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The influence of phosphine cone angle on the synthesis and structures of $[Rh(PR_3)(Binor{-}S)]^+$ complexes that show C–C sigma interactions

Adrian B. Chaplin [1], Andrew S. Weller*

Department of Chemistry, University of Oxford, Chemistry Research Laboratories, Mansfield Road, Oxford OX1 4TA, UK

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ABSTRACT

Complexes that show C–C···Rh sigma interactions have been synthesized and characterised by NMR spectroscopy and X–ray diffraction: $[Rh(PR_3)(Binor{-}S)][BAr^F{}_4]$, R = P^tBu_2Me, PCy_2Ph; Ar = $C_6H_3(CF_3)_2$, Binor–S = 1,2,4,5,6,8-dimetheno-S-indacene. These studies, in concert with previously published work, show that there is a rather narrow window of phosphine steric profile that supports the isolation of these interesting complexes, with the phosphine cone angle lying between 160° and 170°.

1. Introduction

The synthesis, structures and reactivity of transition metal complexes in which a saturated single bond interacts with the metal centre via a 3-centre 2-electron bond, the so called sigma-complexes [1], are now well established. Examples include: C–H intramolecular agostic interactions, C–H···M [2]; dihydrogen complexes, H_2···M [1]; sigma boranes, R_3NBH_3···M [3]; and silanes, R_3Si–H···M. [4]. Intermolecular sigma-alkane complexes of transition metals are also known, but are generally difficult to isolate in solution due to the facile loss of alkane [5–7]. Compared to those with C–H agostic interactions, complexes in which a C–C saturated bond forms a sigma-complex with a transition metal are rarer: a consequence of the relative inaccessibility and orbital directionality of a C–C bond [8]. Despite this there are a growing number of examples reported [8–21], some of which are of direct relevance to C–C activation processes [8,22]. Related Si–Si···M interactions have also been reported [23,24]

Over the fast few years we have reported on the synthesis of $[M(PR_3)(Binor{-}S)]^+$ cations (Binor–S = 1,2,4,5,6,8-dimetheno-S-indacene; R = Cy, ^{i}Pr, cyclopentyl; M = Rh, Ir) in which there is a close approach of one cyclopropyl fragment in the Binor–S derived ligand to the metal centre that results in an M···C–C sigma interaction, while the other cyclopropyl group has undergone C–C activation to form a metallacyclobutane (Scheme 1) [25–29]. These complexes also have a weak supporting C–H···M agostic interaction from the alkyl phosphine. In solution (Rh and Ir) and the solid-state (Ir) these complexes undergo reversible C–C activation of the Binor–S fragement. For Rh we have also shown that they undergo reductive elimination of Binor–S readily on addition of exogenous Lewis base, and thus serve as a useful source of the reactive 10-electron $\{Rh(PR_3)\}^+$ fragment [25,30–32]

The synthetic methodology used for the synthesis of these complexes is one in which a $[M(PR_3)(NBD)_2]^+$ cation, usually partnered with the $[BAr^F{}_4]^-$ counterion, {NBD = norbornadiene; Ar^F = 3,5-$C_6H_3(CF_3)_2$; M = Rh, R = Cy, ^{i}Pr, Cyp (Cyp = cyclopentyl) [25,26]; M = Ir, R = ^{i}Pr [27]} undergoes a cyclodimerization of the two bound-dienes to give the Binor–S fragment directly on the metal centre [33]. $[M(PR_3)(NBD)_2]^+$ can be generated by reaction of an alkyl phosphine (e.g. P^iPr_3 or PCy_3) with $[Rh(NBD)_2]^+$ or by addition of NBD/Na$[BAr^F{}_4]$ to $[RhCl(PR_3)(NBD)]$ or $[IrCl(P^iPr_3)(COE)]$ (COE = cyclooctene) [26,27]. In the case of Rh the intermediates $[Rh(PR_3)(NBD)_2]^+$ cannot be isolated, or even observed, as formation of the Binor–S complex is fast. However for Iridium this intermediate can be isolated, i.e. $[Ir(P^iPr_3)(NBD)_2][BAr^F{}_4]$, a consequence of the stronger Ir–C bonds. In all cases it is the addition of the phosphine that induces the dimerization of NBD. This reaction is also catalytic, using the $[Rh(NBD)_2]^+/PR_3$ system [34], and we have shown that $[M(PR_3)(Binor{-}S)]^+$ are intermediates in this process [25]

* Corresponding author.
E-mail address: andrew.weller@chem.ox.ac.uk (A.S. Weller).
[1] Present address: Department of Chemistry, University of Warwick, CV34 7AL, UK.

