Rhodium Pincers

Oxidative Addition of Biphenylene and Chlorobenzene to a Rh(CNC) Complex

Amy E. Kynman,[a] Samantha Lau,[a] Sean O. Dowd,[b] Tobias Krämer,*[b,c] and Adrian B. Chaplin*,[a]

Abstract: The synthesis and organometallic chemistry of rhodium(I) complex [Rh(CNC–Me)(SOMe2)] [BArF$_4$], featuring NHC-based pincer and labile dimethyl sulfoxide ligands, is reported. This complex reacts with biphenylene and chlorobenzene to afford products resulting from selective C–C and C–Cl bond activation, [Rh(CNC–Me)(2,2′-biphenyl)(OSMe2)][BArF$_4$] and [Rh(CNC–Me)(Ph)Cl(OSMe2)][BArF$_4$], respectively. A detailed DFT-based computational analysis indicates that C–H bond oxidative addition of these substrates is kinetically competitive, but in all cases endergonic: contrasting the large thermodynamic driving force calculated for insertion of the metal into the C–C and C–Cl bonds, respectively. Under equivalent conditions the substrates are not activated by the phosphine-based pincer complex [Rh(PNP-iPr)(SOMe$_2$)][BArF$_4$].

Introduction

Combining their strong σ-donor characteristics with the favourable thermal stability and reaction control possible with a mer-tridentate geometry, pincer ligands featuring flanking NHC groups have emerged as an attractive ligand class with a diverse variety of applications, particularly in transition metal catalysis.[1,2] The ability of NHCs to form adducts across the periodic table notably allows for rich and varied coordination chemistry. Curiously and despite the enduring prominence of rhodium complexes in organometallic chemistry and catalysis,[3] however, NHC-based pincer complexes of this precious metal have not been widely explored beyond rather innocuous rhodium(I) carbonyl derivatives.[4,5] Guisado-Barrios and Bezuidenhout's mesionic carbene complex A, that promotes selective alkyne homocoupling and hydrothiolation reactions,[6] and Kunz's complexes of homoallyl functionalised CNC ligands, which catalyse the isomerisation of epoxides into ketones in the presence of lithium salts,[7] are notable exceptions and highlight the merit of such endeavour (Scheme 1). As part of our work exploring the chemistry of NHC-based pincer ligands, we have also recently prepared rhodium(I) ethylene complex C and shown it to be a highly effective catalyst for terminal alkyne homocoupling reactions and, in the case of aryl-substituted substrates, the subsequent formation of bicyclo[4.2.0]octa-1,5,7-trienes.[8,9]

Scheme 1. Reactivity and catalytic activity of selected Rh(CNC) pincer complexes.

In the context of advancing the organometallic chemistry of rhodium complexes of NHC-based pincer ligands relevant to

---

[a] A. E. Kynman, Dr. S. Lau, Dr. A. B. Chaplin
Department of Chemistry, University of Warwick,
Gibbet Hill Road, Coventry CV4 7AL, UK
E-mail: a.b.chaplin@warwick.ac.uk
http://go.warwick.ac.uk/abchaplin

[b] S. O. Dowd, Dr. T. Krämer
Department of Chemistry, Maynooth University,
Co. Kildare, Maynooth, Ireland.
E-mail: tobias.kraemer@mu.ie
http://www.maynoothuniversity.ie/people/tobias-kr-mer

[c] Dr. T. Krämer
Hamilton Institute, Maynooth University,
Co. Kildare, Maynooth, Ireland.

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000780.

© 2020 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

This manuscript is part of the Special Collection Pincer Chemistry and Catalysis.
catalysis, we herein report the capacity of dimethyl sulfoxide complex 1 to undergo the selective oxidative addition of the C–C bond of biphenylene, and C–Cl bond of chlorobenzene. There is precedent for reactivity of this type for rhodium, but examples involving pincer ligands are limited to the activation of aryl chlorides by neutral systems. DFT calculations have been used to gain molecular insight and the reactivity of 1 is contrasted to that of [Rh(PNP(Ni)Mes)2] [14] and subsequent transmetallation with Milstein’s underexploited rhodium(I) precursor [RhCl(SOMe2)3] in dichloromethane. In this way pristine 1 was obtained in 50% isolated yield, following straightforward crystallisation from dichloromethane/hexane at RT. The spectroscopic characteristics of 1 obtained in this manner are fully congruent with those previously reported, with the N–Me (δ1H 4.95, 5.87) proton resonances the most diagnostic in CD2Cl2.

