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A CH₂Cl₂ complex of a [Rh(pincer)]⁺ cation^{\dagger}

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The CH₂Cl₂ complex [Rh(^{tBu}PONOP)(κ^1 -ClCH₂Cl)][BAr^F₄] is reported, that also acts as a useful synthon for other complexes such as N₂, CO and H₂ 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(OEt₂)₂][BAr^F₄] in $CDF_2Cl-CH_2Cl_2$ solvent to give $[Rh(^{tBu}PONOP)(H-R)][BAr^F_4]$ $[^{tBu}PONOP = 2,6-(^{t}Bu_2PO)_2C_5H_3N; R = Me, Et; Ar^F = 3,5-(CF_3)_2C_6H_3],$ 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 ³¹P NMR spectroscopy as [Rh(^{tBu}PONOP)(solv)][BAr^F₄] (solv = CDF₂Cl or CD₂Cl₂). 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- $(^{t}Bu_2PCH_2)_2C_5H_3N$] 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 coworkers). $[BAr^{F}_{4}]^{-}$ anions are not shown.⁴

Addition of Na[BAr^F₄] to a CH₂Cl₂ solution of Rh(^{*t*Bu}PO-NOP)Cl, **1**, ^{4*a*} results in the formation of orange [Rh(^{*t*Bu}PONOP)-(κ^1 -ClCH₂Cl)][BAr^F₄], **2** (Scheme 2). Filtration and removal of the solvent affords **2** in good isolated yield as a powder. Complex **2** can be recrystallised from CH₂Cl₂–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(^{*t*Bu}PONOP)(κ^1 -N₂)][BAr^F₄], **3**, in an approximate **1**:1 ratio (as measured by ³¹P 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 N₂ comes from trace (1–2 ppm) levels of N₂ present in the argon, as has been noted previously,⁵ and is driven by relative solubilities of



Scheme 2 Synthesis of complex **2**. $[BAr_{4}^{F}]^{-}$ 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 $[BAr_4^{F}]^-$ 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(^{Bu}PNP)(H)Cl]-[BAr^F₄], **6**, at the same lattice position in a 50 : 50 ratio.‡

2 and 3; as in neat CD₂Cl₂ under the same Ar atmosphere 2 does not go onto to form 3 to the detection limit of ³¹P{¹H} NMR spectroscopy. The solid-state structure (Fig. 1A) shows a pseudo square planar cationic $[Rh(^{Hu}PONOP)]^+$ centre coordinated in the fourth position by a CH₂Cl₂ molecule. The Rh–Cl1 distance [2.350(2) Å] is significantly shorter than reported for related $[RhCp^*(PMe_3)(Ph)(\kappa^1-ClCH_2Cl)][BAr^F_4]$, 6 2.512(2) Å, and $[RhCp^*(PMe_3)(Me)(\kappa^1-ClCH_2Cl)][BAr^F_4]$, 2.488(1) Å Cp* = η^5 –C₅Me₅).⁷ Complex 2 adds to the relatively small number of CH₂Cl₂ complexes that have been crystallographically characterised, and in particular CH₂Cl₂ 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 ^tBu 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 ${}^{31}P{}^{1}H$ 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 $[Rh({}^{tBu}PONOP)(CH_2Cl_2)][BArF_4]$, *i.e.* **2**. The ${}^{t}Bu$ groups are observed as a single environment in the ${}^{1}H$ NMR spectrum. The bound CH_2Cl_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. 11 The electrospray ionisation mass spectrum of **2** using N₂ 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 H₂ to a CD₂Cl₂ solution of 2 forms the previously reported dihydrogen complex [Rh(^{*t*Bu}PONOP)(η^2 -H₂)][BAr^F₄]¹² [δ (¹H) -8.27, lit. -8.26]. Addition of N₂ forms the new complex [Rh(^{*t*Bu}PONOP)(κ^{-1} -N₂)]-



Scheme 3 Reactivity of complex 2. CH_2Cl_2 solvent. $[BAr^F_4]^-$ anions are not shown.

 $[BAr_{4}^{F}]$, 3, for which a solid-state structure is shown in Fig. 1B. This demonstrates an end-on bound, monomeric, N₂ adduct [N–N, 1.063(5); Rh–N2, 1.967(3) Å]. The ${}^{31}P{}^{1}H{}$ NMR spectrum displays a single environment at δ 211.0 [*I*(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 $[Rh(^{tBu}PNP)(\kappa^1-N_2)][OTf]$ 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 N2 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^F₄], 4 $[2020 \text{ cm}^{-1}]$ and $[Rh(^{tBu}PNP)(CO)][BAr_{4}^{F}]$ [1982 cm⁻¹].¹⁴ Complex 4 was prepared by adding CO to a CH₂Cl₂ solution of 2, further demonstrating the utility of complex 2 in synthesis.

The difference in electron-donating power of the ^{*t*Bu}PONOP *versus* ^{*t*Bu}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 ³¹P{¹H} NMR spectroscopy. Analysis of single crystals suitable for an X-ray



Scheme 4 Reactivity of $Rh(^{tBu}PNP)Cl^{15}$ with $Na[BAr_4^F]$. CH_2Cl_2 solvent. $[BAr_4^F]^-$ 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 ¹H 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 H₂ to this mixture of 5 and 6 in CD_2Cl_2 afforded mixture of products, from which $[Rh(^{tBu}PNP)-(\eta^2-H_2)][BAr^F_4]$ could be identified as the major species present.¹⁶

Conclusions

The CH_2Cl_2 complex $[Rh(^{tBu}PONOP)(\kappa^1-ClCH_2Cl)][BAr^F_4]$ 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 N₂, CO and H₂ 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.

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Notes and references

[‡]Crystal data: (2) RhP₂O₂NCl₂C₂₂H₄₁·C₃₂H₁₂BF₂₄, Monoclinic (*C*2/*c*), *a* = 16.9996(5) Å, *b* = 18.1716(4) Å, *c* = 39.8254(10) Å, *α* = *γ* = 90°, *β* = 96.458(2)°, volume = 12 224.4(5) Å³, *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, w*R*₂ = 0.1692 [*I* > 2*σ*(*I*)]. CCDC: 1044744; (3): RhP₂O₂N₃C₂₁H₃₉·C₃₂H₁₂BF₂₄, Monoclinic (*C*2/*c*), *a* = 16.8578(4) Å, *b* = 18.1533(3) Å, *c* = 39.7792(7) Å, *α* = *γ* = 90°, *β* = 95.9972(17)°, volume = 12 106.8(4) Å³, *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, w*R*₂ = 0.1183 [*I* > 2*σ*(*I*)].

CCDC: 1044745; (5/6) RhP₂NCl₂C₂₄H₄₅·C₃₂H₁₂BF₂₄: RhP₂NCl₂₃H₄₄·C₃₂H₁₂BF₂₄, Monoclinic (P_{21}/c), a = 13.8327(2) Å, b = 23.4907(3) Å, c = 20.1051(2) Å, $a = \gamma = 90^{\circ}$, $\beta = 97.5982(11)^{\circ}$, volume = 6475.59(4) Å³, Z = 2, $\lambda = 1.54180$ Å, T = 150(2) K, $\mu = 4.12$ mm⁻¹, 12 878 independent reflections [R(int) = 0.029], $R_1 = 0.1064$, w $R_2 = 0.2958$ [$I > 2\sigma(I$]]. CCDC: 1044741.

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