Revised manuscript om-2014-00332n

Rhodium(I) Complexes of the Conformationally Rigid IBioxMe$_4$ Ligand: Preparation of Mono-, Bis- and Tris-Ligated NHC Complexes

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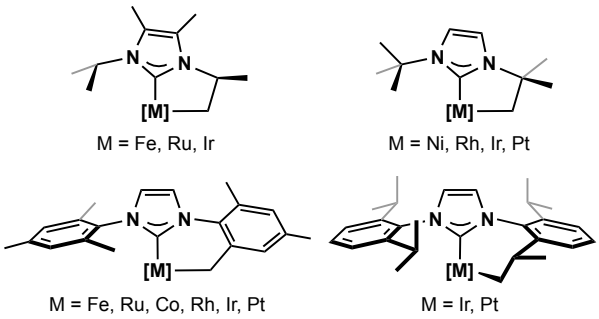
Abstract

The preparation and characterisation of a series of mono-, bis- and tris-ligated rhodium(I) complexes of Glorius' conformationally rigid bioxazoline derived *N*-heterocyclic carbene ligand IBioxMe$_4$ are described. Through reaction of [Rh(COE)$_2$Cl]$_2$ (COE = *cis*-cyclooctene) with isolated IBioxMe$_4$, [Rh(IBioxMe$_4$)(COE)Cl]$_2$ (**1**), *trans*-[Rh(IBioxMe$_4$)$_2$(COE)Cl] (**2**) and [Rh(IBioxMe$_4$)$_3$Cl] (**3**) were each isolated by careful choice of the reaction conditions. Further substitution and salt metathesis reactions of **1** – **3** were investigated and derivatives containing CO, norbornadiene and cyclopentadienyl ancillary ligands were readily isolated. Notably, halide abstraction from **2** and **3** using Na[BAr$^F_4$] (Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$) resulted in the formation of low coordinate T-shaped *cis*-[Rh(IBioxMe$_4$)$_2$(COE)][BAr$^F_4$] (**9**) and [Rh(IBioxMe$_4$)$_3$][BAr$^F_4$] (**11**). The solid-state structures of **2**, **9** and **11** each feature IBioxMe$_4$ ligands that bind unusually with tilted coordination geometries.

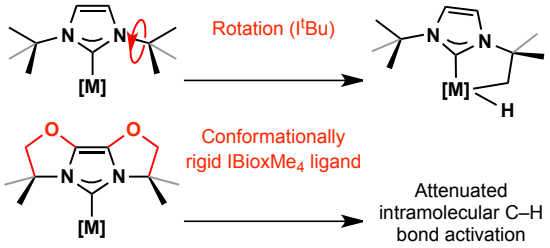
Introduction

With generally stronger σ-donating characteristics and orthogonal steric profiles to phosphine ligands, *N*-heterocyclic carbenes (NHCs) have quickly emerged as a powerful class of carbon-based ligand in organometallic chemistry and catalysis.[1] While in the majority of applications spectator roles are intended, intramolecular C(sp^3)–H bond activation reactions of coordinated NHC ligands are increasingly being observed when partnered with reactive late transition metal fragments.[2] Examples include activation of the *N*-aryl and alkyl substituents of common NHC ligands: 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($I^iPr_2Me_2$), 1,3-bis-*tert*-butylimidazol-2-ylidene (I^tBu), 1,3-bis-mesitylimidazol-2-ylidene (IMes), and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr), amongst others (Chart 1).[3,4,5,6,7] The IMes ligand has even been shown to support double cyclometalation[8] and subsequent reactivity of NHC-based metallocycles can lead to alkyl dehydrogenation.[6a,7,9] However, although cyclometalation reactions are of interest in their own right,[10] they can represent unwanted and potentially detrimental reactivity characteristics of NHC based metal complexes.

Chart 1: Cyclometalated NHC topologies.



Scheme 1: Hypothesised reactivity modulation.



Recognising that substituent flexibility, particularly rotation about *N*-aryl/alkyl bonds, is a key prerequisite for cyclometalation reactions of NHC ligands, conformationally rigid analogues were targeted as a means to attenuate such reactivity, whilst retaining the desirable electronic and steric properties of the ligand class. With such features in mind, bioxazoline-derived NHC ligands (IBiox) developed by Glorius and co-workers were identified from the literature.[11,12] IBiox ligands are particularly notable for their application in palladium catalysed cross coupling reactions, although their coordination chemistry has not been widely explored. Given the structural similarity with $I^iPr_2Me_2$ and I^tBu, the tetramethyl-substituted IBiox ligand, $IBioxMe_4$, was chosen for investigation (Scheme 1). With a view of contrasting the cyclometalation

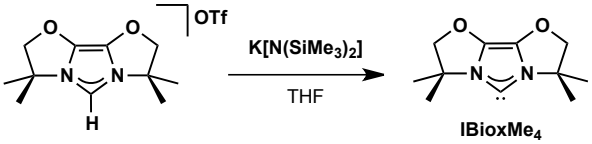
processes observed by Nolan and others in rhodium complexes of I^{t}Bu,[3,4] the coordination chemistry of IBioxMe$_4$ with rhodium was targeted and a range of mono-, bis- and tris-ligated derivatives are reported herein. Some aspects of this chemistry were published as a communication (i.e. tris-NHC complexes **11** and **12**).[13]

Results and discussion

Synthesis of free carbene

The target imidazolium pro-ligand IBioxMe$_4$.HOTf was synthesised in four steps, from commercially available 2-amino-2-methyl-propanol and diethyloxalate, as previously described by Glorius and co-workers.[11] The corresponding free carbene ligand was readily formed by reaction of the pro-ligand with the strong hindered base K[N(SiMe$_3$)$_2$] in THF (Scheme 2).[13] In this manner IBioxMe$_4$ was isolated in 80% yield, following removal of volatiles in vacuo and extraction with pentane, and stored under argon in a glove box. Satisfactory microanalyses were obtained and the free carbene was fully characterised in C_6D_6 solution by NMR spectroscopy. C_{2v} symmetry is observed in solution with the carbene resonance at 190.1 ppm, significantly downfield from the pro-ligand (112.4 ppm) and consistent with other systems.[12b,14]

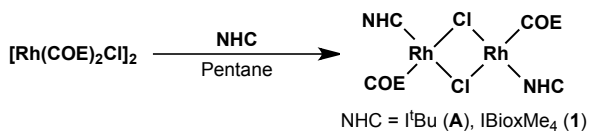
Scheme 2: Preparation of IBioxMe$_4$.



Reaction of IBioxMe$_4$ with [Rh(COE)$_2$Cl]$_2$

Following the procedure of Nolan and co-workers,[3] reaction of IBioxMe$_4$ with the rhodium(I) precursor [Rh(COE)$_2$Cl]$_2$ (COE = *cis*-cyclooctene) in pentane resulted in the formation of dimeric chloro-bridged rhodium(I) complex [Rh(IBioxMe$_4$)(COE)Cl]$_2$ **1**, which was isolated in good yield following recrystallisation from benzene–heptane (66%, Scheme 3). Coordination of the COE and carbene ligands is confirmed by the observation of ^{13}C doublet resonances at δ 60.4 ($^1J_{RhC}$ = 17 Hz) and δ 158.3 ($^1J_{RhC}$ = 59 Hz), respectively, by NMR spectroscopy. Likewise, coordinated alkene protons are observed at 2.97 ppm as an integral 2H multiplet in the ^{1}H NMR spectrum. These data are in good agreement with those of the I^{t}Bu analogue (**A**)[3] and related dimeric complexes [Rh(NHC)(H$_2$C=CH$_2$)Cl]$_2$ (NHC = IMes, SIMes, IPr, SIPr, I^{t}Bu (**B**))[15] previously prepared by Crudden and co-workers.[4]

Scheme 3: Preparation of dimeric **1**.

