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

Coordinatively and electronically unsaturated transition-metal pincer complexes, [M(pincer)], are key intermediates in alkane dehydrogenation processes,$^1$ as well as other catalytic transformations.$^2$ 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.$^3$ Recently, Brookhart and co-workers reported the synthesis of transition-metal methane and ethane sigma complexes, by a low temperature solvent molecule.

Addition of Na[$^{\text{BARF}}_4$] to a CH$_2$Cl$_2$ solution of Rh($^{\text{Bu}}$PONOP)Cl$_2$, $^4$ results in the formation of orange [Rh($^{\text{Bu}}$PONOP)-(κ$^1$-CICH$_2$Cl)]$^{\text{BARF}}_4$, 2 (Scheme 2). Filtration and removal of the solvent affords 2 in good isolated yield as a powder. Complex 2 can be recrystallised from CH$_2$Cl$_2$–pentane under an Ar atmosphere to give crystals suitable for an X-ray diffraction study. Under these conditions, orange 2 crystallises alongside the dinitrogen adduct, [Rh($^{\text{Bu}}$PONOP)(κ$^1$-N$_2$)]$^{\text{BARF}}_4$, 3, in an approximate 1 : 1 ratio (as measured by $^{31}$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.$^4$ Presumably the exogenous N$_2$ comes from trace (1–2 ppm) levels of N$_2$ present in the argon, as has been noted previously,$^5$ and is driven by relative solubilities of

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2 and 3; as in neat CD$_2$Cl$_2$ under the same Ar atmosphere 2 does not go onto to form 3 to the detection limit of $^{31}$P$^{1}$H NMR spectroscopy. The solid-state structure (Fig. 1A) shows a pseudo square planar cationic [Rh($^{31}$PONOP)]$^+$ centre coordinated in the fourth position by a CH$_2$Cl$_2$ molecule. The Rh–Cl1 distance [2.350(2) Å] is significantly shorter than reported for related [RhCp*(PMe$_3$)(Ph)(κ$^3$-ClCH$_2$Cl)][BAR$_4$]$_2$, 2.512(2) Å, and [RhCp*(PMe$_3$)(Me)(κ$^3$-ClCH$_2$Cl)][BAR$_4$], 2.488(1) Å $^{Cp^* = \eta^5-C_5Me_5}$. Complex 2 adds to the relatively small number of CH$_2$Cl$_2$ complexes that have been crystallographically characterised, and in particular CH$_2$Cl$_2$ adducts of pincer, or closely related, complexes. 

Although the short Rh–Cl distance might suggest a stronger interaction in 2, in solution (vide infra) rapid exchange between solvent and bound CH$_2$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 CH$_2$Cl$_2$ complexes in which the bound C–Cl bond is longer. 

Complex 2 is stable in the solid-state under an Ar atmosphere, and in solution (CD$_2$Cl$_2$) for at least 1 week. In the $^{31}$P$^{1}$H NMR spectrum (CD$_2$Cl$_2$) a single resonance is observed at δ 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 [Rh($^{31}$PONOP)(CH$_2$Cl$_2$)][BAR$_4$]$_2$, i.e. 2. The $^1$Bu groups are observed as a single environment in the $^1$H NMR spectrum. The bound CH$_2$Cl$_2$ ligand is not observed, even at –80 °C in the $^{13}$C$^{1}$H NMR spectrum, presumably as it is undergoing fast exchange with the solvent. The electrospray ionisation mass spectrum of 2 using 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 H$_2$ to a CD$_2$Cl$_2$ solution of 2 forms the previously reported dihydrogen complex [Rh($^{31}$PONOP)(κ$^3$-H$_2$)][BAR$_4$]$_2$ $^\delta$(H) = –8.27, lit. –8.26. Addition of N$_2$ forms the new complex [Rh($^{31}$PONOP)(κ$^1$-N$_2$)][BAR$_4$]$_2$, 3, for which a solid-state structure is shown in Fig. 1B. This demonstrates an end-on bound, monomeric, N$_2$ adduct [N–N, 1.063(5); Rh–N$_2$, 1.967(3) Å]. The $^{31}$P$^{1}$H NMR spectrum displays a single environment at δ 211.0 $^J$(RhP) 132 Hz, while in the IR spectrum the N–N stretch is observed at 2201.9 cm$^{-1}$. The N–N bond length is very similar (albeit a little shorter) than that in free N$_2$ [1.09 Å], suggesting only a small degree of activation. Complex 3 can also be compared with previously reported [Rh($^{31}$PONOP)(κ$^1$-N$_2$)][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 cm$^{-1}$ respectively; suggesting greater N$_2$ activation for this more electron rich pincer ligand. This greater metal-based basicity in the $^{31}$P$^{1}$PONOP complexes is reflected in the CO stretching frequencies of the corresponding CO-adducts: [Rh($^{31}$PONOP)(CO)][BAR$_4$]$_2$, 4 [2020 cm$^{-1}$] and [Rh($^{31}$PONOP)(CO)][BAR$_4$] [1982 cm$^{-1}$].

