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Coordination chemistry of a calix[4]arene-based NHC ligand: dinuclear complexes and comparison to I^{i}Pr$_2$Me$_2$†

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The preparation and coordination chemistry of 5,17-bis(3-methyl-1-imidazol-2-ylidene)-25,26,27,28-tetrapropoxycalix[4]arene (**1**) is described. Starting from the bis(imidazolium) pro-ligand **1**·2HI, the free carbene **1** was readily generated in solution through deprotonation using K[O^{t}Bu] and its reactivity with rhodium(I) dimers [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) and [Rh(CO)$_2$Cl]$_2$ investigated. Dinuclear complexes were isolated in both cases, where the calix[4]arene-based NHC ligand adopts a bridging μ^2-coordination mode, and in one case characterised in the solid-state by X-ray diffraction. Using instead an isolated and well-defined (mononuclear) silver transfer agent, generated by reaction of **1**·2HI with Ag$_2$O in the presence of a halide extractor, reactions with [Rh(COD)Cl]$_2$ and [Rh(CO)$_2$Cl]$_2$ produced cationic dinuclear complexes bearing μ^2-**1** and μ^2-Cl bridging ligands. The structural formulation of the novel dinuclear adducts of **1** was aided through spectroscopic congruence with model complexes, containing monodentate 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^{i}Pr$_2$Me$_2$).

Introduction

In addition to desirable donor properties, the structural versatility of N-heterocyclic carbenes (NHCs) has proven to be a major contributing factor in the widespread application of these ligands throughout organometallic chemistry and catalysis.[1] The root of this diversity lies in the numerous and generally straightforward preparative procedures available for the construction of the respective NHC pro-ligands; synthetic methodologies that have enabled access not only a plethora of monodenate ligands, but also an extensive range of polydentate variants.[2,3]

As polydentate ligand scaffolds, calix[4]arenes are well suited building blocks with scope for functionalisation across the upper and/or lower rims of these 'bowl' shaped macromolecules.[4] Despite extensive investigation of heteroatom-based donor systems, the coordination chemistry of NHC-functionalized calix[4]arenes is not well developed.[5] 5,17-Difunctionalised examples, bearing NHC donors on opposite faces of the upper rim, are of particular interest for positioning bound metal centres across the macrocycle cavity. Well-defined complexes of these ligands are, however, limited to imidazol-2-ylidene based **A–D** (Chart 1). Complexes **A** illustrate this principle well, positioning square planar palladium centres directly over the macrocycle cavity.[6] The incorporation of a methylene spacer between the calix[4]arene rim and the NHC donor group in **B** results instead in unfavourable twisting of the donor groups that skews the bound metal centres to one side of the ligand, while in **C** and **D**, the cavity is pinched closed as

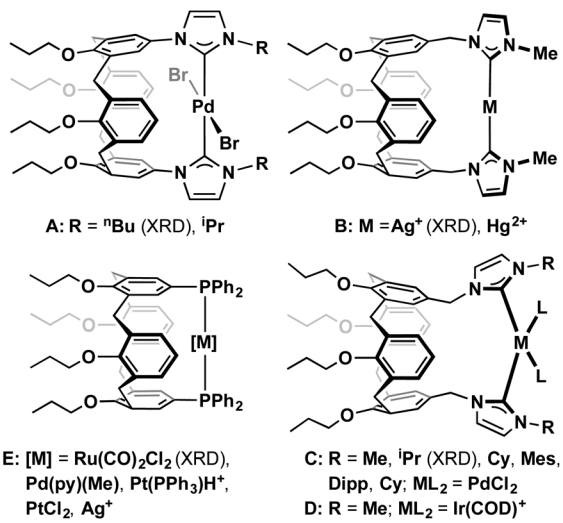

Chart 1 Complexes of upper rim functionalised calix[4]arene NHC and phosphine ligands.

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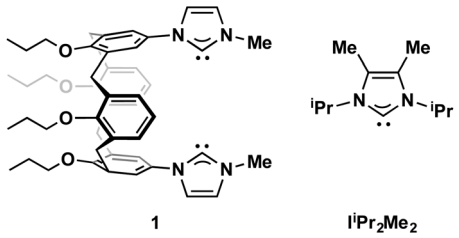


Chart 2 NHC systems of interest.

a consequence of the *cis*-coordination geometry of the metal centres.[7] Closely related to **A**, phosphine-based systems **E** have also been described, where the ligand backbone enforces *trans*-coordination.[8,9]

In this report the preparation and coordination chemistry of an upper rim functionalised calix[4]arene pro-ligand **1**·2HI are described (Chart 2). Through generation of the free NHC ligand (**1**) and use of transmetallation methodology, reactions with rhodium(I) dimers $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) and $[Rh(CO)_2Cl]_2$ lead to a range of dinuclear complexes containing either discrete or chloro-bridged metal fragments depending on the reagents employed. To help understand the influence of the calix[4]arene scaffold and corroborate the structural formulations of these species, the spectroscopic characteristics of complexes of **1** are contrasted with analogues containing the monodentate NHC ligand $I^iPr_2Me_2$.[10]

Results and discussion

The synthesis of 5,17-(3-methyl-1-imidazole)-functionalised pro-ligand **1**·2HI was achieved through straightforward adaption of literature protocols for related *N*-butyl and *N*-isopropyl analogues, involving alkylation of **F** with methyl iodide and isolated in 84% yield (Scheme 1).[11] The known precursor **F** was obtained following a five step synthesis, starting from commercially available 4-*tert*-butylcalix[4]arene (*ca.* 2 weeks, 8% yield in our hands), giving an overall yield of 7% for the six step procedure.[12] The formation of the new bis(imidazolium) salt was fully corroborated through a combination of NMR spectroscopy, ESI-MS, combustion analysis and X-ray crystallography. In solution the pre-carbenic centre is characterized by ^1H and ^{13}C resonances at δ 9.20 and δ 134.9 (CD_2Cl_2), respectively, while the mass spectrum showed a strong dication signal centred at 377.2220 *m*/*z* (calcd 377.2224) with half-integer spacing. The solid-state structure features two independent but structurally similar dications that adopt distinctive 'pinched-cone' conformations, reflecting intra-charge repulsion between the imidazolium groups (C2···C8, 13.43(2) Å/C102···C108, 13.09(2) Å; Fig. 1).[13] In order to quantify this distortion, the angles between the least squares planes (Mpln) of opposing aryloxy groups $\Theta_{CALIX}(R)$, where R = the aryl *para* substituent and the sign reflects the relative disposition of the R substituents (+ve, outwards; –ve, inwards), have been measured. Using this approach distortion from an ideal C_{4v} symmetric 'cone' to C_{2v} symmetric 'pinched cone' conformation of the calix[4]arene skeleton was found to be most pronounced in the independent molecule shown in Fig. 1 with $\Theta_{CALIX}(NHC{\cdot}H^+)/\Theta_{CALIX}(H)$ = +80.8(2)/-19.3(2)° ($\Delta\Theta_{CALIX}$ = 100.1(4)°); the other is characterised by $\Theta_{CALIX}(NHC{\cdot}H^+)/\Theta_{CALIX}(H)$ = +86.4(2)/−2.8(2)° ($\Delta\Theta_{CALIX}$ = 89.2(4)°).

Deprotonation of **1**·2HI with strong hindered base K[O^{t}Bu] in C_6D_6 or d_8-THF at 293 K resulted in quantitative formation of the free carbene **1**, which was thoroughly characterised *in situ* using NMR spectroscopy. The deprotonation was corroborated by the absence of the ^1H NCHN resonance and characteristically high frequency ^{13}C resonance at δ 213.2

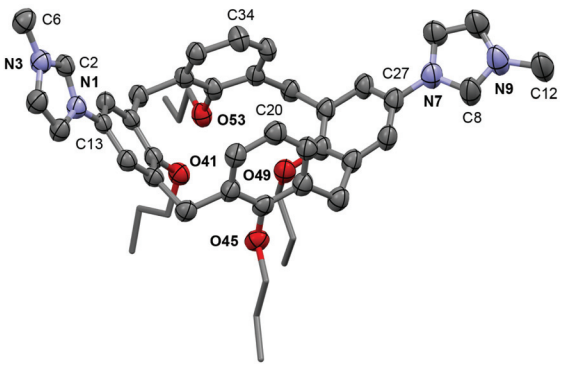
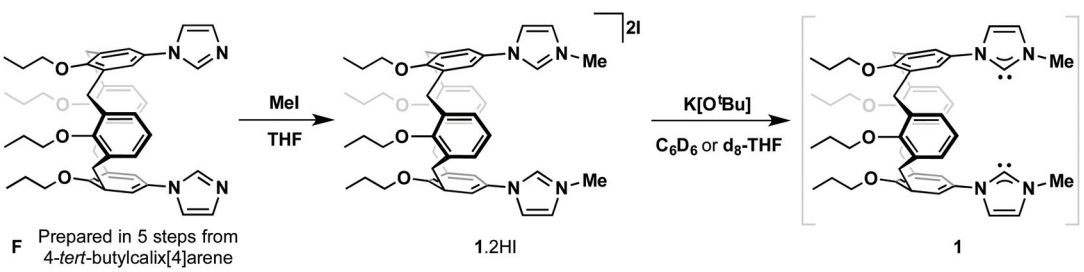