Results and discussion

1. Convenient new synthesis of 1

We have previously reported that 1 can by isolated following reaction of C with dimethyl sulfoxide, however, the preparation of C is a rather involved three-step procedure from the proligand CNC–Me2HBr, the intermediates involved are appreciably air-sensitive, and 1 was only obtained with an overall yield of 26%. As a more accessible method for this latent source of the reactive (Rh(CNC–Me)+) fragment, we have therefore developed the procedure depicted in Scheme 2. This procedure involves in situ generation of the silver(I) carbene transfer agent [Ag(CNC–Me)]+[BArF4]2 [15] and subsequent transmetallation with Milstein’s underexploited rhodium(I) precursor [RhCl(SOMe2)3] in dichloromethane. In this way pristine 1 was obtained in 50% isolated yield, following straightforward crystallisation from dichloromethane/hexane at RT. The spectroscopic characteristics of 1 obtained in this manner are fully congruent with those previously reported, with the N–Me (δ1H 4.95, 5.87) and diastereotopic N–CH2 (δ1H 4.59, 5.87) proton resonances the most diagnostic in CD2Cl2.

Scheme 2. Convenient synthesis of 1 ([BArF4]2−: counter anion omitted).

2. Reaction of 1 with biphenylene

In the weakly coordinating solvent 1,2-difluorobenzene (DFB), 1 reacts readily with biphenylene (2 equiv.) at RT to afford the rhodium(III) complex [Rh(CNC–Me)(2,2′-biphenyl)-(OSMe2)] [BArF4]2, with 74% conversion observed after 24 h (Figure 1). No intermediates were observed in situ by 1H NMR spectroscopy during the reaction and when this reaction was repeated at 50 °C, 3 was obtained in quantitative spectroscopic yield within 3 h. The new complex was subsequently isolated in 74% yield on a larger scale under similar conditions and fully characterised, including in the solid state by single-crystal X-ray diffraction. The formation of 3 is marked in solution by an up-field shift of the N–Me (δ1H 2.68 cf. 3.83) and enhanced separation of the diastereotopic N–CH2 (δ1H 5.01, 6.02 cf. 4.95, 5.87) proton resonances, but overall C2 symmetry indicates dynamic dissociation of dimethyl sulfoxide (δ1H 2.26 cf. free 2.55) and fast pseudo rotation of the 2,2′-biphenyl ligand on the NMR timescale. In the solid state the sulfoxide is bound through the oxygen atom (2.307(2) Å) and this change in coordination mode compared to 1 is in line with expectation for the increase in metal oxidation state. The structure is also notable for an appreciable disparity in the Rh–C contacts associated with the 2,2′-biphenyl ligand (2.013(4), 1.997(4) Å), with the shorter bond trans to weakly bound sulfoxide in accord with trans-influence arguments: in a closely related macrocyclic analogue, where the coordination sphere is completed instead by an agostic interaction, the difference in Rh–C contacts is more pronounced (2.021(2), 1.992(3) Å). The formation of 3 is faster than activation of biphenylene by [Rh(PPr3)2(C6H5F)][BArF4] (5 days @ 40 °C), which proceeds under similar conditions via an intermediate η5-biphenylene derivative and results in the formation of [Rh(PPr3)2(2,2′-biphenyl)][BArF4]. Calculations support a mechanism involving ring slippage and concerted C–C bond oxidative addition in this case. Insertion of the metal into the C–C bond of biphenylene has been reported for iridium pincer complexes (Ir(PCP)) (PCP = 2,6-(bPyCH2)2C6H4, 2,6-(iPrCH2)2C6H4) and these more structurally similar systems are a valuable mechanistic reference point. Formation of the 2,2′-biphenyl product is complete within 30 min at RT for the less bulky iPr-substituted variant, but thermolysis at 125 °C for 24 h is required for the iBu-substi-
tuted variant. The attenuated nature of the latter usefully, how-
however, enabled kinetic products of biphenylene C–H bond activa-
tion (6-position) to be isolated. As we have previously demon-
strated the CNC–Me pincer ligand is able to interconvert be-
tween mer- and fac-coordination modes,[9] both aforemen-
tioned mechanistic scenarios – π complex formation and inter-
mediate C–H bond activation – are possible and we turned to
DFT calculations using the M06-L/SDD/6-31G(d,p) level of the-
ory to help quantify the viability of these possibilities (Figure 2).

