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$[B(3,5\text{-}C_6H_3Cl_2)_4]^-$ as a Useful Anion for Organometallic Chemistry

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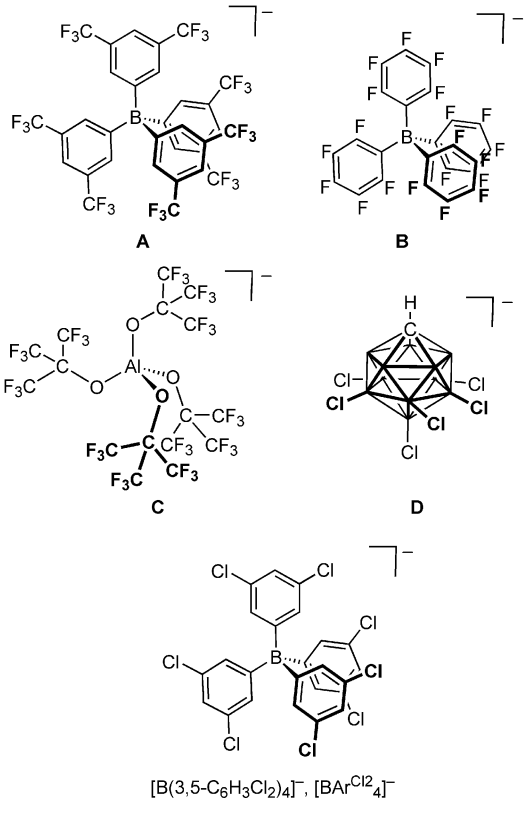
We highlight the use of the robust $[B(3,5\text{-}C_6H_3Cl_2)_4]^-$ anion in organometallic chemistry. When partnered with organometallic cations, compared with $[BAr^F{}_4]^-$ it presents desirable solubility properties, a lack of anion disorder in the solid-state, different coordinating properties with metal fragments and convenient metathetical routes for utilisation in synthesis.

Introduction

Weakly coordinating anions are commonplace in the synthesis of cationic organometallic and main-group salts, as well as organic synthetic routes that use cationic transition metal catalysts. They are used when vacant, or latent, sites are required at a metal centre, either as an integral part of the desired structure or for onward reactivity, either stoichiometric or catalytic.[1] The design of such anions thus incorporates noncoordinating peripheries, in which the overall negative charge is buried within the molecule. As the desired cationic species that partner these anions are often rather reactive, any associated anion is also required to be robust to metal-promoted reactivity. Thus, the anions $[PF_6]^-$ and $[BF_4]^-$, although ubiquitous, are often not the choice for demanding applications due to hydrolysis by adventitious water or fluoride abstraction.[2] Although the range of possible anions is large, only a handful are used routinely (Scheme 1). The anions $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ (**A**) and $[B(C_6F_5)_4]^-$ (**B**) (and derivatives[3]) are perhaps the most widely used, but other anions have also found popularity: $[Al\{OC(CF_3)_3\}_4]^-$ (**C**[4]) and [*closo*-$CB_{11}H_6Cl_6]^-$ (**D**[5]) (and derivatives thereof[6,7]). Of the fluorinated anions (e.g., **A** and **C**), rotational disorder of the CF_3 groups or the formation of clathrates can potentially hamper the accurate structural determination of the resulting complexes in the solid-state – especially when any structural study involves a charge-density analysis in which electron density has to be precisely modelled. We report here the use of an easily prepared anion, $[BAr^{Cl2}{}_4]^-$ (Ar^{Cl2} = 3,5-$C_6H_3Cl_2$), that shows no disorder in the solid-state for the complexes isolated and, importantly, is readily substituted into a synthetic pathway in place of anions such as $[BAr^F{}_4]^-$ [Ar^F = $C_6H_3(CF_3)_2$]. We demonstrate its coordinating properties by the synthesis of two sets of complexes that use the recently reported $[Rh\{\kappa^3\text{-}PtBu_2CH_2CH(CH_2)_2\}]^+$[8] and $[Rh(BINOR\text{-}S)(PiPr_3)]^+$[9] fragments (BINOR-S = *endo*,*cis*,*endo*-heptacyclo[5.3.1.1.^{2,6}1.^{4,12}1.^{9,11}0.^{3,5}0^{8,10}]tetradecane). The former is a 12-electron Rh^{III} fragment that binds arenes (e.g., fluorobenzene) in an η^6-manner, whereas the latter is formally a 12-electron Rh^{III} centre with a supporting C–C σ-bond and an agostic C–H interaction. Although the $[BAr^{Cl2}{}_4]^-$ anion was originally reported in the open literature by Pacey as the Cs^+ salt,[10] with a refine-



