## COMMUNICATION

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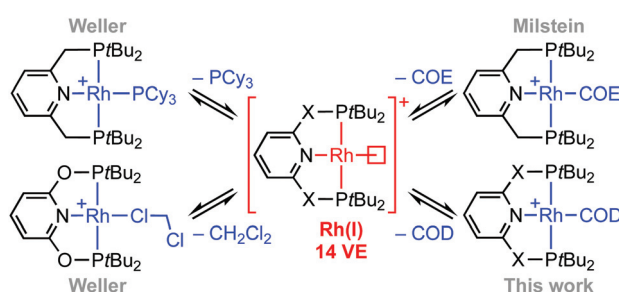# A convenient method for the generation of {Rh(PNP)}+ and {Rh(PONOP)}+ fragments: reversible formation of vinylidene derivatives†

Matthew R. Gyton, [ID] Thomas M. Hood [ID] and Adrian B. Chaplin [ID] *

The substitution reactions of $[Rh(COD)_2][BAr^F_4]$ with PNP and PONOP pincer ligands 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine and 2,6-bis(di-*tert*-butylphosphinito)pyridine in the weakly coordinating solvent $1,2-F_2C_6H_4$ are shown to be an operationally simple method for the generation of reactive formally 14 VE rhodium(I) adducts in solution. Application of this methodology enables synthesis of known adducts of CO, $N_2$, $H_2$, previously unknown water complexes, and novel vinylidene derivatives $[Rh(pincer)(CCHR)][BAr^F_4]$ (R = *t*Bu, $3,5-tBu_2C_6H_3$), through reversible reactions with terminal alkynes.

**Scheme 1** Latent sources of the {Rh(PNP)}+ and {Rh(PONOP)}+ fragments (X = O, $CH_2$). COE = cyclooctene; COD = 1,5-cyclooctadiene.

## Introduction

Phosphine-based pincers are a prominent ligand class in contemporary organometallic chemistry and catalysis, conferring thermal stability whilst permitting a wide range of metal-based reactivity.[1,2] From a fundamental perspective, their capacity to support the generation of reactive low-coordinate metal fragments provides an attractive framework for gaining insights into the mechanism of small molecule activation reactions. The synthesis and characterisation of a rhodium(I) σ-methane complex in solution is a particularly outstanding example, with direct mechanistic relevance to $C(sp^3)$–H bond activation and alkane dehydrogenation processes mediated at iridium homologues.[2,3] Other group 9 highlights include the $C(sp^2)$–H bond oxidative addition of aryl halides[4,5] and the selective $C(sp^3)$–F bond activation of fluorocarbons.[6] In the context of supporting such endeavours and building on preceding work (Scheme 1),[4,7–9] we herein report a convenient method for accessing reactive formally 14 VE rhodium(I) adducts of the widely studied PNP (2,6-bis(di-*tert*-butylphosphinomethyl)pyri-

dine) and PONOP (2,6-bis(di-*tert*-butylphosphinito)pyridine) ligands, exploiting metastable coordination of 1,5-cyclooctadiene (COD) in the weakly coordinating 1,2-difluorobenzene solvent (DFB).[10] We showcase this methodology for the preparation of previously unknown water complexes and the reversible formation of vinylidene derivatives.

## Results and discussion

As an operationally simple entry point into the organometallic chemistry of cationic rhodium(I) pincer complexes, we targeted substitution reactions of the readily accessible (and commercially available) rhodium precursor $[Rh(COD)_2][BAr^F_4]$ ($Ar^F$ = $3,5-(CF_3)_2C_6H_3$); postulating that alongside chelation of the pincer, steric buttressing from the phosphine substituents would promote efficient liberation of the comparatively bulky COD ligand and access to reactive {Rh(pincer)}+ fragments in solution.[11] To this end, stoichiometric reactions between PNP/PONOP and $[Rh(COD)_2][BAr^F_4]$ in DFB under an argon atmosphere were first studied *in situ*, resulting in quantitative coordination of the pincer and establishment of dynamic equilibrium mixtures containing monomeric **1a** (PNP, $\delta_{31P}$ 63.4, 52.6, $^2J_{PP}$ ~320 Hz; PONOP, $\delta_{31P}$ 202.5, $^1J_{RhP}$ = 134 Hz) as

*Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK. E-mail: a.b.chaplin@warwick.ac.uk*
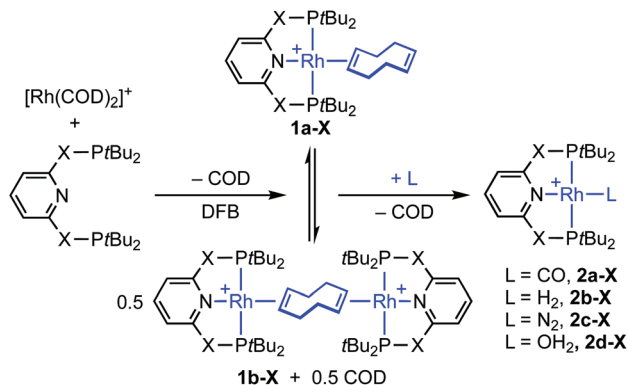
**Scheme 2** Synthesis and reactivity of **1** (X = O, CH$_2$). [BAr$^F_4$]$^-$ counter anions omitted for clarity.

the major components and dimeric **1b** as the minor components, alongside liberated COD (Scheme 2). The former were formed exclusively when the reactions were repeated in the presence of 10 equivalents of COD, while the latter dications were isolated in high yield by crystallisation from DFB/hexane (PNP, 90%; PONOP, 96%), structurally characterised in the solid state using X-ray diffraction and the bulk purity established by microanalysis (see Fig. 1 for **1b-O**).† The synthetic utility of this methodology was then assessed by reacting mixtures of **1a/b**, generated as described above in DFB, with CO, H$_2$, and N$_2$ (1 atm) and analysis *in situ* using $^1$H and $^{31}$P NMR spectroscopy. Introduction of strongly coordinating CO resulted in rapid ($t$ < 5 min) and quantitative formation of the known carbonyl complexes **2a**, with only free COD as the by-product.[7,8] Reactions of H$_2$ and N$_2$ with **1a/b** likewise afforded the corresponding (known) adducts **2b** (with concomitant hydrogenation of COD) and **2c**,[7,8,12] respectively, but under disparately longer timeframes for the PONOP ($t$ ~ 2 days) compared to PNP complexes ($t$ < 3 h). These reactions all proceeded to completion with the exception of **2c-O** (*ca.* 95%), which instead required use of isolated **1b-O** to presumably counter recoordination of COD ($t$ ~ 2 days).

Application of our methodology allows access to novel rhodium(I) pincer adducts of water **2d**. PNP variant **2d-CH$_2$** ($\delta_{31P}$ 63.1, $^1J_{RhP}$ = 144 Hz) was formed quantitatively on addition of excess degassed water (40 equiv.) to an equilibrium mixture of **1a/b-CH$_2$** generated from stoichiometric reaction between [Rh(COD)$_2$][BAr$^F_4$] and PNP in DFB ($t$ ~ 3 h). Consistent with the aforementioned reactivity trends PONOP variant **2d-O** ($\delta_{31P}$ 199.1, $^1J_{RhP}$ = 150 Hz) was, however, only formed with 88% conversion after 3 days under these conditions. Analytically pure samples of the **2d-CH$_2$** (71% yield) and **2d-O** (49% yield) were obtained using **1a/b-CH$_2$** or **1b-O**, respectively, and excess water (500 equiv./Rh). The structural formulation of both new aqua complexes was confirmed using a combination of NMR spectroscopy, X-ray diffraction (see Fig. 1 for **2d-O**) and satisfactory microanalysis. The solid-state structures of **2d** are notable for and Rh–OH$_2$ bond lengths of *ca.* 2.15 Å and the presence of an additional hydrogen bonded water molecule in the lattice (RhOH$_2$···OH$_2$ = 2.7–2.8 Å).[13]

As a means of showcasing our new methodology and as part of our work exploring C(sp)–H activation reactions mediated by cationic rhodium(I) pincers,[14] we set about studying the reactivity of the associated {Rh(pincer)}$^+$ fragments with two bulky terminal alkynes (Scheme 3). Using isolated **1b-CH$_2$** as the precursor, reaction with both HCC$t$Bu and HCCAr′ (Ar′ = 3,5-$t$Bu$_2$C$_6$H$_3$) in DFB under an argon atmosphere resulted in rapid ($t$ < 5 min) and quantitative formation of vinylidene derivatives **3a/b-CH$_2$**, the formation of which was readily apparent due to their striking deep green colours. Both complexes were subsequently isolated from solution and fully characterised in solution and the solid state.† The NMR spectra of **3a/b-CH$_2$** are notable for the presence of vinylidene $^{13}$C resonances at $\delta$ 317.5/326.9 (located by HMBC experiments), time-averaged $C_{2v}$ symmetry – reconciled by free



