Rhodium(I) complexes of the conformationally rigid IBiox-Me$_4$ ligand: isolation of a stable low-coordinate T-shaped complex

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Supporting Information Placeholder

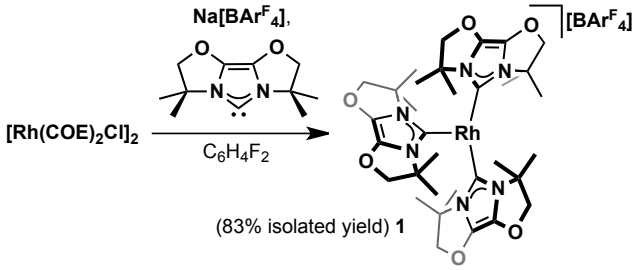
ABSTRACT: The isolation, characterization and reactivity of a T-shaped rhodium(I) complex containing Glorius' bioxazoline derived *N*-heterocyclic carbene ligand IBioxMe$_4$ is described: [Rh(IBioxMe$_4$)$_3$][BAr$^F_4$] (**1**, Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$). **1** represents a rare example of a solution stable 'naked' 14-electron complex and is characterized in the solid-state by highly distorted ligand geometries and Rh···C distances > 3.1 Å for the IBioxMe$_4$ alkyl substituents. Consistent with the bulky nature of the NHC ligand, no reaction is observed with excess IBioxMe$_4$, PCy$_3$ or norbornadiene. Reaction of **1** with CO, however, leads to coordinatively saturated [Rh(IBioxMe$_4$)$_3$(CO)][BAr$^F_4$] **2**.

Coordinatively unsaturated complexes are key intermediates in transition metal catalysed reactions.[1] Understanding the structure and onward reactivity of these unsaturated species is of fundamental mechanistic importance for the targeted development of more effective catalysts and new catalytic transformations, although their inherent high reactivity generally precludes isolation.[2,3,4] Reflecting the importance of *N*-heterocyclic carbene (NHC) ligands in transition metal catalysis,[5] the chemistry of low-coordinate NHC complexes is a particularly topical area. The ability of unsaturated metal complexes containing NHC ligands to undergo cyclometalation via C–H bond activation of alkyl and aryl appendages, however, represents a notable limitation, particularly for the isolation of low-coordinate metal centres in low oxidation states.[6,7]

Observing that substituent flexibility is key requirement for cyclometalation reactions of NHC ligands, it was reasoned that the use of conformationally rigid bioxazoline-derived variants (IBiox), developed by Glorius and co-workers,[8] would prove more resilient to such reactivity. Bioxazolines are excellent scaffolds for the synthesis of bulky (chiral or achiral) NHCs. IBiox ligands have found notable application in palladium catalysed cross coupling reactions, although well-defined IBiox complexes are currently limited to a narrow range of palladium, iridium and group 11 systems.[8]

Given the close structural similarities to the commonly employed I^{i}Pr$_2$Me$_2$ and I^{t}Bu ligands,[9] the coordination chemistry of IBioxMe$_4$ (see Scheme 1 for structure) was selected for investigation. With cationic T-shaped rhodium(I) *tris*-phosphine complexes [Rh(PR$_3$)$_3$]$^+$ (**A**, R = Ph, ^{i}Pr) as precedents,[10] the synthesis of an analogous *tris*-NHC complex was targeted. Pleasingly the desired, formally 14-electron, complex [Rh(IBioxMe$_4$)$_3$][BAr$^F_4$] (**1**, Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$) was readily prepared through reaction of the rhodium(I) precursor [Rh(COE)$_2$Cl]$_2$ (COE = *cis*-cyclooctene) with an excess (3.2 equiv./Rh) of isolated IBioxMe$_4$ in 1,2-difluorobenzene solvent, using Na[BAr$^F_4$] as a halide abstractor (Scheme 1). Subsequent crystallisation from CH_2Cl_2/pentane or heptane afforded **1**.$^1/_2$(CH_2Cl_2) as large purple blocks in 83% isolated yield.

Scheme 1. Preparation of 1.