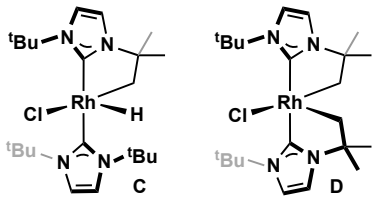


NHC = I^{t}Bu (**A**), IBioxMe$_4$ (**1**)

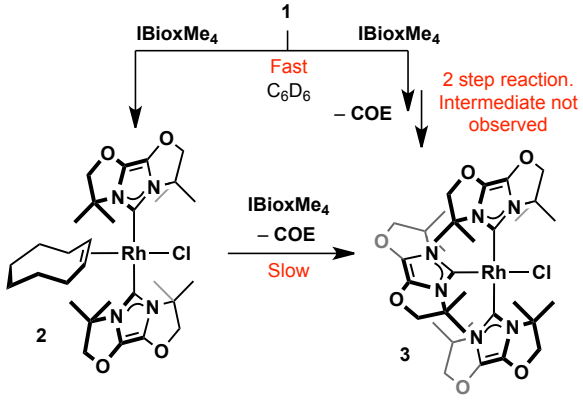
Isolated **1** is stable in solution, showing no apparent reaction after 7 days in C_6D_6 solution (293 K) by ^{1}H NMR spectroscopy. While **A** has also been reported to be stable in benzene solution,[3] in the presence of

excess I^{t}Bu sequential formation of monomeric cyclometalated derivatives **C** and **D** occurs; where these complexes contain one and two cyclometalated I^{t}Bu ligands (I^{t}Bu'), respectively (Chart 2). Addition of excess IBioxMe$_4$ to isolated **1** in C_6D_6 similarly resulted in fragmentation of the chloride bridge. However, instead of intramolecular activation of the NHC ligand, mixtures of the bis- and tris-NHC complexes *trans*-[Rh(IBioxMe$_4$)$_2$(COE)Cl] (**2**) and [Rh(IBioxMe$_4$)$_3$Cl] (**3**) were obtained; the later almost completely insoluble in benzene (Scheme 4). Following this reaction in situ by NMR spectroscopy (C_6D_6, 293 K) revealed a significant rate dependence on the concentration of the NHC ligand. With 4 equivalents IBioxMe$_4$ the initial rate for the disappearance of **1** was *ca* 3.7 × 10^{-6} mol·L^{-1}s^{-1}, which increased to *ca* 8.2 × 10^{-6} mol·L^{-1}s^{-1} when using 8 equivalents of the ligand. After 90% consumption of **1**, the resulting ratios of **2**:**3** were 5.8 and 4.5, respectively. These data indicate approximate first order dependence on [IBioxMe$_4$] and a faster rate of formation for **2** relative to **3**. Given that reaction between **2** and IBioxMe$_4$ to give **3** is two orders of magnitude slower than the reaction of **1** with IBioxMe$_4$ (*vide infra*), the most plausible mechanism for this reaction involves bifurcated (associative) ligand substitution chemistry of **1** (Scheme 4); a suggestion that invokes the presence of transient (unobserved) bis-NHC complex, *cis*-[Rh(IBioxMe$_4$)$_2$(COE)Cl] or [Rh(IBioxMe$_4$)$_2$Cl]$_2$, in the formation of **3**. Throughout these in situ reactions no evidence for ligand cyclometalation was observed supporting the hypothesised reactivity attenuation of the conformationally rigid ligand in comparison to I^{t}Bu. A feature of the IBioxMe$_4$ complexes further contrasted by the reported reactivity of isolated **B**, which undergoes spontaneous intramolecular activation of the NHC ligand, resulting in formation of the rhodium(III) dimer [Rh(I^{t}Bu')(CH$_2$CH$_3$)Cl]$_2$, **C** and metallic rhodium.[4]

Chart 2: Cyclometalated rhodium complexes of I^{t}Bu.



Scheme 4: Reaction of **1** with IBioxMe$_4$.



Complexes **2** and **3** are most conveniently prepared by direct reaction between [Rh(COE)$_2$Cl]$_2$ and excess IBioxMe$_4$ (4.6 eqv.) in benzene and were obtained in this way with isolated yields of 47% and 24% respectively; the insolubility of **3** enabled easy separation of the two complexes. The structures of **2** and **3**

were determined by X-ray crystallography (Figure 1) and corroborated in solution by NMR spectroscopy. Both complexes adopt the expected square planar geometries, although for **2** (with two crystallographically independent, but structurally similar complexes) there is a significant degree of distortion: the C11-Rh1-C26 angle deviating from linearity (167.49(7)º; 167.47(7)º for Rh1A equivalent). Interestingly, one of the IBioxMe$_4$ ligands binds unusually, pitching significantly out of plane as quantified by a non-linear NHC centroid–C$_{NCN}$–Rh angle (Θ_{NHC})[16] of 156.50(14)º (164.72(13)º for Rh1A equivalent). Such large deviations from planar coordination are rare in transition metal complexes,[17,18] and notably more pronounced in **2** in comparison to related [Rh(SIMes)(PPh$_3$)(H$_2$C=CH$_2$)Cl] (Θ_{NHC} = 170.5º)[4], *trans*-[Rh(SIMes)$_2$LCl] (L = N$_2$, O$_2$, CO (**E**); Θ_{NHC} = 177.4 – 178.5º)[19] and *trans*-[Ir(NHC)$_2$(COE)Cl] (Θ_{NHC} = 169.6 – 178.4º).[20] This tilting is attributed to steric interactions between the NHC and the coordinated COE ligands and born out through the presence of close {COE}C̲H$_2$···H$_3$C̲{IBioxMe$_4$} contacts of *ca* 3.6 Å (sum of Van der Waal radii = 3.4 Å). Moreover in line with this reasoning, essentially planar IBioxMe$_4$ coordination is observed when COE is replaced with a less bulky ancillary ligand (i.e. **7**, *vide infra*). Complex **3** is an NHC analogue of Wilkinson's catalyst, examples of which have been previously reported by Lappert et al.[21] The IBioxMe$_4$ ligands twist in a helical fashion and all Θ_{NHC} are greater than 175º in the solid-state structure of **3**.

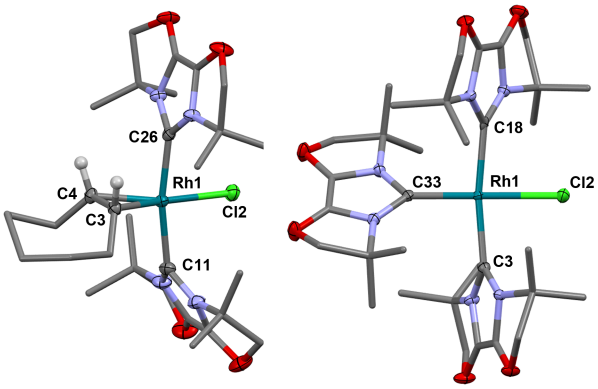


Figure 1: Solid-state structures of **2** (left) and **3** (right). Thermal ellipsoids for selected atoms are drawn at the 50% probability level; most hydrogen atoms are omitted for clarity; only one of the two independent molecules shown for each complex (*Z'* = 2 for both **2** and **3**). Selected bond lengths (Å) and angles(º): **2** – Rh1-Cl2, 2.4231(5); Rh1-C3, 2.125(2); Rh1-C4, 2.117(2); Rh1-C11, 2.100(2); Rh1-C26, 2.026(2); C3-C4, 1.411(3); Cl2-Rh1-Cnt(C3,C4), 175.10(2); C11-Rh1-C26, 167.49(7); Θ_{NHC}(@C11), 156.50(14); Θ_{NHC}(@C26), 172.98(13); Θ_{NHC}(@C11A), 164.72(13); Θ_{NHC}(@C26A), 170.1(2); **3** – Rh1-Cl2, 2.4224(14); Rh1-C3, 2.046(5); Rh1-C18, 2.060(5); Rh1-C33, 2.016(5); Cl2-Rh1-C33, 177.3(2); C3-Rh1-C18, 169.2(2); all Θ_{NHC} > 175.

