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Coordination chemistry of a calix[4]arene-based NHC ligand: Dinuclear complexes and comparison to $I^iPr_2Me_2$

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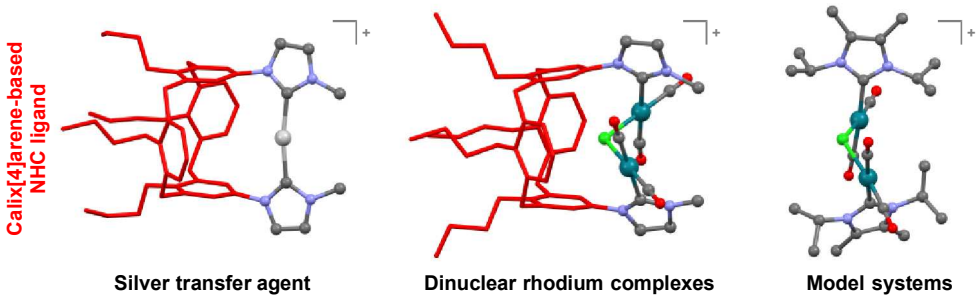
TOC graphic



Abstract

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 $[Rh(CO)_2Cl]_2$ 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_2O in the presence of a halide extractor, reactions with $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ 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 ($I^iPr_2Me_2$).

Introduction

In addition to desirable donor properties, the structural versatility of *N*-heterocyclic carbenes (NHCs) has proven to be 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 possible 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 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]

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

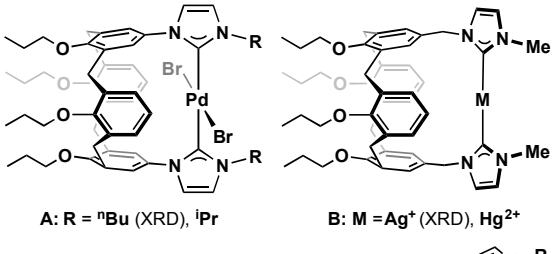
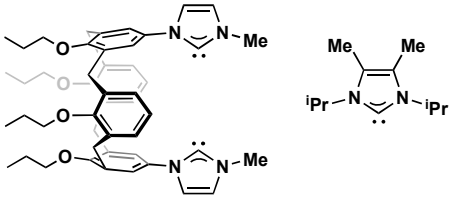


Chart 2: NHC systems of interest.



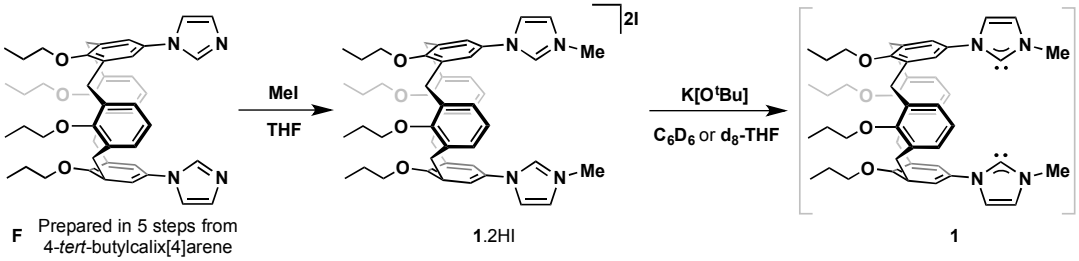
In this report the preparation and coordination chemistry of an upper rim functionalised calix[4]arene pro-ligand **1**.2HI are described (Chart 2). Through generation of the free NHC ligand (**1**) and use of transmetallation methodology, reactions with rhodium(I) dimers $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene)

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 ^{1}H 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; Figure 1).[13] In order to quantify this distortion, the angles between the least squares planes (Mpln) of opposing aryloxy groups Θ_{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 Figure 1 with $\Theta_{CALIX}(NHC.H^+)/\Theta_{CALIX}(H)$ = +80.8(2)/-19.3(2)º ($\Delta\Theta_{CALIX}$ = 100.1(4)º); the other is characterised by $\Theta_{CALIX}(NHC.H^+)/\Theta_{CALIX}(H)$ = +86.4(2)/-2.8(2)º ($\Delta\Theta_{CALIX}$ = 89.2(4)º).