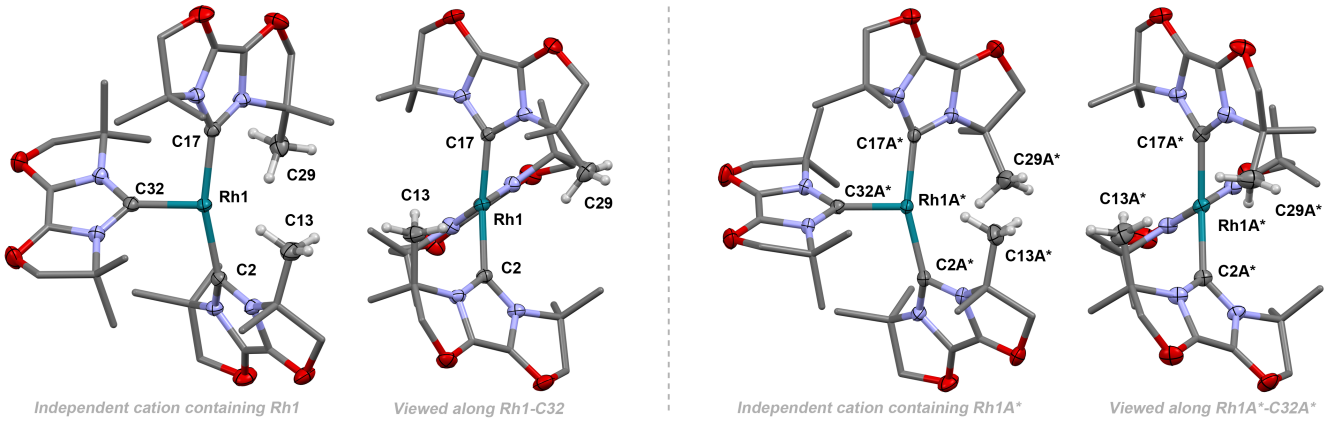
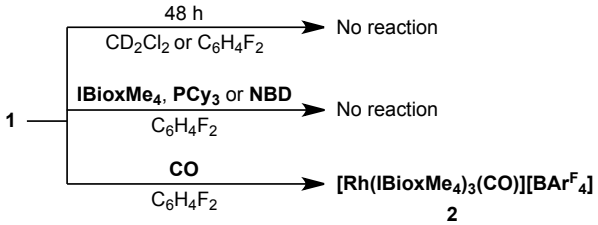


Figure 1. Solid-state structure of **1** ($\mathcal{Z}' = 2$). Thermal ellipsoids for selected atoms drawn at 50%; most hydrogen atoms, anions, solvent molecule and minor disordered components omitted for clarity. For ease of comparison, chiral cations of the same absolute configuration are shown: that containing Rh1A* was generated by inversion. Selected bond lengths (Å) and angles (°): Rh1-C2, 2.053(2); Rh1-C17, 2.037(2); Rh1-C32, 1.941(2); Rh1-C13, 3.273(3); Rh1-C29, 3.574(3); C2-Rh1-C17, 161.80(9); Cnt(C2)-C2-Rh1, 163.9(2); Cnt(C17)-C17-Rh1, 173.1(2); Cnt(C32)-C32-Rh1, 176.9(2); Rh1A-C2A, 2.071(2); Rh1A-C17A, 2.012(2); Rh1A-C32A, 1.934(2); Rh1A-C13A, 3.421(3); Rh1A-C29A, 3.191(3); C2A-Rh1-C17A, 160.21(9); Cnt(C2A)-C2A-Rh1A, 160.0(2); Cnt(C17A)-C17A-Rh1A, 166.5(2); Cnt(C32A)-C32A-Rh1A, 178.2(2).[11]