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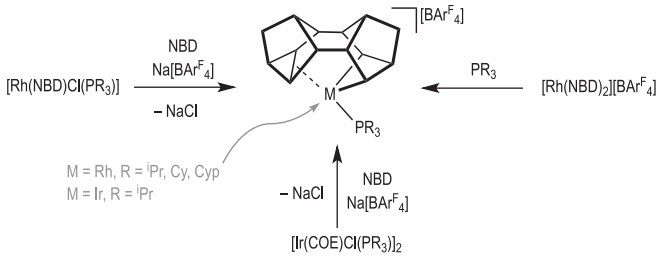


Scheme 1. Generic Routes to $[M(PR_3)(Binor–S)]^+$ complexes.

In this contribution we explore the synthesis of $[Rh(PR_3)(Binor–S)][BAr^F_4]$ complexes using a number of different phosphines in which the sterics (i.e. cone angle [35,36]) are varied while the electronic contribution remains similar [35]. We find that, within the sample of phosphines used, there is a rather narrow window for the production of the C–C···Rh sigma complexes, being supported by phosphines with cones-angles 160° to 170°.

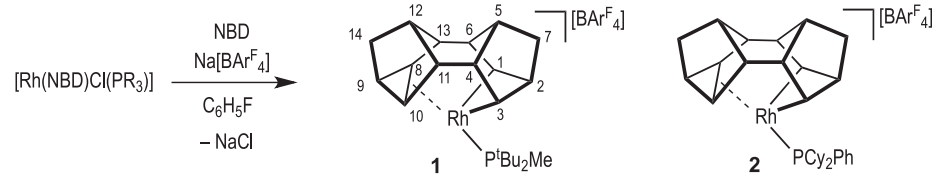
2. Results and discussion

Taking a range of phosphines with different cone angles ranging from P^iBu_3 (cone angle 143°) to P^tBu_3 (182°) the precursor complexes [RhCl(NBD)(PR_3)] where prepared. These were characterised by NMR spectroscopy and elemental analysis and their data are unremarkable showing all to be Rh(I) species in solution. Addition of $Na[BAr^F_4]$, as a halide abstracting reagent, in C_6H_5F solvent in the presence of NBD was used to generate the desired Binor–S complexes. For some phosphines this resulted in intractable mixtures of products. However, for P^tBu_2Me and PCy_2Ph the clean formation of the Binor–S complexes were observed, $[Rh(PR_3)(Binor–S)][BAr^F_4]$ (R = P^tBu_2Me, **1**; PCy_2Ph, **2**), which could be isolated in good yields, 66% and 89% respectively, as crystalline materials, Scheme 2.

These results show that there is a range in the steric profile of the phosphine that supports the isolation of these C–C···M sigma complexes, lying between 160° and 170°. Smaller or larger than this and intractable mixtures were formed. The solid-state structures of **1** and **2** are shown in Figs. 1 and 2 respectively. For **1** there are two independent molecules in the unit cell ($Z' = 2$), but the structural metrics of the $\{Rh(Binor–S)\}^+$ fragment are the same for both within 3σ (Table 1), the two differing by subtle differences in the relative orientation of the phosphine, essentially being an enantiomeric pair in the solid-state which would not be retained in solution (vide infra).