Ring flipping of one of the bridging methylene groups of
the pincer backbone (ΔG‡ = 11.4 kcal mol⁻¹), is predicted to
enable coordination of biphenylene through the central cyclo-
butadiene ring, viz., [Rh(fac-CNC–Me)(η⁴-biphenylene)]⁺, upon
substitution of dimethyl sulfoxide and is associated with a small
energetic penalty of ΔG = +11.2 kcal mol⁻¹. Subsequent C–C
bond insertion, however, gives rise to a prohibitively high calcu-
lated barrier (ΔG‡ = 40.7 kcal mol⁻¹ from 1) ruling out this
mechanism. Eight distinct pathways were identified for the
C–H bond activation of biphenylene, with calculated activation
barriers ranging from ΔG‡ = 17.8 to 25.8 kcal mol⁻¹, but all give
rise to thermodynamically unfavourable rhodium(III) products
(ΔG = +4.2–9.0 kcal mol⁻¹). Whilst C–C bond oxidative addition
is associated with a generally higher calculated barrier (ΔG‡ = 23.7 kcal mol⁻¹ from 1), the reaction proceeds downhill by ΔG = −34.1 kcal mol⁻¹ in line with expectation for the associated relief
of ring strain.[20] The computational analysis thus suggests: (a)

the pincer ligand maintains a mer-coordination mode through-
out the reaction, (b) whilst faster, competing C–H bond is re-
versible, and (c) formation of 3 is the only thermodynamically
favoured product and is irreversible. These conclusions are fully
consistent with experiment; notably the lack of intermediates
observed experimentally during the formation of 3.

In contrast to the activation observed for 1, no reaction was
apparent upon heating 2 with biphenylene (2 equiv.) in DFB at
50 °C for 24 h.

3. Reaction of 1 with Chlorobenzene

On turning to the reaction between 1 and chlorobenzene, it
quickly became apparent from in situ NMR experiments that
more forcing conditions were required to induce reactivity com-
pared to the oxidative addition of biphenylene. Using 100 equiva-
lents of substrate, 15% conversion into [Rh(CNC–Me)(Ph)Cl-
(OSEMe₂)][BARF₄] 4 was observed at RT after 24 h (Figure 3). Higher
conversion could be achieved at 50 °C (62% after 24 h), with 4
obtained in quantitative spectroscopic yield within 6 h when the
reaction was repeated at 85 °C. This new rhodium(III) complex
was subsequently prepared on a larger scale and fully character-
ised, including in the solid state by single-crystal X-ray diffraction.
Complex 4 is characterised in CD₂Cl₂ solution by sharp ¹H and
¹³C resonances that indicate adoption of C₂ symmetry (N–Me,
δ₁H 3.32, 4.39; N-CH₂, δ₁H 4.13, 4.57, 5.11, 6.44; Rh–C(Ph), δ₁³C 142.7, 1JRhC = 32 Hz. Coordination of dimethyl sulfoxide is presumed to be dynamic on the NMR time scale by comparison to