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



F Prepared in 5 steps from 4-*tert*-butylcalix[4]arene

1.2HI

1

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 ^{1}H NCHN resonance and characteristically high frequency ^{13}C resonance at δ 213.2 (C_6D_6) / 216.0 (d_8-THF) of the carbenic centre.[14]

For comparison, the equivalent signal in $^{i}Pr_2Me_2$ 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.

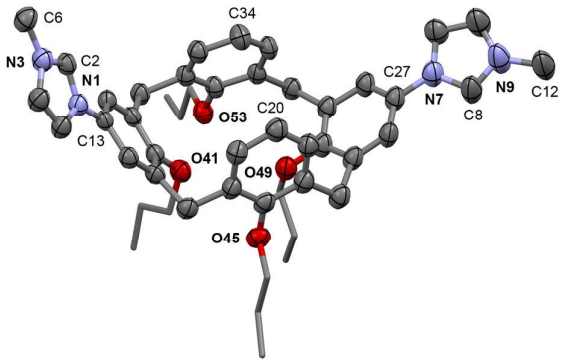
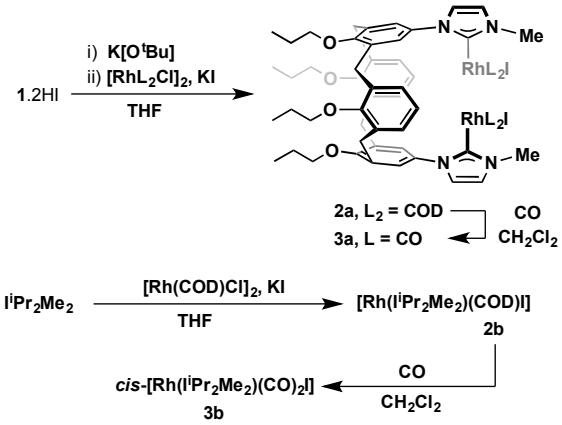


Figure 1: Solid-state structure of **1**.2HI. Thermal ellipsoids for selected atoms drawn at the 30% probability level; only one of the two unique molecules shown (Z' = 2); hydrogen atoms and anions are omitted for clarity. Selected bond lengths (Å) and angles (º): C2···C8, 13.43(2); ∠Mpln(C13-C18,O41)-Mpln(C27-32,O49), 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).

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 eqv) to avoid formation of mixed halide products. Using either 0.5 or 1 eqv 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 $^{i}Pr_2Me_2$, **2b** and **3b**, were readily obtained through direct adaptions of the aforementioned procedures (Scheme 2).

Scheme 2: Reactions of **1** and $^{i}Pr_2Me_2$ with rhodium dimers



For both NHC ligands, the rhodium-diene complexes **2** were characterised in the solid-state by X-ray crystallography (Figure 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)º, **2a**; 100.1(4)/89.2(4)º, **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), **2a**; 2.021(3), **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 (Δδ = 2.03), with the high frequency signal at δ 7.95 presumably a consequence of the close 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.

