



Cite this: *Dalton Trans.*, 2019, **48**, 2877

Received 21st December 2018,

Accepted 28th January 2019

DOI: 10.1039/c8dt05049j

rsc.li/dalton

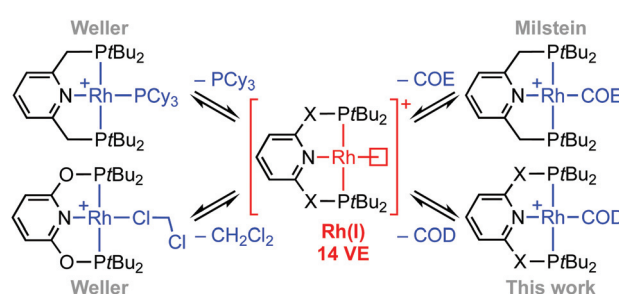
A convenient method for the generation of $\{\text{Rh}(\text{PNP})\}^+$ and $\{\text{Rh}(\text{PONOP})\}^+$ fragments: reversible formation of vinylidene derivatives†

Matthew R. Gytton, Thomas M. Hood and Adrian B. Chaplin*

The substitution reactions of $[\text{Rh}(\text{COD})_2][\text{BAR}^{\text{F}}_4]$ 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- $\text{F}_2\text{C}_6\text{H}_4$ 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 $[\text{Rh}(\text{pincer})(\text{CCHR})][\text{BAR}^{\text{F}}_4]$ ($\text{R} = \text{tBu}$, 3,5- $\text{tBu}_2\text{C}_6\text{H}_3$), through reversible reactions with terminal alkynes.

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 $\text{C}(\text{sp}^3)\text{--H}$ bond activation and alkane dehydrogenation processes mediated at iridium homologues.^{2,3} Other group 9 highlights include the $\text{C}(\text{sp}^2)\text{--H}$ bond oxidative addition of aryl halides^{4,5} and the selective $\text{C}(\text{sp}^3)\text{--F}$ 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-



Scheme 1 Latent sources of the $\{\text{Rh}(\text{PNP})\}^+$ and $\{\text{Rh}(\text{PONOP})\}^+$ fragments ($\text{X} = \text{O}, \text{CH}_2$). COE = cyclooctene; COD = 1,5-cyclooctadiene.

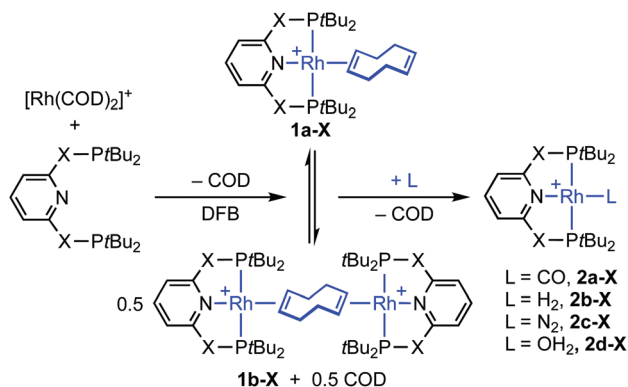
dine) and PONOP (2,6-bis(di-*tert*-butylphosphinito)pyridine) ligands, exploiting metastable coordination of 1,5-cyclooctadiene (COD) in the weakly coordinating 1,2-difluorobenzene solvent (DFB).¹⁰ We showcase this methodology for the preparation of previously unknown water complexes and the reversible 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 $[\text{Rh}(\text{COD})_2][\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$); 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 $\{\text{Rh}(\text{pincer})\}^+$ fragments in solution.¹¹ To this end, stoichiometric reactions between PNP/PONOP and $[\text{Rh}(\text{COD})_2][\text{BAR}^{\text{F}}_4]$ 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, $\delta_{31\text{P}}$ 63.4, 52.6, $^2J_{\text{PP}} \sim 320$ Hz; PONOP, $\delta_{31\text{P}}$ 202.5, $^1J_{\text{RhP}} = 134$ Hz) as

Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK. E-mail: a.b.chaplin@warwick.ac.uk

† Electronic supplementary information (ESI) available: Full experimental details and NMR spectra of new compounds and selected reactions (PDF). Primary NMR data (MNOVA). CCDC 1886657–1886664. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt05049j



Scheme 2 Synthesis and reactivity of **1** (X = O, CH₂). [BAR^F₄][−] 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, H₂, and N₂ (1 atm) and analysis *in situ* using ¹H and ³¹P 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 H₂ and N₂ 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 pro-

ceeded 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-CH₂** (δ_{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-CH₂** generated from stoichiometric reaction between [Rh(COD)₂][BAR^F₄] and PNP in DFB (*t* ~ 3 h). Consistent with the aforementioned reactivity trends PONOP variant **2d-O** (δ_{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-CH₂** (71% yield) and **2d-O** (49% yield) were obtained using **1a/b-CH₂** 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–OH₂ bond lengths of ca. 2.15 Å and the presence of an additional hydrogen bonded water molecule in the lattice (RhOH₂...OH₂ = 2.7–2.8 Å).¹³

As a means of showcasing our new methodology and as part of our work exploring C(sp)³–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-CH₂** as the precursor, reaction with both HCC*t*Bu and HCCAr' (Ar' = 3,5-*t*Bu₂C₆H₃) in DFB under an argon atmosphere resulted in rapid (*t* < 5 min) and quantitative formation of vinylidene derivatives **3a/b-CH₂**, 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-CH₂** are notable for the presence of vinylidene ¹³C resonances at δ 317.5/326.9 (located by HMBC experiments), time-averaged C_{2v} symmetry – reconciled by free

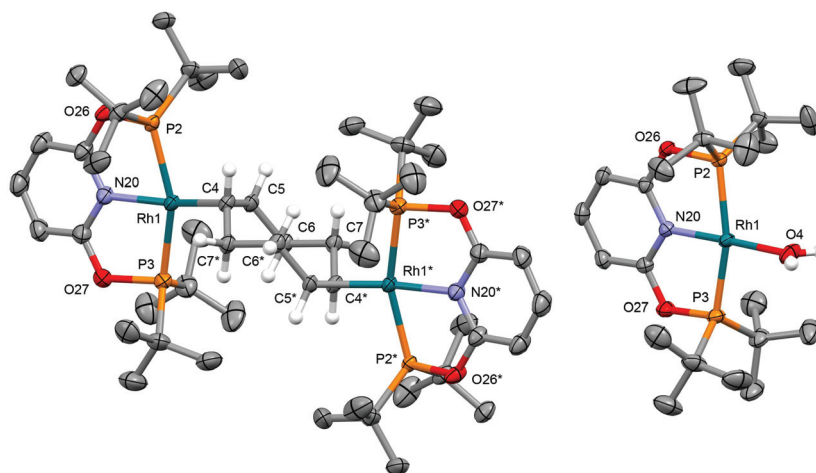


Fig. 1 Solid-state structures of **1b-O** and **2d-O**. Thermal ellipsoids drawn at 50% probability; anions and most hydrogen atoms omitted for clarity. The starred atoms are generated using the symmetry operation $-x, 1 - y, 1 - z$. Selected bond lengths (Å): **1b-O**: Rh1–Cnt(C4,C5), 2.083(2); cf. **1b-CH₂**, Rh1–Cnt(C4,C5), 2.058(2); **2d-O**: Rh1–O4, 2.154(2); cf. **2d-CH₂**, 2.152(7).