Figure 3. Activation of chlorobenzene, [BARF₄]⁻ counter anions omitted (top). Solid-state structure of 4, with thermal ellipsoids drawn at 30% probability and solvent omitted (bottom). Selected bond lengths [Å] and angles [deg]: Rh1–N101, 2.091(3); Rh1–C109, 2.053(4); Rh1–C115, 2.063(4); Rh1–C3, 2.006(4); Cl2–Rh1–C115, 175.12(16); C3–Rh1–Cl2, 91.44(12); N101–Rh1–Cl2, 176.57(9); O15–Rh1–C3, 179.20(14). 3 and the magnitude of the ¹H chemical shift (δ₁H 2.51 cf. free 2.55). On the basis of the solid-state structure and supported by a computational analysis of the possible isomers, we assign a square pyramidal structure in solution with the free coordination site trans to the aryl. A conclusion congruent with the considerably larger trans-influence of the aryl compared that of the halide. Indeed, this difference can be quantified directly by comparison of the solid-state metrics of 3 and 4, where a considerably shorter Rh–N contact is evident for the latter (2.091(3) cf. 2.239(3) Å) despite the other common metal-based being very similar (e.g. Rh1–C3 = 2.013(4) Å, 3; 2.006(4) Å, 4).

Computational analysis of the activation of chlorobenzene by 1 yields a similar picture to that found for biphenylene (Figure 4). In this case, the ability of the pincer ligand to adopt a fac-coordination mode enables a sequence involving η⁴-coordination of the substrate, ring slippage, and oxidative addition of the C–Cl bond to be more competitive with “direct” insertion (ΔΔG° = +2.4 kcal mol⁻¹ from 1) than the biphenylene equivalent (ΔΔG° = +17.0 kcal mol⁻¹ from 1). The “direct” insertion pathway proceeds via formation of a κ¹Cl-adduct of chlorobenzene and is associated with an overall calculated barrier of ΔG‡i = +26.1 kcal mol⁻¹, which is higher than that predicted for the C–C bond activation of biphenylene (ΔG‡i = +23.7 kcal mol⁻¹) but in line with the relative reactivity observed experimentally. Ten distinct pathways were identified for the C–H bond activation of chlorobenzene. Some of these compete kinetically with the thermodynamically preferred insertion of the metal into the C–Cl bond (ΔG = –22.3 kcal mol⁻¹), but all are distinctly endergonic. Computational analysis of the activation of chlorobenzene by a related neutral Rh(PNP) pincer come to a similar conclusion. 21, 22
In contrast to the activation observed for 1, no reaction was apparent upon heating 2 with chlorobenzene (100 equiv.) in DFB at 85 °C for 24 h.

Conclusions

We have shown that [Rh(CNC–Me)(SOMe2)][BArF4] is a readily accessible rhodium(I) complex of a NHC-based pincer ligand, which undergoes the selective oxidative addition of the C–C bond of biphenylene and the C–Cl bond of chlorobenzene. A detailed DFT-based computational analysis indicates that C–H bond activation of these substrates is kinetically competitive, but in all cases endergonic: contrasting the large thermodynamic driving force calculated for insertion of the metal into the C–C and C–Cl bonds, respectively. The decisive role of the flanking NHC donor groups was confirmed by comparison to a structural NMR of biphenylene and chlorobenzene. A decomposition observed after 24 h. Spectroscopic data are consistent with the literature.[8]

1H NMR (300 MHz, CD2Cl2): δ 7.69–7.75 (m, 8H, ArF), 7.68 (t, JHH = 7.9, 1H, py), 7.55 (br, 4H, ArF) 7.32 (d, JHH = 7.8, 2H, py), 7.07 (br, 2H, NCH), 6.80 (br, 2H, NCH), 5.87 (vbr, 2H, CH2) 4.95 (vbr, 2H, CH2) 3.83 (s, 6H, NCH3) 3.15 (s, 6H, SOMe2).

