Transition metal (Rh and Fe) complexes and main-group (Se and B) adducts with \(N,N'-\)diphosphanyl NHC ligands: a study of stereoelectronic properties†

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Attempts to evaluate experimentally the donor characteristics of the \(N,N'-\)bis(di-tert-butylphosphanyl)-imidazole-2-ylidene (PCNHCP) hybrid ligand are described. Thus, reactions of PCNHCP with [Rh(µ-Cl)(COD)]₂ and [Rh(µ-Cl)(CO)]₂ led to the formation of the mononuclear and dinuclear complexes, [Rh(PCNHCP-κ²,N₂)(κ₂,N₂)]Cl (PCNHCP-RhCl) and [Rh(PCNHCP,κ²,N₂)(κ²,N₂)]Cl (PCNHCP-RhCl), respectively, the latter resulting after in situ cleavage of one (t-Bu)₂P–N₄₁₁₃ bond of PCNHCP. With ligands acting as a P,C-chelate, a straightforward evaluation of the Tolman electronic parameter (TEP) of the C₄NH₄ donor is problematical; the viability of dangling P- and bound C₄NH₄ donors (i.e. κ₄C₄NH₄) has been observed in the trinuclear Fe(µ) chain complex \([\text{Fe}_3\text{Cl}_4\lambda\text{(THF)}_2]\) (PCNHCP,κ²,N₂) and [RhPCNHCP,κ²,N₂] (PCNHCP-Rh₂), which were prepared from the free PCNHCP (and Dipp-PCNHCP) and Se. The α-acidity of PCNHCP is found to be higher than that of Dipp-PCNHCP but lower than that of SīPr. The donor ability of the C₄NH₄ in PCNHCP was explored by its reaction with the Lewis acids tri(pentafluorophenyl)borane (B(C₆F₅)₃) and tri(s-pentafluorophenyl)boroxine ([(C₆F₅)BO]₃), which resulted in stable donor–acceptor adducts with no FLP reactivity. The steric properties of PCNHCP and Dipp-PCNHCP are conformation dependent, with the percent buried volume (% V₄₁₁₃) of PCNHCP in the structurally characterised conformer calculated at 67.6, the largest value currently reported for NHC ligands.

Introduction

N-heterocyclic carbene (NHC) ligands have become ubiquitous in molecular chemistry and find extensive applications in e.g. catalytic transformations, medicinal chemistry and material sciences.¹ Both experimental and theoretical studies on their electronic properties have established synergism resulting from their strong σ donor and weaker π acceptor properties. The most commonly used method for the experimental evaluation of the donor properties of NHCs is the Tolman electronic parameter (TEP), originally developed for phosphines by Tolman in 1970,² which is based on the value of the A₁, ν(CO) infrared-stretching frequencies in \([\text{Ni}(\text{CO})_4\lambda\text{L}]\) or the average ν(CO) frequencies in \(\text{cis-}[\text{Ir}(\text{CO})_2\lambda\text{L}]\) and \(\text{cis-}[\text{Rh}(\text{CO})_2\lambda\text{L}]\) (Chart 1), the latter two complexes being more widely used nowadays owing to the toxicity of \([\text{Ni}(\text{CO})_4]\).³ However, the TEP quantifies the overall NHC electronic properties and does not separate the σ donation and π back-donation components.

Recently, Bertrand and coll.⁴ and Ganter and coll.⁵ separately reported the use of phosphinidene (NHC)PPh and selenium adducts (NHC)Se (Chart 1) to probe the NHC π back-bonding ability, on the basis of the δₚ chemical shift in the ³¹P NMR and the δₙe chemical shift in the ⁷⁷Se NMR, respectively. These adducts can be represented by two limiting canonical structures: the polarized form A with a NHC–E (E = PPh or Se) single bond indicating little π accepting ability and the resonance form B with a NHC–E (E = PPh or Se) double bond consistent with a high π accepting ability of NHCS. In contrast to the narrow range of TEP values, the chemical shifts of the phosphinidene/selenium adducts are very sensitive to subtle changes of the electronic structures of NHCS and offer a finer grading of the NHCS.

