Isolation of [Ru(IPr)₂(CO)H]⁺ (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) and reactivity towards E-H (E = H, B) bonds

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ABSTRACT: Halide abstraction from the ruthenium N-heterocyclic carbene complex Ru(IPr)₂(CO)HCl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with NaBAR₄⁺ (BAR₄⁻ = B(C₆H₄(3,5-CF₃))₄) gave the salt [Ru(IPr)₂(CO)H]BAR₄⁻ (2), which was shown through a combined X-ray/neutron structure refinement and Quantum Theory of Atoms in Molecules (QTAIM) study to contain a bifurcated Ru--η⁴-H₂C ξ-agostic interaction involving one IPr substituent of the IPr ligand. This system complements the previously reported [Ru(IMes)₂(CO)H]⁺ cation (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene: Organometallics 2009, 28, 1758) where a non-agostic form is favored. Treatment of 2 with CO, H₂ and the amineboranes H₂B-NR₂H (R = Me, H) gave [Ru(IPr)₂(CO)₄]BAR₄⁻ (3), [Ru(IPr)₂(CO)(η⁴-H₂)H]BAR₄⁻ (4) and [Ru(IPr)₂(CO)(κ²-H₂B-NR₂H)]BAR₄⁻ (R = Me, 5, R = H, 6) respectively. Heating 5 in the presence of Me₅SiCH=CH, led to alkene hydroboration and formation of the C-H activated product [Ru(IPr)(IPr)(CO)]BAR₄⁻ (7). X-ray characterization of 3 and 5-7 was supplemented by DFT calculations and the mechanism of H₂/H exchange in 4 was also elucidated. Treatment of 2 with HBcat resulted in Ru-H abstraction to form the boryl complex [Ru(IPr)₂(CO)(Bcat)]BAR₄⁻ (8), which proved to be competent in the catalytic hydroboration of 1-hexene. In 8, a combined X-ray/neutron structure refinement and QTAIM analysis suggested the presence of a single Ru--η¹-HC ξ-agostic interaction.

INTRODUCTION

The preparation of coordinatively unsaturated transition metal complexes is a widespread pursuit for practitioners of organometallic chemistry with an eye to developing new or improved reactivity of organic substrates. In the case of ruthenium, efforts to generate low-coordinate Ru(0) species date from the mid 1960’s with Chatt’s attempted synthesis of the 16-electron chelating phosphine complex Ru(dmpe)₂(dmpe = 1,2-bis(dimethylphosphino)ethane), which was employed in some of the earliest attempts to bring about intra- and intermolecular C-H bond activation. It is now known that this species is far too reactive to exist as anything other than a transient intermediate that can only be detected at very low temperature in inert gas matrices or in solution on very short, picosecond to nanosecond timescales. However, some 30 years after Chatt’s studies, Caulton and Werner demonstrated that Ru(0)L₄ species could indeed be isolated (and even structurally characterized) given the appropriate choice of L ligands, namely bulky phosphines in combination with π-accepting carbonyl or nitrosyl groups.

Arguably, the preparation of four-coordinate Ru(II)L₄ species is an even greater synthetic challenge on the grounds of their greater electron deficiency i.e. 14-electron count. Such species are therefore, unsurprisingly, rare (Chart 1). The chelate complexes Ru(PNP)Cl (A) and Ru(PO)₃ (B) adopt triplet ground states, which appear to be enough to reduce their Lewis acid character. Upon changing N(SiMe₂CH₃,PBu₃)₂ for N(CH₂CH₃,PBu₃)₂, Ru(PNP)Cl (C) displays a square planar structure and a...
singlet ground state due to the combination of high ligand steric and strong N→Ru π-donation. This same combination of steric and electronic donor properties also appears to help rationalize the stability of (Cy-PSiP)Ru-O′Bu (D). In other species, such as [Ru(P'Bu,Me),₂(CO)]⁺ (R = Ph, H) and Ru(PPh₃,₂,B₆-C₆H₄Me₂)Cl₂ (Chart 2), stabilization benefits from the presence of Ru–H–C agostic interactions to afford complexes which react as latent t₄-electron species. Thus, the X-ray structures of both [Ru(P'Bu,Me),₃(CO)PPh]⁺ and [Ru(P'Bu,Me),₂(CO)H]⁺ exhibit sawhorse configurations, in which both of the remaining vacant coordination sites at ruthenium are occupied by agostic interactions from the phosphine 'Bu groups. In the case of Ru(PPh₃,₂,B₆-C₆H₄Me₂)Cl₂, neutron diffraction reveals an even more unusual stabilizing effect involving two sets of bifurcated agostic Ru–η¹-H₃C interactions.

Chart 2

Our interest in Ru(I)₄ species was raised by the report of Gunnoe and co-workers from a number of years ago which identified the cationic N-heterocyclic carbene (NHC) derivative, [Ru(Imes),₂(CO)H]⁺ (1, Scheme 1: Imes = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene) as a true, four-coordinate Ru(II) species devoid of any agostic stabilization. All attempts to isolate 1 for structural verification proved, unfortunately, unsuccessful, and hence characterization was based upon DFT calculations and chemical trapping experiments. Given that variations of NHC N-substituents can often be used to bring about significant changes in the structure/reactivity of coordinately unsaturated M(NHC)₂ complexes, we have employed the bulkier IPr (1,3-bis(2,6-dialkylphenyl)imidazol-2-ylidene) ligand for the generation of [Ru(IPr),₂(CO)H]⁺ (2). Structural methods (neutron/X-ray diffraction) and DFT calculations have shown that 2 is stabilized by a symmetric bifurcated Ru–η¹-H₃C ζ-agostic interaction involving an IPr methyl group. In solution, 2 undergoes facile coordination of neutral donor ligands (CO, H₂B,NMe₂H (R = Me, H)), B-H activation of a borane as well as intramolecular C-H activation of an IPr ligand.