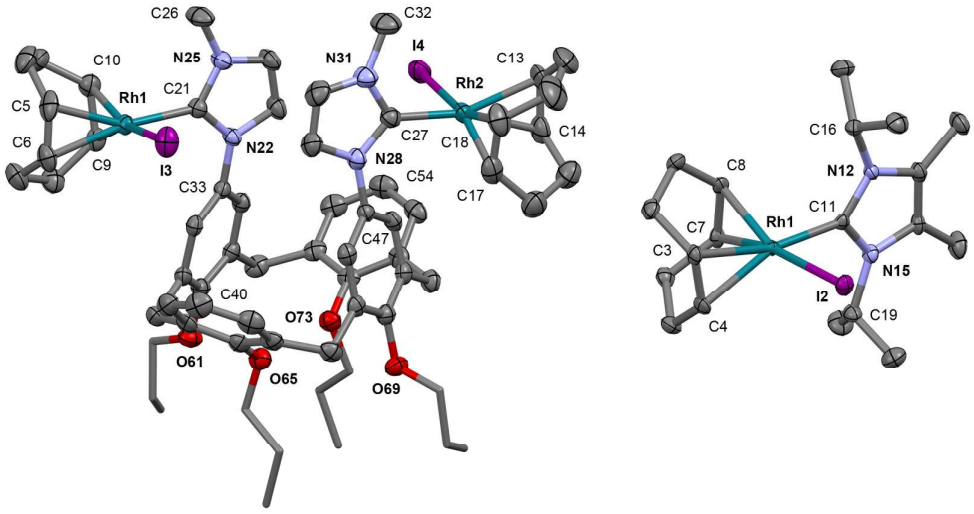
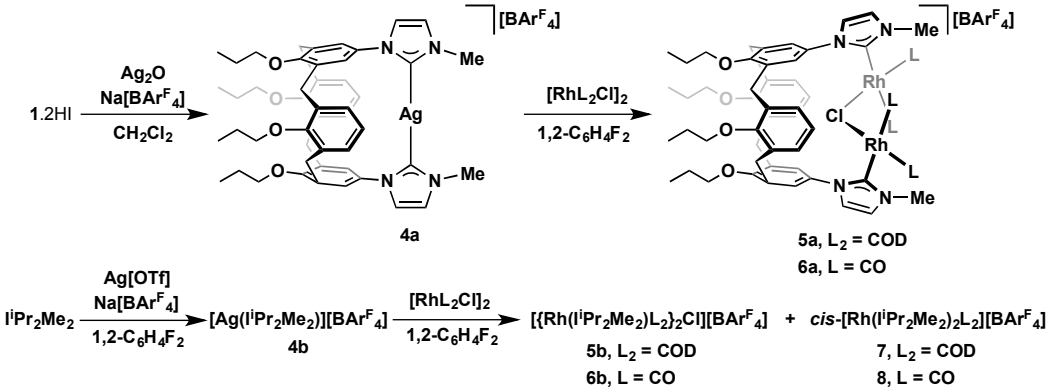


Figure 2: Solid-state structures of **2a** and **2b**. Thermal ellipsoids for selected atoms drawn at the 50% probability level; minor disordered components (two O^{n}Pr groups in **2a**), and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (º): **2a**: Rh1-I3, 2.6905(3); Rh1-Cnt(C5,C6), 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).

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**].

Scheme 3: Preparation and transmetallation reactions of silver NHC complexes



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)º] and essentially equivalent Ag-C bond lengths (Ag1-C2, 2.085(4); Ag1-C8, 2.083(4); Figure 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 eqv $I^iPr_2Me_2$ 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)º **4a**; |N3-C2-C15-N19| = 77.0(5)º, **4b**; |N-C-C-N| = 20.6(6)º, **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)º], 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**.