Various groups have recently reported N-phosphanyl-functionalized NHC ligands, which feature the two adjacent, strong σ-donors groups linked by a direct P–N bond.⁶ Because of the
rigidity and ease of tuning of their steric and electronic properties, they have not only been used as bridging ligands for d10 coinage metals but also as small bite angle (ca. 68.2°) chelating ligands for platinum group or late transition metals. We have recently reported the synthesis of the new tridentate ligand N,N′-bis(di-tert-butylphosphanyl)-imidazole-2-ylidene (PCNHCP) (Scheme 1) and its behaviour as bridging ligand with coinage metals or palladium, resulting in polynuclear complexes, and as PCNHCP chelating ligand with chromium or palladium. However, a more precise experimental estimate of the stereoelectronic properties of CNHC donor in the PCNHCP ligand is not straightforward, due to the high nucleophilicity of both donors and the propensity of formation of small ring chelates with the metals used as probes for the TEP. Herein, we describe Rh(I) carbonyl complexes with PCNHCP which display κP,κC coordination, thus rendering the evaluation of the TEP cumbersome; in contrast, the selective access of NHC-Se adducts permits the evaluation of the π accepting ability of the CNHC in PCNHCP; furthermore we give an estimate of the steric bulk of PCNHCP, and describe adducts with B(C6F5)3 and FeCl2 in which CNHC coordination predominates.

Results and discussion

Mono- and dinuclear rhodium complexes and trinuclear iron complex

Since no rhodium complex with the PCNHCP has yet been prepared, with the objective to prepare cis-[RhCl(CO)2(PCNHCP)] we firstly reacted PCNHCP with [Rh(µ-Cl)(COD)]2 in THF in a 1:1 ligand/Rh ratio (Scheme 1). However, instead of the expected adduct [RhCl(COD)(PCNHCP),κC],[6,7] the mononuclear complex [Rh(PCNHCP),κP,κC]Cl (PCNHCP-RhCl) was isolated, the two PCNHCP ligands acting as P,C-chelates. This was confirmed by single-crystal X-ray diffraction analysis (Fig. 1).

The unit cell of PCNHCP-RhCl contains two similar complex cations with slightly different metrical data and isolated chloride anions (Rh–Cl distance 7.418/7.359 Å). In each cation, the tetracoordinated Rh atom occupies a centre of symmetry and is chelated by two PCNHCP ligands through their CNHC and one phosphorus donor, with a bite angle of 67.26(11)/67.31(13)°. The solution31P{1H} NMR spectrum of PCNHCP-RhCl contains a doublet at \( \delta = 113.1 \) (\( J(P-Rh) = 146.9 \) Hz) and a singlet at \( \delta = 83.8 \), Chart 1 Three experimental methods used to evaluate the electronic properties of NHC ligands.

![Chart 1](image)

![Scheme 1](image)
corresponding to the coordinated and the uncoordinated phosphines, respectively. The latter value is slightly different from that of the free PCNHCP-P (δ 98.7),66 indicating electronic communication between the P donors on coordination.

