The Rh–P distances in the major component [2.166(2) and 2.171(2) Å] are ~0.04 Å shorter than in $[2\text{-NBA}]\text{[BAr}^4]$. Whether this reflects a weaker trans-influence of the bis-agostic Rh–H–C interactions in $[2]\text{[COACBa}^4]$ compared with the intermolecular interactions in $[2\text{-NBA}]\text{[BAr}^4]$, or is a consequence of the metal’s unusual disposition, is not clear. Although formally 2-coordinate group 9 complexes are known, albeit rare, as far as we are aware the cation in $[2]\text{[COACBa}^4]$ is the first example reported with a chelating phosphine.

The expelled alkane, COA, sits encapsulated within the anion framework (Figure 3D), essentially equally disordered between two boat–chair conformations. The closest Rh–C distance is 3.74(1) Å (C28), approaching the Rh center above the square plane, suggesting no significant, and at best very weak, interaction with the metal center. This distance is similar to that measured in $[\text{U(ArO)}_2(\text{neo-hexane})] \ [3.731(8) \text{Å}]$, albeit U versus Rh where a bonding interaction was suggested, although studies on related uranium complexes suggest that such distance reflects a nonbonding interaction.

Figure 3. (A) Cation of $[2]\text{[COACBa}^4]$. 50% displacement ellipsoids, only the major disordered component shown. Selected bond lengths (Å) and angles (deg): Rh1–C29, 2.912(10); Rh1–C9, 2.873(10); Rh1–P1, 2.171(2); Rh1–P2, 2.166(2); P1–Rh1–P2, 91.21(8); $\angle$P1P2C52C7/Rh1P1P2, 42.6(2). (B) Displacement of the Rh center in $[2]^\ddagger$ toward the agostic C–H bonds in the major disordered component. (C) Ball and stick representation of the two disordered components in $[2]^\ddagger$. (D) Packing diagram of $[2]\text{[COACBa}^4]$ showing the O$_2$ arrangement of [BAr$^4$], COA (C = red) shown at van der Waals radii, and only one disordered component shown, Rh1–C28, 3.74(1) Å.

Figure 4. (A) $^{13}$C($^1$H) SSNMR spectra (10 kHz, 158 K) and NQS spectra of $[2]\text{[COACBa}^4]$ (10 kHz, 158 K). $^*$ = spinning sideband. (B) Proposed fluxional processes ($^\ddagger$ = [BAr$^4$]).
2.5. (Rh(Cy,P(CH\textsubscript{2})\textsubscript{3}PCy\textsubscript{2}))\textsubscript{n}/NBA: An \(\eta^1\eta^2\eta^2\)-Alkane Complex. Addition of \(\text{H}_2\) to single-crystals of [Rh(Cy,P-(CH\textsubscript{2})\textsubscript{3}PCy\textsubscript{2})(NBD)][BAr\textsubscript{4}], [3-NBD][BAr\textsubscript{4}], resulted in a fast (~5 min as measured by \(\text{\textsuperscript{\text{31}}P}[\text{\textsuperscript{\text{1}}H}]\) SSNMR spectroscopy) SC-SC transformation to give the corresponding \(\sigma\)-alkane complex [Rh(Cy,P(CH\textsubscript{2})\textsubscript{3}PCy\textsubscript{2})(\eta^1\eta^2\eta^2\text{-NBA})][BAr\textsubscript{4}], [3-NBA][BAr\textsubscript{4}], Figure 6. The solid-state structure of [3-NBA][BAr\textsubscript{4}] reveals a \(\sigma\)-bound NBA ligand, with two Rh...H interactions using the endo C–H bonds (H atoms located). Despite the bite-angle increasing further compared with those of [1-NBA][BAr\textsubscript{4}] and [2-NBA][BAr\textsubscript{4}], the key metrics associated with this interaction remain essentially unchanged: Rh1–C1, 2.399(2) Å; Rh1–C2, 2.396(2) Å; Rh1–P1, 2.215(4) Å; Rh1–P2, 2.221(5) Å; P1–Rh1–P2, 97.87(2)°.