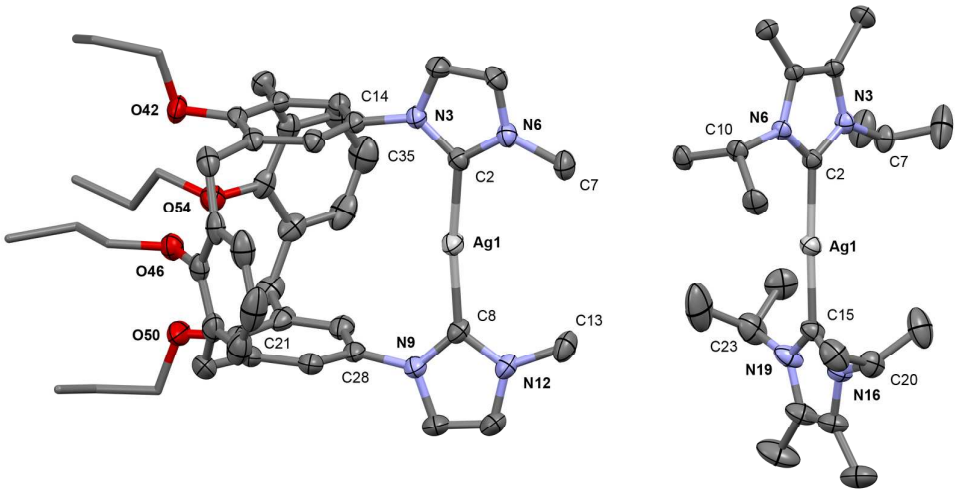


Figure 3: Solid-state structures of **4a** and **4b**. Thermal ellipsoids for selected atoms drawn at the 30% probability level; minor disordered components (four O^{n}Pr groups in **4a**), hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å) and angles (º): **4a**: Ag1-C2, 2.085(4); 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-C40,054), 97.44(10); **4b**: Ag1-C2, 2.093(4); Ag1-C15, 2.092(4); C2-Ag1-C15, 176.81(15).

Silver complex **4a** acts as an effective carbene transfer agent, resulting in the formation of dinuclear complexes **5a** ad **6a** bearing both μ^2**–1** and μ^2–Cl ligands on reaction with 1 eqv 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 eqv 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**/**3b** and supported through preparation of direct I^{i}Pr$_2$Me$_2$ analogues (*vide infra*), the formulation of the structures of **5a**/**6a** was achieved through a combination of ^{1}H, ^{13}C NMR and IR spectroscopy, ESI-MS and in the case of **5b** a low resolution X-ray structure (Figure 4). The ESI-MS in particular evidenced formation of these dinuclear monocationic species, with parent cation signals at 1209.3986 (calcd 1209.3973) and 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 and where 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 ≥ 2σ (I)]. The data nevertheless can affirm the structural formulation, with a reduced pinching of calix[4]arene core [$\Delta\Theta_{CALIX}$ = -83.1(7)º] relative to **2a** [$\Delta\Theta_{CALIX}$ = -98.41(12)º] and **4a** [$\Delta\Theta_{CALIX}$ = -96.4(2)º].

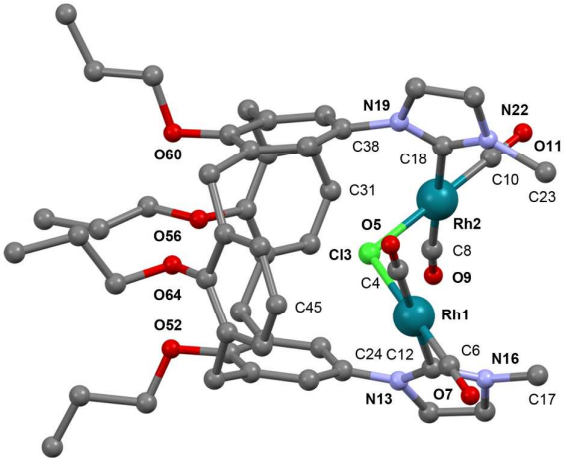
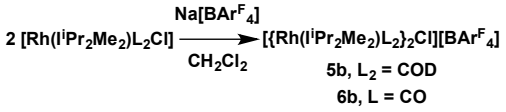


Figure 4: Solid-state structure of **6a** (ball and stick, poor quality data). Minor disordered component (CO), hydrogen atoms and anion omitted for clarity. Selected bond lengths (Å) and angles(º): Rh1-Cl3, 2.353(5); Rh2-Cl3, 2.360(5); Rh1···Rh2, 3.861(3); Rh1-Cl3-Rh2, 110.0(3); ∠Mpln(C24-C29,O52)-Mpln(C38-C43,O60),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

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 eqv of Na[BAr$^F{}_4$] in CH_2Cl_2 (Scheme 4). These structurally simple and fully characterised species (solution and solid-state, Figure 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** [δ 176.9 ($^1J_{RhC}$ = 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 in comparison of 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 **4b**, the calix[4]arene scaffold promotes the selective formation of dinuclear complexes. For instance, when **4b** is

reacted with 1 eqv of $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ 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 ^1H 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).