In view of the lability of the COD ligand that prevented the preparation of [RhCl(COD)(PCNHCP)], the complex [Rh(μ-Cl)(CO)] was used as precursor and was directly reacted with PCNHCP in THF. However, instead of the expected cis-[RhCl(CO)₂(PCNHCP,kPCNHCP)], the neutral, dinuclear complex [Rh(CO)₂(PCNHCP,kPCNHCP,κNHC)]₂ (PCNHCP-RhCO) containing two monononic PCNHCP ligands was obtained after cleavage of one (t-Bu)₂P=N₃ bond of PCNHCP-P (Scheme 1). The formation of (t-Bu)₂PCl was evidenced in the reaction mixture as the only other P-containing product (δ 145 in 31P{¹H} NMR). A similar P–N bond cleavage reaction has also been observed when PCNHCP-P was reacted with [AuCl(tht)] and rationalised by the reactivity of the P–N bond toward the nucleophilic chloride ligand.66 The 31P{¹H} NMR spectrum of PCNHCP-RhCO contains a doublet at δ 128.4 (J(P–Rh) = 142.8 Hz). The structure of this complex exhibits an approximate C₂ symmetry and the square-planar environment around each Rh atom contains one chelating PCNHCP ligand, bonded through the P and C atoms to the metal, two CO ligands occupying axial positions, and two THF molecules completing the octahedral environment. The thermal ellipsoid representation (30% probability level) of the structure of one cation in PCNHCP-P-RhCl(THF) is shown in Fig. 1. Selected bond lengths (Å) and angles (°): Rh1–C1 2.077(4)/2.082(4), Rh1–P1 2.300(1)/2.304(1), C1–Rh1–P1 67.2(1)/67.3(1). H atoms, the –Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-C1 2.071(10), Rh2–C12 2.080(9), Rh1–C23 1.833(10), Rh2–C24 1.842(11), Rh1–N4 2.080(8), Rh2–N2 2.065(8), Rh1–P1 2.249(3), Rh2–P2 2.243(3), C23–O1 1.166(12), C24–O2 1.152(12), C1–Rh1–P1 67.3(3), C12–Rh2–P2 67.2(3).

NHC adducts with main group elements (Se, B)

Based on the results we shifted our attention to alternative adducts that may disclose information on the donor characteristics of the PCNHCP-P. The first attempt focused on the synthesis of phosphinidene adducts of NHCs, which carry information on the π-accepting strength of the NHC precursor.4 Two known synthetic routes were explored for the synthesis of the adducts (Scheme 2): (i) the direct reaction of PCNHCP-P with pentaphenylcyclpentaphosphane ([PPh]₃); (ii) the reaction of PCNHCP-P with PhPCL₂ followed by reduction with Mg. However, both failed: the former gave no reaction even after heating to 70 °C, and the latter led to the cleavage of a P–N bond of PCNHCP-P by PhPCL₂, with formation of (t-Bu)₂PCl.

Fig. 1 Thermal ellipsoid representation (30% probability level) of the structure of one cation in PCNHCP-P-RhCl. H atoms and the t-Bu methyl groups, the second complex cation and the chloride anions are omitted for clarity. Selected bond lengths (Å) and angles (°): the two values are for the two independent cations in the unit cell: Rh1–C1 2.077(4)/2.082(4); Rh1–P1 2.300(1)/2.304(1), C1–Rh1–P1 67.2(1)/67.3(1).

Fig. 2 Thermal ellipsoid representation (30% probability level) of the structure of PCNHCP-RhCO. H atoms and the t-Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–C1 2.071(10), Rh2–C12 2.080(9), Rh1–C23 1.833(10), Rh2–C24 1.842(11), Rh1–N4 2.080(8), Rh2–N2 2.065(8), Rh1–P1 2.249(3), Rh2–P2 2.243(3), C23–O1 1.166(12), C24–O2 1.152(12), C1–Rh1–P1 67.3(3), C12–Rh2–P2 67.2(3).
The second attempt focused on the synthesis of selenium adducts; herein, the π-accepting properties of NHCs precursors can also be correlated with the 77Se NMR chemical shift observed.\(^5\) Thus, reaction of elemental selenium with PCNHCP-Se\(^4\) in a 1:1 ratio in THF afforded selectively the desired adduct PCNHCP-Se\(^\text{P}_\text{Se}\), with intact phosphine groups (Scheme 2), as indicated by a \(^{31}\)P NMR shift (\(s, \delta 91.0\)) \((\text{cf. PCNHCP-P} \delta s, 98.7)\). The structure of the product was further confirmed by an X-ray diffraction analysis (Fig. 4). The Se–NHC bond distance 1.839(8) Å is intermediate between that of a Se–C single bond (aver. 1.94 Å) and of a typical Se=C double bond (aver. 1.74 Å).\(^\text{12c}\) Its value is similar to that found in other selenium–NHC adducts.\(^\text{5,h,12e–c}\) Compared to the free carbene PCNHCP, the N–C\(\text{NHC}\) bond lengths \((1.36(1)/1.37(9))\) Å, cf. \(1.376(1)/1.378(1)\) Å in PCNHCP-P\(^\text{Se}\)) are shortened and the N1–C1–N2 angle \((108.2(6)^\circ\text{, cf. 102.5(1)}^\circ\)) in PCNHCP-P\(^\text{Se}\) enlarged.