Scheme 1.

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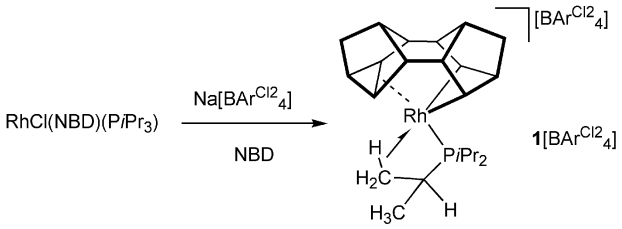
ment in the synthesis by Serwatowski and co-workers in 2003,[11] as far as we are aware it has not been utilised in organometallic chemistry to generate and stabilise potentially reactive metal cations.[12] We believe that this anion will be of use to the organometallic and catalysis communities as well as those interested in the structural determination of cationic species given its ease of preparation, attractive solubility properties, lack of anion disorder in the solid-state, comparable coordinating properties to C_6H_5F and [$BAr^F{}_4$]$^-$, and its expedient use in synthesis. This paper demonstrates these properties and the comparison with the [$BAr^F{}_4$]$^-$ anion and C_6H_5F arene ligand/solvent.

Results and Discussion

The anion [B(3,5-$C_6H_3Cl_2)_4$]$^-$ is best prepared as the Na^+ salt, Na[$BAr^{Cl2}{}_4$], by a slight modification of the published route,[11] in that additional drying is necessary to obtain anhydrous material necessary for organometallic chemistry. This is simply achieved by heating under vacuum overnight. Metathesis (CH_2Cl_2, filtration) with [Bu_4N][BH_4] affords the corresponding ammonium salt, for which the solid-state structure is described in the Supporting Information. No anion disorder is apparent in the structure. In solution [Bu_4N][$BAr^{Cl2}{}_4$] shows sharp resonances in the ^{1}H NMR spectrum (CD_2Cl_2) that show complicated, presumably second-order, coupling in the aromatic region (δ = 7.05–7.00 ppm). The $^{13}C\{^1H\}$ NMR spectrum is simpler, with four resonances observed, as expected, for the anion between δ = 165.2 and 123.6 ppm. The ^{11}B NMR spectrum (CD_2Cl_2) indicates a single, relatively sharp, environment at δ = –6.9 ppm.

To demonstrate that [$BAr^{Cl2}{}_4$]$^-$ can support complexes that show weak and unusual interactions, we have synthesised the complex [Rh(BINOR-S)(P*i*Pr_3)][$BAr^{Cl2}{}_4$] (**1**[$BAr^{Cl2}{}_4$]) by the addition of Na[$BAr^{Cl2}{}_4$] to a mixture of RhCl(P*i*Pr_3)(NBD)/excess NBD (Scheme 2) and precipitation of NaCl (NBD = norbornadiene). This new salt is analogous to the previously reported [Rh(BINOR-S)(P*i*Pr_3)][$BAr^F{}_4$] salt,[9] and contains a C–C σ and a C–H agostic interaction. It cannot be synthesised by using anions such as [BF_4]$^-$ or [PF_6]$^-$ due to decomposition. Thus, the anion [$BAr^{Cl2}{}_4$]$^-$ supports potentially reactive late transition metal centres. Figure 1 shows the solid-state structure of **1**[$BAr^{Cl2}{}_4$], which demonstrates that there are no close contacts between the anion and the metal centre (Rh···Cl distances longer than 4.5 Å). It also demonstrates no anion disorder, a highly desirable property for charge-density analysis in which the rotational disorder in [$BAr^F{}_4$]$^-$-type anions is problematic. The NMR spectroscopic data for the cation are as reported previously,[9] and the anion resonances in the ^{1}H NMR spectrum are essentially unchanged from those of the [Bu_4N][$BAr^{Cl2}{}_4$] salt.