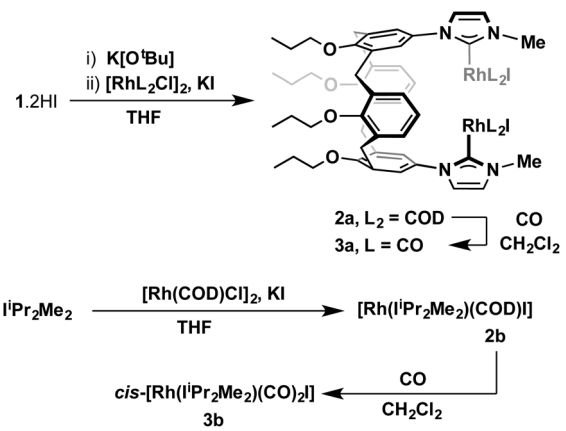
Fig. 1 Solid-state structure of **1**·2HI. Thermal ellipsoids for selected atoms drawn at the 30% probability level; only one of the two unique molecules shown (*Z*′ = 2); hydrogen atoms and anions are omitted for clarity. Selected bond lengths (Å) and angles (°): C2···C8, 13.43(2); ∠Mpln(C13–C18,O41)–Mpln(C27–32,O49), 80.8(2); ∠Mpln(C20–C25, O45)–Mpln(C34–C39,O53), 19.3(2); C102···C108, 13.09(2); ∠Mpln (C113–C118,O141)–Mpln(C127–132,O149), 86.4(2); ∠Mpln(C120–C125, O145)–Mpln(C134–C139,O153), 2.8(2).



Scheme 1 Preparation and deprotonation of pro-ligand **1**·2HI.

(C_6D_6)/216.0 (d_8-THF) of the carbenic centre.[14] For comparison, the equivalent signal in $I^iPr_2Me_2$ is located at δ 212.7 (C_6D_6).[10] Multiple attempts at isolating **1** from solution proved unsuccessful and instead it was generated *in situ* in subsequent studies.

Reactions of **1**, generated as described above, with rhodium(I) dimers $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ were explored in THF, using excess KI (*ca.* 10 equiv.) to avoid formation of mixed halide products. Using either 0.5 or 1 equiv. of rhodium precursor per ligand, the only well-defined species that could be identified were dinuclear complexes **2a** and **3a**, where **1** adopts a bridging μ^2-coordination mode (Scheme 2). In this manner, rhodium-diene-based **2a** was obtained in good isolated yield of 53% following purification over alumina. Isolation of **3a**, however, proved to be very low yielding (*ca.* 17%) and in order to acquire a more meaningful quantity of **3a**, alterative preparation from **2a** *via* diene displacement with CO (1 atm) in CH_2Cl_2 solution was required (quantitative conversion by ^{1}H NMR spectroscopy, 37% isolated yield). Mononuclear analogues of these new complexes bearing $I^iPr_2Me_2$, **2b** and **3b**, were readily obtained through direct adaptions of the aforementioned procedures (Scheme 2).



Scheme 2 Reactions of **1** and $I^iPr_2Me_2$ with rhodium dimers.

For both NHC ligands, the rhodium-diene complexes **2** were characterised in the solid-state by X-ray crystallography (Fig. 2). The conformation of the calix[4]arene backbone in **2a** is notable for a dramatic conformational inversion in comparison to the pro-ligand **1**·2HI, that appears to be driven by a favourable (off-centre) π-stacking interaction between the imidazolylidene rings (Cnt-Cnt = 3.608(5) Å; $\Delta\Theta_{CALIX}$ = −98.41(12)°, **2a**; 100.1(4)/89.2(4)°, **1**·2HI), and pseudo C_2 symmetry. As expected for d^8-metal complexes of this type, the rhodium centres adopt square planar coordination geometries in **2** and the associated metal–ligand bonding metrics are in line with related literature precedents.[15] The similarity of the metal-NHC bonding characteristics in the new systems is apparent in both the solid-state (Rh–C = 2.021(3)/2.024(3) Å, **2a**; 2.021(3) Å, **2b**) and in solution by ^{13}C NMR spectroscopy [δ 180.4 ($^1J_{RhC}$ = 49 Hz), **2a**; 178.4 ($^1J_{RhC}$ = 49 Hz), **2b**]. The structures were fully corroborated in solution by ^{1}H and ^{13}C NMR spectroscopy, with intact coordination of the diene ligands readily established by presence of alkene ^{13}C signals at *ca.* δ 95 ($^1J_{RhC}$ = 7 Hz) and 72 ($^1J_{RhC}$ = 14 Hz) displaying coupling to ^{103}Rh. Loss of C_s symmetry in the {Rh(COD)I} fragment and C_{2v} symmetry of the ligand **1** is observed on complexation, with C_2 symmetry evident on inspection of the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a**. Moreover, a large difference in chemical shift is observed for the now inequivalent ^{1}H resonances of the imidazolylidene functionalised aryl ring ($\Delta\delta$ = 2.03), with the high frequency signal at δ 7.95 presumably a consequence of the close

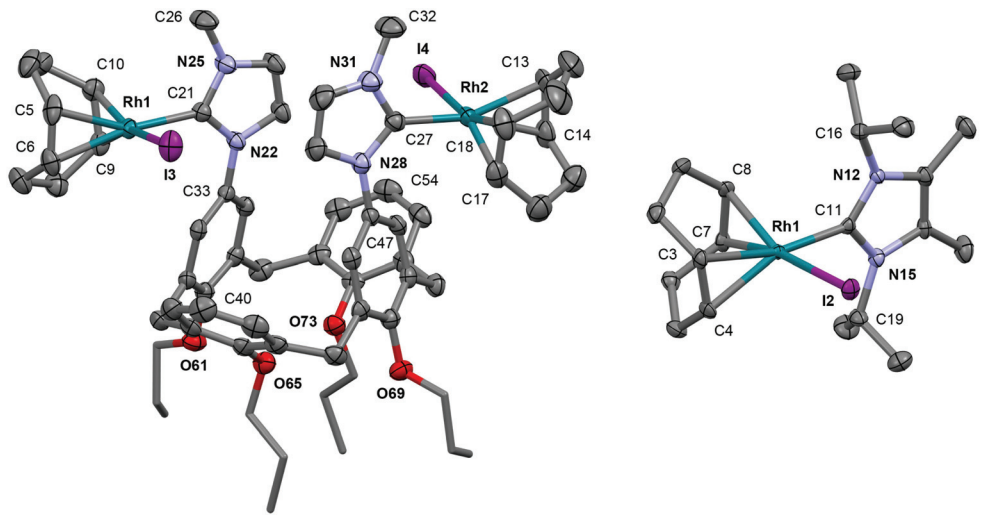


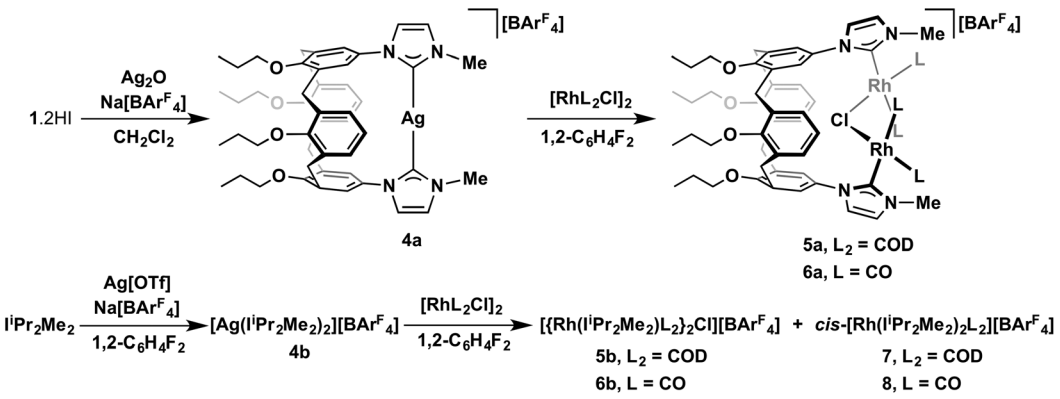
Fig. 2 Solid-state structures of **2a** and **2b**. Thermal ellipsoids for selected atoms drawn at the 50% probability level; minor disordered components (two O^{n}Pr groups in **2a**), and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): **2a**: Rh1–I3, 2.6905(3); Rh1–Cnt(C5,C6), 2.089(3); Rh1–Cnt(C9,C10), 2.001(3); Rh1–C21, 2.021(3); Rh2–I4, 2.6934(3); Rh2–Cnt(C13,C14), 2.098(3); Rh1–Cnt(C17,C18), 1.990(4); Rh2–C27, 2.024(3); Rh1···Rh2, 8.5698(3); Cnt(C21–N25)–Cnt(C27–N31), 3.608(5); ∠Mpln(C33–C38,O61)–Mpln(C47–C52,O69), 22.35(6); ∠Mpln(C40–C45, O65)–Mpln(C54–C59,O73), 76.06(6); **2b**: Rh1–I2, 2.6729(2); Rh1–Cnt(C3,C4), 2.109(2); Rh1–Cnt(C7,C8), 2.00(3); Rh1–C11, 2.021(3).

proximity of the halogen atom (*cf.* C–H···I = 4.139(3)/4.295(3) Å observed in the solid-state and δ 6.61 for **1**·2HI), as previously noted in a related calix[4]arene-based system.[5b] Combined, these NMR data of **2a** are consistent with retention of solid-state structure in solution.

