



Cite this: *Dalton Trans.*, 2015, **44**, 6340

Received 2nd February 2015,  
Accepted 5th March 2015

DOI: 10.1039/c5dt00481k

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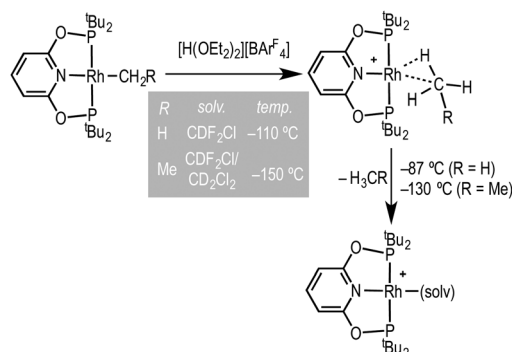
The  $\text{CH}_2\text{Cl}_2$  complex  $[\text{Rh}(\text{}^t\text{BuPONOP})(\kappa^1\text{-ClCH}_2\text{Cl})][\text{BAR}^{\text{F}}_4]$  is reported, that also acts as a useful synthon for other complexes such as  $\text{N}_2$ ,  $\text{CO}$  and  $\text{H}_2$  adducts; while the analogous PNP complex undergoes C–Cl activation.

Coordinatively and electronically unsaturated transition-metal pincer complexes,  $[\text{M}(\text{pincer})]$ , are key intermediates in alkane dehydrogenation processes,<sup>1</sup> as well as other catalytic transformations.<sup>2</sup> They have also played a major role in the elucidation of fundamental bond transformations, such as C–H, C–C and C–X breaking and making.<sup>3</sup> Recently, Brookhart and co-workers reported the synthesis of transition-metal methane and ethane sigma complexes, by a low temperature (*ca.*  $-110$  °C to  $-150$  °C) protonation of the corresponding  $\text{Rh}(\text{}^t\text{BuPONOP})\text{R}$  precursors using  $[\text{H}(\text{OEt}_2)_2][\text{BAR}^{\text{F}}_4]$  in  $\text{CDF}_2\text{Cl}-\text{CH}_2\text{Cl}_2$  solvent to give  $[\text{Rh}(\text{}^t\text{BuPONOP})(\text{H-R})][\text{BAR}^{\text{F}}_4]$  [ $\text{}^t\text{BuPONOP} = 2,6\text{-}(\text{}^t\text{Bu}_2\text{PO})_2\text{C}_5\text{H}_3\text{N}$ ;  $\text{R} = \text{Me, Et}$ ;  $\text{Ar}^{\text{F}} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$ ], Scheme 1.<sup>4</sup> Such complexes are key, but transient, intermediates in C–H bond activation processes. On warming above  $-87$  °C ( $\text{R} = \text{Me}$ ) or  $-130$  °C ( $\text{R} = \text{Et}$ ) they lose alkane and generate complexes tentatively characterised *in situ* on the basis of  $^{31}\text{P}$  NMR spectroscopy as  $[\text{Rh}(\text{}^t\text{BuPONOP})(\text{solv})][\text{BAR}^{\text{F}}_4]$  ( $\text{solv} = \text{CDF}_2\text{Cl}$  or  $\text{CD}_2\text{Cl}_2$ ). These solvent adducts remain to be definitively characterised. They are particularly interesting given their role in alkane coordination chemistry, and more generally as latent-low coordinate intermediates in catalytic processes.

We now report the full characterisation of the  $\text{CH}_2\text{Cl}_2$  adduct accessed *via* a different, halide abstraction, route including a single crystal X-ray diffraction study and its onward reactivity. We also demonstrate that changing the pincer ligand to the more electron donating  $\text{}^t\text{BuPNP}$  [ $2,6\text{-}(\text{}^t\text{Bu}_2\text{PCH}_2)_2\text{C}_5\text{H}_3\text{N}$ ] results in C–Cl bond activation of the solvent molecule.