Scheme 2.

With a more open coordination environment the [$BAr^{Cl2}{}_4$]$^-$ anion can bind in an η^6-motif to the metal centre, as we have recently reported for the [$BAr^F{}_4$]$^-$ anion in both rhodium and iridium complexes with a chelating phosphane–alkene ligand [M{P(C_5H_9)$_2$(η^2-C_5H_7)}({η^6-$C_6H_3(CF_3)_2$}$BAr^F{}_3$)] (M = Rh,[13a] Ir[13b]). Here we use the closely related Rh^{III} complex [Rh(η^6-C_6H_5F){κ^3-P*t*$Bu_2CH_2CH(CH_2)_2$}][$BAr^F{}_4$][8] (**2**[$BAr^F{}_4$]) as a suitable starting material as this provides an open coordination site on displacement of the weakly bound fluoroarene ligand. The addition of [Bu_4N][$BAr^{Cl2}{}_4$] to **2**[$BAr^F{}_4$] in a solution of CH_2Cl_2 results in the displacement of the bound fluo-

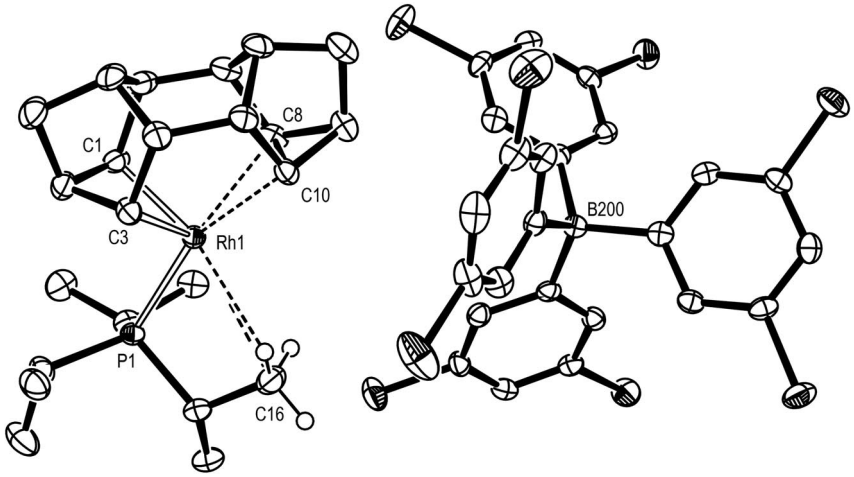


Figure 1. Solid-state structure of **1**[$BAr^{Cl2}{}_4$]. Thermal ellipsoids drawn at the 50% probability level. Most H atoms and the solvent molecule (CH_2Cl_2) are omitted for clarity.