An X-ray structure determination on crystals of the compound isolated from fluorobenzene/hexane revealed two components, which in each case, showed the presence of an ζ-agostic interaction between the metal and one of the methyl substituents. This agostic C-H interaction lies trans to the CO group, with the hydride ligand disordered over the remaining two coordination sites, trans to each other, in the equatorial plane. To examine this in more detail, neutron diffraction data were combined with those from the X-ray measurement in a joint refinement. The cation of the major (55%) component (2a) is shown in Figure 1. Interestingly, the presence of two similar, short Ru–H–C contacts (Ru(1)...H(51A) 2.21(2)), Ru(1)...H(51B) 2.14(2) Å, Ru(1)...H(51C) 2.32(3) Å) supported the presence of a bifurcated Ru–η¹-H₃C agostic interaction far more symmetric in nature than that seen in Ru(PPh₃,₂,B₆-C₆H₄Me₂)Cl₂, where the Ru–H–C distances ranged from 2.13(10)...2.57(11) Å. Conjeero has reported that the C-H activated NHC complex [Pt(IPr),(IPr)'],SbF₆, exhibits a single ζ-agostic interaction to the non-activated IPr ligand with Pt–H and Pt–C distances of 2.07(6) and 2.8760(1) Å respectively, and Pt–H–C angle of 145°. In 2a, the Ru(1)...C(51) distance is considerably shorter (2.58(3) Å), with Ru–H–C angles (Ru(1)...H(51A)...C(51)/Ru(1)...H(51B)...C(51)) of 97.4(11) and 100.2(11)°.

Scheme 1 Gunnoe’s reported synthesis of [Ru(Imes),₂(CO)H]BAR₄⁺ (1).7

RESULTS AND DISCUSSION

Synthesis and Characterization of [Ru(IPr),₂(CO)H]⁺. The BAR₄⁺ (B[C₆H₃{(3,5-CF₃)},₂]₄) salt of [Ru(IPr),₂(CO)H]⁺ (2) was isolated in high yield (80%) as a highly air- and moisture-sensitive dark orange solid upon chloride abstraction from Ru(IPr),₂(CO)HCl with NaBAR₄⁺ in C₆H₆ at room temperature over 12 h (Scheme 2).

Scheme 2 Synthesis of the BAR₄⁺ salt of [Ru(IPr),₂(CO)H]⁺ (2). Both here and in later figures, the dotted contact between Ru and an IPr methyl group represents the likelihood that some H₃C...Ru agostic interaction is retained in solution.
Further insight into the nature of the agostic interaction in 2a was obtained from a quantum theory of atoms in molecules (QTAIM) study where the experimental structure of 2a was used directly in the QTAIM analysis (Figure 2). This highlights curved bond paths associated with both the Ru···H₅a and Ru···H₅b contacts, indicative of bonding interactions and so consistent with a bifurcated Ru···H-C structure. This is further confirmed by the presence of a ring critical point (RCP) enclosed by the [Ru···H₅b-C₅i···H₅a] unit. The computed BCP electron densities, ρ(r), are relatively low at ca. 0.035 au, and suggest that, despite the short Ru···H₅a/H₅b and Ru···C₅i distances, the resultant agostic interactions are relatively weak.  

![Figure 1. Combined neutron/X-ray structure of the cation in [Ru(IPr)(CO)H]BAR₆ (major component, 2a). Ellipsoids are shown at the 30% level with all hydrogen atoms (except Ru-H and those on the agostic methyl group) removed for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-C(2) 2.102(3), Ru(1)-C(29) 2.091(4), Ru(1)-C(51) 2.589(3), Ru(1)-H(51A) 2.21(2), Ru(1)-H(51B) 2.14(2), C(51)-H(51A) 1.09(2), C(51)-H(51B) 1.13(2), C(1)-O(i) 1.160(5), C(2)-Ru(1)-C(29) 176.51(13).](image1)

![Figure 2. QTAIM molecular graph of the cation of the major component, 2a, focusing on the Ru···H₅a/H₅b interactions. Calculations were based on the experimental X-ray/neutron structure and used the BP86 functional. Bond critical points (BCPs) and ring critical points (RCPs) are shown as green and magenta spheres respectively. Selected ρ(r) values (au): BCPs – Ru···H₅b 0.038; Ru···H₅a 0.033; RCP – Ru···H₅b-C₅i-H₅a 0.033. See ESI for full QTAIM metrics.](image2)

2b, the cation within the second component present in the combined neutron/X-ray structure of 2, shows a very similar geometry around Ru to 2a, with Ru···H₅a and Ru···H₅b contacts of 2.23(2) Å and 2.16(2) Å respectively and a short Ru-C(51) contact of 2.590(3) Å. QTAIM calculations also confirm a bifurcated structure. In addition, a third Ru···η²-HC contact of 2.44(2) Å to a η²-IPr substituent located trans to the hydride ligand is seen, although the associated BCP has a low ρ(r) value of only 0.012 au (see Computational ESI).

We were unable to affirm that the Ru···H-C interactions persisted in solution as the four doublets and two septets of the η² groups observed by ¹H NMR spectroscopy at room temperature simply broadened rather than separated upon cooling to 194 K. Low temperature (200 K) ¹C¹H and ¹C²H NMR spectra showed neither any low frequency shifted methyl resonance nor any reduced JCH coupling constant (ESI). The low frequency of the hydride chemical shift (δ -23.9 at 298 K) was similar to that of both Ru(IPr)(CO)HCl and 1 as a result of the vacant trans coordination site. Notably, NMR measurements of 2 (including overnight accumulated ¹C² spectra) could be recorded in CD₂Cl₂ and gave near identical spectra to those recorded in fluorobenzene, revealing that unlike [Ru(PBu₃Me)₂(CO)H]⁺, there was no binding of dichloromethane. Presumably, the Lewis acidity of 2 is lowered by the presence of the two strongly α-donating NHC ligands which, in combination with their steric bulk, disfavor interaction with a poor base like CH₃Cl. A small amount of decomposition of 2 was evident by NMR spectroscopy (only after several days) in chlorinated solvents or upon warming to 343 K in C₆H₆F, although there was no evidence to suggest that this involved dehydrogenation of the carbene N-substituent as seen for [Ir(IPr)₂H]⁺.  