In the solid-state, **1** adopts a pseudo C_2 symmetric distorted T-shaped geometry, C_{NCN}-Rh-C_{NCN} ≈ 161° (Figure 1). Two independent, but structurally similar, cations are observed; the most notable difference being a slightly different oxazoline ring conformation in one of the trans-disposed IBioxMe$_4$ ligands (containing C17/C17A). Complexes **A** and chelating ligand systems [Rh(^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)(CH$_2$^{t}Bu)] (**B**),[12] [Rh(P^{i}Bu$_3$){P^{t}Bu$_2$(CH$_2$)$_2$CH=CH$_2$}]$^+$ (**C**),[13] [Rh{(P^{t}Bu$_2$CH$_2$)$_2$(BN$_2$C$_6$H$_4$)}] (**D**)[14] and [Rh{((2,6-Me$_2$C$_6$H$_3$)NMeC)$_2$CH}(COE)] (**E**)[4] are crystallography characterized rhodium(I) precedents. Platinum(II) NHC and their cyclometalated derivatives are also known to adopt T-shaped geometries.[7] The mutually trans NHC ligands in **1** exhibit highly distorted coordination geometries, with significant pitching *and* yawing, as quantified by non-linear NHC centroid-C_{NCN}-Rh angles [160.0(2) – 173.1(2)°].[11] Such distorted NHC binding is very unusual in transition metal complexes.[15,16] Notably, the methyl substituents of the IBioxMe$_4$ ligand remain distant from the metal centre, with the smallest Rh···C distances being 3.273(3) and 3.191(3) Å in the independent cations, suggesting the absence of any significant agostic interactions in **1**. The observed alkyl Rh···C distances are significantly longer than those reported in genuinely low-coordinate (and also purple) **E** [2.89, 2.97 Å][4] and are in marked contrast to **A** – **C**, which all display strong agostic interactions [Rh···C = 2.41 – 2.49 Å].[10,12,13] Similarly, a stabilising intermolecular σ-CH bond interaction is observed for **D** in the solid-state [Rh···C = 2.77 Å].[14] Complex **1** therefore presents the structural characteristics of a 'naked' low-coordinate rhodium complex.[3,4] Consistent with this formulation, the NHC ligands trans to a free coordination site bind with shorter Rh-C_{NCN} distances than the ligands cis [1.941(2), 1.934(2) vs 2.012(2) – 2.071(2) Å].

In solution, **1** is highly fluxional showing time averaged D_3 symmetry in both CD_2Cl_2 and 1,2-difluorobenzene at 298 K (500 MHz). The coordinated carbene is observed as a doublet resonance at δ 154.6 with a $^1\mathcal{J}_{RhC}$ coupling constant of 64 Hz and the hydride region of the ^{1}H NMR spectrum of **1** is completely featureless. The onset of decoalescence is observed on cooling, although the slow exchange limit is not reached at 200 K (see ESI); at this low temperature the ^{1}H NMR spectrum shows no evidence for agostic interactions of the methyl groups with the metal centre.

Scheme 2. Reactivity of 1.



Coordinatively unsaturated **1** is completely stable in solution (under an argon atmosphere), with invariant ^{1}H NMR spectra recorded over 48 hours in 1,2-difluorobenzene and CD_2Cl_2 solution at 293 K. Moreover, preliminary reactivity studies involving addition of excess IBioxMe$_4$, PCy$_3$ or norbornadiene, as potential ligands, did not result in any reaction after 18 h at 293 K (Scheme 2). A rapid reaction was, however, observed upon placing **1** under an atmosphere of carbon monoxide, resulting in the quantitative formation of [Rh(IBioxMe$_4$)$_3$(CO)][BAr$^F_4$] **2** (NMR spectroscopy).

This carbonyl complex was subsequently isolated in good yield (77%) and fully characterized. Complex **2** shows C_2 symmetry in solution, carbene resonances at δ 158.3 ($^1\mathcal{J}_{RhC}$ = 44 Hz) and δ 157.0 (d, $^1\mathcal{J}_{RhC}$ = 41 Hz), and a single carbonyl stretching frequency [1977 cm^{-1} (ATIR)]. The solid-state structure of **2** (Figure 2) reveals the expected square planar geometry [sum of angles = 359.9(11)°] and notably shows no evidence for the distorted NHC coordination modes observed for **1**; all NHC centroid-C_{NCN}-Rh angles > 175°.[11] Moreover, in line with the coordination of CO the Rh1-C34 bond distance, associated with the $IBioxMe_4$ ligand trans to CO, is elongated significantly in comparison to the analogous bonds in **1** [2.176(4) vs 1.941(2) and 1.934(2) Å].