roarene ligand by the $[BAr^{Cl2}{}_4]^-$ anion and formation of zwitterionic $[Rh\{\kappa^3\text{-}PtBu_2CH_2CH(CH_2)_2\}\{(\eta^6\text{-}C_6H_3Cl_2)\text{-}BAr^{Cl2}{}_3\}]$ (**3**) (Scheme 3). Alternatively, **3** can be prepared from the tetramer $[RhCl\{\kappa^3\text{-}PtBu_2CH_2CH(CH_2)_2\}]_4$[8] by the addition of $Na[BAr^{Cl2}{}_4]$ in a solution of 1,2-$C_6H_4F_2$. The solid-state structure is shown in Figure 2, and the structural metrics are unremarkable. The anion in **3** is coordinated through one arene ring, similar to that observed in the closely related complex $[Rh\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}(\{\eta^6\text{-}C_6H_3(CF_3)_2\}BAr^F{}_3)]$[13a] and for other Rh^I zwitterionic salts of $[B(C_6H_5)_4]^-$.[14] In solution (CH_2Cl_2), the anion remains coordinated, as demonstrated by the observation of a 6:3:1:2 set of resonances in the ^1H NMR spectrum that are all broadened compared with those of the free anion, and which are spread over a wider chemical shift range than those of the free anion (δ = 7.14–6.65 ppm). The higher-field pair is assigned to the arene ring bound to the metal centre. The ^{11}B NMR spectrum of the reaction mixture shows signals of free $[BAr^F{}_4]^-$ and a broad resonance at δ = –7.6 ppm for the coordinated anion in **3**; this is shifted upfield by 1 ppm from that of the free anion. Dissolution of **3** in C_6H_5F results in an equilibrium being established with the arene adduct **2**$[BAr^{Cl2}{}_4]$ (2:1, respectively, as measured by ^1H, ^{31}P and ^{11}B NMR spectroscopy). Given the large excess of C_6H_5F present as solvent, this result demonstrates that $[BAr^{Cl2}{}_4]^-$ binds relatively strongly compared with C_6H_5F. Complex **2**$[BAr^{Cl2}{}_4]$ is less soluble than **3** and crystallises out of solution on standing; a solid-state structure confirms the identity of this new species (see the Supporting Information). In addition, complex **2**$[BAr^{Cl2}{}_4]$ is significantly less soluble than the corresponding $[BAr^F{}_4]^-$ salt and is readily isolated as crystalline material by mixing **2**$[BAr^F{}_4]$ and $[Bu_4N][BAr^{Cl2}{}_4]$ in C_6H_5F, demonstrating the potential versatility of the $[BAr^{Cl2}{}_4]^-$ anion for anion-exchange reactions. Redissolving **2**$[BAr^{Cl2}{}_4]$ in CD_2Cl_2 reforms **3** as evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, as well as free C_6H_5F. Addition of mesitylene to **3** results in the displacement of the anion and the formation of the arene adduct **4**$[BAr^{Cl}{}_4]$ (Scheme 3) (see the Supporting Information for the solid-state structure).

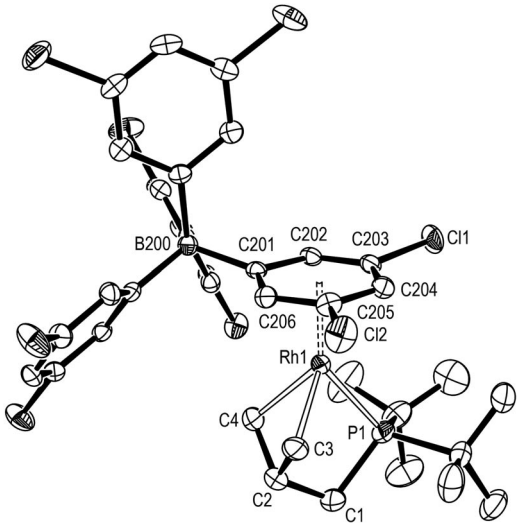
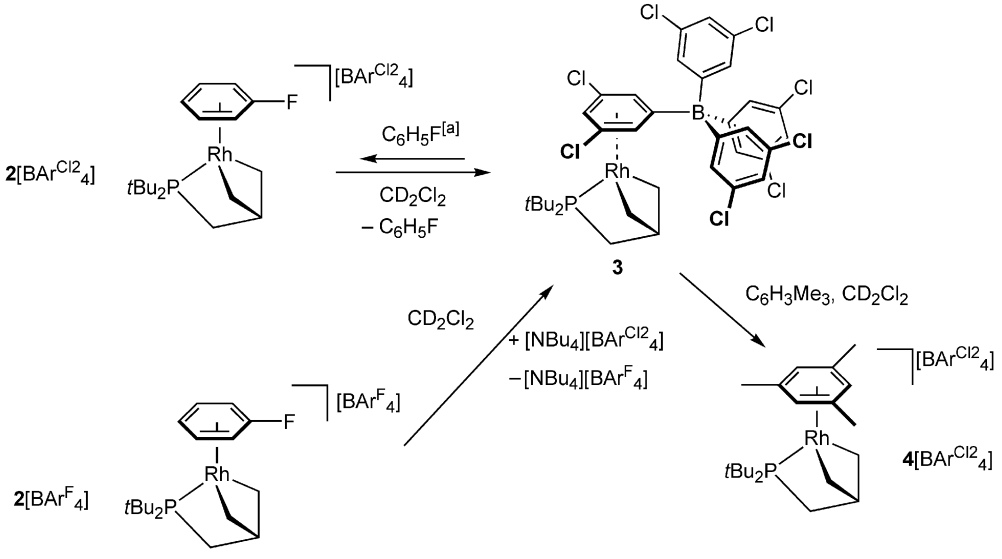