3. NMR scale reactions of [Rh(CNC-Me)(SOMe2)][BArF4] (1)

Reactions were performed using 20 mmol·L−1 solutions of Rh(COD)2][BArF4] by the pincer ligand (Scheme 3), and thereafter SOMe2 using a methodology developed in our laboratories.[14]

4. Experimental Section

1. General Methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C in vacuo overnight. CD2Cl2 was freeze-pump-thaw degassed and dried with 3 Å molecular sieves. 1,2-Difluorobenzene (DFB) and fluorobenzene were pre-dried with alumina, distilled from CaH2 and dried twice over 3 Å molecular sieves. CNC-Me · 2HBr, [23] Na[BArF4]· 2HBr,[23] Na[BArF4]· 2HBr (100 mg, 0.293 mmol) and PNP-Pr (87.7 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 to give an orange solution. The solution was layered with hexane to yield an orange crystalline solid, which was characterised in the solid state by X-ray diffraction and combustion analysis. Yield: 316 mg (45%). This structure of this compound is less well-defined in solution as a result of dynamic fragmentation.

31P[1H] NMR (121 MHz, DFB/C6D6): δ = 44.4 (d, 1JPP = 134).

NMR spectra of Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-Pr (45.1 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

4.1. Preparation of [(PNP-Pr)2Rh(PCOD)2][BArF4] (2)

A solution of Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-Pr (45.1 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

4.2. Preparation of [Rh(PNP-Pr)(SOMe2)][BArF4] (2)

A solution of [Rh(CNC-Me)(SOMe2)][BArF4] (19.8 mg, 7.3 μmol) and SOMe2 (0.10 mL) in DFB (2 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

1H NMR (300 MHz, CD2Cl2): δ 7.73 (t, 1JHH = 7.8, 1H, py), 7.97–7.69 (m, 8H, ArF), 7.56 (br, 4H, ArF) 7.36 (d, 1JHH = 7.8, 2H, py), 3.41 (vbr, 2H, CH2) 3.26 (s, 6H, SOMe2) 2.24–2.39 (m, 4H, 2 × CH), 1.34 (app q, J = 8, 12H, CH3), 1.09 (app q, J = 7, 12H, CH3).

31P[1H] NMR (121 MHz, DFB/C6D6): δ = 338.4 (d, 1JPP = 134).

NMR spectra of Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-Pr (45.1 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

4.1. Preparation of [(PNP-Pr)2Rh(PCOD)2][BArF4] (2)

A solution of [Rh(CNC-Me)(SOMe2)][BArF4] (19.8 mg, 7.3 μmol) and SOMe2 (0.10 mL) in DFB (2 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

4.2. Preparation of [Rh(PNP-Pr)(SOMe2)][BArF4] (2)

A solution of [Rh(CNC-Me)(SOMe2)][BArF4] (19.8 mg, 7.3 μmol) and SOMe2 (0.10 mL) in DFB (2 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

1H NMR (300 MHz, CD2Cl2): δ 7.73 (t, 1JHH = 7.8, 1H, py), 7.97–7.69 (m, 8H, ArF), 7.56 (br, 4H, ArF) 7.36 (d, 1JHH = 7.8, 2H, py), 3.41 (vbr, 2H, CH2) 3.26 (s, 6H, SOMe2) 2.24–2.39 (m, 4H, 2 × CH), 1.34 (app q, J = 8, 12H, CH3), 1.09 (app q, J = 7, 12H, CH3).

31P[1H] NMR (121 MHz, DFB/C6D6): δ = 338.4 (d, 1JPP = 134).

NMR spectra of Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-Pr (45.1 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

1H NMR (300 MHz, CD2Cl2): δ 7.73 (t, 1JHH = 7.8, 1H, py), 7.97–7.69 (m, 8H, ArF), 7.56 (br, 4H, ArF) 7.36 (d, 1JHH = 7.8, 2H, py), 3.41 (vbr, 2H, CH2) 3.26 (s, 6H, SOMe2) 2.24–2.39 (m, 4H, 2 × CH), 1.34 (app q, J = 8, 12H, CH3), 1.09 (app q, J = 7, 12H, CH3).

31P[1H] NMR (121 MHz, DFB/C6D6): δ = 338.4 (d, 1JPP = 134).