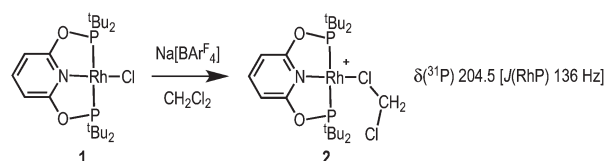
## A $\text{CH}_2\text{Cl}_2$ complex of a $[\text{Rh}(\text{pincer})]^+$ cation<sup>†</sup>

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**Scheme 1** Formation of a sigma alkane complex and decomposition to give tentatively characterised solvent complexes (Brookhart and co-workers).  $[\text{BAR}^{\text{F}}_4]^-$  anions are not shown.<sup>4</sup>

Addition of  $\text{Na}[\text{BAR}^{\text{F}}_4]$  to a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Rh}(\text{}^t\text{BuPONOP})\text{Cl}$ , **1**,<sup>4a</sup> results in the formation of orange  $[\text{Rh}(\text{}^t\text{BuPONOP})(\kappa^1\text{-ClCH}_2\text{Cl})][\text{BAR}^{\text{F}}_4]$ , **2** (Scheme 2). Filtration and removal of the solvent affords **2** in good isolated yield as a powder. Complex **2** can be recrystallised from  $\text{CH}_2\text{Cl}_2$ –pentane under an  $\text{Ar}$  atmosphere to give crystals suitable for an X-ray diffraction study. Under these conditions, orange **2** crystallises alongside the dinitrogen adduct,  $[\text{Rh}(\text{}^t\text{BuPONOP})(\kappa^1\text{-N}_2)][\text{BAR}^{\text{F}}_4]$ , **3**, in an approximate 1 : 1 ratio (as measured by  $^{31}\text{P}$  NMR spectroscopy, *vide infra*). Single crystals of **2** suitable for an X-ray diffraction study were obtained by mechanical separation from orange/brown **3**.<sup>‡</sup> Presumably the exogenous  $\text{N}_2$  comes from trace (1–2 ppm) levels of  $\text{N}_2$  present in the argon, as has been noted previously,<sup>5</sup> and is driven by relative solubilities of

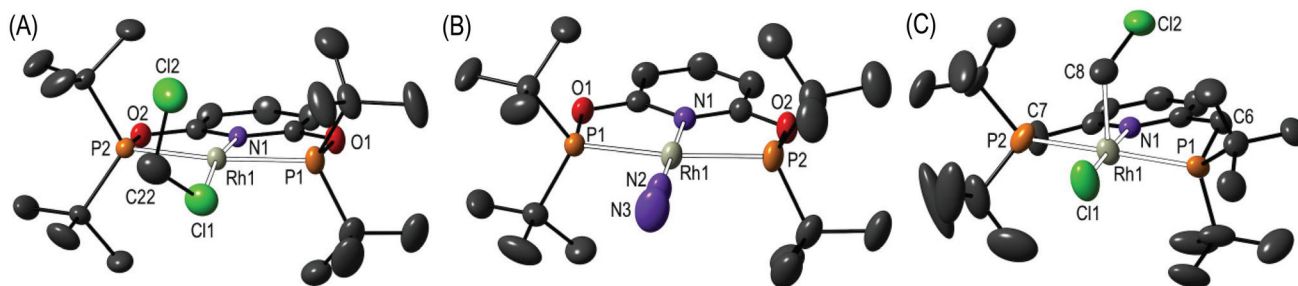


**Scheme 2** Synthesis of complex **2**.  $[\text{BAR}^{\text{F}}_4]^-$  anion is not shown.

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<sup>†</sup>Electronic supplementary information (ESI) available: Full experimental, characterisation and X-ray crystallography details. CCDC 1044741, 1044743, 1044744 and 1044745. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00481k