Figure 2. Solid-state structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Rh1–C201 2.434(2), Rh1–C202 2.412(4), Rh1–C203 2.389(2), Rh1–C204 2.380(2), Rh1–C205 2.290(2), Rh1–C206 2.286(2) Å.

Conclusions

We highlight the use of the $[B(3,5\text{-}C_6H_3Cl_2)_4]^-$ anion in organometallic chemistry. When partnered with organometallic cations, compared with $[BAr^F{}_4]^-$ it presents different, possibly desirable, solubility properties, a lack of anion disorder in the solid-state, different coordinating properties and convenient metathetical routes allowing for its utilisation in synthesis. An approximate coordinating ability can also be established compared with $[BAr^F{}_4]^-$ and C_6H_5F in



Scheme 3. [a] Equilibrium established between **2**$[BAr^{Cl2}{}_4]$ and **3** in a solution of C_6H_5F. See text for details.

which [$BAr^{Cl2}{}_4$]$^-$ interacts with very open metal centres more strongly than [$BAr^F{}_4$]$^-$, but is competitive, although more strongly binding, with the weakly coordinating solvent C_6H_5F. With less available, albeit reactive, metal centres, e.g., **1**[$BAr^{Cl2}{}_4$], the coordinating properties of the anions are levelled and neither interact. Indeed in this respect, [$BAr^{Cl2}{}_4$]$^-$ has very recently been used in the isolation of a two-coordinate-at-boron, 18-valence-electron, cationic, iron–borylene complex, in which these desirable properties of solubility, ease of synthesis and chemical robustness are further highlighted.[12] Of course, in systems in which oxidative addition to a metal centre of aryl chlorides is a straightforward process,[15] such as in cross-coupling reactions,[16] these anions might be of less use, although this offers potential opportunities for derivatisation of the anion itself.

Experimental Section

General: All manipulations, unless otherwise stated, were performed under argon by using Schlenk and glove-box techniques. Glassware was oven-dried at 130 °C overnight and flamed under vacuum prior to use. CH_2Cl_2, pentane and hexane were dried by using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[17] CD_2Cl_2, C_6H_5F and 1,2-$C_6H_4F_2$ were dried with CaH_2, vacuum-distilled and stored over molecular sieves (3 Å). [Rh(NBD)(P*i*Pr$_3$)Cl],[9] [RhCl{κ^3-P*t*Bu$_2$$CH_2CH(CH_2)_2$}]$_4$[8] and [Rh{κ^3-P*t*Bu$_2$$CH_2CH(CH_2)_2$}($C_6H_5F$)][$BAr^F{}_4$][8] were prepared according to literature methods. Na[$BAr^{Cl2}{}_4$] was prepared according to a literature procedure[11] and dried at 120 °C under dynamic vacuum (5×10^{-3} Torr). All other chemicals are commercial products and were used as received. NMR spectroscopic data were recorded with a Varian Mercury VX 300 MHz, Varian Unity Plus 500 MHz or Bruker AVC 500 MHz spectrometer at room temperature, unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. Microanalyses were performed by Elemental Microanalysis Ltd.