NMR spectra of Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-Pr (45.1 mg, 0.26 mmol) in DFB (3 mL) was stirred at RT for 12 h. The solution was layered with hexane to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (7%).

1H NMR (300 MHz, CD2Cl2): δ 7.73 (t, 1JHH = 7.8, 1H, py), 7.97–7.69 (m, 8H, ArF), 7.56 (br, 4H, ArF) 7.36 (d, 1JHH = 7.8, 2H, py), 3.41 (vbr, 2H, CH2) 3.26 (s, 6H, SOMe2) 2.24–2.39 (m, 4H, 2 × CH), 1.34 (app q, J = 8, 12H, CH3), 1.09 (app q, J = 7, 12H, CH3).

31P[1H] NMR (121 MHz, DFB/C6D6): δ = 338.4 (d, 1JPP = 134).
Reactions were performed using 20 mmolL⁻¹ solutions of [Rh(CNC-Me)(Ph)Cl(OSMe₂)][BArF₄] (3) in DFB (0.5 mL) and biphenylene (3.04 mg, 0.01 mmol) in DFB (0.5 mL) was heated at 50 °C for 16 h. The resulting solution was layered with hexane to afford the yellow crystalline product on diffusion. Yield: 23 mg (78%).

A solution of 1 (26.2 mg, 20.0 μmol) and biphenylene (3.04 mg, 20.0 μmol) in DFB (0.5 mL) was heated at 50 °C for 16 h. The resulting solution was layered with hexane to afford the yellow crystalline product on diffusion. Yield: 23 mg (78%).

**Preparation of [Rh(CNC-Me)(Ph)Cl(OSMe₂)][BArF₄]**

A solution of 1 (150 mg, 0.114 mmol) in chlorobenzene (6 mL) was heated at 50 °C for 8 h. The product was precipitated with excess hexane (ca. 10 mL), isolated by filtration, washed with hexane and dried in vacuo. Yield: 120 mg (74%).

**NMR scale reactions of [Rh(PNP-Pr)(OSMe₂)][BArF₄]**

Reactions were performed using 20 mmolL⁻¹ solutions of 2 in DFB within J. Young valve NMR tubes and monitored periodically by ¹H and ³¹P NMR spectroscopy.

**6. Preparation of [Rh(CNC-Me)(Ph)Cl(OSMe₂)][BArF₄]**

A solution of 1 (26.2 mg, 20.0 μmol) and biphenylene (3.04 mg, 20.0 μmol) in DFB (0.5 mL) was heated at 50 °C for 16 h. The resulting solution was layered with hexane to afford the yellow crystalline product on diffusion. Yield: 23 mg (78%).

1H NMR (500 MHz, CD₂Cl₂): δ 0.84 (t, J_HH = 7.7, 1H, py), 7.69–7.76 (m, 8H, ArF), 7.64 (d, J_HH = 7.7, 2H, py), 7.56 (br, 4H, ArF), 7.36 (d, J_HH = 7.5, 2H, biph), 7.03 (br, 2H, NCH), 6.99 (d, J_HH = 7.6, 2H, biph), 6.73 (t, J_HH = 7.5, 2H, biph), 6.64 (br, 2H, NCH), 6.02 (vbr, 2H, CH₂), 5.01 (vbr, 2H, CH₂), 2.68 (s, 6H, NCH₃), 2.26 (s, 6H, SOMe₂).

13C{¹H} NMR (126 MHz, CD₂Cl₂): δ 175.6 (d, J_{BC} = 43, NCH₃), 163.2 (HMBC, biph), 162.3 (q, J_{CB} = 50, ArF), 156.7 (s, py), 154.3 (s, biph), 140.6 (s, py), 135.3 (s, ArF), 135.1 (s, biph), 129.4 (qq, J_{FC} = 32, J_{CB} = 3, ArF), 125.8 (s, py), 125.2 (q, J_{CB} = 272, ArF), 125.0 (s, biph), 124.2 (s, NCH), 123.1 (s, biph), 121.6 (s, NCH), 120.5 (s, biph), 118.0 (sept, J_{JCB} = 4, ArF), 55.7 (s, CH₂), 40.2 (s, SOMe₂), 37.1 (s, NCH₃).