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



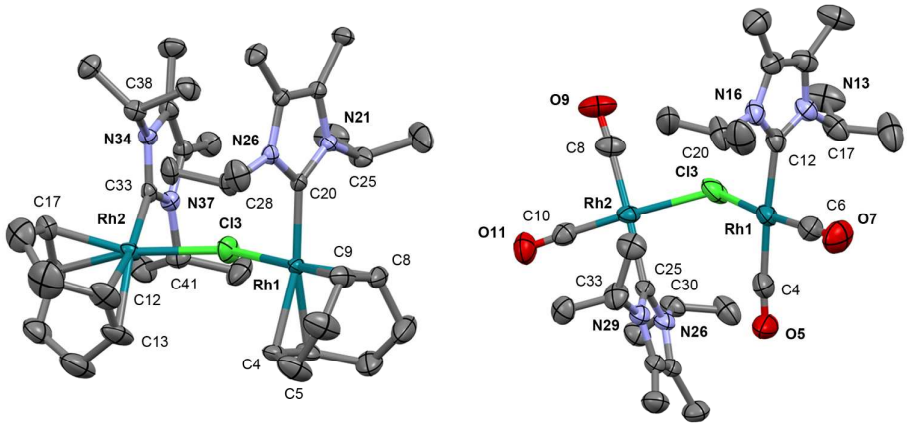


Figure 5: Solid-state structures of **5b** and **6b**. Thermal ellipsoids drawn at the 50% probability level; minor disordered components (two ^{i}Pr groups in **6b**), hydrogen atoms, solvent (**6a**), and anions omitted for clarity. Selected bond lengths (Å) and angles (º): **5b**: Rh1-Cl3, 2.3988(9); 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).

Summary

Using both free carbene and transmetallation methodologies the coordination chemistry of the 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 this 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 150ºC 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 multiplets. $^{13}C\{^1H\}$ 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, $C\underline{H}_2CH_3$), 1.12 (t, $^3J_{HH}$ = 7.4, 6H, $CH_2C\underline{H}_3$), 0.93 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$).

$^{13}C\{^1H\}$ 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{$\underline{C}N$}), 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$\underline{H}_2CH_3$), 1.92 – 1.99 (m, 4H, C$\underline{H}_2CH_3$), 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{$\underline{C}$N}), 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$\underline{H}_2CH_3$), 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{$\underline{C}$N}), 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 x 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, $^{2}J_{HH}$ = 13.3, 2H, ArC$\underline{H}_2$Ar), 4.50 (d, $^{2}J_{HH}$ = 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, $^{2}J_{HH}$ = 13.4, 2H, ArC$\underline{H}_2$Ar), 3.21 – 3.26 (m, 2H, COD{CH}), 3.19 (d, $^{2}J_{HH}$ = 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$\underline{H}_2CH_3$), 1.83 – 1.97 (m, 6H, C$\underline{H}_2CH_3$ + COD{CH_2}), 1.58 – 1.79 (m, 4H, COD{CH_2}), 1.27 – 1.46 (m, 4H, COD{CH_2}), 1.15 (t, $^{3}J_{HH}$ = 7.4, 6H, $CH_2C\underline{H}_3$), 0.95 (t, $^{3}J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 180.4 (d, $^{1}J_{RhC}$ = 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, $^{1}J_{RhC}$ = 7, COD{CH}), 95.0 (d, $^{1}J_{RhC}$ = 7, COD{CH}), 77.7 (s, OCH_2), 77.3 (s, OCH_2), 71.4 (d, $^{1}J_{RhC}$ = 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, $^{3}J_{HH}$ = 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, C$\underline{H}_3$), 1.87 – 1.98 (m, 2H, COD{CH_2}), 1.73 – 1.83 (m, 2H, COD{CH_2}), 1.56 (d, $^{3}J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$), 1.50 (d, $^{3}J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 178.4 (d, $^{1}J_{RhC}$ = 49, NCN), 126.0 (s, $\underline{C}CH_3$), 95.2 (d, $^{1}J_{RhC}$ = 7, COD{CH}), 71.5 (d, $^{1}J_{RhC}$ = 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 x 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): δ 7.26 (s, 2H, Ar), 7.02 (br, 4H, Ar), 6.82 (t, $^{3}J_{HH}$ = 7.4, 2H, Ar), 6.77 (s, 2H, imid.), 6.46 (s, 2H, imid.), 6.41 (s, 2H, Ar), 4.51 (d, $^{2}J_{HH}$ = 13.3, 2H, ArC$\underline{H}_2$Ar), 4.48 (d, $^{2}J_{HH}$ = 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, $^{2}J_{HH}$ = 14.1, 2H, ArC$\underline{H}_2$Ar), 3.22 (d, $^{2}J_{HH}$ = 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, $^{1}J_{RhC}$ = 54, CO), 181.6 (d, $^{1}J_{RhC}$ = 78, CO), 171.5 (d, $^{1}J_{RhC}$ = 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 x 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, $^{3}J_{HH}$ = 7.1, 2H, NCH), 2.22 (s, 6H, CCH_3), 1.501 (d, $^{3}J_{HH}$ = 7.1, 6H, CHC$\underline{H}_3$), 1.496 (d, $^{3}J_{HH}$ = 2.7, 6H, CHC$\underline{H}_3$).
^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 188.7 (d, $^{1}J_{RhC}$ = 53, CO), 182.7 (d, $^{1}J_{RhC}$ = 78, CO), 166.8 (d, $^{1}J_{RhC}$ = 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, $^{3}J_{HH}$ = 7.4, 4H, Ar), 6.92 (d, $^{3}J_{HH}$ = 1.7, 2H, imid.), 6.85 (t, $^{3}J_{HH}$ = 7.5, 2H, Ar), 6.81 (d, $^{3}J_{HH}$ = 1.7, 2H, imid.), 6.40 (s, 4H, Ar), 4.57 (d, $^{2}J_{HH}$ = 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, $^{3}J_{HH}$ = 7.1, 4H, OCH_2), 3.24 (d, $^{2}J_{HH}$ = 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, $^{3}J_{HH}$ = 7.4, 6H,