For comparison with PCNHCP-P\(^\text{Se}\), the selenium adduct Dipp-PCNHCP-Se\(^\text{P}_\text{Se}\) of a ligand containing only one phosphine donors in PCNHCP-P\(^\text{Se}\) was prepared under similar reaction conditions (Scheme 2). The \(^{77}\text{Se}\) NMR spectra feature a triplet at \(\delta 166.9\) \((\gamma_{\text{SeP}} = 46.5\text{ Hz})\) for PCNHCP-P\(^\text{Se}\) and a doublet at \(\delta 131.1\) \((\gamma_{\text{SeP}} = 40.0\text{ Hz})\) for Dipp-PCNHCP-Se. Accordingly, and by comparison with literature data, it can be concluded that the π-acidity of PCNHCP-P\(^\text{Se}\) is stronger than that of Dipp-PCNHCP-P\(^\text{Se}\) and that both ligands are stronger π-acids than SIMes (\(\delta 110\) \(^{77}\text{Se}\) NMR), but weaker π-acids than SIPr (\(\delta 190\) \(^{77}\text{Se}\) NMR) (Scheme 3).\(^\text{13}\)

To further explore the donor abilities of the C\(\text{NHC}\) and P donors in PCNHCP-P\(^\text{Se}\), the latter was reacted with tris(pentafluorophenyl)borane B(C\text{6F\text{5}})\(_3\) in toluene (Scheme 4). The \(^{11}\text{B}\) NMR spectrum of the resulting product (PCNHCP-P\(^\text{Se}\)) shows a single resonance at \(\delta -17.5\), which is indicative of a four-coordinate boron centre and suggests the formation of a NHC–borane Lewis adduct with a stable B–C\(\text{NHC}\) bond.

Broad NMR resonances were not only observed for the three pentafluorophenyl groups in the \(^{19}\text{F}\) NMR and \(^{13}\text{C}\) NMR spectra but also for the phosphine groups (one broad singlet at \(\delta 110.5\) and C\(\text{NHC}\)) (broad multiplet at \(\delta 177.1\)). This, together with the singlet at \(\delta 7.69\) for the two protons on the imidazolylidene ring, indicates fast free rotation of the B(C\text{6F\text{5}})\(_3\) moiety around the B–C\(\text{NHC}\) bond. A single-crystal

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**Scheme 2** Reactions of PCNHCP and Dipp-PCNHCP with PhPCl\(_2\), (PPh)\(_3\) and elemental selenium.

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**Fig. 3** Thermal ellipsoid representation (30% probability level) of the structure of PC\(\text{NHC-P-Fe}\). H atoms and the t-Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1–C1 2.103(6), Fe1–C1 2.255(7), Fe1–C1 2.3807(17), Fe1–Cl1 2.4118(18), Fe2–C1 2.4781(14), Fe2–C1 2.4755(14), Fe2–O1 2.158(4), Fe1–C1–Fe2 91.98(5), Fe1–Cl1–Fe2 91.50(5), Fe1–C1–Fe2 91.98(5), Cl1–Fe1–Cl1 112.98(16), Cl1–Fe1–Cl2 115.81(15), Cl1–Fe1–Cl2 115.31(16), Cl1–Fe1–Cl2 111.90(7), Cl1–Fe1–Cl3 109.59(6), Cl2–Fe1–Cl8 88.99(6), O1–Fe2–Cl3 88.33(11).

**Fig. 4** Thermal ellipsoid representation (30% probability level) of the structure of PC\(\text{NHC-P-Se}\). H atoms and the t-Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles [°]: Cl1 2.2587(19), Fe1 2.103(6), Cl2 2.3807(17), Fe1–C1 2.1839(8), C1–N1 1.36(1), C1–N2 1.370(9), N1–P1 1.760(7), N2–P2 1.775(7), N1–C1–N2 108.2(6).
X-ray diffraction analysis showed that the three C₆F₅ groups adopt a typical C₃ propeller-type orientation (Fig. 5). For steric reasons, the lone pair on the P atoms is oriented toward the borane moiety.