Preparation of [*n*Bu$_4$N][$BAr^{Cl2}{}_4$]: CH_2Cl_2 (3 mL) was added to a Schlenk flask charged with [*n*Bu$_4$N][BH_4] (0.208 g, 0.808 mmol) and Na[$BAr^{Cl2}{}_4$] (0.501 g, 0.810 mmol). The resulting suspension was placed in an ultrasound bath for 20 min and then filtered. The filtrate was concentrated to dryness under vacuum and then washed with hexane (3× 5 mL) to yield 0.54 g (80%) as a white microcrystalline solid. Crystals suitable for X-ray diffraction were grown from layering a CH_2Cl_2 solution of the complex with hexane at room temperature (see the Supporting Information). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.00–7.05 {m, 12 H, $BAr^{Cl2}{}_4$ [δ = 7.04 (*m*-CH), 7.01 (*p*-CH) ppm]}, 2.92–2.98 (m, 8 H, NCH_2), 1.47–1.58 (m, 8 H, $NCH_2C\mathit{H}_2$), 1.35 (apparent sext, $^3J_{HH}$ = 7 Hz, $C\mathit{H}_2$Me), 0.98 (t, $^3J_{HH}$ = 7.3 Hz, 12 H, Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 76 MHz): δ = 165.2 (q, $^1J_{BC}$ = 49 Hz, $BAr^{Cl2}{}_4$), 133.6 [$BAr^{Cl2}{}_4$ (*m*-CH)], 133.4 (q, $^3J_{BC}$ = 4 Hz, $BAr^{Cl2}{}_4$), 123.6 [$BAr^{Cl2}{}_4$ (*p*-CH)], 59.5 (m, NCH_2), 24.3 ($NCH_2C\mathit{H}_2$), 20.2 ($C\mathit{H}_2$Me), 13.9 (Me) ppm. ^{11}B NMR (CD_2Cl_2, 160 MHz): δ = –6.9 ppm. $C_{40}H_{48}BCl_8N$ (837.3): calcd. C 57.38, H 5.78, N 1.67; found C 57.38, H 5.81, N 1.69.

Preparation of [Rh(BINOR-S)(P*i*Pr$_3$)][$BAr^{Cl2}{}_4$] (1[$BAr^{Cl2}{}_4$]): A solution of NBD (0.040 mL, 0.393 mmol) in C_6H_5F (3 mL) was added to a Schlenk flask charged with [Rh(NBD)(P*i*Pr$_3$)Cl] (0.050 g, 0.128 mmol) and Na[$BAr^{Cl2}{}_4$] (0.077 g, 0.125 mmol). The resulting suspension was stirred at room temperature for 1 h and then filtered. The residue was extracted with CH_2Cl_2 (2 mL) and the product precipitated as a yellow powder by the addition of excess hexane. Yield: 0.043 g (33%). Crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution of the complex with pentane at 5 °C. NMR spectroscopic data for the cation are in good agreement with the literature values for the corresponding [$BAr^F{}_4$]$^-$ salt.[9] Resonances due to [$BAr^{Cl2}{}_4$]$^-$ are essentially unchanged from [*n*Bu$_4$N][$BAr^{Cl2}{}_4$].