Although, we have so far been unable to grow suitable samples of **3** for structural elucidation by X-ray crystallography, the solution data points strongly to equivalent structural formations as **2**. For instance, the relative *cis*-configuration of the carbonyl ligands was established through observation of two bands in the respective IR spectra (υ(CO) = 2071, 2002, **3a**; 2072, 1998 cm^{-1}, **3b**) and two distinct high frequency doublet resonances in the $^{13}C\{^1H\}$ NMR spectra [δ 188.4 ($^1J_{RhC}$ = 54 Hz), 181.6 ($^1J_{RhC}$ = 78 Hz), **3a**; 188.7 ($^1J_{RhC}$ = 53 Hz), 182.7 ($^1J_{RhC}$ = 78 Hz), **3b**]. ^1H and $^{13}C\{^1H\}$ NMR spectra of **3a** also exhibit C_2 symmetry. In comparison to **2**, the carbenic resonances are notable for a shift to lower frequency by *ca.* 10 ppm and there is a reduction in the magnitude of the coupling to ^{103}Rh [δ 171.5 ($^1J_{RhC}$ = 44 Hz), **3a**; 166.8 ($^1J_{RhC}$ = 41 Hz), **3b**].

To further explore the coordination chemistry of **1**, we sought to utilise widely employed transmetallation methodology based on silver transfer agents.[1c,16] To this end, **1**·2HI was reacted with a slight excess of Ag_2O in the presence of Na[BAr^F_4] (Ar^F = 3,5-$C_6H_3(CF_3)_2$), as a halide extractor, resulting in chelation of **1** and subsequent isolation of **4a** in 73% yield (Scheme 3). The structural formulation of the new silver(I) complex was readily established in solution though a combination of ^1H and ^{13}C NMR spectroscopy and ESI-MS. The ^1H NMR spectrum of isolated **4a** shows C_{2v} symmetry, with the *N*-methyl signal located to lower frequency than found in the pro-ligand (δ 3.80 *vs.* 4.17). A strong parent ion is observed by ESI-MS in positive ion mode at 859.3340 *m*/*z* (calcd 859.3347 *m*/*z*) with a correct isotope pattern. Moreover the cation : [BAr^F_4] ratio was verified by integration of ^1H NMR data and elemental analysis. The $^{13}C\{^1H\}$ NMR spectrum is notable for the carbenic signal at δ 180.7 that shows coupling to both ^{109}Ag ($^1J_{AgC}$ = 211 Hz) and ^{107}Ag ($^1J_{AgC}$ = 183 Hz); the chemical shift and relative magnitudes of these coupling constants are in good agreement with literature values.[16a] Interrogation of single crystals of **4a** by X-ray diffraction provides further evidence to the mononuclear formulation of **4a** in solution, revealing a distorted linear geometry of the silver cation [C2–Ag1–C8 = 171.00(14)°] and essentially equivalent Ag–C bond lengths (Ag1–C2, 2.085(4); Ag1–C8, 2.083(4); Fig. 3). The biscarbene silver complex of $I^iPr_2Me_2$ bearing the tetrafluoroborate counter anion [$Ag(I^iPr_2Me_2)_2$][BF_4] **G** has previously been prepared,[17] however, for comparison the analogue bearing the [BAr^F_4]$^-$ counter anion **4b** was generated *in situ* through reaction of Ag[OTf], Na[BAr^F_4] and 2 equiv. $I^iPr_2Me_2$ in 1,2-$C_6H_4F_2$. The solid-state structure of **4b** is notable for a significantly more orthogonal orientation of the NHC ligands in comparison to **4a** and **G** [*e.g.* |N6–C2–C8–N12| = 3.7(5)°, **4a**; |N3–C2–C15–N19| = 77.0(5)°, **4b**; |N–C–C–N| = 20.6(6)°, **G**]. The near coplanar disposition of the NHC donors in **4a** is fully in line with expectation, and readily attributed to the calix[4]arene scaffold [$\Delta\Theta_{CALIX}$ = −96.4(2)°], while the conformational differences in **4b**/**G** are presumably attributed to crystal packing effects, induced by disparate anion sizes, and enabled through low-energy Ag–NHC bond rotation. The Ag–C bond lengths are all within experimental error [2.085(4)/2.083(4) Å, **4a**; 2.093(4)/2.092(4) Å, **4b**; 2.078(11) Å, **G**], although we note an apparent trend of bond length contraction for **4a** in comparison to **4b** and that this parameter was not determined with high precision for **G**.

Silver complex **4a** acts as an effective carbene transfer agent, resulting in the formation of dinuclear complexes **5a** and **6a** bearing both μ^2-**1** and μ^2-Cl ligands on reaction with 1 equiv. of $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$, respectively, in 1,2-$C_6H_4F_2$ – established by NMR spectroscopy and ESI-MS. The reaction stoichiometries were maintained when using 0.5 equiv. of rhodium dimer instead, indicating selective formation **5a** and **6a**. Both dinuclear products were obtained in moderate isolated yields (63% and 59% respectively) and were difficult to fully purify, due to limited solution stability. Aided by comparison to **2a**/**3a** and supported through preparation of direct $I^iPr_2Me_2$ analogues (*vide infra*), the formulation of the structures of **5a**/**6a** was achieved through a combination of ^1H, ^{13}C NMR and IR spectroscopy, ESI-MS and in the case of **5b** a low resolution X-ray structure (Fig. 4). The ESI-MS in particular evidenced formation of these dinuclear monocationic species, with parent cation signals at 1209.3986 (calcd 1209.3973) and



Scheme 3 Preparation and transmetallation reactions of silver NHC complexes.

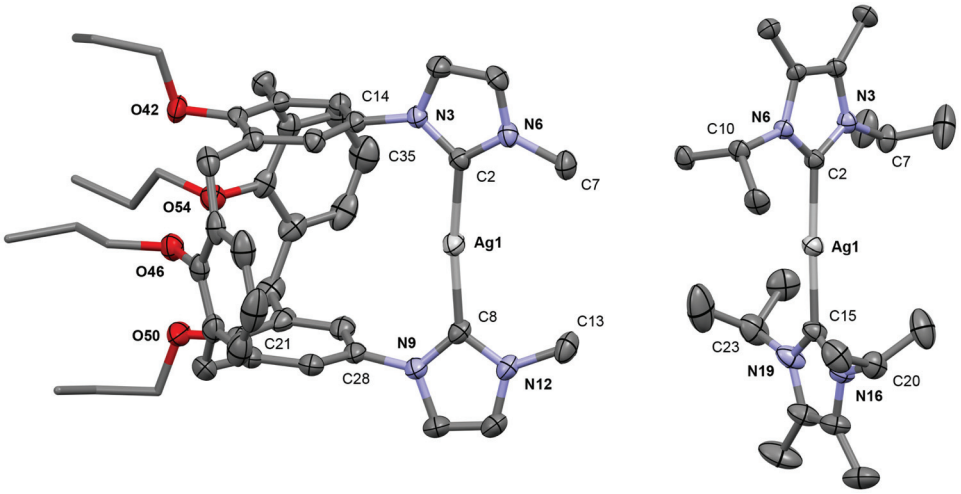


Fig. 3 Solid-state structures of **4a** and **4b**. Thermal ellipsoids for selected atoms drawn at the 30% probability level; minor disordered components (four O^{n}Pr groups in **4a**), hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (°): **4a**: Ag1–C2, 2.085(4); Ag1–C8, 2.083(4); C2–Ag1–C8, 171.00(14); ∠Mpln(C14–C19,O42)–Mpln(C28–C33,O50), 1.01(8); ∠Mpln(C21–C26,O46)–Mpln(C35–C40,O54), 97.44(10); **4b**: Ag1–C2, 2.093(4); Ag1–C15, 2.092(4); C2–Ag1–C15, 176.81(15).

