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A CH_2Cl_2 complex of a $[Rh(pincer)]^+$ cation†

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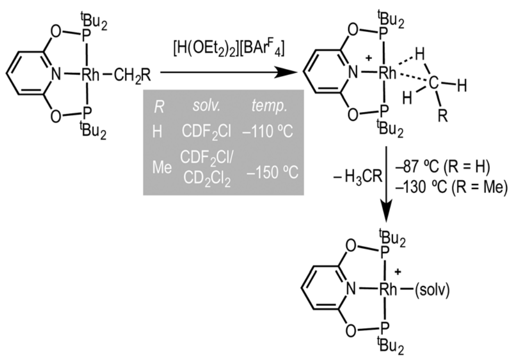
The CH_2Cl_2 complex $[Rh(^{tBu}PONOP)(\kappa^1\text{-}ClCH_2Cl)][BAr^F{}_4]$ is reported, that also acts as a useful synthon for other complexes such as N_2, CO and H_2 adducts; while the analogous PNP complex undergoes C–Cl activation.

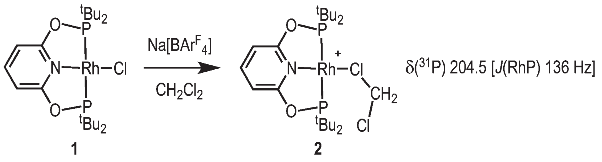
Coordinatively and electronically unsaturated transition-metal pincer complexes, [M(pincer)], are key intermediates in alkane dehydrogenation processes,[1] as well as other catalytic transformations.[2] They have also played a major role in the elucidation of fundamental bond transformations, such as 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 (*ca.* −110 °C to −150 °C) protonation of the corresponding $Rh(^{tBu}PONOP)R$ precursors using $[H(OEt_2)_2][BAr^F{}_4]$ in $CDF_2Cl–CH_2Cl_2$ solvent to give $[Rh(^{tBu}PONOP)(H\text{-}R)][BAr^F{}_4]$ [$^{tBu}PONOP = 2,6\text{-}(^tBu_2PO)_2C_5H_3N$; R = Me, Et; $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$], Scheme 1.[4] Such complexes are key, but transient, intermediates in C–H bond activation processes. On warming above −87 °C (R = Me) or −130 °C (R = Et) they lose alkane and generate complexes tentatively characterised *in situ* on the basis of ^{31}P NMR spectroscopy as $[Rh(^{tBu}PONOP)(solv)][BAr^F{}_4]$ (solv = CDF_2Cl or CD_2Cl_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 CH_2Cl_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 ^{tBu}PNP [$2,6\text{-}(^tBu_2PCH_2)_2C_5H_3N$] results in C–Cl bond activation of the solvent molecule.



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

Addition of $Na[BAr^F{}_4]$ to a CH_2Cl_2 solution of $Rh(^{tBu}PONOP)Cl$, **1**,[4a] results in the formation of orange $[Rh(^{tBu}PONOP)(\kappa^1\text{-}ClCH_2Cl)][BAr^F{}_4]$, **2** (Scheme 2). Filtration and removal of the solvent affords **2** in good isolated yield as a powder. Complex **2** can be recrystallised from CH_2Cl_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, $[Rh(^{tBu}PONOP)(\kappa^1\text{-}N_2)][BAr^F{}_4]$, **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**.‡ 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



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

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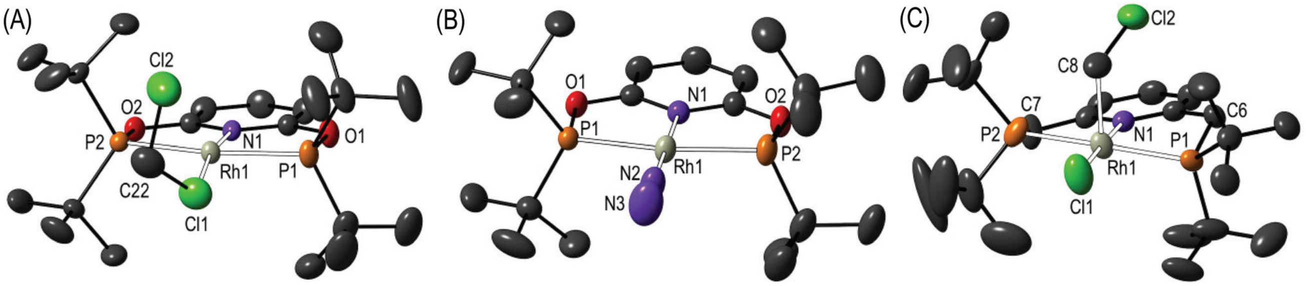