In the solid-state both **1** and **2** show the expected [25,26] overall structure with a Binor–S derived fragment coordinated to a, formally, Rh(III) centre through a metallacyclobutane (Rh/C1/C2/C3) and C–C···Rh sigma interaction (Rh/C8/C10). The metallacyclobutane shows Rh–C distances as expected for 2–centre–2 electron interactions (e.g. Rh1–C1 = 2.029(3) Å in **2**), while the C–C···Rh sigma interaction is longer as expected (e.g. Rh–C8 2.370(4) Å in **2**). The C–C bond C8-C10 is also lengthened compared to a close–analogue of free BINOR–S, consistent with the formation of the sigma interaction [cf. C8–C10 1.616(5) Å **2**, the dione–derivative of Binor–S, 1.49(3) Å] [37]. Although there might appear to be γ C–H and β C–H agostic interactions from the ^{t}Bu and Me groups in **1** and similar interactions from the cyclohexyl and phenyl groups in **2**, the Rh–C distances are all long for such interactions (e.g. Rh1–C17 3.244(6) Å, **1**; Rh1–C32 3.307(4) Å, **2**) [38]. While computational and experimental charge density studies on the Cy analogue to **1** and **2**, $[Rh(PCy_3)(Binor–S)]^+$ [28], support the presence of a weak agostic interaction with a comparably shorter Rh–C distance of 3.018(2) Å, these data for **1** and **2** suggest that any C–H···Rh interactions present are even weaker than this, at best. These weak agostic interactions are fully consistent with the strong *trans*-influence Rh–C bonds that lie opposite [39]. The overall structural motif (Rh(III), two weak agostic C–H bonds trans to Rh–C bonds) is similar to that reported for *trans*–[Rh(2,2′–biphenyl)(P^iPr_3)$_2$][BAr^F_4] [40]. The C–H agostic interaction aside, the structural metrics for the Binor–S fragment are very close to those previously reported for ^{i}Pr, Cy and Cyp analogues (Table 1 compares selected structural data), for which NMR data [25,26], X-ray crystallography [25,26], experimental charge–density measurements [28] and DFT calculations [25,28] all support the C–C···Rh motif.

Solution NMR data for **1** and **2** are also consistent with the previously reported Binor–S complexes of Rh and Ir. Time-averaged C_{2v} symmetry (rather than the pseudo C_s in the solid-state) is observed in solution at room temperature, i.e. only 4 Binor-S environments are observed in the $^{13}C\{^1H\}$ NMR spectrum [41], while in the ^1H NMR spectrum only 5 environments are observed in a 4:2:2:4:4 ratio. As previously outlined this fluxional process occurs via C–C bond making in the metallacyclobutane and C–C bond breaking in the C–C···Rh bond that make the two sides of the Binor-S fragment equivalent. Calculations indicate that this occurs via a Rh(V) intermediate [26], and for $[Ir(P^iPr_3)(Binor–S)][BAr^F_4]$ we have shown that such an intermediate can be formed in the solid-state [27]. For both **1** and **2** rotation around the Rh–P bond must also be occurring at room temperature to produce the observed C_{2v} symmetry. In the $^{13}C\{^1H\}$ NMR spectrum for **1** the time-averaged carbon environment assigned to C1/3/8/10 is observed as a broad doublet [J = 12 Hz], as previously noted in other systems [25,26]. Interestingly for **2** this signal is further resolved as a doublet of doublets [J = 13, 4 Hz] consistent with coupling to both ^{103}Rh and ^{31}P, as reported for the ^{i}Pr-analogue [26]. In **1** the other coupling is clearly too small to be resolved.



	P^{i}Bu$_3$	PPh$_3$	P^{i}Pr$_3$	P^{t}Bu$_2$Me	PCy$_2$Ph	PCyp$_3$	PCy$_3$	PAd$_2$^{n}Bu	P^{t}Bu$_3$
Binor–S complex formed?	no	no	yes[a]	yes	yes	yes[a]	yes[a]	no	no
Cone–angle [b]	143°	145°	160°	~161°	~162°	165°	170°	176°	182°

Scheme 2. Synthesis of compounds **1** and **2**: dependence on the phosphine cone angle. (a)See reference [26]. (b) For cone angle calculations see references [35] and [36]. Generic NMR and X-ray labelling scheme shown for **1**.