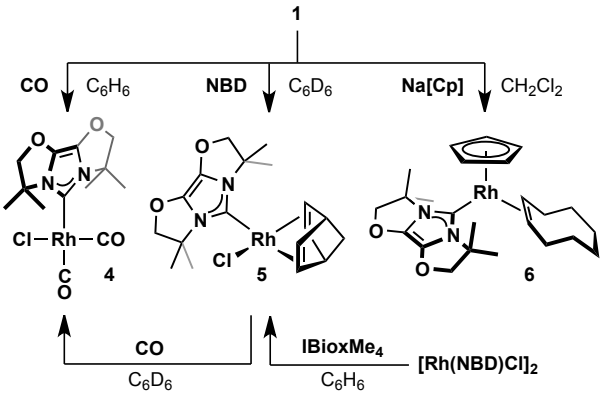
To establish if **2** is a kinetically relevant intermediate in the formation of **3** from **1**, in situ NMR experiments were carried out involving reaction of **2** with excess IBioxMe$_4$ (2 and 4 eqv.) in C$_6$D$_6$ (293 K). A slow reaction was observed, involving substitution of the COE ligand independent of [IBioxMe$_4$], with an initial rate for the disappearance of **2** of *ca* 7.0 × 10^{-8} mol·L^{-1}s^{-1} and approximate half-life of 82 h. These data suggest a dissociative mechanism for the substitution of the COE ligand and clearly show the formation of **3** via **2** is not a kinetically relevant pathway in the reaction of dimeric **1** with IBioxMe$_4$. Consistent with this suggestion, isolated **2** slowly lost COE in solution (*ca* 15% decomposition after 24 h in C$_6$D$_6$ at 293 K). Complex **3** is observed during the decomposition; however, the other species involved have eluded

identification so far.

Coordination chemistry of 1 – 3

Seeking to further explore the coordination chemistry of these rhodium(I) IBioxMe$_4$ complexes, incorporation of other carbon based ancillary ligands was targeted. To this end, reactions of **1** with CO, norbornadiene (NBD) and Na[Cp] were investigated (Scheme 5). Under an atmosphere of CO, **1** was rapidly (< 10 min) and quantitatively (by NMR spectroscopy) converted to the bis-carbonyl complex *cis*-[Rh(IBioxMe$_4$)(CO)$_2$Cl] **4** (solid-state structure in Figure 2). Complexes of the formulation *cis*-[M(NHC)(CO)$_2$Cl] (M = Rh, Ir) have been widely used to probe the electronic and steric characteristics of NHC ligands (Table 1).[22] In particular, these complexes allow the determination of the Tolman electronic parameter (TEP)[23] for the NHC ligand from the carbonyl stretching frequencies of *cis*-[M(NHC)(CO)$_2$Cl], avoiding the need to prepare toxic nickel adducts.[24,25] Using this approach the calculated TEP for IBioxMe$_4$ using **4** (2053 cm^{-1}) is in good agreement with that determined using the previously reported iridium analogue *cis*-[Ir(IBioxMe$_4$)(CO)$_2$Cl] (2052 cm^{-1})[11] and both are marginally larger in magnitude than those of I^{i}Pr$_2$Me$_2$ (2051 cm^{-1}) and I^{t}Bu (2050 cm^{-1}), inline with the presence of the electronegative oxygen substituents. The steric characteristics of IBioxMe$_4$ have also been quantified through measurement of it's percentage buried volume (%V$_{bur}$) using the solid-state structure of **4** for the relevant calculation.[26,27] Steric bulk increases in the order I^{i}Pr$_2$Me$_2$ < IBioxMe$_4$ < I^{t}Bu, with the %V$_{bur}$ of IBioxMe$_4$ (32.0) notably similar to that of aryl substituted IMes (33.8)

Scheme 5: Preparation of **4 – 6**.



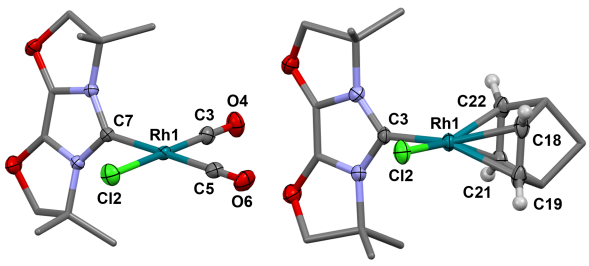


Figure 2: Solid-state structures of **4** (left) and **5** (right). Thermal ellipsoids for selected atoms are drawn at the 50% probability level; most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles(º): **4** – Rh1-Cl2, 2.3519(5); Rh1-C3, 1.830(2); Rh1-C5, 1.897(2); Rh1-C7, 2.069(2); Θ_{NHC}(@C7), 178.97(13); **5** – Rh1-Cl2, 2.3642(15); Rh1-C3, 2.048(6); Rh1- C18, 2.197(6); Rh1-C19, 2.182(6); Rh1-C21, 2.098(6); Rh1-C22, 2.105(6); Θ_{NHC}(@C3), 177.2(4).

Table 1: Steric and electronic properties of NHC ligands derived from *cis*-[M(NHC)(CO)$_2$Cl]

M	NHC	ν(CO) [CH_2Cl_2] /cm^{-1}		TEP [calc.][a] (expt.) /cm^{-1}	%V_{bur} [b]	Ref.
Rh	IBioxMe$_4$	2081	2000	2053	32.0	This work
Ir	IBioxMe$_4$	2066	1982	2052	-	11
Rh	I^{i}Pr$_2$Me$_2$	2076	1996	2051	28.0[c]	28
Ir	ICy[d]	2065	1981	2051 (2050)[29]	28.1	25
Ir	I^{t}Bu	2065	1980	2050	37.6	25
Ir	IMes	2066	1980	2051 (2051)[29]	33.8	25

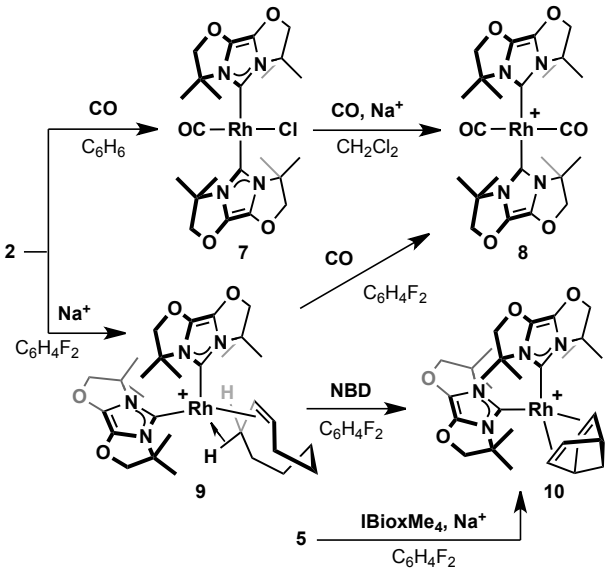
[a] Tolman electronic parameter calculated from regression using the average ν(CO) value.[22] [b] Calculated using SambVca (sphere radius = 3.5, distance from centre of sphere = 2.0, mesh spacing = 0.5, hydrogens omitted, bondi radii scaled by 1.17).[27] [c] Estimated from X-ray structure of [Rh(I^{i}Pr$_2$Me$_2$)(COD)(OH)].[30] [d] ICy = = 1,3-bis-cyclohexylimidazol-2-ylidene.

In comparison to the reaction with CO, the reaction between **1** and NBD to afford [Rh(IBioxMe$_4$)(NBD)Cl] **5** occurred significantly slower, with an approximate half-life of 3.6 h. Indeed, **5** was more readily prepared by reaction of IBioxMe$_4$ with the dimeric rhodium(I) precursor [Rh(NBD)Cl]$_2$ (88% isolated yield). The solid-state structure of **5** (Figure 2) resembles that of **4** and is otherwise unremarkable, as are NMR data. Placing **5** under an atmosphere of CO quantitatively afforded **4** (by NMR spectroscopy) alongside free NBD – therefore offering an alternative synthetic route to the bis-carbonyl compound (Scheme 5).

Cyclopentadienyl complex [Rh(IBioxMe$_4$)(Cp)(COE)] (**6**) resulted from salt metathesis of **1** in CH_2Cl_2 using Na[Cp] and was isolated in good yield (72%). Coordination of the hydrocarbon ligands are apparent by the presence of a 5H and 2H signals at δ 5.11 and 2.11 together with characteristic doublets in the $^{13}C\{^1H\}$ NMR spectrum at δ 86.2 ($^1J_{RhC}$ = 3 Hz) and 53.1 ($^1J_{RhC}$ = 17 Hz) for the [Cp]$^-$ and COE ligands, respectively; the carbene signal was observed at δ 159.7 (d, $^1J_{RhC}$ = 66 Hz). Surprisingly, few examples of non-chelating NHC rhodium(I) cyclopentadienyl complexes are known; [Rh(IMes)(C_5R_5)(H_2C=CH_2)] (R = H (**F**), Me) and [Rh(SIMe)(Cp)(CO)] (SIMe = 1,3-bis-methylimidazolin-2-ylidene) being the only precedents.[31] The NMR characteristics of **6** are in agreement with those reported for **F**; $\delta_{\underline{C}5H5}$ 84.7 (d, $^1J_{RhC}$ = 4 Hz), $\delta_{\underline{C}2H4}$ 24.3 (d, $^1J_{RhC}$ = 16 Hz) and $\delta_{N\underline{C}N}$ 185.0 ($^1J_{RhC}$ = 70 Hz).

