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)][BArF4], 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)][BArF4] and [Rh(CNC–Me)(Ph)Cl(OSMe2)][BArF4], 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)(SOMe2)][BArF4].

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 mesoionic 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
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 activa-
tion 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(PCP)(SOMe2)][BARF4](2, PN
iPr = 2.65(Pr3PCH2)3C6H3(N)), containing a less strongly donating
but more commonly employed phosphine-based pincer
ligand.

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 prol-
gand CNC–Me2HBr, the intermediates involved are appreciably
air-sensitive, and 1 was only obtained with an overall yield of
26%.[8] As a more accessible method for this latent source of
the reactive {Rh(CNC–Me)}+ fragment, we have therefore devel-
oped the procedure depicted in Scheme 2. This procedure in-
volves in situ generation of the silver(I) carbene transfer agent
[Ag(CNC–Me)][BARF4] and subsequent transmetallation
with Milstein’s underexploited rhodium(l) precursor
[RhCl(SOMe2)] in dichloromethane.[16] In this way pristine 1
was obtained in 50% isolated yield, following straightforward
crystallisation from dichloromethane/hexane at RT. The spectro-
scopic characteristics of 1 obtained in this manner are fully con-
gruent with those previously reported, with the
N–Me (δ1H 4.95, 5.87) proton resonances the most diagnostic in CD2Cl2.[8]

![Scheme 2. Convenient synthesis of 1 ([BARf4]– counter anion omitted).](image)

2. Reaction of 1 with biphenylene

In the weakly coordinating solvent 1,2-difluorobenzene
(DBF),[11a] 1 reacts readily with biphenylene (2 equiv.) at RT to
afford the rhodium(III) complex [Rh(CNC–Me)(2,2′-biphenyl)-
(OSMe2)][BARf4], 3, 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 separa-
tion 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.[5b,18] 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
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 interac-
tion, the difference in Rh–C contacts is more pronounced
(2.021(2), 1.992(3) Å).[15c]

![Figure 1. Activation of biphenylene, [BARf4]– counter anions omitted (top). Solid-state structure of 3, with thermal ellipsoids drawn at 30% probability and solvent omitted (bottom). Selected bond lengths [Å] and angles [deg]: Rh–N101, 2.239(3); Rh–C14, 2.051(4); Rh–C115, 2.077(4); Rh–C3, 2.013(4); Rh–C14, 1.997(4); Rh–O15, 2.307(2); C109–Rh1–C115, 173.99(16); C3–Rh1–C14, 86.34(15); N101–Rh1–C14, 177.40(15); O15–Rh1–C3, 174.94(12).](image)

The formation of 3 is faster than activation of biphenylene
by [Rh(Pr3P)2(C6H5F)][BARf4] (5 days @ 40 °C), which proceeds
under similar conditions via an intermediate ν2-biphenylene
derivative and results in the formation of [Rh(Pr3P)2(2,2′-bi-
phenyl)][BARf4].[10a] Calculations support a mechanism involving
ring slippage and concerted C–C 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-(Pr3PCH2)3C6H3, 2,6-(iPr3PCH2)3C6H3) and these more struc-
turally similar systems are a valuable mechanistic reference
point.[19] 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 tBu-substi-
tuated variant. The attenuated nature of the latter usefully, however, enabled kinetic products of biphenylene C–H bond activation (6-position) to be isolated. As we have previously demonstrated the CNC–Me pincer ligand is able to interconvert between mer- and fac-coordination modes,[9] both aforementioned mechanistic scenarios – π complex formation and intermediate C–H bond activation – are possible and we turned to DFT calculations using the M06-L/SDD/6-31G(d,p) level of theory to help quantify the viability of these possibilities (Figure 2).