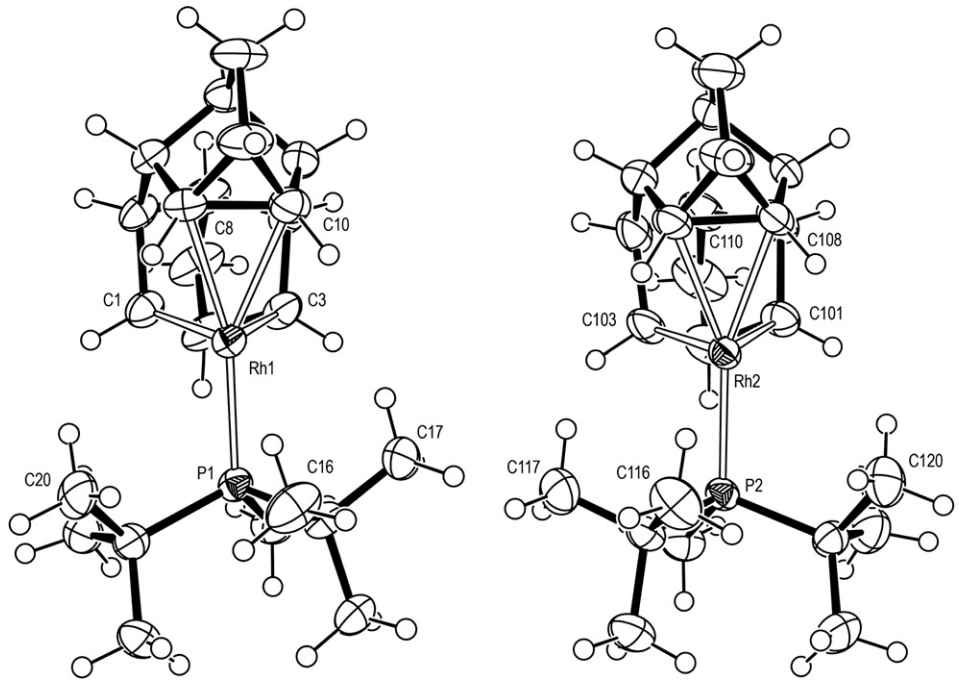


Fig. 1. Solid-state structures of **1** ($Z' = 2$). Thermal ellipsoids are drawn at 50%, solvent molecules and anions omitted for clarity. Selected bond lengths (Å): Rh1–P1, 2.2707(13); Rh1–C1, 2.039(5); Rh1–C3, 2.020(5); Rh1–C8, 2.372(5); Rh1–C10, 2.382(5); Rh1–C16, 3.504(6); Rh1–C17, 3.244(6); Rh1–C20, 3.446(6); C8–C10, 1.605(7); Rh2–P2, 2.2749(12); Rh2–C101, 2.027(5); Rh2–C103, 2.021(5); Rh2–C108, 2.372(5); Rh2–C110, 2.372(5); Rh2–C116, 3.394(6); Rh2–C117, 3.451(6); Rh2–C120, 3.310(6); C108–C110, 1.611(7).

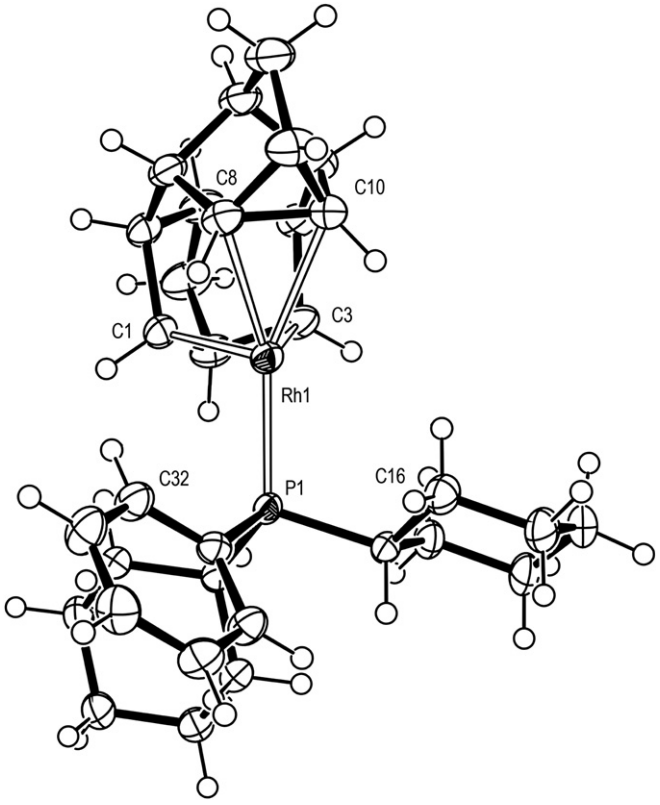


Fig. 2. Solid-state structure of **2**. Thermal ellipsoids are drawn at 50%, anion omitted for clarity. Selected bond lengths (Å): Rh1–P1, 2.2531(9); Rh1–C1, 2.029(3); Rh1–C3, 2.027(4); Rh1–C8, 2.370(4); Rh1–C10, 2.369(4); Rh1–C16, 3.344(4); Rh1–C32, 3.307(4); C8–C10, 1.616(5).