HR ESI-MS (180 °C, 4 kV) positive ion: 482.0606 ([M – OSMe₂]+, calcd. 482.0613) m/z.

Anal. Calcd for C₅₃H₅₃BF₂₄NOP₂RhS (1383.67 g mol⁻¹): C, 46.01; H, 2.68; N, 4.92. Found: C, 46.48; H, 2.68; N, 4.92.

**Crystallographic details**

Data were collected on a Rigaku Oxford Diffraction SuperNova AtlasS2 CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.5418 Å) radiation and an Oxford Cryosystems N-HeliX low temperature device [150(2) K]. Data were collected and reduced using CrysalisPro and refined using SHELXL,[²⁷] through the Olex2 interface.[²⁸]

Deposition Numbers 2022453 ([Rh(PNP-Pr)(Bu₂η₂-η³-η⁷-COD)][BArF₄]), 2022454 (2), 2022455 (3), 2022456 (4) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Computational methods**

All electronic structure calculations presented in this paper were carried out using the Gaussian 09 (Revision E01)[²⁹] program suite at the DFT level of theory. Geometries of all compounds were fully optimized without imposing symmetry constraints (C₁ symmetry), employing the Minnesota M06-L local meta-generalized gradient approximation (meta-GGA) functional.[³⁰] The Stuttgart-Dresden (SDD)[³¹] relativistic effective core potential in combination with the associated basis sets were used to describe the Rh centre, augmented with an additional f-type polarisation function (ζ = 1.350).[³²] The 6-31G(d,p) basis sets[³³] developed by Pople and coworkers were used on all lighter atoms (C, Cl, N, and H). Optimized stationary points were characterized by analysis of their analytical second derivatives, with minima having only positive eigenvalues and transition states having exactly one imaginary eigenvalue. In order to identify the minima linked by each transition state, subsequent geometry optimizations were performed in both forward and reverse direction of the transition vector of the transition state coordinate. The frequency calculations also provided thermal and entropic corrections to the total energy in gas phase at T = 298.15 K and p = 1 atm within the rigid-rotor/harmonic oscillator (RRHO) approximation. Dispersion effects were accounted for by applying Grimme’s van der Waals correction (D3 parameterization)[³⁴] during geometry optimizations of all stationary points. Effects due to the presence of a solvent were treated implicitly with a polarisable dielectric model, using the IEFPCM formalism in conjunction with Truhlar’s SMD model[³⁵] in the absence of defined parameters for DFB solvent, default SMD parameters were selected for fluorobenzene and the relative permittivity adjusted to that of DFB (ε = 13.4).[³⁶] All Gibbs energies are reported in kcal mol⁻¹. All structures were visualized using the Chemcraft tool.[³⁷]

**Conflicts of interest**

There are no conflicts to declare.

**Supporting information**

- Additional computational details (PDF) and optimised geometries (XYZ)
- Primary NMR data (MINOVA)
- Accession Codes: CCDC 2022453–2022456 contain the supplementary crystallographic data for this paper.

**Acknowledgments**

We thank the European Research Council (ERC, grant agreement 637313; A. E. K., S. L., A. B. C.) and Royal Society (UF100592, UF150675, A. B. C.) for financial support. T. K. acknowledges the
Keywords: oxidative addition · rhodium · pincer ligands · computational analysis · DFT calculations

[1] a) C. M. Storey, H. Lee, W. Yang, K. S. Chan, J. Organomet. Chem. 2015, 791, 82–89; d) T. M. Douglas, A. B. Chaplin, A. S. Weller, Organometallics 2008, 27, 2918–2921; e) V. V. Grushin, W. J. Marshall, J. Am. Chem. Soc. 2004, 126, 3068–3069; f) S. Willems, P. Budzelaar, N. Moonen, R. de Gelder, J. Smits, A. Gal, Chem. Eur. J. 2002, 8, 1310–1320.