$CH_2C\underline{H}_3$), 0.98 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$).

$^{13}C\{^1H\}$ 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, 2xAr{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 $I^iPr_2Me_2$ (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).

^1H 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, $CHC\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (1,2-$C_6H_4F_2$, 126 MHz): δ 162.5 (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.

$^{19}F\{^1H\}$ 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.

^1H 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, Ar$\underline{C}H_2$Ar), 4.49 (d, $^2J_{HH}$ = 13.6, 2H, Ar$\underline{C}H_2$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, Ar$\underline{C}H_2$Ar), 3.23 – 3.33 (m), 3.09 (d, $^2J_{HH}$ = 13.6, 2H, Ar$\underline{C}H_2$Ar), 1.35 – 2.50 (m, CH_2), 1.03 (t, $^3J_{HH}$ = 6.9, 6H, $CH_2C\underline{H}_3$), 0.85

(t, $^3J_{HH}$ = 6.9, 6H, $CH_2C\underline{H}_3$), 0.7 – 1.1 (m, COD{CH_2}). Not all signals unambiguously assigned and some signals obscured by solvent peak.

$^{13}C\{^1H\}$ NMR (1,2-$C_6H_4F_2$/C_6D_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_3CN, 180°C, 3 kV): Positive ion: 1209.3986 *m/z*, $[M]^+$ (calcd 1209.3973 *m/z*).

Preparation of 5b

A solution of [Rh($I^iPr_2Me_2$)(COD)Cl] (23.6 mg, 0.0553 mmol) and Na[BAr^F_4] (24.5 mg , 0.0275 mmol) in CH_2Cl_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).

^1H NMR (CD_2Cl_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, $CHC\underline{H}_3$), 1.36 (d, $^3J_{HH}$ = 7.0, 12H, $CHC\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (CD_2Cl_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, $\underline{C}CH_3$), 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, $CH\underline{C}H_3$), 22.2 (s, $CH\underline{C}H_3$), 10.5 (s, $C\underline{C}H_3$).