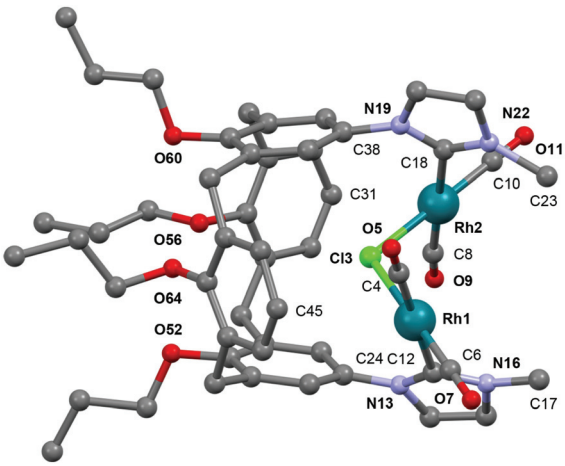
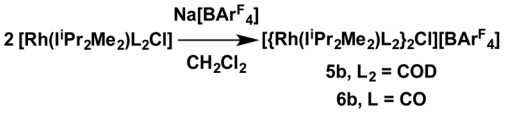


Fig. 4 Solid-state structure of **6a** (ball and stick, poor quality data). Minor disordered component (CO), hydrogen atoms and anion omitted for clarity. Selected bond lengths (Å) and angles(°): Rh1–Cl3, 2.353(5); Rh2–Cl3, 2.360(5); Rh1···Rh2, 3.861(3); Rh1–Cl3–Rh2, 110.0(3); ∠Mpln (C24–C29,O52)–Mpln(C38–C43,O60), 9.7(3); ∠Mpln(C31–C36,O56)–Mpln(C45–C50,O64), 92.8(4).

1105.1680 (calcd 1105.1891) *m*/*z*, respectively for **5a** and **6a**, with correct isotope patterns and integer mass spacing. Moreover the cation : [BAr$^F_4$] ratio was verified by integration of ^{1}H NMR data. In both cases, single carbene resonances [δ 176.9 ($^1J_{RhC}$ = 50 Hz), **5a**; 168.1 ($^1J_{RhC}$ = 43 Hz), **6a**] with very similar chemical shifts and $^1J_{RhC}$ coupling constants to the respective neutral analogues [δ 180.4 ($^1J_{RhC}$ = 49 Hz), **2a**; 171.5 ($^1J_{RhC}$ = 44 Hz), **3a**], alongside ^{103}Rh coupled alkene and carbonyl signals, were observed by ^{13}C NMR spectroscopy. For **6a** both carbonyl stretching bands are perturbed (as expected) to higher frequency relative to neutral **3a** [υ(CO) = 2083, 2016, **6a**; 2071, 2002 cm^{-1}, **3a**]. Bond connectivity and conformational features of **6a** were established through X-ray diffraction, using a poor quality crystalline sample [R_1 = 0.2744, $I \geq 2\sigma(I)$]. The data nevertheless can affirm the structural formulation, with a reduced pinching of calix[4]arene core [$\Delta\Theta_{CALIX}$ = −83.1(7)°] relative to **2a** [$\Delta\Theta_{CALIX}$ = −98.41(12)°] and **4a** [$\Delta\Theta_{CALIX}$ = −96.4(2)°].

Starting from the known precursors [Rh(I^{i}Pr$_2$Me$_2$)(COD)Cl] and [Rh(I^{i}Pr$_2$Me$_2$)(CO)$_2$Cl], the new μ^2-Cl bridged dinuclear complexes **5b** and **6b** were readily prepared by partial halide extraction using 0.5 equiv. of Na[BAr$^F_4$] in CH_2Cl_2 (Scheme 4). These structurally simple and fully characterised species (solution and solid-state, Fig. 5) help verify the formulation of **5a** and **6a**, with excellent agreement of the related spectroscopic data *e.g.* carbene ^{13}C signals of **5** [δ176.9 ($^1J_{RhC}$ = 50 Hz), **5a**; 175.6 ($^1J_{RhC}$ = 50 Hz), **5b**] and carbonyl stretching bands of **6** [υ(CO) = 2083, 2016, **6a**; 2090, 2019 cm^{-1}, **6b**] – see Experimental section for full details. Although iridium NHC and rhodium phosphine examples have been reported, there are no proceeding crystallographically characterised examples of rhodium NHC complexes featuring a single otherwise unsupported bridging halogen atom to the best of our knowledge.[18] Conformational differences, associated with the relative orientation of the NHC ligands about the Rh–Cl–Rh bridge, are evident when comparing the solid-state structures of **6a** (*anti*) **5b** (*syn*) **6b** (*anti*); ^{1}H and ^{13}C NMR data for **5a** and **6a** are most consistent with C_2 symmetry and *anti*-configurations in solution. Contrasting reactions of **4a** and **4b**, the calix[4]arene scaffold promotes the selective formation of dinuclear com-



Scheme 4 Preparation of dinuclear complexes **5b** and **6b**.

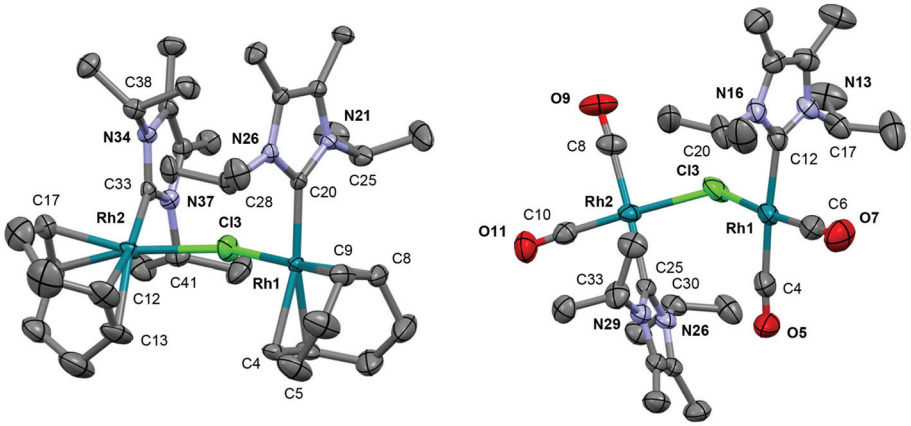


Fig. 5 Solid-state structures of **5b** and **6b**. Thermal ellipsoids drawn at the 50% probability level; minor disordered components (two ^{i}Pr groups in **6b**), hydrogen atoms, solvent (**6a**), and anions omitted for clarity. Selected bond lengths (Å) and angles (°): **5b**: Rh1–Cl3, 2.3988(9); Rh1–Cnt(C4,C5), 2.092(5); Rh1–Cnt(C8,C9), 1.974(4); Rh1–C20, 2.025(3); Rh2–Cl3, 2.4067(9); Rh2–Cnt(C12,C13), 2.101(4); Rh2–Cnt(C16,C17), 1.972(4); Rh2–C33, 2.022(3); Rh1–Cl3–Rh2, 144.13(4); **6b**: Rh1–Cl3, 2.4045(9); Rh1–C4, 1.915(4); Rh1–C6, 1.833(4); Rh1–C22, 2.069(3); Rh2–Cl3, 2.3987(9); Rh2–C8, 1.920(4); Rh2–C10, 1.817(4); Rh2–C25, 2.069(3); Rh1–Cl3–Rh2, 122.26(4).

plexes. For instance, when **4b** is reacted with 1 equiv. of $[Rh(COD)Cl]_2$ or $[Rh(CO)_2Cl]_2$ in 1,2-$C_6H_4F_2$ mixtures of **5b**/*cis*-$[Rh(I^iPr_2Me_2)_2(COD)][BAr^F{}_4]$ **7** (2 : 1) and **6b**/*cis*-$[Rh(I^iPr_2Me_2)_2(CO)_2][BAr^F{}_4]$ **8** (5 : 2) are the organometallic species produced as determined by ^{1}H NMR spectroscopy (Scheme 3) – with the structures of **7** and **8** verified by independent synthesis and full characterisation, including in the solid-state by X-ray diffraction (see experimental for full details).

Summary

Using both free carbene and transmetallation methodologies the coordination chemistry of bis(imidazolium) pro-ligand **1**·2HI with rhodium(I) dimers $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ has been investigated, culminating in the isolation of neutral and cationic dinuclear complexes where the calix[4]arene based-NHC is bound in a μ^2-coordination mode. These dinuclear complexes have been well characterised in solution using NMR spectroscopy, IR spectroscopy (CO derivatives) and ESI-MS (cationic complexes), and their structural formulation corroborated through excellent agreement of these data with that associated with simpler model complexes containing instead $I^iPr_2Me_2$. Structures determined though X-ray diffraction highlight the flexibility of the calix[4]arene ligand scaffold, which undergoes significant conformational change driven by charge repulsion (bis-cationic **1**·2HI), π-stacking of the imidazolylidene rings (**2a**), *trans*-coordination to silver (**4a**), or presence of a bridging μ^2-Cl ligand (**6a**).