**Experimental and Computational Comparison of [Ru(IPr)(CO)H]⁺ and [Ru(IMes)₂(CO)H]⁺.** In Gunnoe’s attempts to prepare 1, benzene was used as the solvent for the attempted NaBAR₆ abstraction. Upon turning to C₆H₆F, we found no discernible change in color of the solution, but did observe a change in the hydride region of the proton NMR spectrum, the signal for 1 at δ ~ -25.4 being replaced by a new resonance at δ -29.9 within the time of mixing Ru(IMes)₂(CO)HCl and NaBAR₆. The species responsible for this new signal proved to be stable for at least 48 h. Comparison with Aldridge’s studies on NaBAR₆ abstraction of chloride from M(IMes)₂H₂Cl (M = Rh, Ir), in particular the shift of the hydride signal to lower frequency, led us to propose the formation of the
sodium inclusion complex, [Ru(IMes)3(CO)HCl(Na)]BAR, where the sodium cation is intercalated between the mesityl rings of the NHC. All efforts to isolate this species with the aim of confirming this assignment were unsuccessful. Similar behavior was found upon re-examining the Ru(IPr)2(CO)HCl/NaBAR, reaction. A 1H NMR spectrum recorded 15 min after mixing the reagents showed loss of the starting Ru-H resonance (δ = 24.5) and formation of new signals at both higher (δ = 23.9) and lower (δ = 28.2) frequencies, assigned to 2 and [Ru(IPr)2(CO)HCl(Na)]BAR, respectively. After 48 h, only the hydride signal for 2 remained, consistent with the inclusion complex being an intermediate on the pathway to full metathesis. Quite why the IMes derivative is so much longer lived than the IPr derivative is unclear. Different behavior was also apparent using [Et3Si(toluene)]BAR, for halide abstraction instead of NaBAR, whereupon Ru(IMes)3(CO)HCl was now converted instantly and cleanly through to halide abstraction with a Ru(IMes)3(CO)HCl(51) fragment (NHC = IMes, IPr) in the agostic structures 1a/1b and 2a/2b which has the effect of destabilizing the LUMO. Orbital plots are provided in the ESI.

**Coordination of CO, H2, and B-H bonds to Ru(IPr)2(CO)H**. Addition of 1 atm CO to a fluorobenzene solution of 2 resulted in displacement of the agostic bonding and coordination of two additional CO ligands to yield the 18-electron tricarbonyl compound, [Ru(IPr)2(CO)2]BAR, (3, Scheme 3). The presence of a high-frequency shifted (δ = 6.8) hydride singlet was indicative of the coordinative saturation.19 Use of 13C CO led to signal enhancement of just the two lowest frequencies of the three 13C(CO)H NMR carbonyl resonances at δ 173, 190 and 193, consistent with the initial Ru-CO group being inert to substitution. The cis-13C labelled CO ligands (Scheme 3) showed the expected small (4 Hz) JHC splitting. Both coupled to the Ru-H resonance, to generate a doublet of doublets signal, with JHC couplings of 26.1 (trans) and 6.7 Hz (cis).

![Scheme 3](image)

Of note in the X-ray structure of 3 (Figure 3) were the distortions of the three distinctly non-linear Ru-C-O bonds. The 81° angle between the two mean planes (each containing the atom of an NHC ring) revealed that the carbene ligands are disposed at the upper limit of a staggered arrangement. Moreover, the three carbonyl ligands about the equatorial girdle of the cation were each seen to lie atop an IPr phenyl ring (C55/O1 above ring based on C16; C56/O2 above ring based on C43 and C57/O3 above ring based on C31). The ensuing steric factors have combined such that the CO ligands are each bent away from the face of the aromatic ring above which each is located.
These features are retained in the BP86-optimized structure of 3, but lost in the less congested model species [Ru(IMe)3(CO)]3+ (3' IMe = 1,3-dimethylimidazol-2-ylidine) confirming their steric origin (similar deviations from linearity can also arise from electronic effects). The carbonyl oxygens appear to have borne the maximum brunt of these distortions away from the plane of the proximate aromatic rings (Ru(1)-C(55)-O(1) 171.9(2)°, Ru(1)-C(56)-O(2) 171.6(2), Ru(1)-C(57)-O(3) 169.1(2)). These compare to the values of 177.6(5), 176.9(5) and 175.1(5)° found in the cationic phosphine derivative [Ru(PPh3)3(CO)]2+.[28] Ultimately, ‘bowing’ of the two trans carbonyl groups in 3 is evidenced by the C(56)-Ru(1)-C(57) angle of 166.09(12)°. The trans-influence of the hydride ligand manifests itself in the elongation of the Ru(1)-C(55) distance (1.976(3) Â) relative to the other two Ru-CO bond lengths (1.945(3) and 1.922(3) Â).

**Figure 3.** Molecular structure of the cation in [Ru(IPr)3(CO)]+[H]BAr4+ (3). Ellipsoids are shown at the 30% level with all hydrogen atoms (except Ru-H) removed for clarity. Selected bond lengths (Â) and angles (°): Ru(1)-C(1) 2.140(2), Ru(1)-C(28) 2.129(3), Ru(1)-C(55) 1.976(3), Ru(1)-C(56) 1.922(3), Ru(1)-C(57) 1.945(3), C(1)-Ru(1)-C(28) 171.64(10), C(55)-Ru(1)-C(56) 91.81(12), C(56)-Ru(1)-C(57) 166.09(12).

Introduction of H2 (1 atm) into a CD3Cl3 solution of 2 brought about an immediate color change from orange to yellow resulting from the formation of the dihydrogen hydride complex [Ru(IPr)3(CO)](η2-H2)H][BAr4]+ (4, Scheme 4). At room temperature, this showed a single, broad hydride resonance at δ -4.95 of relative integral 3, suggestive of rapidly exchanging Ru-H/(η2-H2) ligands. Even at 182 K, the exchange could not be frozen out, an observation that is in line with other ruthenium complexes containing a cis-arrangement of dihydrogen and hydride ligands.29,30 Freeze-pump-thaw degassing failed to completely remove the η2-H2 ligand and the resonance at δ -4.95 could still be seen even after 10 degassing cycles. Upon reducing the solution of 4 to complete dryness, 2 was regenerated.