Increasing the bite-angle of the phosphine promoted different reactivity in the resulting \(\sigma\)-alkane complex. Surprisingly given that the structural metrics have not changed significantly from the smaller bite-angle congeners, [3-NBA][BAr\textsubscript{4}] is not stable when exposed to a moderate vacuum for 3 days. Crystallinity is lost, and SSNMR spectroscopy shows the formation of multiple species, as yet unidentified. Thus, although the binding of the NBA ligand appears to not be influenced significantly by the increase in bite-angle of the chelating phosphine, in the measured ground-state structure steric pressure and/or enhanced stability of any decomposition products as driven by the change in phosphine appear to promote reactivity toward loss of NBA. Hydrogenation of single-crystals of [3-COD][BAr\textsubscript{4}] in a solid/gas reaction resulted in loss of crystallinity.\textsuperscript{39} We have not characterized the product of this further.

2.6. (Rh(Cy,P(CH\textsubscript{2})\textsubscript{3}PCy\textsubscript{2}))\textsubscript{n}/COA and NBA: Phosphine Ligand Backbone C–H Activation, Structural Reorganization with Retention of Crystallinity, and Rh(III) \(\eta^1\eta\)-Alkane Complexes. Addition of \(\text{H}_2\) to crystalline [4-NBD][BAr\textsubscript{4}] resulted in a rapid (~5 min as measured by \(\text{\textsuperscript{\text{31}}P}[\text{\textsuperscript{\text{1}}H}]\) SSNMR spectroscopy) SC-SC reaction. Analysis of the product formed using single-crystal X-ray diffraction was hampered by long-range disorder, which is also present in the starting material. The structure was modeled using a supercell (\(Z=2\)) which gave a satisfactory solution (\(R=15.7\%\)) that allowed for the gross structure of the cation to be determined, Figure 7, but does not allow for detailed metrics to be discussed.
These distances reflect weak (at best) σ-interactions compared to, e.g., [2-NBA][BAR₄]₄, while this spread suggests that the NBA fragment finds a better spatial fit with the {RhPCP}⁺ fragment for some conformations of the reactant. The data clearly do not allow the precise binding mode of the alkane (η⁴-HC, η³-H₂C₇⁰) to be determined. A related SC–SC N–C oxidative addition at a Rh(I) center has been reported in Rh–PnP pincer complexes.⁷¹ [4-NBA][BAR₄] is stable indefinitely in an Ar-filled glovebox or under vacuum.

The 298 K ¹³C ([¹]H) SSNMR spectrum of [4-NBA][BAR₄] shows a featureless region between δ 116 and 59, demonstrating hydrogenation of the diene. The 298 K ¹³P ([¹]H) SSNMR shows a tightly coupled ABX system,⁷² which is less well-resolved at 158 K, consistent with inequivalent trans-phosphines that are in chemically very similar environments bound to a Rh(III) center: δ 64.1, 63.4 [J(RhP) = ~105, J(PP) = 325 Hz] (Figures S49 and S50). The ¹³C NQs spectrum at 158 K shows at least four signals grouped between δ 38–35 and δ 29–27, in the region associated with aliphatic C–H groups, that indicate a low-energy molecular motion of the NBA ligand within the cavity of the cage (Figure S54). Such a low-energy process is consistent with the disorder of the NBA fragment modeled in the solid-state. In the 158 K FSLG HETCOR spectrum, cross peaks between these aliphatic signals in the ¹³C SSNMR spectrum and low-field peaks in the ¹H projection (δ −1.8 to −2.6) are observed. We assign these to the Rh–H–C interactions, although we cannot discount ring-current effects from the proximal Ar⁺ groups causing such a high-field shift in other C–H bonds.¹⁸,²⁶