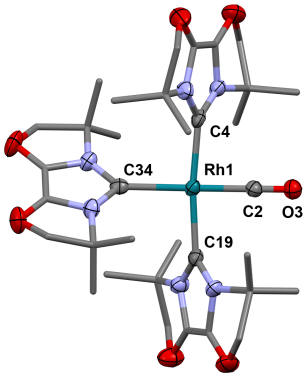


Figure 2. Solid-state structure of **2**. Thermal ellipsoids for selected atoms drawn at 50%; hydrogen atoms, anion and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-C2, 1.825(6); Rh1-C4, 2.072(4); Rh1-C19, 2.075(4); Rh1-C34, 2.176(4); C2-Rh1-C34, 179.5(4); C4-Rh1-C19, 172.9(2); all NHC Cnt-C_{NCN}-Rh1 > 175.[11]

In summary, the isolation of a low-coordinate and solution stable *tris*-NHC rhodium(I) complex, $[Rh(IBioxMe_4)_3]^+$, has been achieved using the bulky and conformationally rigid $IBioxMe_4$ ligand. The fixed geometry of the constituent NHCs appears to prohibit interaction of the metal centre with the ligand substituents and formation of stabilising agostic interactions, while the steric profile is sufficient to prevent any reaction with solvent (CH_2Cl_2, $C_6H_4F_2$), a fourth $IBioxMe_4$ ligand, or other large donor groups (e.g. PCy_3). Formation of the carbonyl complex $[Rh(IBioxMe_4)_3(CO)]^+$ can, however, be achieved by reaction with carbon monoxide; the structure of which serves to highlight the distorted nature of the NHC ligands in its precursor.

EXPERIMENTAL

General experimental methods. All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 150°C overnight and flamed under vacuum prior to use. Anhydrous THF, 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 was dried over Na, vacuum distilled and stored over thoroughly vacuum dried 3 Å molecular sieves. $IBioxMe_4$.HOTf,[8d] $[Rh(COE)_2Cl]_2$,[17] and $Na[BAr^F_4]$[18] were synthesised using literature procedures. All other 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 shifts 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.

Preparation of $IBioxMe_4$. To a mixture of $IBioxMe_4$.HOTf (1.500 g, 4.19 mmol) and $K[N(SiMe_3)_2]$ (0.877 g, 4.40 mmol) was added ice cold THF (15 mL) and the resulting suspension stirred at room temperature for 90 minutes. The volatiles were thoroughly removed in vacuo (> 1 hour at < 1 × 10^{-2} mbar). The residue was extracted with pentane (4 × 50 mL) and the product obtained following removal of the solvent from the combined fractions. Yield = 0.70 g (80%, white powder). ^{1}H NMR (C_6D_6, 400 MHz): δ 3.91 (s, 4H, CH_2), 1.30 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz): δ 190.1 (s, NCN), 123.6 (s, $\underline{C}OCH_2$), 87.6 (s, CH_2), 58.4 (s, $\underline{C}(CH_3)_2$), 26.4 (s, CH_3). $^{19}F\{^1H\}$ NMR (C_6D_6, 282 MHz): no signal. Anal. Calcd for $C_{11}H_{16}N_2O_2$ (208.26 $gmol^{-1}$): C, 63.44; H, 7.74; N, 13.45. Found: C, 63.43; H, 7.93; N, 13.13.

Preparation of $[Rh(IBioxMe_4)_3][BAr^F_4]$ (1). To a mixture of $[Rh(COE)_2Cl]_2$ (0.054 g, 0.075 mmol), $IBioxMe_4$ (0.101 g, 0.485 mmol) and $Na[BAr^F_4]$ (0.140 g, 0.158 mmol) was added $C_6H_4F_2$ (3 mL). The resulting suspension was shaken for 15 minutes at room temperature before all volatiles were removed in vacuo. The crude material was extracted into CH_2Cl_2 solution, filtrated and layered with pentane to afford the crystalline product upon diffusion. Yield = 0.204 g (83%, purple crystals). Crystals for microanalysis and X-ray diffraction were grown from CH_2Cl_2/heptane – the presence of half a molecule of dichloromethane solvate was established by both methods and further corroborated by ^{1}H NMR spectroscopy (in $C_6H_4F_2$ solution). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.70 – 7.74 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 4.47 (d, $^2\mathcal{J}_{HH}$ = 8.4, 6H, CH_2), 4.38 (d, $^2\mathcal{J}_{HH}$ = 8.4, 6H, CH_2), 2.11 (s, 18H, CH_3), 1.22 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 162.3 (q, $^1\mathcal{J}_{BC}$ = 50, Ar^F), 154.6 (d, $^1\mathcal{J}_{RhC}$ = 64, NCN), 135.4 (s, Ar^F), 129.4 (qq, $^2\mathcal{J}_{FC}$ = 32, $^3\mathcal{J}_{BC}$ = 3, Ar^F), 127.1 (s, $\underline{C}OCH_2$), 125.2 (q, $^1\mathcal{J}_{FC}$ = 272, Ar^F), 118.0 (sept, $^3\mathcal{J}_{FC}$ = 4, Ar^F),