Ring flipping of one of the bridging methylene groups of the pincer backbone ($\Delta G^\ddagger = 11.4 \text{ kcal mol}^{-1}$), is predicted to enable coordination of biphenylene through the central cyclobutadiene ring, viz., $[\text{Rh}(\text{fac-CNC–Me})(\eta^4\text{-biphenylene})]^+$, upon substitution of dimethyl sulfoxide and is associated with a small energetic penalty of $\Delta G = +11.2 \text{ kcal mol}^{-1}$. Subsequent C–C bond insertion, however, gives rise to a prohibitively high calculated barrier ($\Delta G^\ddagger = 40.7 \text{ kcal mol}^{-1}$ 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 $\Delta G^\ddagger = 17.8$ to 25.8 kcal mol$^{-1}$, but all give rise to thermodynamically unfavourable rhodium(III) products ($\Delta G = +4.2$–9.0 kcal mol$^{-1}$). Whilst C–C bond oxidative addition is associated with a generally higher calculated barrier ($\Delta G^\ddagger = 23.7 \text{ kcal mol}^{-1}$ from 1), the reaction proceeds downhill by $\Delta G = -34.1 \text{ kcal mol}^{-1}$ 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 throughout the reaction, (b) whilst faster, competing C–H bond is reversible, 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 compared to the oxidative addition of biphenylene. Using 100 equivalents of substrate, 15% conversion into $[\text{Rh}(\text{CNC–Me})(\text{Ph})\text{Cl}(\text{OSMe}_2)]^\ddagger [\text{BARF}_4]$ 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 characterised, including in the solid state by single-crystal X-ray diffraction. Complex 4 is characterised in CD$_2$Cl$_2$ solution by sharp $^1\text{H}$ and $^{13}\text{C}$ resonances that indicate adoption of C$_1$ symmetry ($N$–Me,
\( \delta_{1H} 3.32, 4.39; N-CH_2, \delta_{1H} 4.13, 4.57, 5.11, 6.44; \text{Rh}-(\text{Ph}), \delta_{13C} 142.7, \quad {^{1}J_{\text{RhC}} = 32 \text{ Hz}} \). Coordination of dimethyl sulfoxide is presumed to be dynamic on the NMR time scale by comparison to the magnitude of the \( ^1H \) chemical shift (\( \delta_{1H} 2.51 \) 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 \textit{trans} to the aryl. A conclusion congruent with the considerably larger \textit{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 \text{Rh–N} contact is evident for the latter (2.091(3) \( \AA \) cf. 2.239(3) \( \AA \)) despite the other common metal-based being very similar (e.g. \text{Rh1–C3} = 2.013(4) \( \AA \), 3; 2.006(4) \( \AA \), 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 \textit{fac}-coordination mode enables a sequence involving \( \eta^4 \)-coordination of the substrate, ring slippage, and oxidative addition of the C–Cl bond to be more competitive with "direct" insertion (\( \Delta G^\ddagger = +2.4 \text{ kcal mol}^{-1} \) from 1) than the biphenylene equivalent (\( \Delta G^\ddagger = +17.0 \text{ kcal mol}^{-1} \) from 1).\(^{[21]} \) The "direct" insertion pathway proceeds via formation of a \( \kappa^{\text{Cl}} \)-adduct of chlorobenzene and is associated with an overall calculated barrier of \( \Delta G^\ddagger = +26.1 \text{ kcal mol}^{-1} \), which is higher than that predicted for the C–C bond activation of biphenylene (\( \Delta G^\ddagger = +23.7 \text{ kcal mol}^{-1} \)) 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 (\( \Delta G = -22.3 \text{ kcal mol}^{-1} \)), but all are distinctly endergonic. Computational analysis of the activation of chlorobenzene by a related neutral Rh(PNP) pincer come to a similar conclusion.\(^{[22]} \)
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 phosphine-based analogue [Rh(PNP-iPr)2(COD)][BArF4], for which activation of biphenylene and chlorobenzene was not observed under the same conditions. The reactivity characteristics of [Rh(CNC–Me)(SOMe2)][BArF4] are of interest from the point of view of homogeneous catalysis and we hope these findings will stimulate greater exploitation of Rh(CNC) complexes in organic synthesis.

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-Me2 was purchased from Sigma Aldrich or Acros and stored over 3 Å molecular sieves. CD2Cl2 and CD2Br2 (100 mg, 0.293 mmol), Na[BArF4·2HBr], [RhCl(SOMe2)2][BArF4], and PNP-iPr2 were prepared following literature procedures.[14] PNP-iPr2 was prepared following literature procedures. All other reagents were commercially available and were used as supplied. NMR spectra were recorded using Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. NMR scale reactions of [Rh(CNC–Me)(SOMe2)][BArF4] are of interest from the point of view of homogeneous catalysis and we hope these findings will stimulate greater exploitation of Rh(CNC) complexes in organic synthesis.