Experimental

General considerations

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flamed under vacuum prior to use. Anhydrous CH_2Cl_2, Et_2O, and pentane (<0.005% H_2O) were purchased from ACROS or Aldrich and freeze–pump–thaw degassed three times before being placed under argon. THF was dried over sodium/benzophenone, vacuum distilled, and freeze–pump–thaw degassed three times before being placed under argon. 1,2-$C_6H_4F_2$ was stirred over neutral alumina, filtered, dried over CaH_2, vacuum distilled, and freeze–pump–thaw degassed three times before being placed under argon over 3 Å molecular sieves. CD_2Cl_2 was dried over CaH_2, vacuum distilled, and freeze–pump–thaw degassed three times before being placed under argon. C_6D_6 was dried over Na, vacuum distilled, and freeze–pump–thaw degassed three times before being placed under argon. d_8-THF was dried over 3 Å molecular sieves and freeze–pump–thaw degassed three times before being placed under argon. 5,17-bis(imidazolium)-25,26,27,28-tetrapropoxycalix[4]arene (**F**),[12] $I^iPr_2Me_2$,[10] $[Rh(COD)Cl]_2$,[19] $[Rh(CO)_2Cl]_2$,[20] $Na[BAr^F{}_4]$,[21] $[Rh(I^iPr_2Me_2)(COD)Cl]$,[22] and *cis*-$[Rh(I^iPr_2Me_2)(CO)_2Cl]$[22] were synthesised using literature protocols. All other solvents and reagents are commercial products and were used as received. NMR spectra were recorded on Bruker AV spectrometers at 298 K unless otherwise stated. ^{1}H NMR spectra recorded in 1,2-$C_6H_4F_2$ were referenced using the highest intensity peak of the highest (δ 6.865) frequency fluoroarene multiplet. $^{13}C\{^1H\}$ NMR spectra recorded in 1,2-$C_6H_4F_2$ were referenced using an internal sealed capillary of C_6D_6. Chemical shifts are quoted in ppm and coupling constants in Hz. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer at 293 K. ESI-MS analyses were recorded on Bruker Maxis Impact instrument. Microanalyses were performed by Stephen Boyer at London Metropolitan University.

Preparation of 1·2HI

A solution of **F** (1.00 g, 1.38 mmol) was stirred with iodomethane (0.84 mL, 13.8 mmol) in THF (30 mL) at 70 °C for

14 hours. The product was isolated by filtration following addition of Et_2O (*ca.* 20 mL), washed with Et_2O (2 × 20 mL) and dried *in vacuo*. Yield = 1.17 g (84%, fine off-white powder).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.20 (br, 2H, NCHN), 8.04 (t, $^3J_{HH}$ = 1.8, 2H, imid.), 7.23 (d, $^3J_{HH}$ = 7.5, 4H, Ar), 7.05 (t, $^3J_{HH}$ = 7.5, 2H, Ar), 6.72 (t, $^3J_{HH}$ = 1.8, 2H, imid.), 6.61 (s, 4H, Ar), 4.54 (d, $^2J_{HH}$ = 13.5, 4H, ArC$\underline{H}_2$Ar), 4.17 (s, 6H, NCH_3), 4.03–4.09 (m, 4H, OCH_2), 3.74 (t, $^3J_{HH}$ = 6.8, 4H, OCH_2), 3.28 (d, $^2J_{HH}$ = 13.5, 4H, ArC$\underline{H}_2$Ar), 1.87–2.06 (m, 8H, C$\underline{H}_2$CH$_3$), 1.12 (t, $^3J_{HH}$ = 7.4, 6H, $CH_2C\underline{H}_3$), 0.93 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ 157.5 (s, $\underline{C}OCH_2$), 157.3 (s, $\underline{C}OCH_2$), 137.7 (s, Ar{$\underline{C}CH_2$}), 135.7 (s, Ar{$\underline{C}CH_2$}), 134.9 (s, NCHN), 130.2 (s, Ar), 129.2 (s, Ar{CN}), 125.6 (s, imid.), 124.4 (s, Ar), 120.8 (s, Ar), 119.9 (s, imid.), 78.1 (s, OCH_2), 77.4 (s, OCH_2), 37.8 (s, NCH_3), 31.4 (s, Ar$\underline{C}H_2$Ar), 23.9 (s, $\underline{C}H_2CH_3$), 23.5 (s, $\underline{C}H_2CH_3$), 10.9 (s, $CH_2\underline{C}H_3$), 10.2 (s, $CH_2\underline{C}H_3$). **ESI-MS** (CH_3CN, 180 °C, 3 kV) positive ion: 377.2220 *m*/*z*, $[M]^{2+}$ (calcd 377.2224 *m*/*z*). **Anal.** Calcd For $C_{48}H_{58}I_2N_4O_4$ (1008.81 g mol^{-1}): C, 57.13; H, 5.80; N, 5.55. Found: C, 56.88; H, 6.00; N, 5.55.

Deprotonation of 1·2HI

A suspension of **1**·2HI (10.2 mg, 0.0101 mmol) and K[O^{t}Bu] (3.1 mg, 0.0276 mmol) in d_8-THF (0.5 mL) was agitated and sonicated for several minutes inside a sealed J. Young's NMR tube. Analysis by NMR spectroscopy indicated quantitative formation of **1** with the concomitant formation of ^{t}BuOH (δ_H 5.33, OH; 1.15, CH_3; δ_C 68.1, $\underline{C}CH_3$; 31.6, CH_3). The reaction was repeated in C_6D_6 with the same outcome. The ^{1}H NMR spectra remained unchanged on standing at 293 K for 24 h in both cases.

^{1}H NMR (d_8-THF, 500 MHz): δ 7.41 (s, 4H, Ar), 7.24 (d, $^3J_{HH}$ = 1.6, 2H, imid.), 6.94 (d, $^3J_{HH}$ = 1.6, 2H, imid.), 6.40 (d, $^3J_{HH}$ = 7.5, 4H, Ar), 6.31 (app t, 2H, J = 8, Ar), 4.51 (d, $^2J_{HH}$ = 13.1, 4H, ArC$\underline{H}_2$Ar), 4.00–4.04 (m, 4H, OCH_2), 3.76–3.79 (m, 4H, OCH_2), 3.76 (s, 6H, NCH_3), 3.20 (d, $^2J_{HH}$ = 13.1, 4H, ArC$\underline{H}_2$Ar), 1.99–2.07 (m, 4H, C$\underline{H}_2$CH$_3$), 1.92–1.99 (m, 4H, C$\underline{H}_2$CH$_3$), 1.10 (t, $^3J_{HH}$ = 7.4, 6H, $CH_2C\underline{H}_3$), 0.98 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$). **^{13}C{^{1}H} NMR** (d_8-THF, 126 MHz): δ 216.0 (s, NCN), 156.7 (s, $\underline{C}OCH_2$), 156.3 (s, $\underline{C}OCH_2$), 137.9 (s, Ar{CN}), 137.6 (s, Ar{$\underline{C}CH_2$}), 134.5 (s, Ar{$\underline{C}CH_2$}),128.9 (s, Ar), 123.1 (s, Ar), 121.6 (s, Ar), 121.1 (s, imid.), 118.1 (s, imid.), 77.9 (s, OCH_2), 77.7 (s, OCH_2), 38.3 (s, NCH_3), 32.0 (s, Ar$\underline{C}H_2$Ar), 24.5 (s, $\underline{C}H_2CH_3$), 24.2 (s, $\underline{C}H_2CH_3$), 11.2 (s, $CH_2\underline{C}H_3$), 10.7 (s, $CH_2\underline{C}H_3$). **^{1}H NMR** (C_6D_6, 500 MHz): δ 7.40 (s, 4H, Ar), 6.74 (d, $^3J_{HH}$ = 7.5, 4H, Ar), 6.71 (br, 2H, imid.), 6.61 (t, $^3J_{HH}$ = 7.5, 2H, Ar), 6.18 (br, 2H, imid.), 4.53 (d, $^2J_{HH}$ = 13.2, 4H, ArC$\underline{H}_2$Ar), 3.87 (t, $^3J_{HH}$ = 7.6, 4H, OCH_2), 3.76 (t, $^3J_{HH}$ = 7.4, 4H, OCH_2), 3.42 (s, 6H, NCH_3), 3.17 (d, $^2J_{HH}$ = 13.3, 4H, ArC$\underline{H}_2$Ar), 1.84–1.95 (m, 8H, C$\underline{H}_2$CH$_3$), 0.93 (app. t, J = 7, 12H, $CH_2C\underline{H}_3$). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz): δ 213.2 (s, NCN), 156.7 (s, $\underline{C}OCH_2$), 155.5 (s, $\underline{C}OCH_2$), 137.1 (s, Ar{CN}), 136.4 (s, Ar{$\underline{C}CH_2$}), 134.7 (s, Ar{$\underline{C}CH_2$}), 128.8 (s, Ar), 123.0 (s, Ar), 121.5 (s, Ar), 120.1 (s, imid.), 117.8 (s, imid.), 77.1 (s, OCH_2), 77.0 (s, OCH_2), 37.8 (s, NCH_3), 31.6 (s, Ar$\underline{C}H_2$Ar), 23.7 (s, $\underline{C}H_2CH_3$), 23.6 (s, $\underline{C}H_2CH_3$), 10.6 (s, $CH_2\underline{C}H_3$), 10.5 (s, $CH_2\underline{C}H_3$).