Reaction of bis-NHC **2** with carbon monoxide readily affords *trans*-[Rh(IBioxMe$_4$)$_2$(CO)Cl] **7**, which can be substituted further with carbon monoxide in the presence of Na[BAr$^F_4$] (Ar^F = 3,5-$C_6H_3(CF_3)_2$), as a halide abstracting agent, to give the bis-carbonyl complex *trans*-[Rh(IBioxMe$_4$)$_2$(CO)$_2$][BArF$_4$] **8** (Scheme 6). The structures of both carbonyl complexes were established through a combination of NMR and IR spectroscopy (C_{2v}, **7**; D_{2h}, **8**), alongside crystallographic characterisation (Figure 3). A more upfield ^{13}C resonance for the NHC (141.0 vs. 160.5 ppm), reduced carbonyl $^1J_{RhC}$ coupling constant (64 vs. 82 Hz) and higher carbonyl stretching frequency (2024 vs. 1942 cm^{-1}) are observed for **8** in comparison to **7**, fully consistent with the more electron deficient nature of the metal centre. While there are a number of examples of complexes of the formulation [Rh(NHC)$_2$(CO)Cl] (e.g. **E**),[5x,19, 28,32] there is only one non-chelating precedent for **8** to the author's knowledge.[33]

Scheme 6: Reactions of bis-IBioxMe$_4$ complexes.[a]



[a] $[BAr^F_4]^-$ anions omitted for clarity

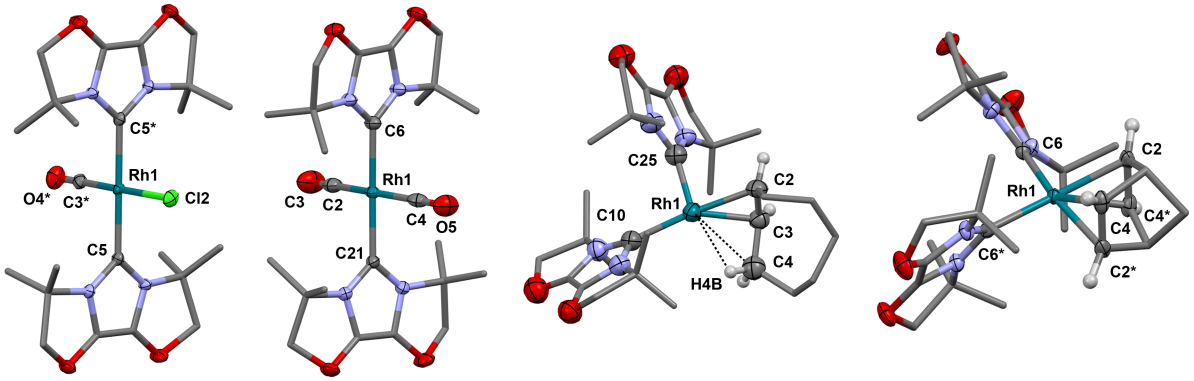


Figure 3: Solid-state structures of **7** – **10** (left to right). Thermal ellipsoids for selected atoms are drawn at the 50% probability level; most hydrogen atoms, minor disordered components, anions and solvent molecules are omitted for clarity; only one of the two independent molecules shown for **9** (*Z*' = 2); symmetry operations *-x,-y,-z* (**7**) and 2-*x*,+*y*,3/2-*z* (**10**) were used to generate the started atoms. Selected bond lengths (Å) and angles(º): **7** – Rh1-Cl2, 2.386(2); Rh1-C3*, 1.807(6); Rh1-C5, 2.050(2); C5-Rh1-C5* 180.00; Θ_{NHC}(@C5), 176.8(2); **8** – Rh1-C2, 1.910(3); Rh1-C4, 1.917(3); Rh1-C6, 2.063(2); Rh1-C21, 2.061(2); C6-Rh1-C21, 177.53(9); all Θ_{NHC}(NHC) > 175; **9** – Rh1-C2, 2.196(14); Rh1-C3, 2.123(14); Rh1-C4, 2.56(2); Rh1-C10, 2.099(14); Rh1-C25, 1.971(15); all other Rh1-C > 3.0; C10-Rh1-C25, 100.5(6); Θ_{NHC}(@C10), 168(1); Θ_{NHC}(@C25), 178.5(12); Rh1A-C4A, 2.94(2); all other non-coordinated Rh1A-C > 3.0; Θ_{NHC}(@C10A), 168.4(11); Θ_{NHC}(@C25A), 177.8(13); **10** – Rh1-C2, 2.163(2); Rh1-C4, 2.159(2); Rh1-C6, 2.121(2); C6-Rh1-C6*, 101.51(9); Θ_{NHC}(@C6), 173.05(12).

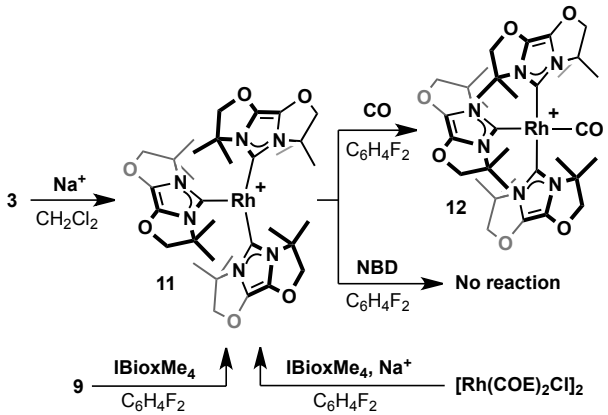
Targeting the preparation of a low-coordinate bis-NHC complex derivative, **2** was reacted with the halide abstracting agent Na[BAr^F_4] in difluorobenzene at reduced temperature (253 K). From this reaction, cationic *cis*-[Rh(IBioxMe$_4$)$_2$(COE)][BAr^F_4] **9** was isolated in good yield (71%). Formally a 14 valence electron complex, formation of **9** was readily apparent by ^{1}H NMR spectroscopy (250 K) by a 2H coordinated alkene resonance centred at δ 3.97, which gave a strong HMQC cross-peak with a ^{13}C signal at δ 76.3, 12H resonances for the $[BAr^F_4]^-$ anion and two singlet signals (8H, 24H) for the IBioxMe$_4$ ligands. The complex is thus highly fluxional in solution (500 MHz). On the basis of the low stability of **9** (*vide infra*) and to reconcile the high time-averaged symmetry implicated from the IBioxMe$_4$ proton resonances (D_{2h}), a mechanism involving

COE ligand dissociation is suggested. Cooling further to 200 K did not halt this process, although the onset of decoalescence was noted – particularly through resolution of inequivalent methylene signals for the NHC backbone (see ESI).

Subsequent to the NMR characterisation, a relatively low quality solid-state structure of **9** was determined, containing two crystallographically independent, but structurally similar molecules (Z' = 2); one of which is shown in Figure 3. The refined structure unambiguously confirms coordination of the COE and IBioxMe$_4$ ligands, with **9** adopting an overall T-shaped coordination geometry. The complex is stabilised by an agostic interaction with the COE ligand; a feature that is much more pronounced in one of the independent molecules (Rh1···C4 = 2.56(2) Å) than the other (Rh1A···C4A = 2.94(2) Å). Notably, the methyl substituents of the IBioxMe$_4$ ligand remain distant from the metal centre, with the closest approaches having Rh···C distances of 3.67(4) and 3.18(3) Å in the independent molecules (containing Rh1 and Rh1A, respectively). [Rh(P^{i}Bu$_3$)(P^{t}Bu$_2$CH$_2$CH$_2$CH=CH$_2$)]$^+$ (**G**) [34] and [Rh{((2,6-Me$_2$C$_6$H$_3$)NMeC)$_2$CH}(L)] (L = norbornene (**H**), COE (**I**))[35] are closely related rhodium(I) alkene complexes; **G** and **H** are stabilised by strong agostic interactions (Rh···C = 2.41 and 2.53 Å, respectively), while **I** is considered a genuinely low coordinate T-shaped complex with Rh···C distances of 2.89 and 2.97 Å. Consistent with the T-shaped formulation of **9**, the NHC binding trans to the open coordination site does so with a significantly shorter Rh-C$_{NCN}$ bond distance (Rh1, 1.971(15) *vs* 2.099(14) Å; Rh1A, 1.921(17) *vs* 2.070(15) Å).