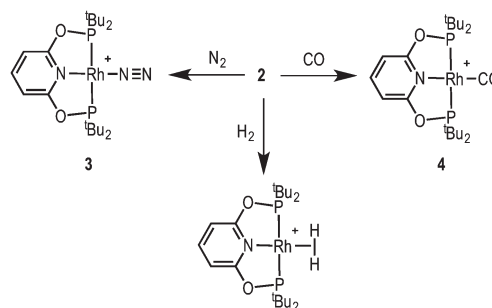
**Fig. 1** Solid-state structures of: (A) Complex 2; (B) Complex 3; (C) Complex 5. Displacement ellipsoids are shown at the 50% probability level, hydrogen atoms and the  $[\text{BAR}^{\text{F}}_4]^-$  anions are not shown. Selected bond lengths (Å) and angles ( $^\circ$ ): (2) Rh1–Cl1, 2.350(2); Rh1–N1, 2.011(4); Rh1–P1, 2.272(1); Rh1–P2, 2.285(1); Cl1–C22, 1.710(8); Cl2–C22, 1.758(7); Cl1–C22–Cl2, 114.3(4); N1–Rh1–Cl1, 169.65(11). (3) Rh1–N1, 2.018(3); Rh1–N2, 1.967(3); Rh1–P1, 2.2745(8); Rh1–P2, 2.2724(8); N2–N3, 1.063(5); Rh1–N2–N3, 179.3(4); N1–Rh1–N2, 179.37(13). (5) Rh1–Cl1, 2.311(2); Rh1–N1, 2.066(6); Rh1–P1, 2.335(2); Rh1–P2, 2.339(2); Rh1–C8, 2.196(15); C8–Cl2, 1.79(2); Rh1–C8–Cl2, 112.5(9). Complex 5 co-crystallises with  $[\text{Rh}(\text{tBuPnP})(\text{H})\text{Cl}][\text{BAR}^{\text{F}}_4]$ , **6**, at the same lattice position in a 50 : 50 ratio.†

**2** and **3**; as in neat  $\text{CD}_2\text{Cl}_2$  under the same Ar atmosphere **2** does not go onto to form **3** to the detection limit of  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The solid-state structure (Fig. 1A) shows a pseudo square planar cationic  $[\text{Rh}(\text{tBuPONOP})]^+$  centre coordinated in the fourth position by a  $\text{CH}_2\text{Cl}_2$  molecule. The Rh–Cl1 distance [2.350(2) Å] is significantly shorter than reported for related  $[\text{RhCp}^*(\text{PMe}_3)(\text{Ph})(\kappa^1\text{-ClCH}_2\text{Cl})][\text{BAR}^{\text{F}}_4]$ ,<sup>6</sup> 2.512(2) Å, and  $[\text{RhCp}^*(\text{PMe}_3)(\text{Me})(\kappa^1\text{-ClCH}_2\text{Cl})][\text{BAR}^{\text{F}}_4]$ , 2.488(1) Å  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ .<sup>7</sup> Complex **2** adds to the relatively small number of  $\text{CH}_2\text{Cl}_2$  complexes that have been crystallographically characterised, and in particular  $\text{CH}_2\text{Cl}_2$  adducts of pincer, or closely related, complexes.<sup>8</sup>

Although the short Rh–Cl distance might suggest a stronger interaction in **2**, in solution (*vide infra*) rapid exchange between solvent and bound  $\text{CH}_2\text{Cl}_2$  occurs. The two C–Cl distances in the bound solvent molecule are similar, 1.710(8) [C22–Cl1] and 1.758(7) [C22–Cl2] Å, although the distal C–Cl bond is the slightly longer of the two. This is in contrast to other reported  $\text{CH}_2\text{Cl}_2$  complexes in which the bound C–Cl bond is longer.<sup>8,9</sup> We suggest that the slight lengthening of C22–Cl2 may be due to a number of weak C–H...Cl hydrogen bonds between proximal tBu groups and Cl2.<sup>10</sup>

Complex **2** is stable in the solid-state under an Ar atmosphere, and in solution ( $\text{CD}_2\text{Cl}_2$ ) for at least 1 week. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ) a single resonance is observed at  $\delta$  204.5 [J(RhP) 136 Hz]. These data are identical to those previously reported by Brookhart and co-workers for the complex tentatively characterised as  $[\text{Rh}(\text{tBuPONOP})(\text{CH}_2\text{Cl}_2)][\text{BAR}^{\text{F}}_4]$ , *i.e.* **2**. The tBu groups are observed as a single environment in the  $^1\text{H}$  NMR spectrum. The bound  $\text{CH}_2\text{Cl}_2$  ligand is not observed, even at  $-80^\circ\text{C}$  in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, presumably as it is undergoing fast exchange with the solvent.<sup>11</sup> The electrospray ionisation mass spectrum of **2** using  $\text{N}_2$  as a desorption gas showed only **3** as the molecular ion.