3. Conclusions

We have extended the number of complexes that show C–C···Rh interactions by the synthesis and characterization of $[Rh(PR_3)(Binor{-}S)][BAr^F{}_4]$, R = P^tBu_2Me, **1**; PCy_2Ph, **2**. When considered alongside our previous work in the area these studies show that there is a rather narrow window of phosphine steric profile that supports the isolation of these interesting complexes, with the phosphine cone angle lying between 160° and 170°.

4. Experimental

4.1. General methods

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. CH_2Cl_2, hexane and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze–pump–thaw cycles [42]. C_6H_5F and CD_2Cl_2 were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. NBD was degassed by successive freeze–pump–thaw cycles and dried over 3 Å molecular sieves. $[Rh(NBD)Cl]_2$ [43], $[Rh(NBD)Cl(PPh_3)]$ [44], $[Rh(NBD)Cl(P^tBu_3)]$ [45] and $Na[BAr^F{}_4]$ [46] were prepared using literature methods. All other chemicals are commercial

Table 1
Comparison of selected structural metrics for the Rh–Binor–S complexes.

$[Rh(PR_3)(Binor{-}S)]^+$	P^iPr_3[a]	PCy_3[a]	$PCyp_3$[a]	P^tBu_2Me **1**[b]	PCy_2Ph **2**
Rh–P/Å	2.2693(7)	2.2621(4)	2.2466(7)	2.273(2)	2.2531(9)
C8–C10/Å	1.604(4)	1.608(3)	1.607(4)	1.608(10)	1.616(5)
Rh–C8/Rh–C10/Å[c]	2.361(4)	2.386(3)	2.352(4)	2.375(10)	2.370(6)
Rh–C1/Rh–C3/Å[c]	2.037(4)	2.026(3)	2.032(3)	2.027(10)	2.028(5)

[a] See reference [26].
[b] Averaged over two independent molecules.
[c] Average value.

products and were used as received. NMR spectra were recorded on a Bruker DRX 500 MHz, Bruker AVC 500 MHz or Varian Mercury VX 300 MHz spectrometers. Chemical shifts are quoted in ppm and coupling constants in Hz. Microanalyses of **1** and **2** were performed at Elemental Microanalysis Ltd; all others were performed at the London Metropolitan University.

4.2. Synthesis of [Rh(NBD)Cl(PR$_3$)]

General procedure: To a solution of [Rh(NBD)Cl]$_2$ (0.150 g, 0.325 mmol) in CH_2Cl_2 (6 mL) was added PR_3 (0.683 mmol) and the resulting yellow solution stirred at room temperature for 2 h. The products were obtained either by recrystallization by addition of hexane (PR_3 = PCy_2Ph) or by removing the solvent in vacuo and washing with hexane at low temperature (−78 °C, PR_3 = P^iBu_3, P^tBu_2Me, PAd^n_2Bu).

[Rh(NBD)Cl(P^iBu_3)] Yield: 75%.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 5.06–5.11 (m, 2H, CH), 3.74–3.80 (m, 2H, CH), 3.37–3.43 (m, 2H, CH), 1.80–1.98 (m, 3H, ^{i}Bu{CH}), 1.41–1.49 (m, 7H, ^{i}Bu{CH_2} + CH_2), 1.37 (dt, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 1.4, 1H, CH_2'), 1.16 (d, $^3J_{HH}$ = 6.6, 18H, ^{i}Bu{Me}).

^{31}P{1H} NMR ($CDCl_3$, 122 MHz, 298 K): δ 9.2 (d, $^1J_{RhP}$ = 164, 1P).

Anal. Calcd for $C_{19}H_{35}ClPRh$ (432.82 gmol^{-1}): C, 52.73; H, 8.15; N, 0.00. Found: C, 52.84; H, 8.24; N, 0.00.

[Rh(NBD)Cl(P^tBu_2Me)] Yield: 53%.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 4.97–5.01 (m, 2H, CH), 3.70–3.75 (m, 2H, CH), 3.34–3.39 (m, 2H, CH), 1.39 (d app. q, $^2J_{HH}$ = 8.7, J = 2, 1H, CH_2), 1.33 (dt, $^2J_{HH}$ = 8.7, $^3J_{HH}$ = 1.6, 1H, CH_2'), 1.35 (d, $^3J_{PH}$ = 13.2, 18H, ^{t}Bu), 0.66 (dd, $^2J_{PH}$ = 7.0, $^3J_{RhH}$ = 1.3, 3H, Me).

^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz, 298 K): δ 36.9 (d, $^1J_{RhP}$ = 166, 1P).