In both CD_2Cl_2 and difluorobenzene solution at 298 K, **9** undergoes decomposition via loss of COE although this process is much faster in the former ($t_{1/2}$ = 0.54 hrs vs. 6.6 hrs) presumably reflecting the differing coordinating ability of the two solvents; the resulting mixtures have so far proven intractable to further characterisation in either solvent. Complex **9** does, however, act as a source of the reactive {Rh(IBioxMe$_4$)$_2$}$^+$ fragment in solution affording **8** and the diene complex [Rh(IBioxMe$_4$)$_2$(NBD)][BAr$^F_4$] **10** quantitatively by NMR spectroscopy on addition of carbon monoxide and NBD, respectively (Scheme 6). The formation of **10** was further verified by independent synthesis from **5**, IBioxMe$_4$ and Na[BAr$^F_4$] and the solid-state structure is shown in Figure 3.

Scheme 7: Reactions of tris-IBioxMe$_4$ complexes.[a]



[a] [BAr$^F_4$]$^-$ anions omitted for clarity

Encouraged by the formation of **9** from **2**, reaction of tris-NHC complex **3** with Na[BAr^F_4] in CH_2Cl_2 at room temperature led to the isolation of cationic formally 14 valence electron Rh(I) complex [Rh($IBioxMe_4$)$_3$][BAr^F_4] **11** in 65% yield (Scheme 7, Figure 4). Complex **11** can also be prepared as previously described using a high yielding one-pot procedure involving reaction between [Rh(COE)$_2$Cl]$_2$ and $IBioxMe_4$ in difluorobenzene, using Na[BAr^F_4] as a halide abstractor (83% isolated yield).[13] In contrast to **9**, the tris-NHC complex was found to be completely stable in CD_2Cl_2 and difluorobenzene solution at room temperature (over 48 hours under argon). This increased stability is readily accounted for by the stronger donor characteristics of $IBioxMe_4$ in comparison to COE and confirmed by rapid COE substitution by $IBioxMe_4$ on addition of the NHC to **9**, forming **11** quantitatively by ^{1}H NMR spectroscopy (Scheme 7).

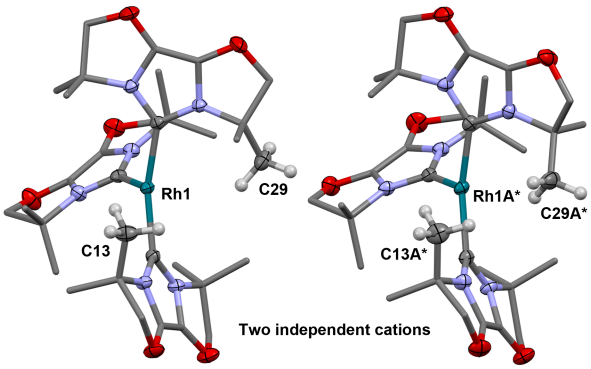


Figure 4: Solid-state structures of **11** (*Z*' = 2)**.** Thermal ellipsoids for selected atoms are drawn at the 50% probability level; most hydrogen atoms, minor disordered components, anions and solvent molecule are omitted for clarity. Selected distances: Rh1-C13, 3.273(3); Rh1-C29, 3.574(3); Rh1A-C13A, 3.421(3); Rh1A-C29A, 3.191(3).[13]

As noted by Reed reporting on the solid-state structure of [Rh(PPh_3)$_3$]$^+$ (**J**), the adoption of a T-shaped geometry is electronically favoured over trigonal planar for three coordinate d^8 metal centres to allow for diamagnetism (Figure 5).[36] Moreover, T-shaped low-coordinate d^8 metal fragments can be stabilised through formation of agostic interactions with alkyl ligand appendages, due to the presence of accessible frontier orbitals of suitable symmetry and energy (i.e. b_1 and $2a_1$). This facet is borne in the solid-state for rhodium(I) phosphine complexes **G**, **H**, **J** (Rh···C = 2.62 Å), [Rh(P^iPr_3)$_3$]$^+$ (Rh···C = 2.49 Å),[37] [Rh(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)(CH$_2$^{t}Bu)] (Rh···C = 2.49 Å)[38], as well as platinum(II) NHC and phosphine complexes [Pt(IPr)(IPr')]$^+$ (Pt···C = 2.89 Å)[6b] and [Pt(P^iPr_3)$_2$(Me)]$^+$ (Pt···C = 2.86 Å).[39] As an additional interesting example, phosphine-boryl-pincer complex [Rh{(P^tBu$_2$CH$_2$)$_2$($BN_2C_6H_4$)}] adopts intermolecular σ-C–H bond interactions between individual complexes in the absence of accessible alkyl groups.[40] In the case of **11**, however, there is no evidence for any significant agostic interactions between the NHC ligands and the metal centre in both solution (highly fluxional at 298 K) and the solid-state (Rh···C distances for the methyl substituents > 3.1 Å).[13] Thus, the rigid geometry of the $IBioxMe_4$ ligand appears to prohibit any significant interaction of the methyl substituents in both **9** and **11**.

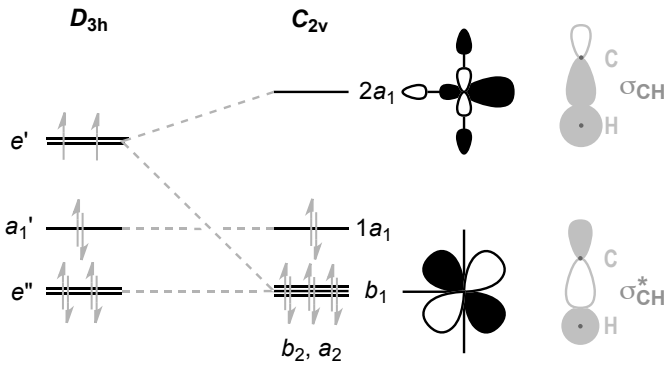


Figure 5: Frontier molecular orbitals for d^8 metal centres in idealised trigonal planar and T-shaped coordination geometries.[41]

Inspection of the $IBioxMe_4$ coordination geometries in **9** and **11** reveals tilted binding for those cis to open coordination sites: Θ_{NHC} = 168(1) / 168.4(11)º for **9** and 160.0(2) − 173.1(2)º for **11**.[13] Given that related distortions observed in coordinatively saturated **2** can be confidently ascribed to steric effects, and taking into account the bulky nature of $IBioxMe_4$ and the absence any significant Rh···H_3C interactions (Rh···C ≥ 3.18 Å and Rh···H ≥ 2.44 Å),[42] it seems reasonable to similarly attribute the unusual NHC geometries in **9** and **11** to steric effects. Related phenomena in main group bis-NHC complexes of gallium and indium have been reported, with Θ_{NHC} values ranging from 144.8 – 154.6º, and attributed to π-bonding interactions [s(M) to p(C_{NCN})].[18a] Contrasting with **11**, all $IBioxMe_4$ ligands in coordinatively saturated tris-NHC complexes **3** and **12** (*vide infra*) bind with and Θ_{NHC} angles > 175º; steric interactions between the ancillary chloride/carbonyl ligand and the cis $IBioxMe_4$ ligands counteracting NHC tilting ($\underline{C}H_3\cdots\underline{Cl}$ = 3.38 – 3.72 Å cf. sum of Van der Waal radii = 3.45 Å; $\underline{C}H_3\cdots O\underline{C}$ = 3.35 – 3.76 Å cf. sum of Van der Waal radii = 3.40 Å).[13] Likewise in the context of **9**, only slight tilting is observed in **10**, containing cis $IBioxMe_4$ ligands (Θ_{NHC} = 173.05(12)º).