Unlike for [2-NBA][BAR₄] or [3-NBA][BAR₄], dissolving [4-NBA][BAR₄] in CD₂Cl₂ gave a stable complex that could be characterized by solution NMR spectroscopy and single-crystal X-ray diffraction (crystals grown from CH₂Cl₂/pentane) as [Rh(C₂H₅P(CH₂)₂CH(CH₃)₂PCy₂)H(k¹-CℓCH₂Cl)] [BAR₄], [4-CH₂Cl₂][BAR₄], Figure 8, in which the NBA ligand has been replaced by a CH₂Cl₂ ligand. Vacuum transfer of the volatiles demonstrates NBA is liberated, consistent with the initial solid/gas hydrogenation of the NBD to form [4-NBA][BAR₄]. The molecular structure of [4-CH₂Cl₂][BAR₄], Figure 8B, does not suffer from disorder and clearly shows the trans-spanning PCP pincer motif suggested for [4-NBA][BAR₄]. The Rh=H-hydride (H1) was located, sitting trans to a vacant site, and anti to the remaining hydrogen associated with the C–H activated methylene group (H3). This stereochemistry is as expected for an intramolecular C–H activation.⁶⁶,⁶⁸ A CH₂Cl₂ molecule has displaced the labile NBA fragment. Displacement of a weakly bound σ-alkane ligand by halogenated solvent is well-established,⁶³,²⁸,³⁰ and the structure is consistent with other crystallographically characterized Rh–ClCH₂Cl complexes.⁴⁹,⁷³,⁷⁴ [4-CH₂Cl₂][BAR₄] is a 16-electron Rh(III) complex, but there is no evidence for any significant supporting agostic interaction from the cyclohexyl groups: closest Rh⋯C = 3.261(3) Å. Although this is not an SC–SC transformation, the O₃ arrangement of anions is retained in the extended solid-state structure of recrystallized material.

Solution NMR data for [4-CH₂Cl₂][BAR₄] at 298 K (CD₂Cl₂) reveal a fluxional process is occurring. In the ¹H NMR spectrum relatively broad signals are observed for the phosphine ligand, and no characteristic signal due to the C–H activated methylene (ca. 3 ppm)⁶⁶ or Rh=H was observed. The ³¹P ([¹]H) NMR spectrum showed a relatively sharp doublet at δ 66 ([J(RhP) 121 Hz]. Cooling to 243 K results in a sharpening of the aliphatic region in the ¹H NMR spectrum, and two new signals at δ 2.71 and −27.2 [d, J (RhH) = 55 Hz, br, fwhm ~40 Hz] appear which integrate to 1 H each. These are assigned to the C–H activated methylene (i.e., C3) and Rh=H, respectively, the latter with a chemical shift that places it trans to a vacant site.⁶⁵,⁷⁵,⁷⁶ A spin-saturation experiment at this temperature shows that these two signals are undergoing slow mutual exchange. The ³¹P ([¹]H) NMR spectrum is still a doublet but is shifted slightly to lower field [δ 64.4]. These low-temperature data are fully consistent with the solid-state structure of [4-CH₂Cl₂][BAR₄]. An exchange process that involves reversible reductive C–H bond forming/C–H oxidative addition is proposed, as suggested for closely related systems,⁶⁶ and DFT calculations confirm this is favored (ΔG°calk = 18.7 kcal/mol) over an alternative α–elimination process via a diphasphino–carbene intermediate (ΔG°calc = 27.4 kcal/mol, see Figure S10S, Supporting Information).⁶⁶ It is also likely that the bound CH₂Cl₂ molecule is undergoing rapid exchange at the metal center with the solvent.