2. Preparation of [Rh(CNC–Me)(SOMe2)][BArF4] (1)

A suspension of CNC-Me2·2HBr (100 mg, 0.293 mmol), Na[BArF4] (284 mg, 0.320 mmol), and Ag2O (70.0 mg, 0.363 mmol) in CH2Cl2 (5 mL) was stirred in the absence of light for 2 h. The solution was filtered through a Celite plug and added dropwise to a stirred solution of [RhCl(SOMe2)2] (92.2 mg, 0.293 mmol) in CH2Cl2 (2 mL). The resulting suspension was stirred in the absence of light for 2 h, filtered and then layered with hexane to afford the product as red crystals on diffusion at RT. Yield: 192 mg (50%). This complex is unstable in the solid-state outside of an inert atmosphere: complete decomposition observed after 24 h. Spectroscopic data are consistent with the literature.[8]

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.[16]

4. Synthesis of [Rh(PNP-iPr)(SOMe2)][BArF4] (2)

This complex was prepared by successive substitution of cyclooctadiene from [Rh(COD)2][BArF4] by the pincer ligand (Scheme 3), and thereafter SOMe2 using a methodology developed in our laboratories.[14]

1H NMR (300 MHz, CD2Cl2): δ 7.69–7.75 (m, 8H, ArH), 7.68 (t, JHH = 7.9, 1H, py), 7.55 (br, 4H, ArH) 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).


4.1. Preparation of [(PNP-iPr)2(μ2-η2:η2-2-COD)][BArF4] (1)

A solution of [Rh(COD)2][BArF4] (302 mg, 0.26 mmol) and PNP-iPr (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.

13C{1H} NMR (126 MHz, D2O): δ 3.83 (s, 6H, NCH3) 3.15 (s, 6H, SOMe2).

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

A solution of [(PNP-iPr)2(μ2-η2:η2-2-COD)][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 (ca. 20 mL) to afford the product as a yellow crystalline solid on diffusion. Yield: 15.0 mg (74%).

1H NMR (500 MHz, CD2Cl2): δ 7.73 (t, JHH = 7.9, 1H, py), 7.47–7.69 (m, 8H, ArH), 7.56 (br, 4H, ArH), 7.36 (d, JHH = 7.8, 2H, py), 3.41 (vt, JHH = 4.4, 4H, 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).

Acknowledgments

This work was supported by the European Commission (Project: G4RDA, 312928) and the University of Manchester. We gratefully acknowledge the use of the Microscopy Unit, School of Chemistry, University of Manchester for access to the JEOL JSM-5800 SEM.


www.eurjic.org
31P[1H] NMR (121 MHz, CD2Cl2): δ = 55.4 (d, JRP= 137).

Anal. Calcd for C56H40BF24N5ORhS (1424.15 g mol–1): C, 46.08; H, 3.86; N, 1.01; found C, 46.18; H, 3.71; N, 1.01.

HR ESI-MS (180 °C, 4 kV) positive ion: 522.1155 (M+), calcd 522.1160.

5. NMR scale reactions of [Rh(PNP–IPr)(OSMe2)][BArF4] (2)

Reactions were performed using 20 mmol−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)(2,2′-biphenyl)(OSMe2)][BArF4] (3)

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%).

7. Preparation of [Rh(CNC-Me)(Ph)(Cl)(OSMe2)][BArF4] (4)

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%).

1H NMR (600 MHz, CD2Cl2): δ 8.04 (t, JHH = 7.7, 1H, py), 7.69–7.76 (m, 8H, ArF), 7.64 (d, JHH = 7.7, 2H, py), 7.56 (br, 4H, ArF), 7.36 (d, JHH = 7.5, 2H, biph), 7.03 (br, 2H, biph), 6.99 (br, 2H, NCH), 6.97 (d, JHH = 7.6, 2H, biph), 6.73 (t, JHH = 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).

8. 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–IPr)(m2C2H4)(OSMe2)][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.

9. 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(dp) basis sets[33] developed by Pople and co-workers 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, subsequence geometry optimizations were performed in both forward and reverse direction of the displacement 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 (MINOA)
• 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

Received: August 16, 2020