**Fig. 1** Solid-state structures of **1b-O** and **2d-O**. Thermal ellipsoids drawn at 50% probability; anions and most hydrogen atoms omitted for clarity. The starred atoms are generated using the symmetry operation −$x$, 1 − $y$, 1 − $z$. Selected bond lengths (Å): **1b-O**: Rh1−Cnt(C4,C5), 2.083(2); *cf.* **1b-CH$_2$**, Rh1−Cnt(C4,C5), 2.058(2); **2d-O**: Rh1−O4, 2.154(2); *cf.* **2d-CH$_2$**, 2.152(7).
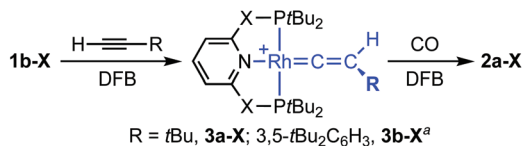
**Scheme 3** Preparation of vinylidene complexes **3** (X = O, CH$_2$). [BAr$^F_4$]$^-$ counter anions omitted for clarity; $^a$ **3b-O** formed as mixture with the corresponding π-complex **2e-O**.

rotation about the Rh=C=C vector – and single phosphorus resonances with large coupling to $^{103}$Rh ($\delta_{31P}$ 65.6/65.9, $^1J_{RhP}$ = 139/137 Hz). The solid-state structures affirm the structural assignments and, in addition to the Rh=C bond lengths of 1.81–1.84 Å that are fully inline with related rhodium precedents,[15] notable for the adoption of both $C_2$ (**3a-CH$_2$**, Z′ = 2) and $C_s$ (**3a-CH$_2$**, Z′ = 2; **3b-CH$_2$**) symmetric pincer ligand conformations; demonstrating the flexibility of lutidene-based pincer backbones.[16] In a similar manner, deep blue vinylidene complex **3a-O** was obtained from HCCtBu and **1b-O**, but over a more protracted time frame than the PNP analogue (ca. 18 h; $\delta_{31P}$ 206.5, $^1J_{RhP}$ = 144 Hz, $\delta_{13C}$(RhC) 330.0, $C_{2v}$ solution symmetry; Fig. 2). Consistent with the aformetioned trends, the reaction between {Rh(PONOP)}$^+$ and HCCAr′ only resulted in the formation of the green vinylidene derivative **3b-O** ($\delta_{31P}$ 208.4, $^1J_{RhP}$ = 143 Hz, $\delta_{13C}$(RhC) 339.5) as the minor component (30%) of a mixture with the balance made up by the corresponding π-complex [Rh(PONOP)(HCCAr′)][BAr$^F_4$] (**2e-O**; $\delta_{31P}$ 194.6. $^1J_{RhP}$ = 129 Hz).[17] This ratio was found even in use of excess alkyne and the co-crystallisation of these two compounds (with the ratio reflected in the corresponding crystallographic occupancies) precluded separation in this manner.† [18]

Curiously, we note reaction of isolated **3** (in the case of **3b-O**, as a mixture with **2e-O**) with CO (1 atm) resulted in complete conversion to **2a** in all cases with concomitant liberation of the corresponding terminal alkynes ($t$ < 90 min). Such reversible vinylidene formation is well documented in ruthenium complexes,[19] and in line with related observations we

have made when studying C(sp)–H bond activation reactions of cationic rhodium complexes of NHC-based pincer ligands.[14]

## Conclusions

We have demonstrated that reaction between the readily accessible (and commercially available) rhodium precursor [Rh(COD)$_2$][BAr$^F_4$] and two phosphine-based pincer ligands (2,6-bis(di-tert-butylphosphinomethyl)pyridine and 2,6-bis(di-tert-butylphosphinito)pyridine) in 1,2-F$_2$C$_6$H$_4$ provides a operationally simple method for generating the corresponding {Rh(pincer)}$^+$ fragments, and subsequent synthesis of adducts of CO, H$_2$, N$_2$ and H$_2$O (**2**). This methodology is underpinned by reversible binding of COD, that leads to dynamic equilibrium mixtures of monomeric [Rh(pincer)(η$^2$-COD)][BAr$^F_4$] **1a** and dimeric [{Rh(pincer)}$_2$(μ-η$^2$:η$^2$-COD)][BAr$^F_4$]$_2$ **1b**, the latter of which were readily isolated by recrystallisation. This methodology was used to study the reaction between {Rh(pincer)}$^+$ and bulky terminal alkynes, which resulted in the (reversible) formation of novel vinylidene derivatives [Rh(pincer)(CCHR)][BAr$^F_4$] (R = tBu, **3a**; 3,5-tBu$_2$C$_6$H$_3$, **3b**).

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

**Fig. 2** Solid-state structure of **3a-O**. Thermal ellipsoids drawn at 50% probability; anion, most hydrogen atoms and disordered component (vinylidene) omitted for clarity. Selected bond lengths (Å): **3a-O**: Rh1–C4, 1.865(5); Rh1–C4A, 1.846(4); cf. **3a-CH$_2$**, Rh–C, 1.826(5)–1.840(3); **3b-CH$_2$**: 1.812(2).[18]

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