Preparation of 2a

A solution of **1**·2HI (99.7 mg, 0.0987 mmol) and K[O^{t}Bu] (27.8 mg, 0.248 mmol) was stirred in THF (10 mL) for 1 hour then added to a flask charged with $[Rh(COD)Cl]_2$ (51.6 mg, 0.105 mmol) and KI (165.1 mg, 1.42 mmol). After a further hour the volatiles were removed *in vacuo*. The product was extracted with CH_2Cl_2 (2 × 10 mL) and purified over alumina (1 : 1 EtOAc/CH_2Cl_2, Air). Yield = 75.5 mg (53%, yellow powder).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.95 (d, $^4J_{HH}$ = 2.8, 2H, Ar), 7.29–7.39 (m, 2H, Ar), 7.04–7.14 (m, 2H, Ar), 6.97 (t, $^3J_{HH}$ = 7.4, 2H, Ar), 6.44 (d, $^3J_{HH}$ = 2.0, 2H, imid.), 6.19 (d, $^3J_{HH}$ = 2.0, 2H, imid.), 5.92 (d, $^4J_{HH}$ = 2.8, 2H, Ar), 5.24–5.29 (m, 2H, COD{CH}), 4.92–5.09 (m, 2H, COD{CH}), 4.62 (d, $^2J_{HH}$ = 13.3, 2H, ArC$\underline{H}_2$Ar), 4.50 (d, $^2J_{HH}$ = 13.5, 2H, ArC$\underline{H}_2$Ar), 3.99–4.18 (m, 4H, OCH_2), 3.85 (s, 6H, NCH_3), 3.65–3.82 (m, 4H, OCH_2), 3.38 (d, $^2J_{HH}$ = 13.4, 2H, ArC$\underline{H}_2$Ar), 3.21–3.26 (m, 2H, COD{CH}), 3.19 (d, $^2J_{HH}$ = 13.7, 2H, ArC$\underline{H}_2$Ar), 2.29–2.39 (m, 2H, COD{CH}), 2.09–2.29 (m, 6H, COD{CH_2}), 1.97–2.09 (m, 4H, C$\underline{H}_2$CH$_3$), 1.83–1.97 (m, 6H, C$\underline{H}_2$CH$_3$ + COD{CH_2}), 1.58–1.79 (m, 4H, COD{CH_2}), 1.27–1.46 (m, 4H, COD{CH_2}), 1.15 (t, $^3J_{HH}$ = 7.4, 6H, $CH_2C\underline{H}_3$), 0.95 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ 180.4 (d, $^1J_{RhC}$ = 49, NCN), 158.2 (s, $\underline{C}OCH_2$), 155.0 (s, $\underline{C}OCH_2$), 137.0 (s, Ar{$\underline{C}CH_2$}), 136.9 (s, Ar{$\underline{C}CH_2$}), 134.9 (s, Ar{C}), 134.7 (s, Ar{C}), 134.3 (s, Ar{C}), 131.5 (s, Ar), 129.6 (s, Ar), 123.6 (s, Ar), 123.4 (s, imid.), 122.9 (s, Ar), 122.5 (s, imid.), 122.5 (s, Ar), 95.0 (d, $^1J_{RhC}$ = 7, COD{CH}), 95.0 (d, $^1J_{RhC}$ = 7, COD{CH}), 77.7 (s, OCH_2), 77.3 (s, OCH_2), 71.4 (d, $^1J_{RhC}$ = 14, 2 × COD{CH}), 39.1 (s, $N\underline{C}H_3$), 33.9 (s, COD{CH_2}), 31.7 (s, CH_2), 31.4 (s, CH_2), 31.0 (s, CH_2), 30.7 (s, CH_2), 29.2 (s, COD{CH_2}), 23.8 (s, $\underline{C}H_2CH_3$), 23.4 (s, $\underline{C}H_2CH_3$), 11.3 (s, $CH_2\underline{C}H_3$), 10.3 (s, $CH_2\underline{C}H_3$). **Anal.** Calcd For $C_{64}H_{80}I_2N_4O_4$ (1428.24 g mol^{-1}): C, 53.79; H, 5.64; N, 3.92. Found: C, 53.71; H, 5.75; N, 4.04.

Preparation of 2b

A solution of I^{i}Pr$_2$Me$_2$ (61.2 mg, 0.336 mmol), $[Rh(COD)Cl]_2$ (166.1 mg, 0.337 mmol) and KI (1072.2 mg, 6.46 mmol) in THF (10 mL) was stirred for 1 hour. The volatiles were removed *in vacuo* and the product obtained after purification over silica (CH_2Cl_2, Air) and subsequent recrystallisation from CH_2Cl_2/pentane. Yield = 55.0 mg (31%, yellow crystals).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 5.97 (sept, $^3J_{HH}$ = 7.1, 2H, NCH), 5.03–5.09 (m, 2H, COD{CH}), 3.50–3.57 (m, 2H, COD{CH}), 2.26–2.36 (m, 4H, COD{CH_2}), 2.16 (s, 6H, CC$\underline{H}_3$), 1.87–1.98 (m, 2H, COD{CH_2}), 1.73–1.83 (m, 2H, COD{CH_2}), 1.56 (d, $^3J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$), 1.50 (d, $^3J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 178.4 (d, $^1J_{RhC}$ = 49, NCN), 126.0 (s, $\underline{C}CH_3$), 95.2 (d, $^1J_{RhC}$ = 7, COD{CH}), 71.5 (d, $^1J_{RhC}$ = 14, COD{CH}), 53.7 (s, NCH), 32.8 (s, COD{CH_2}), 30.0 (s, COD{CH_2}), 22.4 (s, CH$\underline{C}H_3$), 21.4 (s, CH$\underline{C}H_3$), 10.7 (s, C$\underline{C}H_3$). **Anal.** Calcd for $C_{19}H_{32}I_2N_2Rh$ (518.29 g mol^{-1}): C, 44.03; H, 6.22; N, 5.41. Found: C, 44.11; H, 6.14; N, 5.47.

Preparation of 3a

Method A: A solution of **1**·2HI (102.1 mg, 0.101 mmol) and K[O^{t}Bu] (28.9 mg, 0.258 mmol) was stirred in THF (10 mL) for 1 hour then added to a flask charged with $[Rh(CO)_2Cl]_2$ (40.7 mg, 0.105 mmol) and KI (165.4 mg, 0.996 mmol). After a further hour the volatiles were removed *in vacuo*. The product was extracted with CH_2Cl_2 (2 × 10 mL) and purified over alumina (1 : 1 Et_2O/CH_2Cl_2, Air). Yield = 22.4 mg (17%, yellow powder). *Method B*: A solution of **2a** (121.2 mg, 0.0848 mmol) in CH_2Cl_2 (10 mL) was stirred under CO (1 atm) for 12 hours, resulting in a colour change from bright to pale yellow. The mixture was dried *in vacuo* and washed with pentane (3 × 5 mL). Yield = 42.1 mg (37%, yellow powder).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ7.26 (s, 2H, Ar), 7.02 (br, 4H, Ar), 6.82 (t, $^3J_{HH}$ = 7.4, 2H, Ar), 6.77 (s, 2H, imid.), 6.46 (s, 2H, imid.), 6.41 (s, 2H, Ar), 4.51 (d, $^2J_{HH}$ = 13.3, 2H, ArC$\underline{H}_2$Ar), 4.48 (d, $^2J_{HH}$ = 13.6, 2H, ArC$\underline{H}_2$Ar), 3.80–4.09 (m, 8H, OCH_2), 3.77 (s, 6H, NCH_3), 3.24 (d, $^2J_{HH}$ = 14.1, 2H, ArC$\underline{H}_2$Ar), 3.22 (d, $^2J_{HH}$ = 14.1, 2H, ArC$\underline{H}_2$Ar), 1.79–2.16 (m, 8H, C$\underline{H}_2$CH$_3$), 1.03–1.13 (m, 6H, CH$_2$C$\underline{H}_3$), 0.92–1.03 (m, 6H, CH$_2$C$\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 188.4 (d, $^1J_{RhC}$ = 54, CO), 181.6 (d, $^1J_{RhC}$ = 78, CO), 171.5 (d, $^1J_{RhC}$ = 44, NCN), 157.5 (s, $\underline{C}OCH_2$), 156.3 (s, $\underline{C}OCH_2$), 136.2, 136.1, 135.9, 135.6, 130.6, 129.4, 123.8, 123.4, 123.2, 122.8, 77.8 (OCH_2), 77.4 (OCH_2), 40.0 (s, NCH_3), 31.5 (br, Ar$\underline{C}H_2$Ar), 24.0 ($\underline{C}H_2CH_3$), 23.7 ($\underline{C}H_2CH_3$), 11.0 (s, CH$_2\underline{C}H_3$), 10.4 (s, CH$_2\underline{C}H_3$). Not all signals were unambiguously identified. **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 2071, 2002. **Anal.** Calcd for $C_{52}H_{56}I_2N_4O_8Rh_2$ (1324.02 g mol^{-1}): C, 47.15; H, 4.26; N, 4.23. Found: C, 46.91; H, 4.12; N, 4.25.