DFT calculations were employed to provide structural insight into 4 and three local minima were again located, two of which feature a single agostic interaction, either trans to CO (4a) or H (4b), and a third, non-agostic form (4c). All three isomers are within 0.9 kcal/mol of each other when computed at the BP86-D3(CH3Cl) level (Figure 4a). A transition state for Ru-H/(η2-H2) exchange, TS(4b-4b), was also located. This process involves H-transfer from the original η2-H2 ligand in 4b (labelled H5-H6, Figure 4b) onto the neighboring hydride (H4). Concomitant rotation of this new η2-H2-H moiety then delivers H2 back onto H4 to complete the exchange. In TS(4b-4b), the agostic interaction shortens significantly (Ru···H4 = 1.91 Å cf. 2.06 Å in 4b) reflecting the lower trans influence of the η2-H2 moiety compared to a hydride. The overall barrier (relative to the lowest energy form 4c) is 13.3 kcal/mol, consistent with rapid exchange on the NMR timescale.

**Figure 4.** (a) Isomers of [Ru(IPr)3(CO)](η2-H2)H]+, 4, with the shortest agostic Ru···H contact indicated; (b) Computed structures of 4b and Ru-H/(η2-H2) exchange transition state TS(4b-4b) with selected distances in Å; non-participating H atoms omitted for clarity. All free energies (kcal/mol) are at the BP86-D3(CH3Cl) level and are quoted relative to 4c set to 0.0 kcal/mol.

The amine-borane complexes22 [Ru(IPr)3(CO)(κ-Cl-H2BH-NMe2-H)]BAr4+ (5) and [Ru(IPr)3(CO)(κ-Cl-H2BH-NH2)]BAr4+ (6) were prepared as alternative examples involving A-E bond coordination to 2 (Scheme 4). 5 and 6 were identical in the first instance by the appearance of 1B NMR signals at δ 4.5 and δ -2.4 respectively, characteristically downfield from those of the free substrates (δ -13.4, -21.6). In the low frequency region of the 1H NMR spectra, sharp hydride signals (5: δ -15.61; 6: δ -15.86) were present in a 1:3 ratio with very broad B-H resonances (5: δ -2.3; 6: δ -2.1). Upon cooling to 190 K, exchange of the bound and terminal B-H groups was frozen.
out to give two distinct, single integral Ru-H-B singlets (5: δ -5.83, -3.94; 6: δ -5.63, -4.13), which sharpened upon 1H decoupling. In the case of 5, 1H[11B] NOESY studies showed that the remaining, unbound B-H signal was hidden underneath resonances from the IPr groups. The X-ray structures of both 5 and 6 (Figure 5) revealed distorted octahedral geometries comprised of a trans arrangement of IPr ligands with the CO and hydride then mutually cis and, therefore, trans to the two metal bound B-H groups of the amine-borane ligands. The Ru···B distances of 2.293(4) and 2.333(2) Å were similar to the values in the large number of known rhodium κ¹-bound derivatives (e.g. [Rh(PBu3)_2(κ²-H_2BH-NMe3)H]H+) (2.318(8) Å),33,35 [Rh(IMes)_2(κ²-H_2BH-NBuH_2)H]H+ (2.305(4) Å),36 although (unsurprisingly) significantly shorter than in the κ¹-bound ruthenium complexes, [Ru(xantphos)(PPh3)(κ²-HBH-NH3)H]H+ (2.939(3) Å)37 and [Cp*Ru(PMe3)(κ²-HBH-NMe3)]H+ (2.648(3) Å).38

The stability of 5 in solution proved to be solvent dependent. Thus, the complex decomposed in CDCl3 over ca. 6 h at room temperature, but was stable for over a week in C6D6F. However, warming to 343 K in C6D6F resulted in dehydrocoupling of the amine-borane ligand to afford [Me,N-BH3] and the dihydrogen hydride complex 4. Coordination of H2 eliminated upon dehydrocoupling was also found37 for [Ru(xantphos)(PPh3)(κ²-HBH-NBuH2)H]H+ whereas, in contrast, amino-borane products of the type [ML2(κ²-H_2B-NR3)H]H+ arise upon the dehydrocoupling of Rh and Ir amine-borane derivatives.39 This difference is not simply due to Ru vs Rh/Ir, since Ru(PCy3)(η²-H2)H2 has also been shown to form the amino-borane product Ru(PCy3)(κ²-H_2B-NR3)H, upon direct addition of H2B-NR3H (R = H, Me).40 Extension of the bonding analysis performed by Alcaraz et al. on the isoelectronic and isostructural complexes [M(PCy3)2(κ²-H_2B-NPr2)H]M+ (M = Ru, n = 0; M = Rh and Ir, n = 1) suggests that the inability of cationic 2 to coordinate an amino-borane ligand may be connected to poor overlap between the contracted metal d-orbitals and empty BN π* orbital.41

Figure 5. Molecular structure of the cations in (left) [Ru(IPr)3(CO)(κ²-H_2BH-NMe3)H]BAR4+ (5) and (right) [Ru(IPr)3(CO)(κ²-H_2BH-NH3)H]BAR4+ (6). Ellipsoids are shown at the 30% level with all hydrogen atoms (except Ru-H and those on B or N) removed for clarity. Selected bond lengths (Å) and angles (°) in 5: Ru(i)-C(i) 2.136(3), Ru(i)-C(28) 2.107(3), Ru(i)-C(55) 1.805(4), Ru(i)-B(1) 2.293(4), C(1)-Ru(i)-C(28) 173.11(13), C(55)-Ru(i)-B(1) 142.06(16). Selected bond lengths (Å) and angles (°) in 6: Ru(i)-C(i) 2.1170(16), Ru(i)-C(28) 2.0950(16), Ru(i)-C(55) 1.813(2), Ru(i)-B(1) 2.333(2), C(i)-Ru(i)-C(28) 176.78(6), C(55)-Ru(i)-B(1) 162.34(10).
In an attempt to promote \( \text{H}_3\text{B}-\text{NMe}_3 \) coordination, 5 was heated with an excess of \( \text{Me}_3\text{SiCH}==\text{CH}_2 \) as a hydrogen acceptor. This led, instead, to formation of the hydaboration product, \( \text{Me}_3\text{SiCH}==\text{CH}_2\text{NMe}_3 \), which was identified by comparison of the “\( ^3 \)B NMR chemical shift to those of \( \text{RCH}_2\text{CH}_2\text{BH}_3\text{NMe}_3 \) (\( \text{R} = \text{Bu}, \text{Me}(\text{CH}_3) \)). The initial organometallic product of the reaction was 2, implying that alkene hydrogenation must occur as well as hydaboration. Continued heating led to the slow disappearance of the hydride signal for 2 (15 days at 323 K in \( \text{C}_6\text{H}_6 \)), alongside a change in color of the solution from orange to red. Spectroscopic identification of the product(s) proved to be a thankless task due to extensive overlap of signals in both the methyl and methine regions of the proton NMR spectrum.