Complex **2** is a useful synthon for the preparation of other pincer complexes (Scheme 3). Addition of  $\text{H}_2$  to a  $\text{CD}_2\text{Cl}_2$  solution of **2** forms the previously reported dihydrogen complex  $[\text{Rh}(\text{tBuPONOP})(\eta^2\text{-H}_2)][\text{BAR}^{\text{F}}_4]$ <sup>12</sup> [ $\delta(^1\text{H})$   $-8.27$ , lit.  $-8.26$ ]. Addition of  $\text{N}_2$  forms the new complex  $[\text{Rh}(\text{tBuPONOP})(\kappa^1\text{-N}_2)]$

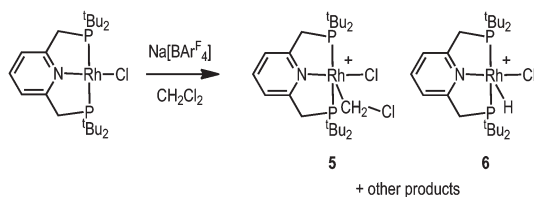


**Scheme 3** Reactivity of complex **2**.  $\text{CH}_2\text{Cl}_2$  solvent.  $[\text{BAR}^{\text{F}}_4]^-$  anions are not shown.

$[\text{BAR}^{\text{F}}_4]$ , **3**, for which a solid-state structure is shown in Fig. 1B. This demonstrates an end-on bound, monomeric,  $\text{N}_2$  adduct [N–N, 1.063(5); Rh–N2, 1.967(3) Å]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum displays a single environment at  $\delta$  211.0 [J(RhP) 132 Hz], while in the IR spectrum the N–N stretch is observed at  $2201.9\text{ cm}^{-1}$ . The N–N bond length is very similar (albeit a little shorter) than that in free  $\text{N}_2$  [1.09 Å], suggesting only a small degree of activation. Complex **3** can also be compared with previously reported  $[\text{Rh}(\text{tBuPnP})(\kappa^1\text{-N}_2)][\text{OTf}]$  which shows a slightly longer N–N bond, a shorter Rh–N bond and a more red-shifted N–N stretch: 1.116(4), 1.898(3) Å, and  $2153\text{ cm}^{-1}$  respectively; suggesting greater  $\text{N}_2$  activation for this more electron rich pincer ligand.<sup>13</sup> This greater metal-based basicity in the tBuPnP complexes is reflected in the CO stretching frequencies of the corresponding CO-adducts:  $[\text{Rh}(\text{tBuPONOP})(\text{CO})][\text{BAR}^{\text{F}}_4]$ , **4** [ $2020\text{ cm}^{-1}$ ] and  $[\text{Rh}(\text{tBuPnP})(\text{CO})][\text{BAR}^{\text{F}}_4]$  [ $1982\text{ cm}^{-1}$ ].<sup>14</sup> Complex **4** was prepared by adding CO to a  $\text{CH}_2\text{Cl}_2$  solution of **2**, further demonstrating the utility of complex **2** in synthesis.

The difference in electron-donating power of the tBuPONOP versus tBuPnP ligands can also be shown by the attempted synthesis of the  $\text{CH}_2\text{Cl}_2$  adduct of the  $\{\text{Rh}(\text{tBuPnP})\}^+$  fragment, analogous to complex **2**. Rather than simple coordination, this resulted in a number of products as measured by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Analysis of single crystals suitable for an X-ray





**Scheme 4** Reactivity of  $\text{Rh}(\text{tBuPNP})\text{Cl}^{15}$  with  $\text{Na}[\text{BarF}_4]$ .  $\text{CH}_2\text{Cl}_2$  solvent.  $[\text{BarF}_4]^-$  anions are not shown.