As reported earlier, complex **11** shows no reaction with excess $IBioxMe_4$, PCy_3, or NBD, but reacts rapidly with carbon monoxide to generate $[Rh(IBioxMe_4)_3(CO)][BAr^F{}_4]$, **12** (Scheme 7).[13] Notably, the static C_{2v} structure observed for **12** in solution at room temperature (400 MHz) contrasts to previously reported tris-NHC complexes $[Rh(NHC)_3(CO)]^+$ [NHC = $I^iPr_2Me_2$, ICy], which undergo restricted rotation of the NHC ligands (about Rh-C_{NCN}) at room temperature (500 MHz).[43] This difference in behaviour is presumably attributed to the more imposing steric profile of $IBioxMe_4$ compared to $I^iPr_2Me_2$ and ICy; a feature quantified by $\%V_{bur}$ values listed in Table 1 (*ca* 32 vs 28).

Summary and Outlook

A series of new rhodium(I) complexes of Glorius' conformationally rigid bioxazoline derived *N*-heterocyclic carbene ligand $IBioxMe_4$ have been prepared. In contrast to non-rigid I^tBu, complexes of $IBioxMe_4$ appear to be more resistant to cyclometalation reactions allowing the coordination of up to three NHC ligands to rhodium via the common (isolated) dimeric intermediate $[Rh(IBioxMe_4)(COE)Cl]_2$ (**1**); i.e. isolation of *trans*-$[Rh(IBioxMe_4)_2(COE)Cl]$ (**2**) and $[Rh(IBioxMe_4)_3Cl]$ (**3**). Substitution and salt metathesis reactions of **1** – **3** were investigated and derivatives containing CO, norbornadiene and cyclopentadienyl ancillary ligands

were readily isolated. In search of low-coordinate complexes of $IBioxMe_4$, **2** and **3** were reacted with $Na[BAr^F_4]$ and led to the isolation of T-shaped *cis*-$[Rh(IBioxMe_4)_2(COE)][BAr^F_4]$ (**9**) and $[Rh(IBioxMe_4)_3][BAr^F_4]$ (**11**). Although **9** exhibits low solution stability, readily losing COE at room temperature, **11** shows excellent stability. Using these complexes as pertinent examples, the rigid geometry of the $IBioxMe_4$ ligand appears to preclude interaction of the metal centre with the ligand's alkyl appendages as hypothesised. The large steric profile of $IBioxMe_4$ ($\%V_{bur}$ = 32.0) also leads to interesting tilted NHC coordination geometries (**2**, **9** and **11**). The electronic structure and additional reactivity of these complexes is currently being investigated together with that of iridium analogues. These results will be reported in due course.

Experimental

General experimental methods

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 130ºC overnight and flamed under vacuum prior to use. Anhydrous C_6H_6, CH_2Cl_2, heptane and pentane (<0.005 % H_2O) were purchased from ACROS or Aldrich and freeze-pump-thaw degassed three times before being placed under argon. C_6D_6, CD_2Cl_2 and 1,2-difluorobenzene ($C_6H_4F_2$) were dried over CaH_2, vacuum distilled and the latter stored over thoroughly vacuum dried 3 Å molecular sieves. Norbornadiene (NBD) was dried over Na, vacuum distilled and stored over thoroughly vacuum dried 3 Å molecular sieves. $IBioxMe_4$.HOTf,[11] $[Rh(COE)_2Cl]_2$,[44] $[Rh(NBD)Cl]_2$[45] Na[Cp][46] and $Na[BAr^F_4]$[47] were synthesised using literature procedures. All other solvents and reagents are commercial products and were used as received. NMR spectra were recorded on Bruker DPX-400, AV-400 and DRX-500 spectrometers at 298 K unless otherwise stated. Chemical shirts are quoted in ppm and coupling constants in Hz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Microanalyses were performed by Stephan Boyer at London Metropolitan University.

Synthesis of new compounds

1.1 $IBioxMe_4$

Prepared from $IBioxMe_4$.HOTf as described in an earlier communication.[13]

1.2 $[Rh(IBioxMe_4)(COE)Cl]_2$ (1)

To a suspension of $[Rh(COE)_2Cl]_2$ (0.100 g, 0.14 mmol) in pentane (30 mL) was added a solution of $IBioxMe_4$ (0.058 g, 0.28 mmol) in pentane (30 mL) drop-wise over 5 minutes. The resulting suspension was stirred at room temperature for 1 hour and then filtered. The filtrate was washed with pentane (2 × 10 mL) and the residue recrystallised from benzene – heptane. Yield = 0.085 g (66%, microcrystalline cream solid).

^{1}H NMR (C_6D_6, 400 MHz): δ 3.76 (d, $^2J_{HH}$ = 8.1, 2H, OCH_2), 3.71 (d, $^2J_{HH}$ = 8.1, 2H, OCH_2), 2.89 – 3.05 (m, 2H, CH), 2.41 – 2.65 (m, 4H, $CHCH_2$), 2.02 (s, 6H, CH_3), 1.80 (s, 6H, CH_3), 1.68 – 1.88 (m, 4H, CH_2{COE}), 1.44 – 1.65 (m, 4H, CH_2{COE}). **$^{13}C\{^1H\}$ NMR** (C_6D_6, 101 MHz): δ 158.3 (d, $^1J_{RhC}$ = 59, NCN), 126.4 (s, $COCH_2$), 87.4 (s,

OCH_2), 62.2 (s, $\underline{C}(CH_3)_2$), 60.4 (d, $^1J_{RhC}$ = 17, CH), 31.2 (s, CH_2{COE}), 30.4 (s, $CH\underline{C}H_2$), 27.5 (s, CH_3), 27.2 (s, CH_2{COE}), 24.9 (s, CH_3). **Anal.** Calcd for $C_{38}H_{60}N_4O_4Rh_2.0.66(C_6H_6)$ ([913.62] 965.18 $gmol^{-1}$): C, 52.22; H, 6.68; N, 5.80. Found: C, 52.21; H, 6.91; N, 5.95. Reproducible microanalyical data were unable to be obtained between different batches of this product due the presence of variable benzene solvate (confirmed by dissolving in CD_2Cl_2). ^{1}H and $^{13}C\{^1H\}$ NMR spectra are provided in the ESI.

1.3 [Rh(IBioxMe$_4$)$_2$(COE)Cl] (2) and [Rh(IBioxMe$_4$)$_3$Cl] (3)

To a solution of $[Rh(COE)_2Cl]_2$ (0.150 g, 0.21 mmol) in benzene (10 mL) was added a solution of $IBioxMe_4$ (0.200 g, 0.960 mmol) in benzene (10 mL) drop-wise (over *ca* 1 min). The resulting solution was stirred at room temperature for 24 hours, during which time **3** crystallised. Complex **3** was isolated by filtration and washed with benzene (2 x 2 mL) – the washings being discarded. Yield = 0.080 g (24% / Rh, deep yellow crystalline solid). Addition of excess heptane to the reaction filtrate afforded **2**. Yield = 0.140 g (47% / Rh, yellow microcrystalline solid). Higher yields of **3** can be achieved using a larger excess of $IBioxMe_4$, e.g. repeating using 8 equivalents of ligand gave a 55% yield of **3** after 24 hours.

Data for **2**:

^{1}H NMR (C_6D_6, 400 MHz): δ 3.93 (d, $^2J_{HH}$ = 7.9, 4H, OCH_2), 3.80 (d, $^2J_{HH}$ = 7.9, 4H, OCH_2), 3.19 – 3.28 (m, 2H, CH), 2.50 – 2.61 (m, 2H, $CH\underline{C}H_2$), 2.13 (s, 12H, CH_3), 1.77 (s, 12H, CH_3), 1.71 – 1.85 (obscured m, 4H, CH_2{COE}), 1.52 – 1.62 (m, 4H, $CH\underline{C}H_2$ + CH_2{COE}), 1.39 – 1.52 (m, 2H, CH_2{COE}). **$^{13}C\{^1H\}$ NMR** (C_6D_6, 101 MHz): δ 169.6 (d, $^1J_{RhC}$ = 42, NCN), 126.5 (s, $\underline{C}OCH_2$), 87.8 (s, OCH_2), 62.5 (s, $\underline{C}(CH_3)_2$), 57.7 (d, $^1J_{RhC}$ = 16, CH), 34.4 (s, $CH\underline{C}H_2$), 31.7 (s, CH_2{COE}), 27.2 (s, CH_2{COE}), 26.7 (s, CH_3), 24.4 (s, CH_3). **Anal.** Calcd for $C_{30}H_{46}ClN_4O_4Rh.0.5(C_6H_6)$ ([665.07] 704.13 $gmol^{-1}$): C, 56.29; H, 7.01; N, 7.96. Found: C, 56.18; H, 7.07; N, 8.17. Benzene solvate is readily apparent from the crystal structure and on dissolving in CD_2Cl_2 (not stable).[48]

Data for **3**:

^{1}H NMR (C_6D_6, 400 MHz): δ 4.00 (d, $^2J_{HH}$ = 7.4, 4H, OCH_2), 3.97 (d, $^2J_{HH}$ = 7.4, 4H, OCH_2), 3.89 (d, $^2J_{HH}$ = 7.7, 4H, OCH_2), 3.82 (d, $^2J_{HH}$ = 7.7, 4H, OCH_2), 3.74 (s, 4H, OCH_2), 2.34 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 0.76 (s, 6H, CH_3), 0.55 (s, 6H, CH_3). **^{13}C NMR** (C_6D_6, 101 MHz): concentration was too low to measure. **Anal.** Calcd for $C_{33}H_{48}ClN_6O_6Rh.0.25(C_6H_6)$ ([763.13] 782.66 $gmol^{-1}$): C, 52.94; H, 6.37; N, 10.75. Found: C, 52.72; H, 6.38; N, 10.68. Benzene solvate was confirmed by dissolving in CD_2Cl_2 (not stable).