Preparation of 3b

A solution of **2b** (40.1 mg, 0.0774 mmol) in CH_2Cl_2 (10 mL) was placed under an atmosphere of CO (1 atm) for 2 hours. The volatiles were removed *in vacuo* to afford the product, which was washed with pentane (3 × 10 mL) and dried thoroughly under vacuum. Yield = 21.4 mg (59%, fine yellow powder).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 5.26 (sept, $^3J_{HH}$ = 7.1, 2H, NCH), 2.22 (s, 6H, CCH_3), 1.501 (d, $^3J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$), 1.496 (d, $^3J_{HH}$ = 2.7, 6H, CHC$\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 188.7 (d, $^1J_{RhC}$ = 53, CO), 182.7 (d, $^1J_{RhC}$ = 78, CO), 166.8 (d, $^1J_{RhC}$ = 41, NCN), 127.2 (s, $\underline{C}CH_3$), 54.3 (s, $\underline{C}HCH_3$), 22.2 (s, CH$\underline{C}H_3$), 21.1 (s, CH$\underline{C}H_3$), 10.7 (s, C$\underline{C}H_3$). **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 2072, 1998. **Anal.** Calcd for $C_{13}H_{20}I_2N_2O_2Rh$ (466.12 g mol^{-1}): C, 33.50; H, 4.33; N, 6.01. Found: C, 33.41; H, 4.25; N, 6.03.

Preparation of 4a

A suspension of **1**·2HI (79.5 mg, 0.0788 mmol), Ag_2O (20.0 mg, 0.0862 mmol) and Na[BAr$^F{}_4$] (69.0 mg, 0.0778 mmol) in CH_2Cl_2 (20 mL) was sonicated periodically over two hours. The solution was filtered and the solvent was removed *in vacuo* to afford the product. Yield = 100.0 mg (73%, white crystals).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72–7.76 (m, 8H, Ar^F), 7.57 (br, 4H, Ar^F), 7.10 (d, $^3J_{HH}$ = 7.4, 4H, Ar), 6.92 (d, $^3J_{HH}$ = 1.7, 2H, imid.), 6.85 (t, $^3J_{HH}$ = 7.5, 2H, Ar), 6.81 (d, $^3J_{HH}$ = 1.7, 2H, imid.), 6.40 (s, 4H, Ar), 4.57 (d, $^2J_{HH}$ = 12.8, 4H, ArC$\underline{H}_2$Ar), 4.10–4.22 (m, 4H, OCH_2), 3.80 (s, 6H, NCH_3), 3.74 (t, $^3J_{HH}$ = 7.1, 4H, OCH_2), 3.24 (d, $^2J_{HH}$ = 12.8, 4H, ArC$\underline{H}_2$Ar), 2.10–2.21 (m, 4H, C$\underline{H}_2$CH$_3$), 1.99 (app. sex., J = 7, 4H, C$\underline{H}_2$CH$_3$), 1.12 (t, $^3J_{HH}$ = 7.4, 6H, CH$_2$C$\underline{H}_3$), 0.98 (t, $^3J_{HH}$ = 7.5, 6H, CH$_2$C$\underline{H}_3$). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ 180.7 (two coincident d, $^1J_{109AgC}$ = 211, $^1J_{107AgC}$ = 183, NCN), 162.3 (q, $^1J_{BC}$ = 50.5, Ar^F), 157.8 ($\underline{C}OCH_2$), 156.7 (s, $\underline{C}OCH_2$), 136.5 (s, 2 × Ar{C}), 135.4 (s, Ar^F), 134.3 (s, Ar{C}), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 129.3 (s, Ar), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 126.4 (s, Ar), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 124.7 (d, $^3J_{AgC}$ = 6, imid.), 123.4 (s, Ar), 121.9 (d, $^3J_{AgC}$ = 6, imid.), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 78.7 (s, OCH_2), 77.2 (s, OCH_2), 38.8 (d, $^3J_{AgC}$ = 3, NCH_3), 31.4 (s, Ar$\underline{C}H_2$Ar), 24.0 (s, $\underline{C}H_2CH_3$), 23.5 (s, $\underline{C}H_2CH_3$), 11.0 (s, CH$_2\underline{C}H_3$), 10.1 (s, CH$_2\underline{C}H_3$). **ESI-MS** (CH_3CN, 180 °C, 3 kV) positive ion: 859.3340 m/z, $[M]^+$ (calcd 859.3347 m/z). **Anal.** Calcd For $C_{80}H_{68}AgBF_{24}N_4O_4$ (1724.09 g mol^{-1}): C, 55.73; H, 3.98; N, 3.25. Found: C, 55.85; H, 4.08; N, 3.33.

In situ reactions of 4b

A suspension of I^{i}Pr$_2$Me$_2$ (9.9 mg, 0.0549 mmol), Ag[OTf] (7.2 mg, 0.0277 mmol) and Na[BAr$^F{}_4$] (24.0 mg, 0.0271 mmol) in difluorobenzene (0.5 mL) was agitated for several minutes. Analysis *in situ* by NMR spectroscopy indicated quantitative formation of **4b** (data below). Solutions of **4b**, prepared in this way, where then filtered onto either $[Rh(COD)Cl]_2$ (13.6 mg, 0.0276 mmol) or $[Rh(CO)_2Cl]_2$ (10.8 mg, 0.0278 mmol), resulting in the formation of **5b** : **7** (2 : 1) and **6b**/**8** (5 : 2).

^{1}H NMR (1,2-$C_6H_4F_2$, 500 MHz): δ 8.11–8.13 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 4.20 (sept, $^3J_{HH}$ = 6.8, 4H, NCH), 1.87 (s, 12H, CCH_3), 1.31 (d, $^3J_{HH}$ = 6.8, 24H, CHC$\underline{H}_3$). **^{13}C{^{1}H} NMR** (1,2-$C_6H_4F_2$, 126 MHz): δ162.5 (q, $^1J_{BC}$ = 50, Ar^F), 135.1 (s, Ar^F), 129.7 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 124.9 (q, $^1J_{FC}$ = 272, Ar^F), 124 (obscured, $\underline{C}CH_3$), 117.6 (sept, $^3J_{FC}$ = 4, Ar^F), 50.1 (s, NCH), 23.3 (s, CHC$\underline{H}_3$), 8.1 (s, C$\underline{C}H_3$). The carbene resonance was not located. **^{19}F{^{1}H} NMR** (1,2-$C_6H_4F_2$, 282 MHz): δ-62.25 (Ar^F). No signal for $[OTf]^-$ detected. **ESI-MS** (CH_3CN, 180 °C, 3 kV) positive ion: 467.2297 m/z, $[M]^+$ (calcd 467.2298 m/z).

Preparation of 5a

A solution of **4a** (29.9 mg, 0.0173 mmol) and $[Rh(COD)Cl]_2$ (9.4 mg, 0.0191 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL) was stirred for 1 hour with the exclusion of light. The solvent was removed *in vacuo* and the resulting crude material washed with pentane and dried *in vacuo*. Yield = 22.3 mg (63%, yellow powder). The product was characterised *in situ*, although has limited stability in solution.

^{1}H NMR (1,2-$C_6H_4F_2$/C_6D_6, 500 MHz): δ 8.09–8.15 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F) 5.44 (br, 2H, COD{CH}), 5.38 (br, 2H, COD{CH}), 4.58 (d, $^2J_{HH}$ = 13.6, 2H, ArC$\underline{H}_2$Ar), 4.49 (d, $^2J_{HH}$ = 13.6, 2H, ArC$\underline{H}_2$Ar), 4.20 (s, 6H, NCH_3), 3.96–4.24 (m), 3.67–3.76 (m), 3.55–3.63 (m), 3.49–3.55 (m), 3.46 (d, $^2J_{HH}$ = 13.6, 2H, ArC$\underline{H}_2$Ar), 3.23–3.33 (m), 3.09 (d, $^2J_{HH}$ = 13.6, 2H,

ArCH$_2$Ar), 1.35–2.50 (m, CH$_2$), 1.03 (t, $^3J_{HH}$ = 6.9, 6H, CH$_2$CH$_3$), 0.85 (t, $^3J_{HH}$ = 6.9, 6H, CH$_2$CH$_3$), 0.7–1.1 (m, COD{CH$_2$}). Not all signals unambiguously assigned and some signals obscured by solvent peak. **^{13}C{^{1}H} NMR** (1,2-C$_6$H$_4$F$_2$/C$_6$D$_6$, 126 MHz, selected signals only): δ 176.9 (d, $^1J_{RhC}$ = 50, NCN), 100.3 (br, COD{CH}), 96.4 (br, COD{CH}), 78.5 (d, $^1J_{RhC}$ = 14, COD{CH}), 71.8 (d, $^1J_{RhC}$ = 13, COD{CH}), 97.7 (d, $^1J_{RhC}$ = 7, COD{CH}), 70.2 (d, $^1J_{RhC}$ = 16, COD{CH}), 37.8 (s, NCH$_3$). **ESI-MS** (CH$_3$CN, 180 °C, 3 kV): positive ion: 1209.3986 *m*/*z*, [M]$^+$ (calcd 1209.3973 *m*/*z*).

Preparation of 5b

A solution of [Rh(I^{i}Pr$_2$Me$_2$)(COD)Cl] (23.6 mg, 0.0553 mmol) and Na[BAr$^F_4$] (24.5 mg, 0.0275 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred for 1 hour. The solution was then filtered and layered with pentane to afford the product on diffusion. Yield = 32.0 mg (69%, yellow crystals).