diffraction study, obtained from recrystallisation of the reaction mixture, demonstrated co-crystallisation of two complexes  $[\text{Rh}(\text{tBuPNP})(\text{CH}_2\text{Cl})\text{Cl}][\text{BarF}_4]$ , **5**, and  $[\text{Rh}(\text{tBuPNP})-(\text{H})\text{Cl}][\text{BarF}_4]$ , **6**, in an approximate 50:50 ratio (Scheme 4); for which the solid-state structure of **5** is shown in Fig. 1C. Because of this co-crystallisation the metrical data associated with **5** should be treated with caution. The  $^1\text{H}$  NMR spectrum of these crystals showed a broad hydride signal at  $\delta -15.48$  (relative integral relative to  $[\text{BarF}_4]$  of  $\sim 0.5$  H) which is assigned to **6**. Given the number of products formed we are reluctant to speculate on mechanism of formation of **6**, but protonation of **5** by trace acid arising from other decomposition pathways could form **6**. Addition of  $\text{H}_2$  to this mixture of **5** and **6** in  $\text{CD}_2\text{Cl}_2$  afforded mixture of products, from which  $[\text{Rh}(\text{tBuPNP})-(\eta^2-\text{H}_2)][\text{BarF}_4]$  could be identified as the major species present.<sup>16</sup>

## Conclusions

The  $\text{CH}_2\text{Cl}_2$  complex  $[\text{Rh}(\text{tBuPONOP})(\kappa^1-\text{ClCH}_2\text{Cl})][\text{BarF}_4]$  has been isolated, confirming its formation in the decomposition of the corresponding alkane adduct at low temperature, itself formed from protonation of an alkyl precursor.<sup>4</sup> Synthesis has been achieved by an alternative halide-abstraction route in  $\text{CH}_2\text{Cl}_2$  solvent, starting from a readily available chloride precursor. This complex, with its weakly bound  $\text{CH}_2\text{Cl}_2$  ligand, also acts as a useful synthon for other complexes such as  $\text{N}_2$ ,  $\text{CO}$  and  $\text{H}_2$  adducts. The corresponding PNP ligand complex undergoes C–Cl activation to form a mixture of products, highlighting the difference in electron donating properties of these two ligands.

## Acknowledgements

The EPSRC for funding (EP/K035908/1) and Dr Adrian Chaplin for the initial synthesis of complex **5**.

## Notes and references

† Crystal data: (2)  $\text{RhP}_2\text{O}_2\text{NCl}_2\text{C}_{24}\text{H}_{41}\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ , Monoclinic ( $C2/c$ ),  $a = 16.9996(5)$  Å,  $b = 18.1716(4)$  Å,  $c = 39.8254(10)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 96.458(2)^\circ$ , volume =  $12\,224.4(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $\lambda = 0.71073$  Å,  $T = 150(2)$  K,  $\mu = 0.53$  mm<sup>-1</sup>, 16 021 independent reflections [ $R(\text{int}) = 0.029$ ],  $R_1 = 0.0814$ ,  $wR_2 = 0.1692$  [ $I > 2\sigma(I)$ ]. CCDC: 1044744; (3):  $\text{RhP}_2\text{O}_2\text{N}_3\text{C}_{21}\text{H}_{39}\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ , Monoclinic ( $C2/c$ ),  $a = 16.8578(4)$  Å,  $b = 18.1533(3)$  Å,  $c = 39.7792(7)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 95.9972(17)^\circ$ , volume =  $12\,106.8(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $\lambda = 1.54180$  Å,  $T = 150(2)$  K,  $\mu = 3.83$  mm<sup>-1</sup>, 12 215 independent reflections [ $R(\text{int}) = 0.031$ ],  $R_1 = 0.0483$ ,  $wR_2 = 0.1183$  [ $I > 2\sigma(I)$ ].

CCDC: 1044745; (5/6)  $\text{RhP}_2\text{NCl}_2\text{C}_{24}\text{H}_{45}\text{C}_{32}\text{H}_{12}\text{BF}_{24} \cdot \text{RhP}_2\text{NClC}_{23}\text{H}_{44}\text{C}_{32}\text{H}_{12}\text{BF}_{24}$ , Monoclinic ( $P2_1/c$ ),  $a = 13.8327(2)$  Å,  $b = 23.4907(3)$  Å,  $c = 20.1051(2)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 97.5982(11)^\circ$ , volume =  $6475.59(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\lambda = 1.54180$  Å,  $T = 150(2)$  K,  $\mu = 4.12$  mm<sup>-1</sup>, 12 878 independent reflections [ $R(\text{int}) = 0.029$ ],  $R_1 = 0.1064$ ,  $wR_2 = 0.2958$  [ $I > 2\sigma(I)$ ]. CCDC: 1044741.

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