Unlike other NHC–borane adducts,¹⁴ PCNHC-P-B₁ exhibits no frustrated-Lewis-pair (FLP) reactivity toward H₂ or THF, which is consistent with a rather strong donor–acceptor CNHC → B interaction, despite a moderate elongation of this bond (1.688(3) Å) when compared to that in the adduct IPr/B(C₆F₅)₃ (1.663(5) Å)¹⁴ and in 1,3,4,5-tetramethyl-1,3-imidazole-2-ylidene/B(C₆F₅)₃ (1.640(2) Å).¹⁵

Another donor–acceptor adduct was obtained by reaction of PCNHC with a suspension of tris(pentafluorophenyl)boroxine [(C₆F₅)BO]₃ in toluene (Scheme 4). An immediate reaction occurred with formation of a clear solution. A crystallographic analysis established again the formation of one CNHC → B bond in the boroxine adduct PCNHC-P-B₂, leaving the other two B atoms intact (Fig. 6). The B–CNHC bond distance 1.670(4) Å.
is slightly shorter than that in PC_{NHC}P-B1. Obvious differences were observed between the three B−C_{6}F_{5} moieties: (i) the B1–C32 bond (1.643(4) Å) is elongated compared to the other two (1.590(4) Å and 1.586(4) Å); (ii) the B2–C20 and B3–C26 bonds are coplanar with the boroxine ring while the B1–C32 bond bends out of the boroxine plane, away from the PC_{NHC}P ligand with a distance of 1.393 Å between the C23 atom and the boroxine plane. This results from the coordination of B1 to C_{NHC} forming a tetrahedral environment around the B1 atom.

The $^{31}$P NMR spectrum shows one singlet at δ 97.6 for the phosphine groups and a doublet is observed in the $^{1}$H NMR spectrum at δ 1.15 ($J_{HP} = 12.9$ Hz) for the $t$-Bu groups, which indicates free rotation of the boroxine moiety around the B−C_{NHC} bond. The $^{11}$B NMR spectrum contains a broad signal at δ 26.4 and a singlet at δ −0.6 ppm corresponding to the three- and four-coordinate B atoms, respectively. Similarly to PC_{NHC}P-B1, it exhibited no frustrated-Lewis-pair (FLP) reactivity toward H$_2$ or THF.

### Percent buried volume of the NHC ligands

Lastly, the steric properties of PC_{NHC}P and Dipp-PC_{NHC} were evaluated from the percent buried volume ($\%V_{bur}$) using the SambVca software, and metrical data from the crystal structures. The results are compiled in Table 1 assuming a 3.50 Å residual solvent resonance ($^{1}$H and $^{13}$C) or external 85% H$_3$PO$_4$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$%V_{bur}$ for M−NHC length at 2.00 Å</th>
<th>$%V_{bur}$ for M−NHC length at 2.28 Å</th>
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<tr>
<td>Dipp-PC_{NHC}</td>
<td>39.4</td>
<td>36.2</td>
</tr>
<tr>
<td>PC_{NHC}P</td>
<td>35.8</td>
<td>31.0</td>
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### Conclusions

Some stereoelectronic properties of the hybrid ligands PC_{NHC}P and Dipp-PC_{NHC} have been evaluated. Initial attempts to prepare cis-[RhCl(CO)]$_2$(PC_{NHC}PκC_{NHC}) by the reaction of PC_{NHC}P with [Rh(μ-Cl)(COD)$_2$]$_2$, or [Rh(μ-Cl)(CO)$_2$]$_2$, led instead to the formation of rhodium complexes with a chelating PC_{NHC}PκP$_2$C_{NHC} or PC_{NHC}κP$_2$C_{NHC}κN ligand, and the additional coordination of the phosphine group hampered the evaluation of the TEP of the sole C_{NHC} donor. However, the π-accepting properties of PC_{NHC}P and Dipp-PC_{NHC} were determined from the $^{77}$Se NMR chemical shift of the corresponding selenium adducts. The σ-donor ability of the carbene donor in PC_{NHC}P was confirmed by the isolation of two stable donor-acceptor adducts with borane or boroxine. The free carbene donor of PC_{NHC}P shows the largest value reported for percent buried volume in NHC ligands in the conformation of the free PC_{NHC}P established crystallographically. Currently, it appears that a coordination mode through the C_{NHC} donor (κC_{NHC}) is more common with 3d metals.