Fortuitous isolation of a very small number of diffraction quality red-orange crystals proved possible. These were characterized by X-ray crystallography (Figure 6) as the C-H activated IPr complex, [Ru(IPr)(IPr')(CO)]BAr\(^f\) (7). The sawhorse structure (C(1)-Ru(1)-C(29): 175.67(9)°; C(28)-Ru(1)-C(12): 96.40(12)°) shows an agostic interaction trans to the activated arm of the IPr ligand (Ru(1)···H(51C) 2.23(2) Å, Ru(1)···C(51) 3.163(3) Å, Ru(1)-H(51C)-C(51) 158(2)°). This was confirmed by a QTAIM calculation based on the heavy atom positions of 7 that showed a Ru(1)···H51C bond path with \( \rho(r) = 0.035 \) au (see Fig. S19, ESI). The metallated C-Ru distance of 2.071(2) Å is much shorter than in either [Ir(IPr)(IPr')(H)]\(^+\) (2.117(7) Å) or [Pt(IPr)(IPr')]\(^+\) (2.226(6) Å)\(^{29}\) which, to the best of our knowledge, are the only other known examples of C-H activated IPr complexes.

\( \text{B-H} \) activation by 2. The electrophilic nature of the Ru-H in 2 was demonstrated by the reaction with HBcat, which generated a rare example of a cationic boryl complex,\(^{44} \) [Ru(IPr)(CO)(Bcat)]BAr\(^f\) (8, Scheme 4). The formation of a boryl ligand was inferred in the first instance by a signal at \( \delta \) 42 in the “\( ^3 \)B NMR spectrum, which is indicative of three-coordinate boron.\(^{45} \) Free rotation about the Ru-B bond (based on the appearance of two proton and three “\( ^3 \)C catechol signals) could be frozen out at 213 K, while lowering the temperature further (to 182 K) resolved the methine protons of the IPr ligands into eight multiplets, each of integral 1. The methyl resonances remained partially overlapping, although one doublet was low frequency shifted to \( \delta \) -0.34, consistent with agostic bonding.

\( \text{Figure 6. Molecular structure of the cation in } [\text{Ru(IPr)(IPr')(CO)]BAr}_2 \text{. Ellipsoids are shown at the 30\% level with all hydrogen atoms (except those on the agostic methyl group) removed for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-C(1) 2.106(2), Ru(1)-C(29) 2.113(2), Ru(1)-C(28) 1.788(3), Ru(1)-C(12) 2.071(2), C(1)-Ru(1)-C(29) 175.67(9), C(12)-Ru(1)-C(28) 96.40(12).} \)
Ru(1)--H(27b) 2.02(3) Å, Ru(1)--H(27a) 2.46(3) Å, Ru(1)--H(27b)--C(27) 109(2)°. The associated QTAIM molecular structure (Figure 8) this time indicates a single Ru-bridge-H-C \textsuperscript{Pr} ζ-agostic, with no bond path evident between Ru and H\textsubscript{27a} and, hence, no RCP that would be indicative of the bifurcated Ru-\textsuperscript{η\textsubscript{1}}-H\textsubscript{C} form. The strong trans-influence boryl ligand\textsuperscript{46-47} occupied the apical site of the square pyramidal structure, with much shorter Ru-B distance (2.030(4) Å) than found in other Ru or Os boryl complexes.\textsuperscript{48} The catechol substituent provided the optimal motif for coordination to Ru, since no reaction at all was observed upon treatment of 2 with HBpin.

The reasons why bifurcated Ru-\textsuperscript{η\textsubscript{1}}-H\textsubscript{C} structures are seen in 2a and 2b while a Ru-\textsuperscript{η\textsubscript{1}}-HC interaction is preferred in 8 are presently not clear to us. Our DFT calculations on the isolated cations of 2a and 2b indicate that structures with different (or indeed no) agostic interactions can be very close in energy. Moreover, a 2\textsuperscript{nd} order perturbation analysis based on the computed natural bond orbitals (NBO) suggests the overall strength of the agostic interaction does not reflect the binding mode. Thus the total σ-donation from the C51-H51a and C51-H51b σ-BMOs is strongest in 2a (21.2 kcal/mol), weakest in 2b (12.4 kcal/mol), and intermediate from the C27-H27a and C27-H27b σ-BMOs in 8 (18.6 kcal/mol). See Figures S21 and S22 in the ESI for full details.

**Catalytic hydroboration of alkenes with 8.** Upon exposure of 8 to 1 atm H\textsubscript{2}, elimination of HBcat took place in the time of mixing with concomitant formation of the dihydrogen hydride complex 4. The reversible coordination of the boryl ligand therefore prompted a preliminary study on the use of 8 as a precursor for catalytic alkene hydroboration. Rhodium, particularly with phosphine ligands,\textsuperscript{49} is typically the element of choice for this transformation, with only a handful of reports detailing the activity of ruthenium complexes.\textsuperscript{50} Catalytic experiments with 1-hexene showed that 8 gave mainly the linear hydroboration product, with a small amount of hexane also generated through competitive alkene hydrogenation (Table 1). The hydride complex 2 gave an identical product composition, suggesting that it is converted to 8 under the catalytic conditions, and that it is the boryl complex which then propagates the subsequent chemistry.\textsuperscript{47}
contain a bifurcated Ru···η3-H2C agnostic interaction at one of the carbene 1Pr substituents. The agnostic bonding appears to play a central role in allowing 2 to be isolated and structurally characterized, in contrast to the non-agnostic IMes derivative. In terms of reactivity, 2 behaves like a coordinatively unsaturated fragment, readily coordinating H2C=O and amine boranes. Treatment with catecholborane highlights the electrophilic nature of the Ru-H bond which results in the formation of the boryl derivative [Ru(IPr)(CO)(Bcat)]BaF, which features a Ru···η3-HC interaction. This mode of reactivity, whereby substrates E-H (E = B, H) can add over the Ru-H bond, appears to be especially promising as a route to new Ru-E containing products and is something we will report more on in due course.