1.4 *cis*-[Rh(IBioxMe$_4$)(CO)$_2$Cl] (4)

A solution of **1** (0.050 g, 0.055 mmol) in benzene (2 mL) was placed under CO (1 atm) and stirred at room temperature for 10 minutes. The solution was placed under argon and the product crystallised by addition of excess heptane (*ca* 40 mL) and cooling to 5ºC. Yield = 0.040 g (90%, pale yellow microcrystalline solid).

^{1}H NMR (C_6D_6, 400 MHz): δ 3.66 (d, $^2J_{HH}$ = 8.3, 2H, CH_2), 3.61 (d, $^2J_{HH}$ = 8.3, 2H, CH_2), 1.51 (s, 12H, CH_3), 1.25 (s, 12H, CH_3). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz): δ 186.7 (d, $^1J_{RhC}$ = 55, CO), 183.9 (d, $^1J_{RhC}$ = 73, CO), 149.4 (d, $^1J_{RhC}$ = 42, NCN), 126.2 (s, $\underline{C}OCH_2$), 87.3 (s, CH_2), 61.3 (s, $\underline{C}(CH_3)_2$), 26.7 (s, CH_3), 25.2 (s, CH_3). **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 2081 (s), 2000 (s). **Anal.** Calcd for $C_{13}H_{16}ClN_2O_4Rh$ (402.64 $gmol^{-1}$): C, 38.78; H, 4.01; N, 6.96. Found: C, 38.83; H, 4.04; N, 6.88.

1.5 [Rh(IBioxMe$_4$)(NBD)Cl] (5)

To a mixture of $[Rh(NBD)Cl]_2$ (0.100 g, 0.22 mmol) and $IBioxMe_4$ (0.100 g, 0.48 mmol) was added benzene. The resulting suspension was stirred at room temperature for 2 hours before the volatiles were removed in vacuo. The residue was chromatographed on silica using 1:3 THF – CH_2Cl_2 (in air) and then recrystallised from CH_2Cl_2 – hexane. Yield = 0.168 g (88%, yellow microcrystalline solid).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.69 (app q, J = 2, 2H, CH=CH), 4.47 (d, $^2J_{HH}$ = 8.2, 2H, OCH_2), 4.42 (d, $^2J_{HH}$ = 8.2, 2H, OCH_2), 3.78 (br, 2H, $CH_2\underline{C}H$), 3.56 (app q, J = 2, 2H, CH=CH), 1.98 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.37 (td, $^2J_{HH}$ = 8.2, $^3J_{HH}$ = 1, 1H, CH_2{NBD}), 1.30 (dt, $^2J_{HH}$ = 8.2, $^3J_{HH}$ = 1, 1H, CH_2{NBD}). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ 162.3 (d, $^1J_{RhC}$ = 56.5, NCN), 126.1 (s, $\underline{C}OCH_2$), 88.0 (OCH_2), 76.9 (d, $^1J_{RhC}$ = 6, CH=CH), 63.9 (d, $^3J_{RhC}$ = 5, CH_2{NBD}), 61.9 (s, $\underline{C}(CH_3)_2$), 51.3 (s, $CH_2\underline{C}H$), 49.2 (d, $^1J_{RhH}$ = 12, CH=CH), 27.1 (s, CH_3), 26.0 (s, CH_3). **Anal.** Calcd for $C_{18}H_{24}ClN_2O_2Rh$ (438.75 $gmol^{-1}$): C, 49.27; H, 5.51; N, 6.38. Found: C, 49.29; H, 5.81; N, 6.22.

1.6 [Rh(IBioxMe$_4$)(Cp)(COE)] (6)

A suspension of **1** (0.060 g, 0.066 mmol) and Na[Cp] (0.012 g, 0.140 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 3 hours. The volatiles were removed in vacuo and the product obtained by extraction of the residue with heptane (2 × 5 mL). Yield = 0.052 g (72%, yellow powder).

^{1}H NMR (C_6D_6, 400 MHz): δ 5.11 (s, 5H, Cp), 3.70 (d, $^2J_{HH}$ = 8.1, 2H, OCH_2), 3.67 (d, $^2J_{HH}$ = 8.1, 2H, OCH_2), 2.48 – 2.58 (m, 2H, $CHC\underline{H}_2$), 2.06 – 2.15 (m, 2H, CH), 1.70 – 1.95 (m, 6H, CH_2{COE}), 1.75 (s, 6H, CH_3), 1.48 – 1.62 (m, 4H, CH_2{COE}), 1.32 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz): δ 159.7 (d, $^1J_{RhC}$ = 66, NCN), 125.6 (s, $\underline{C}OCH_2$), 87.2 (s, OCH_2), 86.2 (d, $^1J_{RhC}$ = 3, Cp), 62.4 (s, $\underline{C}(CH_3)_2$), 53.1 (d, $^1J_{RhC}$ = 17, CH), 34.7 (s, CH_2{COE}), 33.9 (s, CH_2{COE}), 27.3 (s, CH_2{COE}), 27.3 (s, CH_3), 23.2 (s, CH_3). **Anal.** Calcd for $C_{24}H_{35}N_2O_2Rh$ (486.45 $gmol^{-1}$): C, 59.26; H, 7.25; N, 5.76. Found: C, 59.40; H, 7.35; N, 5.83.

1.7 *trans*-[Rh(IBioxMe$_4$)$_2$(CO)Cl] (7)

A solution of **2** (0.050 g, 0.071 mmol) in benzene (2 mL) was placed under CO (1 atm) and stirred at room temperature for 24 hours. The volatiles were removed in vacuo and the crude product recrystallised from CH_2Cl_2 – heptane at room temperature. Yield = 0. 035 g (85%, pale yellow microcrystalline solid).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.56 (d, $^2J_{HH}$ = 8.3, 4H, CH_2), 4.52 (d, $^2J_{HH}$ = 8.3, 4H, CH_2), 1.93 (s, 12H, CH_3),

1.91 (s, 12H, CH_3). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 101 MHz): δ 188.0 (d, $^1J_{RhC}$ = 82, CO), 160.5 (d, $^1J_{RhC}$ = 39, NCN), 125.5 (s, $\underline{C}OCH_2$), 88.6 (s, CH_2), 61.3 (s, $\underline{C}(CH_3)_2$), 27.3 (s, CH_3), 26.3 (s, CH_3). **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 1942 (s). **Anal.** Calcd for $C_{23}H_{32}ClN_4O_5Rh$ (582.88 $gmol^{-1}$): C, 47.39; H, 5.53; N, 9.61. Found: C, 47.41; H, 6.04; N, 9.69.

1.8 *trans*-[Rh(IBioxMe$_4$)$_2$(CO)$_2$][BAr$^F{}_4$] (8)

A suspension of **7** (0.020 g, 0.034 mmol) and Na[BAr$^F{}_4$] (0.034 g, 0.038 mmol) in CH_2Cl_2 was placed under CO (1 atm) and stirred at room temperature for 30 minutes. The reaction was placed under an argon atmosphere, the solution filtered and the filtrate layered with heptane to afford a crystalline product upon diffusion. Yield = 0.034 g (70%, yellow crystals).