Anal. Calcd for $C_{16}H_{29}ClPRh$ (390.74 gmol^{-1}): C, 49.18; H, 7.48; N, 0.00. Found: C, 49.29; H, 7.39; N, 0.00.

[Rh(NBD)Cl(PCy_2Ph)] Yield: 85%.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.35–7.46 (m, 5H, Ph), 5.08–5.13 (m, 2H, CH), 3.73–3.79 (m, 2H, CH), 3.34–3.39 (m, 2H, CH), 1.10–2.26 (m, 24H, Cy + CH_2).

^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz, 298 K): δ 31.6 (d, $^1J_{RhP}$ = 166, 1P).

Anal. Calcd for $C_{25}H_{35}ClPRh$ (504.88 gmol^{-1}): C, 59.47; H, 6.99; N, 0.00. Found: C, 59.56; H, 7.11; N, 0.00.

[Rh(NBD)Cl(PAd^n_2Bu)] Yield: 83%.

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 4.84–4.90 (m, 2H, CH), 3.68–3.74 (m, 2H, CH), 3.55–3.61 (m, 2H, CH), 2.20–2.35 (m, 12H, Ad), 2.00 (br, 6H, Ad), 1.75 (app. q, J = 13, 12H, Ad), 1.55–1.66 (m, 2H, ^{n}Bu{CH_2}), 1.41 (d app. q, $^2J_{HH}$ = 8.7, J = 2, 1H, CH_2), 1.24–1.37 (m, 5H, 2 × ^{n}Bu{CH_2} + CH_2'), 0.93 (t, $^3J_{HH}$ = 7.3, 3H, ^{n}Bu{Me}).

^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz, 298 K): δ 36.6 (d, $^1J_{RhP}$ = 160, 1P).

Anal. Calcd for $C_{31}H_{47}ClPRh$ (589.05 gmol^{-1}): C, 63.21; H, 8.04; N, 0.00. Found: C, 63.34; H, 7.94; N, 0.00.

4.3. Synthesis of [Rh(BINOR–S)(P^tBu_2Me)][BAr$^F_4$] **1**

To a Schlenk flask charged with [Rh(NBD)Cl(P^tBu_2Me)] (0.0200 g, 0.051 mmol) and Na[BAr$^F_4$] (0.0450 g, 0.051 mmol) was added a solution of NBD (0.1 mL, excess) in C_6H_5F (2 mL). The resulting suspension was stirred at RT for 90 min and then filtered. The filtrate was layered with pentane and held at 5 °C for 72 h to afford the product as yellow crystals. Yield: 0.056 g (84%).

^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): δ 7.70–7.74 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 3.18 (br, 4H, H$^{1/3/8/10}$), 2.34 (br, 2H, H$^{2/9}$), 2.14 (s, 2H, H$^{5/12}$), 1.94 (br, 4H, H$^{4/6/11/13}$), 1.38 (br, 4H, H$^{4/9}$), 1.35 (d, $^3J_{PH}$ = 13.6, 18H, ^{t}Bu), 1.28 (dd, $^2J_{PH}$ = 9.2, $^3J_{RhH}$ = 2.0, 3H, Me).

^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz, 298 K): δ 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 135.4 (s, Ar^F), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 125.2 (q, $^1J_{FC}$ = 273, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 43.9 (br, C$^{4/6/11/13}$), 36.4 (d, $^1J_{PC}$ = 23, ^{t}Bu{C}), 35.3 (br, C$^{5/12}$), 33.2 (br, C$^{4/9}$), 30.5 (d, $^2J_{PC}$ = 3, ^{t}Bu{Me}), 26.3 (br d, J = 12, C$^{1/3/8/10}$), 2.2 (dd, $^1J_{PC}$ = 23, $^2J_{RhC}$ = 3, Me). C$^{2/9}$ was not unambiguously located at this temperature.

^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 298 K): δ 54.8 (d, $^1J_{RhP}$ = 224, 1P).

Anal. Calcd. for $C_{55}H_{49}BF_{24}RhP$ (1310.65 gmol^{-1}): C, 50.40; H, 3.77; N, 0.00. Found: C, 50.52; H, 3.67; N, 0.00.