Scheme 3 Preparation of vinylidene complexes **3** (X = O, CH₂). [Bar^F₄][−] 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 ¹⁰³Rh ($\delta_{31\text{P}}$ 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 C₂ (**3a-CH₂**, Z' = 2) and C_s (**3a-CH₂**, Z' = 2; **3b-CH₂**) symmetric pincer ligand conformations; demonstrating the flexibility of lutidine-based pincer backbones.¹⁶ In a similar manner, deep blue vinylidene complex **3a-O** was obtained from HCC*t*Bu and **1b-O**, but over a more protracted time frame than the PNP analogue (*ca.* 18 h; $\delta_{31\text{P}}$ 206.5, ¹J_{RhP} = 144 Hz, $\delta_{13\text{C}}$ (RhC) 330.0, C_{2v} solution symmetry; Fig. 2). Consistent with the aforementioned trends, the reaction between {Rh(PONOP)}⁺ and HCC*Ar*' only resulted in the formation of the green vinylidene derivative **3b-O** ($\delta_{31\text{P}}$ 208.4, ¹J_{RhP} = 143 Hz, $\delta_{13\text{C}}$ (RhC) 339.5) as the minor component (30%) of a mixture with the balance made up by the corresponding π -complex [Rh(PONOP)(HCC*Ar*')] [Bar^F₄][−] (**2e-O**; $\delta_{31\text{P}}$ 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

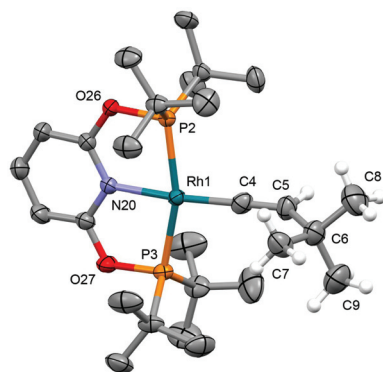


Fig. 2 Solid-state structure of **3a-O**. Thermal ellipsoids drawn at 50% probability; anion, most hydrogen atoms and disordered component (vinylidene) omitted for clarity. Selected bond lengths (Å): **3a-O**: Rh1–C4, 1.865(5); Rh1–C4A, 1.846(4); cf. **3a-CH₂**, Rh–C, 1.826(5)–1.840(3); **3b-CH₂**, 1.812(2).¹⁸

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^F₄] and two phosphine-based pincer ligands (2,6-bis(di-*tert*-butylphosphinomethyl)pyridine and 2,6-bis(di-*tert*-butylphosphinito)pyridine) in 1,2-F₂C₆H₄ provides a operationally simple method for generating the corresponding {Rh(pincer)}⁺ fragments, and subsequent synthesis of adducts of CO, H₂, N₂ and H₂O (**2**). This methodology is underpinned by reversible binding of COD, that leads to dynamic equilibrium mixtures of monomeric [Rh(pincer)(η^2 -COD)][Bar^F₄] **1a** and dimeric [{Rh(pincer)}₂(μ - η^2 : η^2 -COD)][Bar^F₄]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)(CCH*R*)] [Bar^F₄] (R = *t*Bu, **3a**; 3,5-*t*Bu₂C₆H₃, **3b**).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the European Research Council (ERC, grant agreement 637313) and Royal Society (UF100592, UF150675, A. B. C.) for financial support. Crystallographic data for **3a-O** were collected using an instrument purchased through support from Advantage West Midlands and the European Regional Development Fund. All other crystallographic data were collected using an instrument that received funding from the ERC under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 637313).

References

- (a) *Pincer Compounds: Chemistry and Applications*, ed. D. Morales-Morales, Elsevier, 2018, vol. 1; (b) Organometallic Pincer Chemistry, in *Topics in Organometallic Chemistry*, ed. G. van Koten and D. Milstein, Springer, 2013, vol. 40; (c) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (d) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750–3781.
- A. Kumar, T. M. Bhatti and A. S. Goldman, *Chem. Rev.*, 2017, **117**, 12357–12384.
- W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg and M. Brookhart, *Science*, 2009, **326**, 553–556.
- (a) E. Ben-Ari, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2003,