88.3 (CH_2), 62.5 (s, $\underline{C}(CH_3)_2$), 27.3 (s, CH_3), 25.4 (s, CH_3). Anal. Calcd for $C_{65}H_{60}BF_{24}N_6O_6Rh.^1/_2(CH_2Cl_2)$ ([1590.89] 1633.35 gmol^{-1}): C, 48.16; H, 3.76; N, 5.15. Found: C, 48.43; H, 3.88; N, 5.23.

[Rh(IBioxMe$_4$)$_3$(CO)][BAr$^F_4$] (2). A solution of **1** (0.050 g, 0.031 mmol) in $C_6H_4F_2$ (2 mL) was placed under CO (1 atm) resulting in an immediate colour change from purple to bright yellow. After 15 minutes the solution was placed under an argon atmosphere and layered with heptane to afford a crystalline product upon diffusion. Yield = 0.045 g (77%, pale yellow crystals). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.70 – 7.74 (m, 8H, Ar^F), 7.57 (br, 4H, Ar^F), 4.50 (d, $^2\mathcal{J}_{HH}$ = 8.2, 4H, CH_2), 4.49 (d, $^2\mathcal{J}_{HH}$ = 8.3, 4H, CH_2), 4.42 (coincident d, $^2\mathcal{J}_{HH}$ ~ 8, 8H, 2×CH_2), 4.40 (d, $^2\mathcal{J}_{HH}$ = 8.2, 4H, CH_2), 4.26 (d, $^2\mathcal{J}_{HH}$ = 8.4, 4H, CH_2), 2.09 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 1.62 (s, 6H, CH_3), 0.94 (s, 6H, CH_3), 0.79 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 192.8 (d, $^1\mathcal{J}_{RhC}$ = 64, CO), 162.3 (q, $^1\mathcal{J}_{BC}$ = 50, Ar^F), 158.3 (d, $^1\mathcal{J}_{RhC}$ = 44, NCN{*trans*-CO}), 157.0 (d, $^1\mathcal{J}_{RhC}$ = 41, NCN{*cis*-CO}), 135.4 (s, Ar^F), 129.4 (qq, $^2\mathcal{J}_{FC}$ = 32, $^3\mathcal{J}_{BC}$ = 3, Ar^F), 128.2 (s, $\underline{C}OCH_2$), 127.7 (s, $\underline{C}OCH_2$), 127.5 (s, $\underline{C}OCH_2$), 125.2 (q, $^1\mathcal{J}_{FC}$ = 272, Ar^F), 118.0 (sept, $^3\mathcal{J}_{FC}$ = 4, Ar^F), 89.3 (CH_2), 88.7 (CH_2), 87.6 (CH_2), 66.7 (s, $\underline{C}(CH_3)_2$), 64.1 (s, $\underline{C}(CH_3)_2$), 62.2 (s, $\underline{C}(CH_3)_2$), 27.4 (s, CH_3), 27.2 (s, CH_3), 26.9 (s, CH_3), 25.3 (s, CH_3), 24.6 (s, CH_3), 22.7 (s, CH_3). IR (solid, cm^{-1}): ν(CO) 1977 (s). Anal. Calcd for $C_{66}H_{60}BF_{24}N_6O_7Rh$ (1618.90 gmol^{-1}): C, 48.97; H, 3.74; N, 5.19. Found: C, 49.15; H, 3.63; N, 5.12.

ASSOCIATED CONTENT

Additional NMR data and experimental details. 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 972107 (**1**) and 972208 (**2**).

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENT

The author thanks the University of Warwick and the Royal Society for financial support.

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