**EXPERIMENTAL SECTION**

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques using dried and degassed solvents, unless otherwise stated. NMR spectra were recorded on Bruker Avance 400 and 500 MHz NMR spectrometers and referenced to residual solvent signals for 2H and 13C spectra for CDCl3 (δ 7.26, 128.0) and CD3CN (δ 5.32, 54.0). Unlocked samples in fluorobenzene were referenced to the center of the downfield multiplet at 6.71. 1H spectra were referenced externally to BF3·OEt2 at δ = 0.0. All complexes, exhibited a singlet at δ -6.6 for the BaF2 anion. IR spectra were recorded on a Nicolet Nexus spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK. GC-MS data were collected on an Agilent Technologies 5975C using an HP-5 column (GC data was collected on the same type of column). Ru(IPr)(CO)HCl was prepared according to the literature.9

[Ru(IPr)(CO)(CO)]BaF2 (2). A 12H2 (8 mL) solution of Ru(IPr)(CO)HCl (0.21 g, 0.22 mmol) was added to a slurry of NaBaF2 (0.192 g, 0.22 mmol) in CD3CN (2 mL) and the suspension stirred for 12 h. After filtration, the reaction mixture was concentrated to ca. 3 mL and layered with hexane to afford dark orange crystals of 2, which were manually separated by hand from colorless crystals of residual NaBaF2. Yield: 0.290 g (80%). 1H NMR (500 MHz, CD3CN, 298 K): δ 7.74 (s, 8H, o-Ar-H), 7.58 (s, 4H, p-Ar-H), 7.45 (t, δH = 7.7 Hz, 4H, p-Ar-H), 7.18-7.21 (overlapping d, 8H, m-Ar-H), 7.06 (s, 4H, NCH), 2.39 (sept, δH = 7.0 Hz, 4H, CH(CH3)2), 2.32 (sept, δH = 6.8 Hz, 4H, CH(CH3)3), 1.09 (d, δH = 6.8 Hz, 12H, CH(CH3)2), 1.05 (d, δH = 7.0 Hz, 12H, CH(CH3)3), 0.82 (d, δH = 6.8 Hz, 12H, CH(CH3)2), 0.73 (d, δH = 7.0 Hz, 12H, CH(CH3)3), -23.69 (s, iH, Ru-H). 13C[1H] NMR (126 MHz, CD3CN, 298 K): δ 200.2 (s, Ru-CO), 185.4 (s, Ru-CNl), 162.2 (q, δC = 50 Hz, i-Ar-C), 145.8 (s, o-Ar-C), 145.7 (s, o-Ar-C), 135.3 (s, o-Ar-C), 135.2 (s, NAr-C), 131.1 (s, p-Ar-C), 129.4 (q, 3CF = 32.2 Hz, 3CF = 31.1 Hz, m-Ar-C), 125.8 (s, NCH), 125.1 (q, JCF = 270 Hz, CF3), 125.0 (s, m-Ar-C), 124.7 (s, m-Ar-C), 117.9 (sept, 3CF = 4 Hz, p-Ar-C), 29.2 (s, CH(CH3)2), 29.2 (s, CH(CH3)3), 24.6 (s, CH(CH3)2), 24.4 (s, CH(CH3)3), 23.8 (s, CH(CH3)2), 22.3 (s, CH(CH3)3). IR (CD3CN, cm-1): 1964 (νCO). Anal. Calcd for CsH20Na2BF3Ru: C 59.02, H 4.84, N 3.16. Found: C 58.91, H 5.01, N 3.20.