4.4. Synthesis of [Rh(BINOR–S)(PCy_2Ph)][BAr$^F_4$] **2**

To a Schlenk flask charged with [Rh(NBD)Cl(PCy_2Ph)] (0.0235 g, 0.047 mmol) and Na[BAr$^F_4$] (0.0412 g, 0.047 mmol) was added a solution of NBD (0.1 mL, excess) in C_6H_5F (3 mL). The resulting suspension was stirred at RT for 90 min and then filtered. The filtrate was layered with pentane and held at 5 °C for 72 h to afford the product as yellow crystals. Yield: 0.044 g (66%).

^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): δ 7.70–7.74 (m, 8H, Ar^F), 7.51–7.65 (m, 9H, Ar^F + Ph), 3.35 (br, 4H, H$^{1/3/8/10}$), 2.42 (app. q, J = 10, 2H, Cy{CH}), 2.31 (br, 2H, H$^{2/9}$), 2.20 (s, 2H, H$^{5/12}$), 2.03 (br, 4H, H$^{4/6/11/13}$), 1.77–1.96 (m, 10H, Cy), 1.43 (br, 4H, H$^{4/9}$), 1.18–1.52 (m, 10H, Cy).

^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz, 298 K): δ 162.3 (q, $^1J_{BC}$ = 50, Ar^F), 135.4 (s, Ar^F), 133.5 (d, $^2J_{PC}$ = 9, Ph), 132.6 (d, $^4J_{PC}$ = 2, Ph), 130.7 (d, $^3J_{PC}$ = 9, Ph), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, Ar^F), 125.5 (d, $^1J_{PC}$ = 39, Ph), 125.1 (q, $^1J_{FC}$ = 272, Ar^F), 118.0 (sept, $^3J_{FC}$ = 4, Ar^F), 43.9 (br, C$^{4/6/11/13}$), 35.3 (br, C$^{5/12}$), 33.5 (dd, $^1J_{PC}$ = 24, $^2J_{RhC}$ = 2, Cy{CH}), 33.4 (br, C$^{4/9}$), 29.6 (br, Cy), 29.1 (br, Cy), 27.4 (d, $^2J_{PC}$ = 12, Cy), 27.3 (d, $^2J_{PC}$ = 11, Cy), 26.4 (br, Cy), 25.9 (dd, J = 13, J = 4, C$^{1/3/8/10}$). C$^{2/9}$ was not unambiguously located at this temperature.

^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 298 K): δ 42.1 (d, $^1J_{RhP}$ = 211, 1P).

Anal. Calcd. for $C_{65}H_{58}BF_{24}RhP$ (1439.83 gmol^{-1}): C, 54.22; H, 4.06; N, 0.00. Found: C, 53.88; H, 3.84; N, 0.00.

4.5. Crystallography

Data for **1** and **2** (Table 2) were collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low-temperature device [150(2) K]

Table 2
Crystallographic data for **1** and **2**.

	1.C_6H_5F	**2**
CCDC	897872	897873
Formula	$C_{61}H_{54}BF_{25}PRh$	$C_{64}H_{55}BF_{24}PRh$
M	1406.73	1424.77
Crystal System	Triclinic	Triclinic
Space group	P-1	P-1
T [K]	150(2)	150(2)
a [Å]	16.9856(3)	12.4297(2)
b [Å]	19.4486(3)	13.9045(2)
c [Å]	19.6501(3)	18.1299(3)
a [deg]	71.3272(8)	81.1817(10)
β [deg]	75.9809(8)	77.5303(10)
g [deg]	89.9118(7)	83.5117(8)
V [Å^3]	5946.04(16)	3012.91(8)
Z	4 (Z' = 2)	2
Density [gcm^{-3}]	1.571	1.571
μ (mm^{-1})	0.433	0.426
θ range [deg]	5.10 ≤ θ ≤ 25.03°	5.12 ≤ θ ≤ 25.03°
Reflns collected	37148	17850
R_{int}	0.0486	0.0288
Completeness	99.0%	99.0%
No. of data/restr/param	20806/805/1760	10563/520/913
R_1 [$I > 2\sigma(I)$]	0.0513	0.0427
wR_2 [all data]	0.1337	0.1078
GoF	1.024	1.026
Largest diff. pk and hole [eÅ^{-3}]	0.735, −0.594	0.906, −0.662

[47]; data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK [48]. The structures were solved by direct methods using SIR2004 [49] and refined full-matrix least squares on F^2 using SHELXL-97 [50]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using the riding model. Further details about the refinement, including disorder modelling and restraints, are documented in the CIF under the heading _refine_special_details. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under CCDC 897872 and 897873 These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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