- 125, 4714–4715; (b) E. Ben-Ari, R. Cohen, M. Gandelman, L. J. W. Shimon, J. M. L. Martin and D. Milstein, *Organometallics*, 2006, **25**, 3190–3210.
- 5 (a) S. A. Hauser, J. Emerson-King, S. Habershon and A. B. Chaplin, *Chem. Commun.*, 2017, **53**, 3634–3636; (b) L. Fan, S. Parkin and O. V. Ozerov, *J. Am. Chem. Soc.*, 2005, **127**, 16772–16773.
- 6 J. Choi, D. Y. Wang, S. Kundu, Y. Choliy, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Science*, 2011, **332**, 1545–1548.
- 7 A. B. Chaplin and A. S. Weller, *Organometallics*, 2011, **30**, 4466–4469.
- 8 G. M. Adams, F. M. Chadwick, S. D. Pike and A. S. Weller, *Dalton Trans.*, 2015, **44**, 6340–6342.
- 9 D. Hermann, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *Organometallics*, 2002, **21**, 812–818.
- 10 S. D. Pike, M. R. Crimmin and A. B. Chaplin, *Chem. Commun.*, 2017, **53**, 3615–3633.
- 11 This approach notably avoids the need for a late stage halogen abstraction step, which can limit the choice of reagents or solvents. For instance, Na[BAR^F₄] is not a very effective chloride abstractor in DFB due to appreciable solubility of NaCl (see ref. 10). Silver salts are also sufficiently oxidising to enact one electron oxidation of rhodium(i) complexes (see: M. Feller, E. Ben-Ari, T. Gupta, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, L. Weiner and D. Milstein, *Inorg. Chem.*, 2007, **46**, 10479–10490.).
- 12 M. Findlater, K. M. Schultz, W. H. Bernskoetter, A. Cartwright-Sykes, D. M. Heinekey and M. Brookhart, *Inorg. Chem.*, 2012, **51**, 4672–4678.
- 13 (a) M. B. Hursthouse, K. M. A. Malik, E. W. Evans, M. B. H. Howlader and M. T. Atlay, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 1782–1784; (b) P. J. Stang, L. Song, Y.-H. Huang and A. M. Arif, *J. Organomet. Chem.*, 1991, **405**, 403–406.
- 14 C. M. Storey, M. R. Gyton, R. E. Andrew and A. B. Chaplin, *Angew. Chem., Int. Ed.*, 2018, **57**, 12003–12006.
- 15 (a) O. Nürnberg and H. Werner, *J. Organomet. Chem.*, 1993, **460**, 163–175; (b) B. Windmüller, O. Nürnberg, J. Wolf and H. Werner, *Eur. J. Inorg. Chem.*, 1999, **1999**, 613–619.
- 16 For comparison to a related NHC-based pincer system see: R. E. Andrew, D. W. Ferdani, C. A. Ohlin and A. B. Chaplin, *Organometallics*, 2015, **34**, 913–917.
- 17 These complexes are presumably in equilibrium (and this suggestion is support by subsequent reaction with CO). See: Y. Wakatsuki, *J. Organomet. Chem.*, 2004, **689**, 4092–4109.
- 18 Due to presence as the minor disordered component in the solid state, the metrics associated with the vinylidene in **3b-O** are unreliable.
- 19 (a) G. Albertin, S. Autoniutti, E. Bordinon, F. Cazzaro, S. Ianelli and G. Pelizzi, *Organometallics*, 1995, **14**, 4114–4125; (b) M. I. Bruce, B. C. Hall and E. R. T. Tiekink, *Aust. J. Chem.*, 1997, **50**, 1097–1100; (c) C. Slugovc, V. N. Sapunov, P. Wiede, K. Mereiter, R. Schmid and K. Kirchner, *J. Chem. Soc., Dalton Trans.*, 1997, 4209–4216; (d) V. Cadierno, M. P. Gamasa and J. Gimeno, *Organometallics*, 1999, **18**, 2821–2832; (e) N. J. Beach, J. M. Walker, H. A. Jenkins and G. J. Spivak, *J. Organomet. Chem.*, 2006, **691**, 4147–4152; (f) M. Bassetti, V. Cadierno, J. Gimeno and C. Pasquini, *Organometallics*, 2008, **27**, 5009–5016; (g) Y. Mutoh, K. Imai, Y. Kimura, Y. Ikeda and Y. Ishii, *Organometallics*, 2011, **30**, 204–207.