Preparation of [Rh{κ^3-P*t*Bu$_2$$CH_2CH(CH_2)_2$}(η^6-$BAr^{Cl2}{}_4$)] (3): 1,2-$C_6H_4F_2$ (2 mL) was added to a Schlenk flask charged with [RhCl{κ^3-P*t*Bu$_2$$CH_2CH(CH_2)_2$}]$_4$ (0.038 g, 0.028 mmol) and Na[$BAr^{Cl2}{}_4$] (0.073 g, 0.118 mmol). After stirring for 1 h, the solution was filtered and the filtrate concentrated to dryness in vacuo. Successive recrystallisation of the residue from CH_2Cl_2/pentane/hexane at –20 °C afforded the product as yellow needles. Yield: 0.052 (49% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.14 [br., 6 H, B(*o*-$C_6\mathit{H}_3Cl_2)_3$], 6.95 [br., 3 H, B(*p*-$C_6\mathit{H}_3Cl_2)_3$], 6.74 [v. br., 1 H, η^6-(*p*-$C_6\mathit{H}_3Cl_2$)], 6.65 [v. br., 2 H, η^6-(*o*-$C_6\mathit{H}_3Cl_2$)], 2.84 (dm, $^3J_{PH}$ = 65.2 Hz, 1 H, CH), 1.75 (br. d, $^2J_{PH}$ = 7.8 Hz, 2 H, PCH_2), 1.68 (apparent q, *J* = 3.4 Hz, 2 H, $RhCH_2$), 1.54 (br., 2 H, $RhCH_2'$), 1.38 (d, $^3J_{PH}$ = 13.7 Hz, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): δ = 160.8 [q, $^1J_{BC}$ = 49 Hz, B(*i*-$C_6H_3Cl_2)_3$], 153.2 [br., η^6-(*i*-$C_6H_3Cl_2$)], 133–134 [m, B(*o*-$C_6H_3Cl_2)_3$ + *m*-$C_6H_3Cl_2$], 125.1 [B(*p*-$C_6H_3Cl_2)_3$], 109.7 [η^6-(*o*-$C_6H_3Cl_2$)], 103.2 [η^6-(*p*-$C_6H_3Cl_2$)], 45.1 (m, CH), 38.7 [d, $^1J_{PC}$ = 17 Hz, *t*Bu (C)], 31.2 [d, $^2J_{PC}$ = 3 Hz, *t*Bu (Me)], 26.1 (d, $^1J_{PC}$ = 24 Hz, PCH_2), 13.6 (d, $^1J_{RhC}$ = 18 Hz, $RhCH_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ = 126.4 (d, $^1J_{RhP}$ = 198 Hz) ppm. ^{11}B NMR (CD_2Cl_2, 160 MHz): δ = –7.6 ppm. $C_{36}H_{37}BCl_8PRh$ (898.0): calcd. C 48.15, H 4.15; found C 47.49, H 4.16. See Supporting Information for selected NMR spectra of the crystalline material.

Reaction of 3 with C_6H_5F: C_6H_5F (0.4 mL) was added to a J. Young NMR tube charged with **3** (0.006 g, 0.007 mmol). Analysis by NMR spectroscopy indicated the formation of a 1:2 mixture of **2**[$BAr^{Cl2}{}_4$] and **3**. NMR spectroscopic data for the cation of **2**[$BAr^{Cl2}{}_4$] are in good agreement with the literature values for the corresponding [$BAr^F{}_4$]$^-$ salt.[8] Resonances due to [$BAr^{Cl2}{}_4$] are essentially unchanged from [*n*Bu$_4$N][$BAr^{Cl2}{}_4$]. On standing at room temperature, **2**[$BAr^{Cl2}{}_4$] crystallised from solution (0.006 g, 90% yield). Dissolving this material in CD_2Cl_2 resulted in quantitative reformation of **3** with the concomitant liberation of C_6H_5F, as observed by NMR spectroscopy, and thus NMR spectroscopic data for **2**[$BAr^{Cl2}{}_4$] could not be obtained. Complex **2**[$BAr^{Cl2}{}_4$] was also prepared by the stoichiometric reaction between **2**[$BAr^F{}_4$] and [*n*Bu$_4$N][$BAr^{Cl2}{}_4$] in C_6H_5F. Crystals of **2**[$BAr^{Cl2}{}_4$] suitable for X-ray diffraction were grown from C_6H_5F at –20 °C (see Supporting Information for the solid-state structure).