Complex 4 was prepared by adding CO to a CH$_2$Cl$_2$ solution of 2, further demonstrating the utility of complex 2 in synthesis.

The difference in electron-donating power of the $^{31}$P$^{1}$PONOP versus $^{31}$PONOP ligands can also been shown by the attempted synthesis of the CH$_2$Cl$_2$ adduct of the [Rh($^{31}$PONOP)]$^-$ fragment, analogous to complex 2. Rather than simple coordination, this resulted in a number of products as measured by $^{31}$P$^{1}$H NMR spectroscopy. Analysis of single crystals suitable for an X-ray
diffraction study, obtained from recrystallisation of the reaction mixture, demonstrated co-crystallisation of two complexes $[\text{Rh}^{(R)}\text{PONOP}]\left(\kappa^1\text{CICH}_{2}\text{Cl}\right)[\text{BARF}_4]$, 5, and $[\text{Rh}^{(R)}\text{PONOP}](\text{HCl})[\text{BARF}_4]$, 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 $^1$H NMR spectrum of these crystals showed a broad hydride signal at $\delta = 15.48$ (relative integral relative to [BARF]$_4$) of $-0.5$ 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 H$_2$ to this mixture of 5 and 6 in CH$_2$Cl$_2$ afforded mixture of products, from which $[\text{Rh}^{(R)}\text{PONOP}](\text{H})[\text{BARF}_4]$ could be identified as the major species present.$^{16}$

Conclusions

The CH$_2$Cl$_2$ complex $[\text{Rh}^{(R)}\text{PONOP}]\left(\kappa^1\text{CICH}_{2}\text{Cl}\right)[\text{BARF}_4]$ 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.$^7$ Synthesis has been achieved by an alternative halide-abstraction route in CH$_2$Cl$_2$ solvent, starting from a readily available chloride precursor. This complex, with its weakly bound CH$_2$Cl$_2$ ligand, also acts as a useful synthetic for other complexes such as N$_2$, CO and 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) Rh$_5$P$_3$O$_6$NCl$_4$C$_9$H$_{17}$C$_2$H$_4$BF$_{20}$, Monoclinic (C2/c), $a = 16.999(5)$ Å, $b = 18.171(6)$ Å, $c = 39.825(10)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 96.458(2)^\circ$, volume = 12 224.4(5) Å$^3$, $Z = 8$, $\omega = 0.7073$ Å, $\mu = 0.53$ mm$^{-1}$, 16 021 independent reflections [R(int) = 0.029], $R_1 = 0.0814$, wR$_2 = 0.1692$ [I > 2σ(I)].

CCDC: 1044745; (5/6) Rh$_5$P$_3$NCl$_4$C$_9$H$_{17}$C$_2$H$_4$BF$_{20}$: Rh$_5$P$_3$NCl$_4$C$_9$H$_{19}$C$_2$H$_4$BF$_{20}$, Monoclinic (P2$_1$/c), $a = 13.8327(2)$ Å, $b = 23.4907(2)$ Å, $c = 20.1031(2)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 97.5982(11)^\circ$, volume = 6 475.59(4) Å$^3$, $Z = 2$, $\mu = 1.51480$ Å, $\mu = 3.83$ mm$^{-1}$, 12 215 independent reflections [R(int) = 0.031], $R_1 = 0.0483$, wR$_2 = 0.1183$ [I > 2σ(I)].