^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.70–7.74 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 5.91 (sept, $^3J_{HH}$ = 7.1, 4H, NCH), 4.75 (s, 4H, COD{CH}), 3.51 (s, 4H, COD{CH}), 2.22–2.36 (m, 8H, COD{CH$_2$}), 2.11 (s, 12H, CCH$_3$), 1.81–1.93 (m, 8H, COD{CH$_2$}), 1.57 (d, $^3J_{HH}$ = 7.0, 12H, CHCH$_3$), 1.36 (d, $^3J_{HH}$ = 7.0, 12H, CHCH$_3$). **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 126 MHz): δ 175.6 (d, $^1J_{RhC}$ = 50, NCN), 162.3 (q, $^1J_{BC}$ = 51, Ar^F), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 31, $^3J_{BC}$ = 3, Ar^F), 126.3 (s, CCH$_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 97.7 (d, $^1J_{RhC}$ = 7, COD{CH}), 70.2 (d, $^1J_{RhC}$ = 16, COD{CH}), 54.3 (s, NCH), 33.1 (s, COD{CH$_2$}), 29.1 (s, COD{CH$_2$}), 22.5 (s, CHCH$_3$), 22.2 (s, CHCH$_3$), 10.5 (s, CCH$_3$). **ESI-MS** (CH$_3$CN, 180 °C, 3 kV) positive ion: 817.2872 *m*/*z*, [M]$^+$ (calcd 817.2924 *m*/*z*). **Anal.** Calcd For C$_{70}$H$_{76}$BF$_{24}$N$_4$Rh$_2$Cl (1434.39 g mol^{-1}): C, 49.97; H, 4.56; N, 3.33. Found: C, 50.18; H, 4.52; N, 3.23.

Preparation of 6a

A solution of **4a** (32.0 mg, 0.0186 mmol) and [Rh(CO)$_2$Cl]$_2$ (7.8 mg, 0.0201 mmol) in 1,2-C$_6$H$_4$F$_2$ (10 mL) was stirred for one hour with the exclusion of light. The cloudy yellow solution was filtered, reduced to dryness and the resulting residue washed with pentane. Yield = 21.4 mg (31%, yellow powder). The product was characterised *in situ*, although has limited stability in solution.

^{1}H NMR (1,2-C$_6$H$_4$F$_2$/C$_6$D$_6$, 500 MHz): δ 8.11–8.15 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 4.52 (d, $^2J_{HH}$ = 12.6, 2H, ArCH$_2$Ar), 4.51 (d, $^2J_{HH}$ = 12.6, 2H, ArCH$_2$Ar), 4.05–4.19 (m, 2H, OCH$_2$), 3.88–3.99 (m, 2H, OCH$_2$), 3.84 (s, 6H, NCH$_3$), 3.51–3.65 (m, 4H, OCH$_2$), 3.18 (d, $^2J_{HH}$ = 12.6, 2H, ArCH$_2$Ar), 3.15 (d, $^2J_{HH}$ = 12.6, 2H, ArCH$_2$Ar), 2.11–2.23 (m, 4H, CH$_2$CH$_3$), 1.79–1.92 (m, 4H, CH$_2$CH$_3$), 0.94 (t, $^3J_{HH}$ = 7.5, 6H, CH$_2$CH$_3$), 0.93 (t, $^3J_{HH}$ = 7.5, 6H, CH$_2$CH$_3$). Some signals obscured by solvent peak. **^{13}C{^{1}H} NMR** (1,2-C$_6$H$_4$F$_2$/C$_6$D$_6$, 126 MHz, selected signals only): δ 182.7 (d, $^1J_{RhC}$ = 53, CO), 181.0 (d, $^1J_{RhC}$ = 80, CO), 168.1 (d, $^1J_{RhC}$ = 43, NCN), 36.3 (s, NCH$_3$). **ESI-MS** (CH$_3$CN, 180 °C, 3 kV) positive ion: 1105.1680 *m*/*z*, [M]$^+$ (calcd 1105.1891 *m*/*z*). **IR** (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2083, 2016.

Preparation of 6b

A solution of [Rh(I^{i}Pr$_2$Me$_2$)(CO)$_2$Cl] (26.5 mg, 0.709 mmol) and Na[BAr$^F_4$] (32.6 mg, 0.368 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred for one hour. The solution was then filtered and layered with pentane to afford the product on diffusion. Yield = 37.1 mg (66%, yellow crystals).

^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 7.67–7.77 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 5.20 (sept, $^3J_{HH}$ = 7.1, 4H, NCH), 2.18 (s, 12H CCH$_3$), 1.55 (d, $^3J_{HH}$ = 7.1, 12H, CHCH$_3$), 1.50 (d, $^3J_{HH}$ = 7.0, 12H, CHCH$_3$). **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 101 MHz): δ 185.4 (d, $^1J_{RhC}$ = 53, CO), 181.0 (d, $^1J_{RhC}$ = 84, CO), 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 128.0 (s, CCH$_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 54.8 (s, NCH), 22.8 (s, CHCH$_3$)$_2$, 22.4 (s, CHCH$_3$)$_2$, (s, 10.6 CCH$_3$). The carbene resonance was not located. **ESI-MS** (CH$_3$CN, 180 °C, 3 kV) positive ion: 713.0829 *m*/*z*, [M]$^+$ (calcd 713.0843 *m*/*z*). **IR** (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2090, 2019. **Anal.** Calcd For C$_{58}$H$_{52}$BClF$_{24}$N$_4$O$_4$Rh$_2$Cl (1577.11 g mol^{-1}): C, 44.17; H, 3.32; N, 3.55. Found: C, 44.51; H, 3.57; N, 3.49.

Preparation of 7

A solution of I^{i}Pr$_2$Me$_2$ (50.8 mg, 0.282 mmol), [Rh(COD)Cl]$_2$ (34.3 mg, 0.0696 mmol) and Na[BAr$^F_4$] (123.4 mg, 0.139 mmol) was stirred in 1,2-C$_6$H$_4$F$_2$ (5 mL) for 2.5 h. The solution was then filtered and layered with pentane to afford the product on diffusion. Yield = 114.0 mg (56%, yellow crystals).

^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.71–7.75 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 5.56 (sept, $^3J_{HH}$ = 7.1, 4H, NCH), 4.27 (s, 4H, COD{CH}), 2.31–2.40 (m, 4H, COD{CH$_2$}), 2.16 (s, 12H, CCH$_3$), 2.01–2.11 (m, 4H, COD{CH$_2$}), 1.55 (d, $^3J_{HH}$ = 7.1, 12H, CHCH$_3$), 1.22 (d, $^3J_{HH}$ = 7.1, 12H, CHCH$_3$). **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 126 MHz): δ 178.1 (d, $^1J_{RhC}$ = 55.8, NCN), 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 127.1 (s, CCH$_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 87.2 (d, $^1J_{RhC}$ = 8, COD{CH}), 54.5 (s, NCH), 31.8 (s, COD{CH}), 22.9 (s, CHCH$_3$), 21.6 (s, CHCH$_3$), 10.9 (s, CCH$_3$). **ESI-MS** (CH$_3$CN, 180 °C, 3 kV) positive ion: 571.3215 *m*/*z* [M]$^+$ (calcd 571.3242 *m*/*z*). **Anal.** Calcd For C$_{62}$H$_{64}$BF$_{24}$N$_4$Rh (1434.39 g mol^{-1}): C, 51.96; H, 4.49; N, 3.90. Found: C, 52.05; H, 4.59; N, 3.93.

Preparation of 8

A solution of 7 (113.9 mg, 0.0794 mmol) in 1,2-C$_6$H$_4$F$_2$ (5 mL) was stirred under an atmosphere of CO (1 atm) for 24 hours. The solvent was removed *in vacuo* and the resulting crude material washed with pentane and recrystallised from CH$_2$Cl$_2$/pentane. Yield = 72.4 mg (66%, orange powder).

^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 7.71–7.75 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 5.05 (sept, $^3J_{HH}$ = 7.1, 4H, NCH), 2.20 (s, 12H, CCH$_3$), 1.46 (d, $^3J_{HH}$ = 7.1, 12H, CHCH$_3$), 1.19 (d, $^3J_{HH}$ = 7.1, 12H, CHCH$_3$). **^{13}C{^{1}H} NMR** (CD$_2$Cl$_2$, 126 MHz): δ 186.9 (d, $^1J_{RhC}$ = 57, CO), 168.2 (d, $^1J_{RhC}$ = 47, NCN), 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 135.3 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 128.2 (s, CCH$_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 55.3 (s, NCH), 22.0 (s, CHCH$_3$), 21.1 (s, CHCH$_3$), 10.9 (s, CCH$_3$).

ESI-MS (CH_3CN, 180 °C, 3 kV) positive ion: 519.2249 *m*/*z* $[M]^+$ (calcd 520.2201 *m*/*z*). **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 2077, 2018. **Anal.** Calcd For $C_{56}H_{52}BF_{24}N_4Rh$ (1382.29 g mol^{-1}): C, 48.64; H, 3.79; N, 4.05. Measured: C, 48.51; H, 3.63; N, 4.15.

Crystallography

Full details about the collection, solution and refinement are documented in the CIF, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1448987–1448996.

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