### Experimental section

#### Synthesis and characterisation

**General methods.** All manipulations involving organometallics were performed under argon using standard Schlenk techniques. Solvents were dried using standard methods and distilled under nitrogen prior to use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. $^{1}$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR spectra were recorded at 298 K, unless otherwise specified, on a Bruker Avance 400, 500 or 600 spectrometer and referenced to the residual solvent resonance ($^1$H and $^{13}$C) or external 85% H$_3$PO$_4$, 85% H$_3$PO$_4$. 

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**Table 1  Percent buried volume ($\%V_{bur}$)**

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<td>PC_{NHC}P</td>
<td>35.8</td>
<td>31.0</td>
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</table>
Synthesis of PCNHCP-RhCl. To a solution of [RhCl(COD)]2 (0.030 g, 0.061 mmol) in THF (5 ml) was added a solution of PCNHCP (0.100 g, 0.281 mmol) in THF (5 ml) at room temperature and the reaction mixture was stirred for 2 h. After evaporation of the volatiles, the residue was washed with pentane (20 ml) and dried under vacuum to give a yellow powder (0.075 g, 87%). X-ray quality crystals were obtained by slow diffusion of pentane into its CH2Cl2 solution. Analysis: Found (Calcd for C23H37N2P2Se) (%): C, 52.30 (52.41), H, 6.41 (6.20). 1H NMR (600 MHz, CDCl3): δ 1.07 (3H, t, JHH = 6.9 Hz, iPr-C3), 1.08 (3H, t, JHH = 6.9 Hz, iPr-C3), 1.10 (6H, d, JHF = 6.9 Hz, iPr-C3), 1.22 (12H, m, C(CH3)3), 23.5 (iPr-CH3), 29.5 (d, JCP = 4.3 Hz, 5H, C(CH3)3), 29.9 (d, JCP = 15.7 Hz, 5H, C(CH3)3), 31P{1H} NMR (161 MHz, CDCl3): δ 113.1 (d, JFRh = 146.9 Hz), 83.8 (s).