^1H NMR (CD_2Cl_2, 400 MHz): δ 7.69 – 7.73 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 4.63 (s, 8H, OCH_2), 1.80 (s, 24H, CH_3). **^1H NMR** ($C_6H_4F_2$, 500 MHz): δ 8.34 (br, 8H, Ar^F), 7.70 (br, 4H, Ar^F), 4.58 (s, 8H, OCH_2), 1.91 (s, 24H, CH_3). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 101 MHz): δ 185.4 (d, $^1J_{RhC}$ = 64, CO), 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 141.0 (d, $^1J_{RhC}$ = 37, NCN), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 128.4 (s, $\underline{C}OCH_2$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 88.1 (OCH_2), 61.9 (s, $\underline{C}(CH_3)_2$), 26.8 (s, CH_3). **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 2024 (s). **Anal.** Calcd for $C_{56}H_{44}BF_{24}N_4O_6Rh$ (1438.65 $gmol^{-1}$): C, 46.75; H, 3.08; N, 3.89. Found: C, 46.91; H, 2.96; N, 4.08.

1.9 *cis*-[Rh(IBioxMe$_4$)$_2$(COE)][BAr$^F{}_4$] (9)

In an inert atmosphere glove box, cold $C_6H_4F_2$ (1.5 mL, -20ºC) was added to a mixture of **2** (0.060 g, 0.090 mmol) and Na[BAr$^F{}_4$] (0.088 g, 0.099 mmol). The resulting suspension was held at -20ºC for 10 minutes with periodic shaking. The mixture was diluted with cold heptane (-20ºC) and rapidly filtered through celite. Addition of excess cold heptane resulted in the precipitation of the product, which was subsequently washed with cold heptane (2 x 2 mL) and dried in vacuo. Yield = 0.095 g (71%, light red-brown solid). The sample for NMR analysis was prepared by vacuum transfer of CD_2Cl_2 into a J Young's NMR tube containing the solid product cooled to -196ºC. The complex dissolved on warming the tube to -78ºC; the sample was then transferred directly into a NMR spectrometer pre-cooled to -23ºC (250 K).

^1H NMR (CD_2Cl_2, 500 MHz, 250 K): δ 7.68 – 7.72 (m, 8H, Ar^F), 7.54 (br, 4H, Ar^F), 4.44 (s, 8H, CH_2), 3.93 – 4.01 (m, 2H, CH), 2.46 – 2.56 (m, 2H, $CHC\underline{H}_2$), 1.66 (s, 24H, CH_3), 1.17 – 1.75 (m, 10H, CH_2{COE}; δ 1.29, 2H, $CHC\underline{H}_2$'). **^1H NMR** ($C_6H_4F_2$, 500 MHz, 298 K): δ 8.34 (br, 8H, Ar^F), 7.70 (br, 4H, Ar^F), 4.45 (s, 8H, CH_2), 4.24 – 4.31 (m, 2H, CH), 2.29 – 2.38 (m, 2H, $CHC\underline{H}_2$), 1.62 (s, 24H, CH_3), 1.26 – 1.85 (m, 10H, CH_2{COE}). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 126 MHz, 250 K): δ 161.9 (q, $^1J_{BC}$ = 50, Ar^F), 134.9 (s, Ar^F), 128.9 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 126.8 (br, $\underline{C}OCH_2$), 124.7 (q, $^1J_{FC}$ = 272, Ar^F), 117.7 (sept, $^3J_{FC}$ = 4, Ar^F), 87.6 (s, CH_2), 76.3 (very br – from HMQC, CH), 62.7 (s, $\underline{C}(CH_3)_2$), 30.2 (br, $CH\underline{C}H_2$) 30.0 (s, CH_2{COE}), 26.0 (s, CH_2{COE}), 25.6 (br, CH_3). The N$\underline{C}$N resonance was not observed, presumably it is very broad. **Anal.** Calcd for $C_{62}H_{58}BF_{24}N_4O_4Rh$ (1492.83 $gmol^{-1}$): C, 49.88; H, 3.92; N, 3.75. Found: C, 49.74; H, 3.87; N, 3.90.

1.10 [Rh(IBioxMe$_4$)$_2$(NBD)][BAr$^F_4$] (10)

To a mixture of **5** (0.056 g, 0.13 mmol), IBioxMe$_4$ (0.030 g, 0.14 mmol) and Na[BAr$^F_4$] (0.124 g, 0.14 mmol) was added $C_6H_4F_2$ (2 mL) and the resulting suspension stirred at room temperature for 90 minutes. The solution was filtered and the product crystallised by addition of excess heptane. Yield = 0.150 g (78%, yellow – orange microcrystalline solid).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.70 – 7.74 (m, 8H, Ar^F), 7.57 (br, 4H, Ar^F), 4.60 (app q, J = 2, 4H, CH=CH), 4.44 (d, $^2J_{HH}$ = 8.3, 4H, OCH_2), 4.40 (d, $^2J_{HH}$ = 8.3, 4H, OCH_2), 3.92 (br, 2H, $CH_2\underline{CH}$), 1.87 (s, 12H, CH_3), 1.60 (s, 12H, CH_3), 1.49 (t, $^3J_{HH}$ = 1, 2H, CH_2{NBD}). **^{1}H NMR** ($C_6H_4F_2$, 500 MHz): δ 8.34 (br, 8H, Ar^F), 7.70 (br, 4H, Ar^F), 4.73 (app q, J = 2, 4H, CH=CH), 4.43 (d, $^2J_{HH}$ = 8.4, 4H, OCH_2), 4.39 (d, $^2J_{HH}$ = 8.4, 4H, OCH_2), 3.95 (br, 2H, $CH_2\underline{CH}$), 1.94 (s, 12H, CH_3), 1.70 (s, 12H, CH_3), 1.53 (t, $^3J_{HH}$ = 1, 2H, CH_2{NBD}). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 157.0 (d, $^1J_{RhC}$ = 57, NCN), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 127.4 (s, $\underline{C}OCH_2$), 125.2 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 88.7 (OCH_2), 67.9 (d, $^1J_{RhC}$ = 8, CH=CH), 66.9 (d, $^3J_{RhC}$ = 4, CH_2{NBD}), 63.8 (s, $\underline{C}(CH_3)_2$), 52.6 (s, $CH_2\underline{C}H$), 27.6 (s, CH_3), 24.4 (s, CH_3). **Anal.** Calcd for $C_{61}H_{52}BF_{24}N_4O_4Rh$ (1474.77 gmol^{-1}): C, 49.68; H, 3.55; N, 3.80. Found: C, 49.87; H, 3.46; N, 3.90.

1.11 [Rh(IBioxMe$_4$)$_3$][BAr$^F_4$] (11)

To a mixture of **3** (0.100 g, 0.131 mmol) and Na[BAr$^F_4$] (0.128 g, 0.144 mmol) was added CH_2Cl_2 (4 mL). The resulting dark purple solution was filtered and the filtrate layered with heptane to afford a crystalline product upon diffusion. Yield = 0.140 g (65%, purple crystals). Complex **11** can also be made from [Rh(COE)$_2$Cl]$_2$ and IBioxMe$_4$ in difluorobenzene, using Na[BAr$^F_4$] as a halide abstractor (83% isolated yield). Details of this alternative procedure and NMR data were reported earlier.[13]

1.12 [Rh(IBioxMe$_4$)$_3$(CO)][BAr$^F_4$] (12)

Prepared from **11** as described in an earlier communication.[13] **IR** (CH_2Cl_2, cm^{-1}): ν(CO) 1968 (s).

Supporting information

Experimental details for NMR scale reactions, selected NMR spectra of **1** – **10**, crystallographic data and the structure of [Rh(IBioxMe$_4$)$_2$Cl$_2$]. This material is available free of charge via the Internet at http://pubs.acs.org. Full crystallographic details are document in CIF format and have been deposited with the Cambridge Crystallographic Data Centre under CCDC 972199 – 972208 and 994089 ([Rh(IBioxMe$_4$)$_2$Cl$_2$] see ESI).

Acknowledgements

The author thanks the University of Warwick and the Royal Society for financial support. Crystallographic data was collected using a diffractometer purchased through support from Advantage West Midlands and the European Regional Development Fund.

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[48] On one occasion single crystals of paramagnetic $[Rh(IBioxMe_4)_2Cl_2]$ were obtained by dissolving **2** in CD_2Cl_2. The formation of this species was accompanied by the presence of very broad signals in the NMR spectrum. The structure derived by X-ray diffraction is given in the ESI.

TOC graphic