[12] a) S. G. Curto, M. A. Estereusel, M. Oliiván, E. Ohate, A. Vélez, Organometallics 2017, 36, 114–128; b) S. D. Timpa, M. R. Crimmin, A. B. Chaplin, Organometallics 2013, 31, 427–4282; d) J. A. Wright, A. A. Caruana, R. Dorta, H. Rozenberg, J. Am. Chem. Soc. 2019, 141, 363–3633.

[13] T. M. Hood, B. Lefebvre, M. R. Gyton, A. B. Chaplin, Inorg. Chem. 2019, 58, 7953–7961.

[14] S. D. Pike, M. R. Crimmin, A. B. Chaplin, Chem. Commun. 2017, 53, 3615–3617.

[15] The tetrafluroborate salt has been previously isolated: D. J. Nielsen, K. J. Nolte, W. D. Jones, W. Jones, D. Krog-Jespersen, A. S. Goldman, Dalton Trans. 2014, 43, 16354–16365.

[16] M. Moser, B. Wucher, D. Kunz, F. Rominger, Organometallics 2020, 39, 3615–3617; b) Y. Zhao, M. A. Koon, D. W. Jones, W. D. Jones, W. Jones, D. Krog-Jespersen, A. S. Goldman, Dalton Trans. 2014, 43, 16354–16365.

[17] a) T. M. Storey, R. E. Andrew, A. B. Chaplin, Chem. Eur. J. 2020, in the press, DoI: https://doi.org/10.1002/chem.202002962; b) M. R. Gyton, A. E. Kynman, B. Lefebvre, A. Gallo, J. R. Lewandowski, A. B. Chaplin, Dalton Trans. 2020, 49, 5791–5793; c) M. R. Gyton, B. Lefebvre, A. B. Chaplin, Organometallics 2018, 37, 3963–3971; d) J. A. Wright, A. A. Caruana, R. Dorta, H. Rozenberg, J. Am. Chem. Soc. 2018, 140, 3551–3554; b) W. E. Buschmann, J. S. Miller, K. Bowman-James, C. N. Miller, Inorg. Synth. 2002, 33, 83–91.

[18] a) J. A. Martínez-Martínez, A. S. Weller, Dalton Trans. 2019, 48, 3551–3554; b) W. E. Buschmann, J. S. Miller, K. Bowman-James, C. N. Miller, Inorg. Synth. 2002, 33, 83–91.

[19] E. Neumann, A. Pfaltz, Organometallics 2005, 24, 2008–2011.

[20] W. P. Leung, Q. W. Y. Ip, S. Y. Wong, T. C. W. Mak, Organometallics 2002, 21, 4604–4609.

[21] G. M. Sheldrick, Acta Crystallogr., Sect. C 2015, 71, 3–8.

[22] a) O. Dolumonov, L. J. Bourhis, R. J. Gidley, A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuta, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. D. Dunning, D. J. Defrees, D. J. Fox, Gaussian 09, Revision E01, Gaussian, Inc., Wallingford CT, 2013.

[24] a) Y. Zhao, D. G. Truhlár, J. Chem. Phys. 2006, 125, 194101; b) Y. Zhao, D. G. Truhlár, Acc. Chem. Res. 2008, 41, 157–167.

[25] a) A. N. Buriakov, M. Dolg, H. Stoll, H. Preuß, Theor. Chim. Acta 1990, 77, 123–141.
[32] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 1993, 208, 111–114.

[33] a) W. J. Hehre, R. Ditchfield, J. A. Pople, J. Chem. Phys. 1972, 56, 2257–2261; b) P. C. Hariharan, J. A. Pople, Theor. Chim. Acta 1973, 28, 213–222.

[34] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.

[35] A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378–6396.

[36] T. R. O’Toole, J. N. Younathan, B. P. Sullivan, T. J. Meyer, Inorg. Chem. 1989, 28, 3923–3926.

[37] G. A. Zhurko, D. A. Zhurko, G. A. Andrienko, Chemcraft, Version 1.8 (Build 536).

Received: August 16, 2020