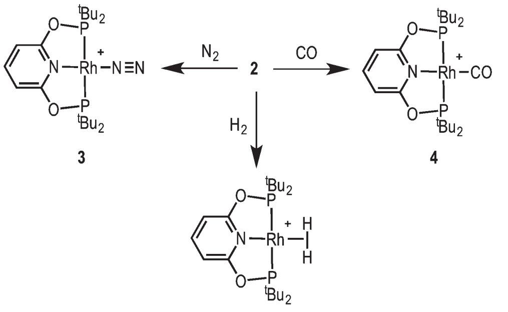
Fig. 1 Solid-state structures of: (A) Complex **2**; (B) Complex **3**; (C) Complex **5**. Displacement ellipsoids are shown at the 50% probability level, hydrogen atoms and the $[BAr^F{}_4]^-$ anions are not shown. Selected bond lengths (Å) and angles (°): (**2**) Rh1–Cl1, 2.350(2); Rh1–N1, 2.011(4); 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 $[Rh(^{tBu}PNP)(H)Cl]$-$[BAr^F{}_4]$, **6**, at the same lattice position in a 50 : 50 ratio.‡

2 and **3**; as in neat CD_2Cl_2 under the same Ar atmosphere **2** does not go onto to form **3** to the detection limit of $^{31}P\{^1H\}$ NMR spectroscopy. The solid-state structure (Fig. 1A) shows a pseudo square planar cationic $[Rh(^{tBu}PONOP)]^+$ centre co-ordinated in the fourth position by a CH_2Cl_2 molecule. The Rh–Cl1 distance [2.350(2) Å] is significantly shorter than reported for related $[RhCp^*(PMe_3)(Ph)(\kappa^1\text{-}ClCH_2Cl)][BAr^F{}_4]$,[6] 2.512(2) Å, and $[RhCp^*(PMe_3)(Me)(\kappa^1\text{-}ClCH_2Cl)][BAr^F{}_4]$, 2.488(1) Å $Cp^* = \eta^5\text{–}C_5Me_5$).[7] Complex **2** adds to the relatively small number of CH_2Cl_2 complexes that have been crystallographically characterised, and in particular CH_2Cl_2 adducts of pincer, or closely related, complexes.[8]

Although the short Rh–Cl distance might suggest a stronger interaction in **2**, in solution (*vide infra*) rapid exchange between solvent and bound CH_2Cl_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_2Cl_2 complexes in which the bound C–Cl bond is longer.[8,9] We suggest that the slight lengthening of C22–Cl2 may be due to a number of weak C–H···Cl hydrogen bonds between proximal ^{t}Bu groups and Cl2.[10]

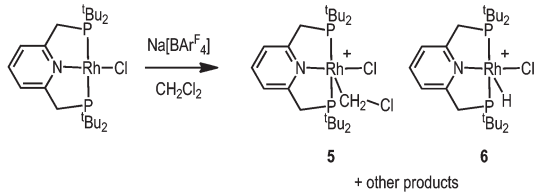
Complex **2** is stable in the solid-state under an Ar atmosphere, and in solution (CD_2Cl_2) for at least 1 week. In the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) a single resonance is observed at δ 204.5 [J(RhP) 136 Hz]. These data are identical to those previously reported by Brookhart and co-workers for the complex tentatively characterised as $[Rh(^{tBu}PONOP)(CH_2Cl_2)][BAr^F{}_4]$, *i.e.* **2**. The ^{t}Bu groups are observed as a single environment in the ^1H NMR spectrum. The bound CH_2Cl_2 ligand is not observed, even at −80 °C in the $^{13}C\{^1H\}$ NMR spectrum, presumably as it is undergoing fast exchange with the solvent.[11] 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_2Cl_2 solution of **2** forms the previously reported dihydrogen complex $[Rh(^{tBu}PONOP)(\eta^2\text{-}H_2)][BAr^F{}_4]^{12}$ [$\delta(^1H)$ −8.27, lit. −8.26]. Addition of N_2 forms the new complex $[Rh(^{tBu}PONOP)(\kappa^1\text{-}N_2)]$-$[BAr^F{}_4]$, **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–N2, 1.967(3) Å]. The $^{31}P\{^1H\}$ 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 $[Rh(^{tBu}PNP)(\kappa^1\text{-}N_2)][OTf]$ 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.[13] This greater metal-based basicity in the ^{tBu}PNP complexes is reflected in the CO stretching frequencies of the corresponding CO-adducts: $[Rh(^{tBu}PONOP)(CO)][BAr^F{}_4]$, **4** [2020 cm^{-1}] and $[Rh(^{tBu}PNP)(CO)][BAr^F{}_4]$ [1982 cm^{-1}].[14] Complex **4** was prepared by adding CO to a CH_2Cl_2 solution of **2**, further demonstrating the utility of complex **2** in synthesis.