If [4-COD][BAR₄] is subjected to H₂ in the solid-state, after 30 min crystallinity is lost. However, if the reaction is stopped after only 10 min and the resulting single crystals are quickly transferred to an X-ray diffractometer and cooled to 150 K, the resulting analysis shows that a new complex is formed in 30% yield in a SC–SC process, with the remainder being unreacted [4-COD][BAR₄]. These data showed this new complex to be [4-COA][BAR₄], [Rh(C₂H₅P(CH₂)₂CH(CH₃)₂PCy₂)H(μ¹-COA)][BAR₄]. Although the single-crystal refinement showed a superpositional mixture of [4-COD][BAR₄] (70%) and [4-COA][BAR₄] (30%) in the O₃-anionic cage, refinement of the constituent components gave a reliable and robust solution (R = 9.6%).

The molecular cation of [4-COA]⁺ is shown in Figure 9. This shows a C–H activated, trans-spanning, diphasphino "PCP" pincer ligand with a cyclooctane located in close proximity to the Rh(II) metal center [Rh1···Cl1a, 2.90(3) Å]. The COA ligand is not disordered and shows that all the C–C bonds are single [1.46(2)–1.48(2) Å]. The Rh–C distance is very long compared with other Rh=H·C σ-alkane complexes, cf. [1-pentene]-[BAR₄], 2.522(5) Å, in which the pentane acts as a bidentate ligand.⁷⁸ However, it is considerably shorter than found in [2][COACBAR₄] (where we propose a minimal interaction at best) and is of a similar distance to the weak agostic interaction in trans-[Rh(2,2'-biphenyl)(PBU₃)] [BAR₄] 2.979(4) Å, as
also interrogated by QTAIM analysis. This distance, combined with a rather open Rh1a···C1a (albeit with the H placed in a calculated position) of 140.7(2)°, points to an η1 Rh···H–C interaction. The hydrogen atoms were not located in [4-COA]⁺, but as dissolution of the crystalline material in CD3Cl, formed [4-CD3Cl][BARF₄] free COA alongside [4-COD][BARF₄] in a 30:70 ratio, Scheme 4, the same Rh–H, C–H activated motif as for [4-NBA][BARF₄] is proposed. As for the other σ-alkane structures reported here, there are multiple stabilizing C–H···F interactions between the alkane and proximal CF₃ groups in the lattice (Figure S91).

Complex [4-COA][BARF₄] is a σ-alkane complex in which only one Rh···H–C interaction is present, being related to structures characterized using solution and DFT techniques, such as [Re(η⁴-C₅Me₂)(CO)₃(C₅H₅)] [Al(OR)₃] or Rh(η⁵-C₅H₅)(CO)₂(C₂H₃), respectively. However, as far as we are aware, this is the first structurally determined example of an alkane interacting with a transition metal center. Such motifs have been probed on the picosecond time scale using fast time-resolved infrared spectroscopy (TRIR) combined with DFT calculations, and these are early intermediates in the oxidative addition of alkanes to coordinatively unsaturated metal centers. Valence isoelectronic amine–borane and silane complexes with η¹-M–H–E coordination have been reported and show comparable structural metrics to [4-COA][BARF₄], such as wide M–H–E angles and long M–E distances: [Ir(POCOP)H(η¹-H5SiEt₅)] [B(C₆F₅)₄], structure A, (POCOP = 2,6-[OP²Bu]₂C₆H₃) and [Rh(k¹-Xantphos)-(H)₂(η¹-H₃B-NMe₃)][BARF₄], structure B, in Chart 1. Of course, the increased polarity of the E–H bond in these analogues will make a significant contribution to bonding, and thus, they are sufficiently stable to observe using solution NMR techniques, unlike [4-COA][BARF₄].

If hydrogenation of [4-COD][BARF₄] is continued for a total of 30 min, decomposition to an, as yet unidentified, product(s) is observed upon dissolution in CD3Cl, from which a featureless 31P(¹H) NMR spectrum and a very broad ¹H NMR spectrum are observed. We speculate that this signals the formation of a paramagnetic Rh(II) dimeric complex on dissolution, but the identity of this species remains to be resolved. Attempts to obtain meaningful SSNMR data for [4-COA][BARF₄] were hampered by temporal and temperature sensitivity that was amplified by the requirement to use finely crushed material for analysis by SSNMR that meant that crystallinity is lost much faster than for larger samples. In the 31P(¹H) SSNMR spectrum at 158 K, a major, broad peak at δ 64 is observed (being similar to that seen for [4-NBA][BARF₄]), alongside [4-COD][BARF₄] and decomposition products. The sensitivity of [4-COA]-[BARF₄] contrasts with the relative stability of [4-NBA][BARF₄] or [2] [COA]BArF₄ and perhaps reflects the combination of the different steric profile of the alkane in the former (NBA versus COA) combined with the stabilizing influence of agostic interactions in the latter.

[4-NBA][BARF₄] and [4-COA][BARF₄] are shown to have very similar structures, with the former’s stability allowing for a more detailed characterization by SSNMR spectroscopy and the latter providing a good structural solution by X-ray crystallography. Combined, they thus provide a convincing analysis as a weakly bound σ-alkane complex bound η¹ at a Rh(III) center. We believe they are the first Rh(III) σ-alkane complexes isolated, or observed, by any method.

2.7. Computational Studies. Periodic DFT calculations were performed on the extended solid-state structures of [X-NBA][BARF₄] (X = 1, 2, and 3), [2] [COA]BArF₄, and [4-COD][BARF₄] to assess the structure and bonding of these species (see Supporting Information for details and tables of computed structures). For the [X-NBA][BARF₄] series geometries optimized with the PBE-D3 approach provided good agreement with the experimental structures. For [2] [COA]BArF₄ both the major and minor components were computed and structural metrics around the Rh centers were again well-reproduced. However, more movement of the COA was seen in these calculations, perhaps reflecting the absence of significant bonded interactions between Rh and the COA (see below). For [4-COA][BARF₄] the calculations slightly underestimate the Rh1···C1 distance (calcd 2.80 Å; expt 2.90 (3) Å).

Chart 1. Examples of η¹-Coordinated σ-Complexes

"Anions are not shown."
Given the variations between computed and experimental structures across the range of systems under consideration, the subsequent analyses were based on computed structures in which the Rh, C, B, and P positions were taken from the crystallographic studies and the H and F atoms were optimized with the PBE-D3 approach. Selected distances involving key H atom positions optimized on this basis are shown in Figure 10.

A more quantitative analysis of bonding was then provided by quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) second order perturbation donor–acceptor interaction analyses performed on the isolated cations shown in Figure 10, while noncovalent interaction (NCI) plots were run on ion pairs featuring the nearest-neighbor [BARF₄]⁻ anion.

2.7.1. [X-NBA][BARF₄] (X = 1, 2, and 3). Computed structures for all three species show short Rh···H11/H21 contacts of around 1.88 Å and elongation of the C1–H11/C2–H21 bonds to ca. 1.15 Å consistent with the presence of two 3c–2e C–H···Rh σ-interactions in each case. QTAIM and NBO analyses on the [2-NBA]⁺ cation confirm this (Figure 11A–C), with the presence of Rh···H11 and Rh···H21 bond paths and reduced bond critical point (BCP) metrics for C1–H11 and C2–H21 compared to the spectator C1–H21/C2–H22 bonds. NBO calculations highlight the dominance of C–H → Rh σ-donation into the trans-σ₄ₛₙ₋₉₋ₘ orbital, reinforced by π-back-donation from a Rh lone pair (d orbital) and the cis-σ₉₋ₘ₋₉₋ₘ bonding orbital. Similar results were computed for [1-NBA]⁺ and [3-NBA]⁺ (see Supporting Information) indicating that changing the bite-angle has a minimal effect on the Rh···NH interaction.

Figure 11D shows the NCI plot of the [2-NBA][BARF₄] ion pair and reveals a broad curved feature running roughly parallel to the H11–C1–C2–H21 bonds. This reflects the chelating nature of the NBA ligand and is predominantly stabilizing (blue) in character, while also exhibiting a central destabilizing (orange/red) region that is consistent with the presence of the ring critical point (RCP) in the QTAIM study. Some destabilizing character is also seen between Rh and the center of the two C–H bonds (see detail in Figure 11E). This suggests two cyclic (RhC) features in the electron density topology that are consistent with an η-interaction and the significant contribution of classical Rh(dx²) to σ₉₋₈₋₉₋₈ π-back-donation identified in the NBO analysis. This also highlights how the NCI approach can amplify the insight gained from the local QTAIM critical points. This features contrast with the more localized η¹-interactions associated with C–H···Rh bonding in

Figure 11. (A) Molecular graph of the [2-NBA]⁺ cation; density contours plotted in the RhH11H21 plane with BCPs (green) and RCPs (red). (B) Key BCP metrics and (C) donor–acceptor interactions associated with the Rh···H11C1 interaction. (D) NCI plot of the [2-NBA][BARF₄] ion pair; isosurface generated for ρ = 0.3 au and −0.07 < ρ < 0.07 au. (E) Detail of the [Rh···NBA] interaction, ‘similar data are obtained for the Rh···H21, C2···H21, and C2···H22 interactions.’

The closest Rh···COA contact in [2][COAcBARF₄] is via H21 with a computed distance of 2.844 Å. This is well within the sum of the van der Waals radii of Rh and H (3.64 Å). A weak BCP is computed between these centers (ρ = 0.011 e Å⁻³). No equivalent donor–acceptor interaction is computed with NBO, although the NCI plot does suggest a weak, stabilizing feature between Rh and H21 (see Figure 12D,E). This is part of a broad area of weakly stabilizing interactions between the COA and the [2⁺] cation, suggesting that any direct covalent Rh···H21 interaction is at best very weak, if it exists at all. The COA is further stabilized within the cavity by dispersive interactions with the two proximate aryl substituents of the [BARF₄]⁻ anion.
somewhat weaker σ-interaction than in the [2]+ cation, although NBO indicates a similar degree of σ-donation and, if anything, greater back-donation in this case. A blue/green disk in the NCI plot confirms this η1 C1–H11 → Rh σ-interaction as well as highlights broad areas of stabilizing dispersion interactions with the cyclohexyl substituents and the [BAr4]+ aryl groups.

An interesting aspect of the NBO analysis of both agostic [2]⁺ and [4-COA]+ is the degree of donation into σ* C–H from the trans-σRHL bonding orbitals (L = P2 or C32, respectively). In [4-COA]+, this is supported by donation from the cis-σRh–H42 bonding orbital (see Figure 14). These interactions reflect the

![Figure 12](image12.png)

Figure 12. (A) Molecular graph of the [2]+ cation; density contours plotted in the Rh(13B)(H9A) plane with BCPs (green) and RCPs (red). (B) Key BCP metrics and (C) donor–acceptor interactions associated with the Rh–H1IC1 interaction. (D) NCI plot of the [2]+[COAcBA4]+ ion pair; isosurface generated for s = 0.3 au and −0.07 < ρ < 0.07 au. (E) Detail highlighting the region around Rh (the narrow disk within the circled region arises from an interaction between cyclohexyl hydrogens and sits well above the coordination plane).

2.7.3. [4-COA][BAr4]+. The computed structure of [4-COA]−[BAr4]+ shows a Rh–H11 distance of 2.002 Å and an elongated C1–H11 distance of 1.13 Å (Figure 10). These, along with the computed Rh···H11 BCP metrics (Figure 13), suggest a

![Figure 13](image13.png)

Figure 13. (A) Molecular graph of the [4-COA]+ cation; density contours plotted in the RhH1IC1 plane, BCPs (green), and RCPs (red). (B) Key BCP metrics and (C) donor–acceptor interactions associated with the Rh–H1IC1 interaction. (D) NCI plot of the [4-COA][BAr4]+ ion pair; isosurface generated for s = 0.3 au and −0.07 < ρ < 0.07 au. (E) Detail highlighting the region around Rh.