ESI-MS (CH_3CN, 180°C, 3 kV) Positive ion: 817.2872 *m/z*, $[M]^+$ (calcd 817.2924 *m/z*).

Anal. Calcd For $C_{70}H_{76}BF_{24}N_4Rh_2Cl$ (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 $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.0201 mmol) in 1,2-$C_6H_4F_2$ (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.

^1H NMR (1,2-$C_6H_4F_2$/C_6D_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, $ArC\underline{H}_2Ar$), 4.51 (d, $^2J_{HH}$ = 12.6, 2H, $ArC\underline{H}_2Ar$), 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, $ArC\underline{H}_2Ar$), 3.15 (d, $^2J_{HH}$ = 12.6, 2H, $ArC\underline{H}_2Ar$), 2.11 – 2.23 (m, 4H, $C\underline{H}_2CH_3$), 1.79 – 1.92 (m, 4H, $C\underline{H}_2CH_3$), 0.94 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$), 0.93 (t, $^3J_{HH}$ = 7.5, 6H, $CH_2C\underline{H}_3$). Some signals obscured by solvent peak.

$^{13}C\{^1H\}$ NMR (1,2-$C_6H_4F_2$/C_6D_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_3CN, 180°C, 3 kV) Positive ion: 1105.1680 *m/z*, $[M]^+$ (calcd 1105.1891 *m/z*).

IR (CH_2Cl_2, cm^{-1}): ν (CO) 2083, 2016.

Preparation of 6b

A solution of $[Rh(I^iPr_2Me_2)(CO)_2Cl]$ (26.5 mg, 0.709 mmol) and $Na[BAr^F{}_4]$ (32.6 mg, 0.368 mmol) in CH_2Cl_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_2Cl_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 CC$\underline{H}_3$), 1.55 (d, $^3J_{HH}$ = 7.1, 12H, CHC$\underline{H}_3$), 1.50 (d, $^3J_{HH}$ = 7.0, 12H, CHC$\underline{H}_3$).

^{13}C{^{1}H} NMR (CD_2Cl_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, CH$\underline{C}H_3)_2$, 22.4 (s, CH$\underline{C}H_3)_2$, (s, 10.6 C$\underline{C}H_3$). The carbene resonance was not located.

ESI-MS (CH_3CN, 180°C, 3 kV) Positive ion: 713.0829 *m/z*, $[M]^+$ (calcd 713.0843 *m/z*).

IR (CH_2Cl_2, cm^{-1}): ν (CO) 2090, 2019.

Anal. Calcd For $C_{58}H_{52}BClF_{24}N_4O_4Rh_2Cl$ (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 $I^iPr_2Me_2$ (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-$C_6H_4F_2$ (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_2Cl_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, CHC$\underline{H}_3$), 1.22 (d, $^3J_{HH}$ = 7.1, 12H, CHC$\underline{H}_3$).

^{13}C{^{1}H} NMR (CD_2Cl_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, $\underline{C}CH_3$), 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, CH$\underline{C}H_3$), 21.6 (s, CH$\underline{C}H_3$), 10.9 (s, C$\underline{C}H_3$).

ESI-MS (CH_3CN, 180°C, 3 kV) Positive ion: 571.3215 *m/z* $[M]^+$ (calcd 571.3242 *m/z*).

Anal. Calcd For $C_{62}H_{64}BF_{24}N_4Rh$ (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-$C_6H_4F_2$ (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_2Cl_2/pentane. Yield = 72.4 mg (66%, orange powder).

^{1}H NMR (CD_2Cl_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, $CHC\underline{H}_3$), 1.19 (d, $^3J_{HH}$ = 7.1, 12H, $CHC\underline{H}_3$).

^{13}C{^{1}H} NMR (CD_2Cl_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, $\underline{C}CH_3$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 55.3 (s, NCH), 22.0 (s, $CH\underline{C}H_3$), 21.1 (s, $CH\underline{C}H_3$), 10.9 (s, $C\underline{C}H_3$).

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. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information available

^{1}H and ^{13}C NMR, IR and ESI-MS spectra of new complexes.

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