Scheme 3 Reactivity of complex **2**. CH_2Cl_2 solvent. $[BAr^F{}_4]^-$ anions are not shown.

The difference in electron-donating power of the ^{tBu}PONOP *versus* ^{tBu}PNP ligands can also been shown by the attempted synthesis of the CH_2Cl_2 adduct of the $\{Rh(^{tBu}PNP)\}^+$ fragment, analogous to complex **2**. Rather than simple coordination, this resulted in a number of products as measured by $^{31}P\{^1H\}$ NMR spectroscopy. Analysis of single crystals suitable for an X-ray



Scheme 4 Reactivity of Rh(^{tBu}PNP)Cl[15] with Na[BAr$^F_4$]. CH_2Cl_2 solvent. [BAr$^F_4$]$^-$ anions are not shown.

diffraction study, obtained from recrystallisation of the reaction mixture, demonstrated co-crystallisation of two complexes [Rh(^{tBu}PNP)(CH_2Cl)Cl][BAr$^F_4$], **5**, and [Rh(^{tBu}PNP)-(H)Cl][BAr$^F_4$], **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 δ −15.48 (relative integral relative to [BAr$^F_4$] 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 CD_2Cl_2 afforded mixture of products, from which [Rh(^{tBu}PNP)-(η^2-H_2)][BAr$^F_4$] could be identified as the major species present.[16]

Conclusions

The CH_2Cl_2 complex [Rh(^{tBu}PONOP)(κ^1-$ClCH_2Cl$)][BAr$^F_4$] 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.[4] Synthesis has been achieved by an alternative halide-abstraction route in CH_2Cl_2 solvent, starting from a readily available chloride precursor. This complex, with its weakly bound CH_2Cl_2 ligand, also acts as a useful synthon 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

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Notes and references

‡ Crystal data: (**2**) $RhP_2O_2NCl_2C_{22}H_{41}\cdot C_{32}H_{12}BF_{24}$, Monoclinic ($C2/c$), a = 16.9996(5) Å, b = 18.1716(4) Å, c = 39.8254(10) Å, $\alpha = \gamma = 90°$, β = 96.458(2)°, volume = 12 224.4(5) Å^3, Z = 8, λ = 0.71073 Å, T = 150(2) K, μ = 0.53 mm^{-1}, 16 021 independent reflections [R(int) = 0.029], R_1 = 0.0814, wR_2 = 0.1692 [$I > 2\sigma(I)$]. CCDC: 1044744; (**3**): $RhP_2O_2N_3C_{21}H_{39}\cdot C_{32}H_{12}BF_{24}$, Monoclinic ($C2/c$), a = 16.8578(4) Å, b = 18.1533(3) Å, c = 39.7792(7) Å, $\alpha = \gamma = 90°$, β = 95.9972(17)°, volume = 12 106.8(4) Å^3, Z = 8, λ = 1.54180 Å, T = 150(2) K, μ = 3.83 mm^{-1}, 12 215 independent reflections [R(int) = 0.031], R_1 = 0.0483, wR_2 = 0.1183 [$I > 2\sigma(I)$]. CCDC: 1044745; (**5**/**6**) $RhP_2NCl_2C_{24}H_{45}\cdot C_{32}H_{12}BF_{24}$: $RhP_2NClC_{23}H_{44}\cdot C_{32}H_{12}BF_{24}$, Monoclinic ($P2_1/c$), a = 13.8327(2) Å, b = 23.4907(3) Å, c = 20.1051(2) Å, $\alpha = \gamma = 90°$, β = 97.5982(11)°, volume = 6475.59(4) Å^3, Z = 2, λ = 1.54180 Å, T = 150(2) K, μ = 4.12 mm^{-1}, 12 878 independent reflections [R(int) = 0.029], R_1 = 0.1064, wR_2 = 0.2958 [$I > 2\sigma(I)$]. CCDC: 1044741.

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