Synthesis of PCNHCP-Se. To a solution of [Rh2(µ-Cl)3(CO)4] (0.088 g, 0.226 mmol) in THF (5 ml) was added a solution of PCNHCP (0.160 g, 0.449 mmol) in THF (5 ml) at room temperature and the reaction mixture was stirred for 2 h. It was then concentrated to ca. 2 ml and 20 ml pentane were added to precipitate the product. The supernatant was removed by filtration and the solid was dried under vacuum to give a brown powder (0.066 g, 44%). X-ray quality crystals were obtained by slow diffusion of pentane into its THF solution. Analysis: Found (Calcd for C23H38N2PSe) (%): C, 61.01 (61.19), H, 8.02 (8.02), N, 6.41 (6.20). 1H NMR (600 MHz, CDCl3): δ 7.44 (t, 1H, JHH = 7.7 Hz, Ar-H), 7.31 (dd, 1H, JHH = 2.1 Hz, JHF = 0.3 Hz, im-H), 7.26 (2H, JHH = 7.7 Hz, Ar-H), 6.87 (dd, 1H, JHH = 2.1 Hz, JHF = 1.3 Hz, im-H), 2.50 (sept, 2H, JHF = 6.9 Hz, iPr-CF3), 1.32 (18H, JHF = 12.5 Hz, C(CH3)3), 1.28 (6H, JHF = 6.9 Hz, iPr-CF3), 1.10 (6H, JHF = 6.9 Hz, iPr-CF3). 13C{1H} NMR (125 MHz, CDCl3): δ 169.1 (d, JCP = 33.1 Hz, C(CH3)3), 162.0 (s), 161.4 (Ar-C), 134.9 (Ar-C), 130.2 (Ar-CH), 124.4 (Ar-CH), 122.0 (d, JCP = 7.6 Hz, im-C), 121.7 (d, JCP = 1.3 Hz, im-C), 116.1 (d, JCP = 1.3 Hz, im-C), 92.3 (d, JCP = 33.1 Hz, C(CH3)3), 29.3 (d, JCP = 17.5 Hz, C(CH3)3), 29.0 (d, iPr-CH3), 24.6 (d, iPr-CH3), 23.5 (d, iPr-CH3). 31P{1H} NMR (243 MHz, CDCl3): δ 90.5 (s). 19F NMR (114 MHz, CDCl3): δ 131.1 (d, JFCF = 40.0 Hz).
Synthesis of PCNHC-P-B2. To a suspension of [(C6F5)BO]3 (0.116 g, 0.199 mmol) in toluene (2 ml) was added a solution of PCNHC-P (0.072 g, 0.202 mmol) in toluene (2 ml) at room temperature and stirring was maintained for 1 h. The reaction mixture was concentrated to 2 ml and 20 ml pentane was added to precipitate the product. After filtration, the residue was dried under reduced pressure to give a white powder (0.120 g, 64%). X-ray quality crystals were obtained by cooling down its toluene solution to ~30 °C for two days. Analysis: Found (Calcd for C17H14Ar4F17N3O28P4) (%): C, 47.72 (47.37), H, 4.17 (4.08), N, 2.97 (2.99). 1H NMR (400 MHz, CDCl3) δ 7.66 (s, 2H, im-H) 1.15 (d, 36H, JHH = 12.9 Hz, C(CH3)3) 13C{1H} NMR (125 MHz, d8-THF): δ 175.9 (br, NAr), 149.9 (dm, JCF = 249.7 Hz, o-ARCF), 148.7 (dm, JCF = 241.6 Hz, p-ARCF) 140.3 (dm, JCF = 241.4 Hz, p-PCNHC-BNHC), 137.8 (dm, JCF = 250.7 Hz, overlapping m-ARCF and m-ARCF-BNHC), 126.0 (im-C), 124.9 (br, ARCB), 109.7 (br, ARCB-CNHC), 35.9 (d, JCF = 35.2 Hz, C(CH3)3), 29.0 (d, JCF = 17.7 Hz, C(CH3)3). 13P{1H} NMR (161 MHz, d8-THF): δ 97.6 (s). 11B NMR (128 MHz, d8-THF): δ 26.4 (br, ARB), −0.6 (s, ArB-CNHC). 19F NMR (282 MHz, d8-THF): δ −132.4 (dm, 4F, JFF = 22.4 Hz, o-ARCF), −135.3 (m, 2F, p-ARCF-BNHC), −156.0 (tt, 2F, JFF = 20.0 Hz, JFB = 3.1 Hz, p-ARCF), −160.4 (t, 1F, JFF = 20.3 Hz, p-ARCF-BNHC), −166.1 (m, 4F, m-ARCF), −168.5 (m, 2F, m-ARCF-BNHC).

X-ray crystallography

Summary of the crystal data, data collection and refinement for the structures of PCP-RhCl2CH2Cl2, PCNHC-RhCO, PCNHC-P-Fe, PCNHC-P-Se, PCNHC-P-B-1 THF and PCNHC-P-B-2 toluene are given in Table S1. For PCNHC-P-RhCl2CH2Cl2, PCNHC-P-Fe, PCNHC-P-Se, PCNHC-P-B-1 THF and PCNHC-P-B-2 toluene, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 12 frames, each at 10s exposure. The structure was solved by direct methods using the program SHELXS-97. The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. A semi-empirical absorption correction was applied using MULTscanABS in PLATON.

Conflict of interest

The authors declare no competing financial interest.

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