Reaction of 3 with $C_6H_3Me_3$: $C_6H_3Me_3$ (0.005 mL, 0.036 mmol) was added to a solution of **3** (0.006 g, 0.007 mmol) in CD_2Cl_2 (0.4 mL) in a J. Young NMR tube. Analysis by NMR spectroscopy indicated the quantitative formation of [Rh{κ^3-P*t*Bu$_2$$CH_2CH(CH_2)_2$}($C_6H_3Me_3$)][$BAr^{Cl2}{}_4$] (**4**[$BAr^{Cl2}{}_4$]); data for the cation are in good agreement with the literature values for the corresponding [$BAr^F{}_4$]$^-$ salt.[8] Resonances due to [$BAr^{Cl2}{}_4$]$^-$ are essentially unchanged from [*n*Bu$_4$N][$BAr^{Cl2}{}_4$]. Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution of the complex layered with pentane at 5 °C (see Supporting Information for solid-state structure).

Reaction of 2[$BAr^F{}_4$] with [*n*Bu$_4$N][$BAr^{Cl2}{}_4$]: CD_2Cl_2 (0.4 mL) was added to a J. Young NMR tube charged with **2**[$BAr^F{}_4$] (0.010 g,

0.008 mmol) and [nBu$_4$N][BAr$^{Cl2}_4$] (0.066, 0.008 mmol). Analysis by NMR spectroscopy indicated the quantitative formation of **3**.

Crystallography: Relevant details about the structure refinements of **1**[BAr$^{Cl2}_4$] and **3** are given in Table 1. Data were collected with an Enraf Nonius Kappa CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a low-temperature device;[18] data were collected by using COLLECT, reduction and cell refinement were performed by using DENZO/SCALEPACK.[19] The structures were solved by direct methods using SIR2004[20] and refined by full-matrix least-squares on F^2 using SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions by using the riding model. Graphical representations of the structures were made by using ORTEP3.[22] CCDC-781556 (for **2**[BAr$^{Cl2}_4$]), -781557 (for **3**), -781558 (for **4**[BAr$^{Cl2}_4$]), -781559 (for [nBu$_4$N][BAr$^{Cl2}_4$]) and -781946 (for **1**[BAr$^{Cl2}_4$]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for **1**[BAr$^{Cl2}_4$] and **3**.

	1[BAr$^{Cl2}_4$]	**3**
Empirical formula	$C_{48}H_{51}BCl_{10}PRh$	$C_{36}H_{37}BCl_8PRh$
M	1127.08	897.95
T /K	150(2)	150(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a /Å	15.54420(10)	12.56750(10)
b /Å	13.39650(10)	16.1160(2)
c /Å	23.9622(2)	20.0126(3)
β /°	95.6384(4)	106.8663(5)
V /Å^3	4965.70(6)	3878.95(8)
Z	4	4
Density /g cm^{-3}	1.508	1.538
μ /mm^{-1}	0.948	1.059
θ range /°	5.11 ≤ θ ≤ 26.37	5.10 ≤ θ ≤ 26.37
Reflections collected	19586	15115
R_{int}	0.0262	0.0249
Completeness	99.2%	99.2%
Data/restraints/parameters	10071/0/556	7874/0/430
R_1 [$I > 2\sigma(I)$]	0.0308	0.0295
wR_2 (all data)	0.0702	0.0723
GoF	1.014	1.033
Largest difference peak/hole /e Å^{-3}	0.606/–0.574	0.571/–0.496

Supporting Information (see footnote on the first page of this article): Solid-state structures of [nBu$_4$N][BAr$^{Cl2}_4$], **2**[BAr$^{Cl2}_4$] and **4**[BAr$^{Cl2}_4$]; selected NMR spectroscopic data.

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