[Ru(IPr)(CO)]H2BaF (3). A J Young’s resealable NMR tube was charged with a solution of 2 (0.019 g, 0.01 mmol) in CD3CN (0.5 mL), degassed via three freeze-pump-thaw cycles and exposed to 1 atm CO. After 3 h, the pale yellow solution was layered with hexane to afford pale yellow crystals of 3. Yield: 0.016 g (36%). 1H NMR (500 MHz, CD3CN, 298 K): δ 7.73 (s, 8H, o-Ar-H), 7.56 (s, 4H, p-Ar-H), 7.51 (t, δH = 8.1 Hz, 4H, p-Ar-H), 7.28 (d, δH = 8.1 Hz, 8H, m-Ar-H), 2.76 (s, 4H, NCH), 2.21 (sept, δH = 7.0 Hz, 8H, CH(CH3)2), 1.09 (d, δH = 7.0 Hz, 24H, CH(CH3)2), 1.00 (d, δH = 7.0 Hz, 24H, CH(CH3)2), -6.81 (s, iH, RuH). 13C[1H] NMR (126 MHz, CD3Cl, 298 K): δ 193.1 (s, Ru-CO), 189.6 (s, Ru-COO), 173.1 (s, Ru-CNl), 162.1 (q, JCF = 51 Hz, 1Ar-C), 146.4 (s, o-Ar-C), 176.6 (s, NAr-C), 135.2 (s, o-Ar-C), 132.0 (s, p-Ar-C), 129.2 (qq, 3CF = 32.2 Hz, 3CF = 31.1 Hz, m-Ar-C), 126.8 (s, NCH), 125.1 (s, m-Ar-C), 125.0 (q, JCF = 271.1 Hz, CF3), 117.8 (m, p-Ar-C), 29.1 (s, CH(CH3)2), 26.3 (s, CH(CH3)2), 22.6 (s, CH(CH3)2). IR (KBr, cm-1): 2040 (νCO), 2025 (νCO). Anal. Calcd for CsH28Ba2N2O2RuH2Cl2F3: C 58.90, H 5.10, N 3.69. Found: C 58.35, H 5.02, N 3.87.
H{Ru(IPr)₃}C(O)CO(Bcat)BAR₅ (H). Bcat (0.003 g, 0.025 mmol) was added to a solution of 2 (0.041 g, 0.023 mmol) in C₄H₆ (0.5 mL) and the reaction mixture allowed to stand for 1 h. The solvent was removed under vacuum to yield a pale brown solid, which was washed with hexane (3 x 0.8 mL) and then redissolved in fluorobenzene/hexane to afford 8 as pale yellow crystals Yield: 0.034 g (78%). Hi NMR (500 MHz, CDCl₃, 298 K): δ 7.73 (s, 8H, o-ArH), 7.57 (s, 4H, p-ArH), 7.27 (m, 4H, ArH), 7.21 (m, 4H, ArH), 7.02 (d, JHH = 7.4 Hz, 4H, ArH), 6.07 (s, 4H, NCH), 6.72 (dd (JHH = 5.4 Hz, JHH = 3.6 Hz, ArH), 5.4 Hz, ArH), 4.75 (s, 4H, CH₂), 2.98 (sept, JHH = 6.8 Hz, 12H, ArH), 2.33 (sept, JHH = 6.8 Hz, 12H, ArH), 2.13 (sept, JHH = 5.7 Hz, 12H, ArH), 1.97 (sept, JHH = 5.8 Hz, 12H, ArH), 1.68 (sept, JHH = 6.5 Hz, 1H, CH(CH₃)₂), 1.38 (br s, 3H, CH₂), 1.26 (br s, 6H, CH(CH₃)₂), 1.20 (br s, 3H, CH₂), 1.15 (br s, 3H, CH₂), 1.10 (br s, 3H, CH₂), 1.07 (br s, 3H, CH₂), 0.88 (br s, 3H, CH₂), 0.83 (br s, 3H, CH₂), 0.76 (d, JHH = 5.1 Hz, 6H, CH₂), 0.62 (d, JHH = 5.7 Hz, 3H, CH₂), 0.49 (d, JHH = 6.5 Hz, 3H, CH₂), 0.32 (br s, 6H, CH₂), -0.34 (d, JHH = 6.0 Hz, 6H, CH₂).

δ(C) NMR (101 MHz, CDCl₃, 298 K): δ 109.4 (s, Ru-C), 162.2 (s, Ru=N), 145.9 (s, O-C), 154.2 (s, O-C), 153.5 (s, N-C), 153.5 (s, O-C), 135.0 (s, O-C), 129.0 (s, O-C), 129.0 (s, O-C), 126.9 (s, N-C), 128.9 (s, m-Ar), 125.0 (q, JCF = 271 Hz, CF₃), 124.6 (s, m-Ar), 120.9 (s, ArC), 117.8 (sept, JCD = 4 Hz, ArC), 121.2 (s, ArC), 29.8 (s, CH₂), 29.1 (s, CH₂), 25.1 (s, CH₂), 24.8 (s, CH₂), 22.4 (s, CH₂), 21.2 (s, CH₂), 18.8 NMR (161 MHz, CDCl₃, 298 K): δ 41.6 (br s, RuH). IR (CDCl₃, cm⁻¹): 1981 (υCCO). Anal. Calcd for C₃₀H₁₂B₃N₃O₆F₄Ru: C: 59.44, H: 4.70, N: 2.97. Found: C: 59.01, H: 4.55, N: 3.08.

Catalytic Hydroboration. To a solution of 2 (0.004 g, 0.0022 mmol) in C₄H₆F (0.5 mL) in a vial in the glovebox was added 1-hexene (0.004 g, 0.0440 mmol) and H{Ru(IPr)₃}C(O)CO(Bcat)BAR₅ (0.001 g, 0.0088 mmol) and the reaction mixture stirred for 24 h. At this time, Hi NMR spectroscopy showed no resonances attributable to any remaining 1-hexene. The composition of the reaction mixture was analyzed by GC-MS; assignment of the linear product (and, by default, the branched product) was made by comparison of retention time to a sample comprising ca. 99% of linear isomer prepared via the hydroboration of ethylene with H{Ru(IPr)₃}C(O)CO(Bcat)BAR₅. respectively. The neutron experiment for 2 was carried out using two single crystals that were mounted in random orientations relative to each other inside a sealed vanadium container filled with argon gas. The vanadium can was loaded into a top-loading closed cycle refrigerator and data collected at 3 different orientations. A Nonius kappaCCD detector was also employed for the data collection of 3, while those for 5 and 6 were effected using an Agilent Xcalibur (Mo-Kα) diffractometer and that for 7 was completed using an Agilent SuperNova (Cu-Kα) diffractometer. The structure of 8 was refined using a combination of X-ray data garnered using Cu-Kα radiation and an Agilent SuperNova diffractometer plus neutron data on the SXD instrument at ISIS. In the latter experiment, one crystal was sealed inside a vanadium container under argon and placed into a top loading closed cycle refrigerator with data collected at 5 different orientations. All diffraction measurements were made at 150 K.

All of the X-ray refinements were carried out using SHELXL. With the exception of 6, the asymmetric unit in all structures comprises one cation and one BAR₅ anion. Hydrides, where present, were located and refined at a distance of 1.6 Å from the metal center in the case of the X-ray-only refinements for 3, 5 and 6. Disorder of the fluorne atoms in some of the anion CF₅ groups was not uncommon. In such instances, C-F and F--F distance restraints were included and, if merited, ADP restraints were added for affected fractional occupancy fluorne atoms. Convergence was reasonably straightforward with the exception of the pertinent details, many of which pertain to disorder, that follow.