3. CONCLUSIONS

The studies reported herein provide a demonstration of the power of solid-state molecular organometallic chemistry (SMOM-Chem), and in particular single-crystal to single-crystal transformations to provide access to and, when combined with periodic DFT calculations, characterize a wide range of different σ-alkane M···H–C coordination motifs by systematic variation of the ligand set. Figure 15 highlights these, alongside selected structural and computationally determined bonding parameters for the Rh···alkane interactions.

![Figure 14](image14.png)

Figure 14. NBO donor–acceptor pairs highlighting σ-donation from (a) the trans-Rh–C32 σ-bond and (b) the cis-Rh–H2 σ-bond into σ* C–H. NBO occupancies are also indicated.

η1-orientation of the C–H bonds in these species ([2]+, ZRhHC,ave = 138°; [4-COA]+, ZRhHC = 133°) Similar σ-donation has been identified with the onset of the C–H···Rh ("pregostic") interaction93,94 and is consistent with the end-on approach of CH4 in Bürgi–Dunitz trajectories95 and of H2 in oxidative addition reactions.

![Figure 15](image15.png)

Figure 15. Snapshots along a continuum of M···H–C interactions provided by the complexes reported in this paper, with key, selected structural and computationally determined bonding parameters for the Rh···alkane interactions.

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described present snapshots along a continuum of M⋯H−C interactions that would be very difficult to probe in σ-alkane complexes using solution techniques due to the instability of such systems combined with fluxionality between different M⋯H−C bonds that often results in time-averaged structures in solution, even at very low temperatures. Thus, with the NBA alkane ligand and simple, chelating phosphines, relatively strong bidentate chelating η^s-η^t motifs are observed, e.g., [2-NBAr^4][BAr^4][4-COA], with a trans-spanning C−H activated PCP pincer ligand, reduced access to the metal center results in unprecedented η^t Rh(III)⋯H−C motifs being observed in the solid-state, e.g., [4-COA][BAr^4], a model for the early stages of C−H activation at metal centers. Finally, when the steric requirement of the phosphine and the alkane combine with the ability for the phosphine to engage in stabilizing intramolecular agostic interactions, the alkane is expelled from the metal center but remarkably stays encapsulated within the anion framework, providing baseline experimental structural data for a close, but essentially nonbonding, approach of an alkane with a metal center: viz. [2][4-COA][BAr^4]. Underpinning these remarkable structures is the stabilizing effect of the anion microenvironment, and in particular the role that intermolecular dispersion interactions play in stabilizing these alkane ligands within the binding pocket. Reflecting this, none of the complexes reported are stable in solution even at low temperature. The SMOM technique thus complements elegant low-temperature in situ solution techniques for the synthesis and characterization of σ-alkane complexes.\(^{29,31,81}\)

That such wide variations of alkane binding modes and structures are observed while a well-defined molecular environment is maintained in the solid-state provides an exemplar of a potentially tunable, molecular heterogeneous system that can be precisely characterized. By using a core metal–ligand fragment, i.e., (Rh(diphosphine))\(^{1}\), it also offers a wide range of potential opportunities for transformations where variation of metal–ligand interactions is likely to influence rate, stability, and selectivity in catalysis.\(^{96}\) It will be interesting to see if this can be translated to productive C−H activation reactions of hydrocarbons using SMOM systems, and our efforts are currently focused in this direction.

## ASSOCIATED CONTENT

[Supporting Information](#)

Synthesis, structural characterization, solution and solid-state NMR experiments, and computational studies (PDF)

Crystallographic data (CIF)

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