The model in 2, which was solved and refined using X-ray data, revealed that two of the isopropyl groups in the cation were disordered, with the positions of C₅₁/C₅₂ and the carbon atoms attached to C₄₁ (C₂₄/C₄₃) each being split over two sites in a 55:45 ratio. Some C-C distance restraints were employed to help convergence to a chemically sensible final. The hydrogen atoms attached to C₅₁ were located and freely refined, subject to being located 0.98 Å from the parent atom. The hydride ligand was seen to be disordered over two trans sites (55:45 ratio) and each fraction was refined at a distance of 1.6 Å from Ru. In the BAR₅ anion, the fluorne atoms attached to C₇₉, C₁₈ and C₂₇ each exhibited disorder over two sites in respective ratios of 70:30, 60:40 and 50:50. The arising converged X-ray model was used as the basis for the results presented here, which were obtained using Xanal06 and a combination of X-ray and neutron data. With the exception of H₅ₐ, H₅ß and H₅c, and the disordered hydride (H₁/H₄) hydrides were initially refined in four groups, namely, those confined to the anion, and, in the cation, primary hydrides, tertiary hydrides and aromatic hydrides. The arising refined C-H distances were used as the basis for the rigid groups with which these non-contentious hydrides were ultimately included. The disordered hydride was modelled subject to both components being equidistant from the ruthenium center. The agostic hydrides attached to C₅₁ were refined freely. All hydrogen atoms were treated isotopically. Disordered fluorne atoms were refined with ADP restraints, and with restrained C-F and F--F distances of 1.330(5) Å and 2.41(3) Å, respectively.

Halide disorder was seen to be evident in many of the CF₅ groups within the anion in 3. In particular, the fluorine atoms attached to C₆₄, C₆₅ C₇₂ C₈₀, C₁₈ and C₁₉ exhibited respective disordered distances of 65:35, 50:50, 70:30, 50:50, 80:20 and 55:45. C-F distance restraints were to being similar within each affected functionality. The isopropyl carbons, C₂₃/C₄₄, belonging to the cation in 6 were modelled as being disordered over two sites in a 55:45 ratio. The hydrogen atom attached to C₂₂ was included at a calculated position based on the major fractional occupancy components of C₃₂/C₄₄. H₅ (attached to N₅) was located and refined subject to being located at a distance of 0.98 Å from the parent atom. The hydrogen atoms attached to the boron center, B₈, were located and refined without restraints. Disorder was also evident in some of the anion CF₅ groups. In particular, the fluorine atoms attached to C₆₄, C₇₂ and C₇₃ were each modelled over two proximate sites in disorder ratios of 50:50, 60:40 and 60:40, respectively. In 6, the hydrogen atoms attached to B₈ and N₅ were readily located and freely refined, without any restraints. There may be some "wagging" disorder associated with the carboxyl ligand. However, efforts to model this did not improve the refinement; hence, these were abandoned. Only one CF₅ group in the anion was modelled for disorder, with the fluorines attached to C₆₂ being treated as located across two sites at a 75:25 ratio. There was also one disordered molecule of fluorobenzene in the asymmetric unit of this structure. This was ultimately treated using PLATON SQUEEZE, as the solvent was disordered over two proximate sites and, in each of these, the fractional occupancy was additionally disordered.

The asymmetric unit in 7 comprises one cation, one anion, half of an ordered molecule of C₆H₅F and a region of diffuse solvent.
C88, C91, H91 and F26 in the ordered solvent moiety are co-incident with a crystallographic 2-fold rotation axis which serves to generate the remainder of the molecule. The disordered region exhibited some evidence for the presence of one fluorobenzene molecule, but this was not accessible to any sensible model and hence was treated via PLATON SQUEEZE. On the basis of the results from this algorithm, the empirical formula (as presented herein) contains one additional formula unit of C1,H,F, to account for the SQUEEZED solvent. The hydrogen atoms attached to C51 were located and refined at a distance of 0.98 Å from the parent atom and subject to being equidistant from each other. In the anion, F16,18 were refined as being disordered over two proximate sites in a 65:35 ratio.

As for 2, the structure of 8 was solved to convergence using X-ray data and the arising model then used as the basis for a combined refinementusing both X-ray and neutron data. In the X-ray only model, the hydrogens attached to C27 were located and refined at a distance of 0.98 Å from the parent atom and with a common Uiso value. Additionally, the hydrogen atoms attached to C12 were included at calculated positions but, again, with a common Uiso value. Two of the CF3 groups in the anion were modelled for disorder (55:45 and 60:40 ratios for fluorine atoms attached to C12 and C13, respectively). The combined X-ray and neutron refinement for this structure, with particular emphasis on the treatment of non-contentious hydrogen atoms, was similar to the strategy adopted for 2. Ultimately, in this instance, the hydrogens attached to C27 were refined without restraints.

Crystallographic data for compounds 2, 3, and 5-8 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1435594-1435599. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Computational Details. DFT calculations were run with Gaussian 03 (Revision D.01) and Gaussian 09 (Revision D.01). Ru centers were described with the Stuttgart RECPs and associated basis sets and 6-31G** basis sets were used for all other atoms. Optimizations employed the BP86 functional and all stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). Exceptions were those structures used for the QTAIM and NBO studies which were either based on the X-ray/neutron structures (2a, 2b, 8) or the experimental heavy atom positions with only the H atoms positions being optimized. TS(4b-4b) was also characterized via IRC calculations and subsequent geometry optimizations to confirm it linked to the expected minima. PCM corrections for the effects of fluorobenzene and CH2Cl2 solvent were computed as appropriate with Gaussian 09 and dispersion corrections applied using Grimme’s D3 parameter set and the BP86-optimized geometries. QTAIM studies employed the AIMALL program and NBO analyses were run with NBO version 5.9.

ASSOCIATED CONTENT

Supporting Information

All data supporting this study are provided as Supporting Information accompanying this paper. The Supporting Information is available free of charge on the ACS Publications website. Multinuclear NMR spectra of 2-6 and 8. Computational Data including full QTAIM data for BCPs and RCPs associated with Ru⋯H agostic interactions, details of TDDFT calculations, optimized geometries and energies and geometries used in QTAIM calculations and an NBO analysis of the agostic interactions in 2a, 2b and 8; an xyz file containing all geometries is also supplied.

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REFERENCES

For cases which seem to be devoid of such stabilization, see:

For non-Ru examples, see:
