DOI: 10.1002/zaac.200600165

Halide Abstraction by Na[B{$C_6H_3(CF_3)_2$-3,5}$_4$]: Synthesis and Structural Characterization of the Rhodium(I) Cations [(η^6-arene)Rh(PPh_3)$_2$]$^+$ (Arene = benzene, toluene)

Oliver Buttler, Amal Al-Fawaz, Deborah L. Kays, Joanna K. Day, Li-Ling Ooi and Simon Aldridge*

Cardiff / UK, Centre for Fundamental and Applied Main Group Chemistry, Cardiff School of Chemistry

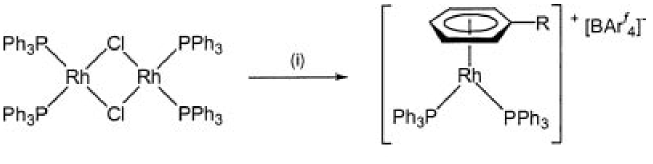
Received June 1st, 2006.

Abstract. Halide abstraction from [(Ph_3P)$_2$Rh(μ-Cl)]$_2$ by the sodium salt of the weakly coordinating [BAr^f_4]$^-$ anion [Ar^f = $C_6H_3(CF_3)_2$-3,5] in the presence of excess arene offers a convenient, high-yielding route to the half-sandwich cations [(arene)Rh(PPh_3)$_2$]$^+$[BAr^f_4]$^-$ [arene = benzene (**1**), toluene (**2**)]. Crystalline samples of **1** and **2** are isomorphous [*a* = 13.1270(2), *b* = 15.3030(2), *c* = 17.5760(3) Å, α = 74.620(1), β = 81.533(1), γ = 88.540(1)° for **1**] and feature the arene ligand bound to the rhodium atom in η^6 fashion.

Keywords: Rhodium; Phosphine; Halide abstraction

Cationic rhodium(I) complexes are known to be active homogeneous catalysts for a range of organic transformations [1]. Thus, for example, the *Schrock-Osborn* diene system [(Ph_3P)$_2$Rh(nbd)]$^+$ (nbd = norbornadiene) represents a benchmark in hydrogenation catalysis [2], and more recent work has demonstrated that complexes of the type [(arene)RhL_2]$^+$ (arene = benzene, toluene; L_2 = a chiral chelating phosphine such as 1,2-bis(2,5-diethylphospholanyl)benzene (Et-DuPHOS)) are effective catalysts for *asymmetric* hydrogenation reactions [3]. Synthetic routes to a range of arene-stabilized rhodium(I) *bis*(phosphine) cations have therefore been demonstrated [3−9] including complexes in which the π-system is provided by an aryl-containing borate counterion (e.g. [BPh_4]$^-$) [8], or by ancillary coordination of one of the phosphine ligands {as in [(Ph_3P)(Ph_2P-$\eta^6C_6H_5$)Rh]$_2$$^{2+}$} [9].

Recent investigation of the reactivity of late transition metal complexes such as [(Ph_3P)$_2$Rh(μ-Cl)]$_2$ towards the strongly Lewis acidic boranes [(C_6F_5)$_2$BCl] and [(C_6F_5)$_2$BH]$_2$ in arene solvents (benzene or toluene) reveals the formation of products due to halide or phosphine abstraction from the metal atom [10]. Given the widespread application of cationic rhodium(I) *bis*(phosphine) systems we were surprised to find, however, that reports concerning the synthesis and spectroscopic characterization of the parent system [(benzene)Rh(PPh_3)$_2$]$^+$ (**1**) were lacking, at that crystallographic studies of **1** (and its toluene analogue, **2**) were similarly absent. Therefore we report herein a straightforward synthesis of complexes **1** and **2**, as the [BAr^f_4]$^-$ salts [Ar^f = $C_6H_3(CF_3)_2$-3,5], and their structural characterization in the solid state.



1: R = H
2: R = Me

Scheme 1 Syntheses of the cationic *bis*(triphenylphosphine)-rhodium arene complexes **1** and **2**:. Reagents and conditions: (i) Na[BAr^f_4] (2 equiv.), arene (*ca.* 300 equiv.), dichloromethane, 20 °C, 90 min, *ca.* 85 % isolated yield.

Reaction of [(Ph_3P)$_2$Rh(μ-Cl)]$_2$ with two equivalents of Na[BAr^f_4] and a vast excess of benzene or toluene (ca. 300 equivalents) using dichloromethane as the solvent (Scheme 1) leads to the formation of [(arene)Rh(PPh_3)$_2$]$^+$[BAr^f_4]$^-$ [arene = benzene (**1**), toluene (**2**)] in good yields (ca. 85 %). **1** and **2** have been characterized by multinuclear (^1H, ^{11}B, ^{13}C, ^{19}F and ^{31}P) NMR, and IR spectroscopies and by elemental analysis. Particularly diagnostic among the spectroscopic signatures are the extremely high $^1J_{RhP}$ coupling constants, typical of Rh(I) arene and cyclopentadienyl systems (*ca.* 205 Hz for both **1** and **2**) [3−5, 9a, 9b, 10], and aromatic ^1H resonances for the coordinated arene (δ_H 5.78 for **1**; δ_H 5.20, 5.55, 6.64 for **2**) shifted upfield from the corresponding free species [3−5, 9b, 10]. Single crystals of **1** and **2** suitable for study by X-ray crystallography could also be obtained, with the results shown in Figure 1 and Table 1.

The principal point of interest concerning the structures of the cationic components of **1** and **2** concerns the mode of interaction of the arene ligand with the *bis*(phosphine)rhodium(I) fragment. Examples of both 16-electron species containing η^4 arenes and 18-electron complexes featuring η^6 binding have previously been reported [3−7]. In the case of **1** and **2**, the metric parameters (notably the Rh-C and C-C distances) *do* reflect slight asymmetry in the arene binding, but the range of Rh-C and C-C distances [e.g.

---

* Dr Simon Aldridge
Cardiff University, Cardiff School of Chemistry
Centre for Fundamental and Applied Main Group Chemistry
Main Building, Park Place
Cardiff, CF10 3AT / UK
Tel: (029) 20875495
Fax: (029) 20874030
AldridgeS@cardiff.ac.uk

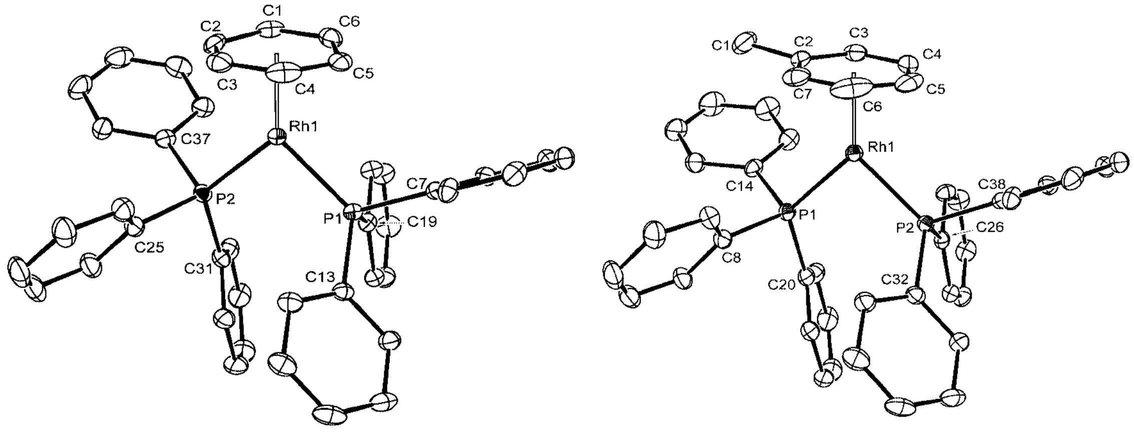


Figure 1 Structure of the cationic component of $[(\eta^6\text{-}C_6H_6)Rh(PPh_3)_2]^+[BAr^f_4]^-$ (**1**, left) and $[(\eta^6\text{-}C_6H_5CH_3)Rh(PPh_3)_2]^+[BAr^f_4]^-$ (**2**, right); hydrogen atoms omitted for clarity and ORTEP ellipsoids shown at the 50 % probability level.
Key bond lengths /Å and angles /°: for **1** Rh(1)-P(1) 2.243(1), Rh(1)-P(2) 2.272(1), Rh(1)-C_6H_6 centroid 1.864(5), Rh(1)-C(1) 2.340(4), Rh(1)-C(2) 2.298(4), Rh(1)-C(3) 2.366(4), Rh(1)-C(4) 2.357(4), Rh(1)-C(5) 2.283(4), Rh(1)-C(6) 2.320(4), C(1)-C(2) 1.413(7), C(2)-C(3) 1.392(7), C(3)-C(4) 1.380(7), C(4)-C(5) 1.410(7), C(5)-C(6) 1.403(7), C(1)-C(6) 1.367(7), P(1)-Rh(1)-P(2) 93.42(4); for **2** Rh(1)-P(1) 2.280(1), Rh(1)-P(2) 2.237(1), Rh(1)-C_6H_5 centroid 1.889(5), Rh(1)-C(2) 2.401(3), Rh(1)-C(3) 2.379(3), Rh(1)-C(4) 2.307(4), Rh(1)-C(5) 2.259(4), Rh(1)-C(6) 2.341(4), Rh(1)-C(7) 2.380(4), C(2)-C(3) 1.382(5), C(3)-C(4) 1.362(6), C(4)-C(5) 1.393(7), C(5)-C(6) 1.422(8), C(6)-C(7) 1.391(7), C(2)-C(7) 1.387(5), P(1)-Rh(1)-P(2) 92.84(3).

Table 1 Details of data collection, structure solution and refinement for compounds **1** and **2**.

Compound		**1**	**2**
Empirical formula		$C_{74}H_{48}BF_{24}P_2Rh$	$C_{75}H_{50}BF_{24}P_2Rh$
Formula weight		1568.78	1582.81
Temperature /K		150(2)	150(2)
CCDC deposit number		609304	609305
Wavelength /Å		0.71073	0.71073
Crystal system		Triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$
Unit cell dimensions /Å, °	a	13.1270(2)	13.1761(2)
	b	15.3030(2)	15.5566(2)
	c	17.5760(3)	17.5140(3)
	α	74.620(1)	74.806(1)
	β	81.533(1)	81.553(1)
	γ	88.540(1)	88.517(1)
Volume /Å^3		3366.8(1)	3426.6(1)
Density (calcd), /Mg m^{-3}		1.547	1.534
Z		2	2
Absorption coefficient /mm^{-1}		0.412	0.405
F(000)		1576	1592
Crystal size /mm^3		0.43 x 0.30 x 0.15	0.38 x 0.35 x 0.25
Theta range /°		3.06 to 27.56	3.52 to 26.37
Index ranges	h	−17 to 17	−16 to 16
	k	−19 to 19	−19 to 19
	l	−22 to 22	−21 to 21
Reflections collected		59933	51378
Independent reflections		15395 [R(int) = 0.1508]	13980 [R(int) = 0.0700]
Completeness to theta max		99.1 %	99.6 %
Absorption correction		Semi-empirical from equivs	Semi-empirical from equivs
Max. and min. transmission		0.941 and 0.843	0.905 and 0.861
Refinement method		Full-matrix least-squares (F^2)	Full-matrix least-squares (F^2)
Data / restraints / parameters		15395 / 144 / 994	13980 / 144 / 1038
Goodness-of-fit on F^2		1.033	1.026
Final R indices [I>2sigma(I)]		R1 = 0.0623, wR2 = 0.1409	R1 = 0.0490, wR2 = 0.1058
R indices (all data)		R1 = 0.1030, wR2 = 0.1608	R1 = 0.0690, wR2 = 0.1154
Largest diff. pk and hole /e Å^{-3}		0.806 and −0.947	0.976 and −0.845

2.283(4)-2.366(4) and 1.367(7)-1.413(7) Å, respectively for the parent benzene system **1**] are within the bounds expected for η^6 coordination {e.g. 2.277-2.343 and 1.365-1.416 Å for $[(\eta^6\text{-}C_6H_6)Rh(S,S\text{-}Me\text{-}DuPHOS)]^+$} [3]. The geometry of the rhodium *bis*(phosphine) fragment [*d*(Rh-P) = 2.243(1), 2.272(1) Å; ∢P-Rh-P = 93.42(4)°] is similar to that of related systems, and shows the expected lengthening of the Rh-P bonds compared to the analogous bis(triphenylphosphite) system [2.184 Å (mean)] [6].

Experimental Section

Syntheses of $[(\eta^6\text{-arene})Rh(PPh_3)_2]^+[BAr^f_4]^-$ *[arene = benzene* (**1**), *toluene* (**2**)*]*

The two compounds were synthesized using a common method exemplified for **1**. All manipulations were carried out using standard Schlenk line techniques, employing dried degassed solvents; precursors were prepared by standard literature methods [11]. A mixture of $[(Ph_3P)_2Rh(\mu\text{-Cl})]_2$ (0.155 g, 0.117 mmol), Na$[BAr^f_4]$ (0.207 g, 0.234 mmol) and benzene (6 ml) in dichloromethane (40 ml) was stirred for 90 min at 20 °C, after which time the reaction was judged to be complete by ^{31}P NMR. Concentration of the reaction mixture (to *ca.* 10 ml), addition of hexanes (50 ml) and cooling to −30 °C for 12 h led to the formation of **1** as a beige solid (yield: 0.361 g, 86 %). Recrystallization by layering a concentrated solution in dichloromethane with hexanes at −30 °C led to the formation of crystals suitable for X-ray diffraction. Elemental analysis: calc. for $C_{74}H_{48}BF_{24}P_2Rh$ (**1**), C 56.65 %, H 3.08 %; found C 56.21 %, H 2.88 %. Elemental analysis: calc. for $C_{75}H_{50}BF_{24}P_2Rh$ (**2**), C 56.91 %, H 3.18 %; found C 56.63 %, H 3.06 %.

Characterizing data for **1**: **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 5.87 (s, 6H, η^6-C_6H_6), 7.15-7.30 (m, 30H, PPh_3), 7.46 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 7.63 (s, 8H, *ortho*-CH of $[BAr^f_4]^-$). **^{13}C NMR** (CD_2Cl_2, 76 MHz): δ 103.5 (CH of η^6-C_6H_6), 117.5 (*para*-CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^f_4{}^-$), 128.8 (q, $^2J_{CF}$ = 32 Hz, *meta*-C of $BAr^f_4{}^-$), 134.8 (*ortho*-CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C of $BAr^f_4{}^-$), 128.3, 130.8, 133.7 (CH of Ph). ^{11}B NMR (CD_2Cl_2, 96 MHz): δ −7.6. **^{19}F NMR** (CD_2Cl_2, 283 MHz): δ −62.8. **^{31}P NMR** (CD_2Cl_2, 122 MHz): δ 44.1 (d, $^1J_{RhP}$ = 205.6 Hz). **IR** (CCl_4 solution, cm^{-1}): 1549 m, 1354 w, 1217 w, 792 s. Characterizing data for **2**: **^{1}H NMR** (CD_2Cl_2, 300 MHz): δ 2.19 (s, 3H, CH_3 of η^6-$C_6H_5CH_3$), 5.20 (d, $^3J_{HH}$ = 6.4 Hz, 2H, *ortho*-CH of η^6-$C_6H_5CH_3$), 5.55 (t, $^3J_{HH}$ = 6.4 Hz, 2H, *meta*-CH of η^6-$C_6H_5CH_3$), 6.64 (t, $^3J_{HH}$ = 6.4 Hz, 1H, *para*-CH of η^6-$C_6H_5CH_3$), 7.19-7.32 (m, 30H, PPh_3), 7.50 (s, 4H, *para*-CH of $[BAr^f_4]^-$), 7.67 (s, 8H, *ortho*-CH of $[BAr^f_4]^-$). **^{13}C NMR** (CD_2Cl_2, 76 MHz): δ 19.9 (CH_3 of η^6-$C_6H_5CH_3$), 100.8, 104.8, 119.3 (CH of η^6-$C_6H_5CH_3$), 117.5 (*para*-CH of $BAr^f_4{}^-$), 124.6 (q, $^1J_{CF}$ = 272 Hz, CF_3 of $BAr^f_4{}^-$), 128.9 (q, $^2J_{CF}$ = 32 Hz, *meta*-C of $BAr^f_4{}^-$), 134.8 (*ortho*-CH of $BAr^f_4{}^-$), 161.8 (q, $^1J_{CB}$ = 50 Hz, *ipso*-C of $BAr^f_4{}^-$), 128.3, 130.8, 133.7 (CH of Ph). **^{11}B NMR** (CD_2Cl_2, 96 MHz): δ −7.6. **^{19}F NMR** (CD_2Cl_2, 283 MHz): δ −62.8. ^{31}P NMR (CD_2Cl_2, 122 MHz): δ 44.4 (d, $^1J_{RhP}$ = 205.4 Hz). **IR** (CCl_4 solution, cm^{-1}): 1550 m, 1353 w, 1217 w, 782 s. ^{1}H and ^{31}P NMR data for compounds thought to contain the $[(\eta^6\text{-toluene})Rh(PPh_3)_2]^+$ cation have been noted previously by *James* [9b] and by *Weller* [9a].

Crystallographic method

Data for compounds **1** and **2** were collected on a Bruker Nonius Kappa CCD diffractometer. Data collection and cell refinement were carried out using DENZO and COLLECT; structure solution and refinement used SIR-92 (**1**) or DIRDIFF-99 (**2**) and SHELXL-97, respectively; absorption corrections were performed using SORTAV [12]. Details of each data collection, structure solution and refinement can be found in Table 1. Relevant bond lengths and angles are included in the figure captions and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1).

---

[1] See, for example, J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Sausalito, California, 1987, chp 10.

[2] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1976**, *98*, 2134.

[3] D. Heller, H.-J. Drexler, A. Spannenberg, B. Heller, J. You, W. Baumann, *Angew. Chem*. **2002**, *114*, 814; *Angew. Chem. Int. Ed.* **2002**, *41*, 777.

[4] J. Wolf, M. Manger, U. Schmidt, G. Fries, D. Barth, B. Weberndörfer, D. A. Vicic, W. D. Jones, H. Werner, *Dalton Trans.* **1999**, 1867.

[5] E. T. Singewald, C. S. Slone, C. L. Stern, C. A. Mirkin, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 3048.

[6] R. Uson, P. Lahuerta, J. Reyes, L. A. Oro, C. Foces-Foces, F. H. Cano, S. Garcia-Blanco, *Inorg. Chim. Acta* **1980**, *42*, 75.

[7] P. Marcazzan, B. O. Patrick, B. R. James, *Organometallics* **2003**, *22*, 1177.

[8] (a) Z. Zhou, G. Facey, B. R. James, H. Alper, *Organometallics* **1996**, *15*, 2496; (b) C. Dai, E. G. Robbins, A. J. Scott, W. Clegg, D. S. Yufit, J. A. K. Howard, T. B. Marder, *Chem. Commun.* **1998**, 1983.

[9] (a) A. Rifat, N. J. Patmore, M. F. Mahon, A. S. Weller, *Organometallics* **2002**, *21*, 2856; (b) P. Marcazzan, M. B. Ezhova, B. O. Patrick, B. R. James, *C. R. Chimie* **2002**, *5*, 373; (c) X.-Y. Yu, M. Maekawa, T. Morita, H.-C. Chang, S. Kitagawa, G.-X. Jin, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 267.

[10] A. Al-Fawaz, S. Aldridge, D. L. Coombs, A. A. Dickinson, D. J. Willock, L.-L. Ooi, M. E. Light, S. J. Coles, M. B. Hursthouse, *Dalton Trans.* **2004**, 4030.

[11] (a) J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711; (b) D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba, M. D. Smith, *Inorg. Chem.* **2001**, *40*, 3810.

[12] (a) Denzo: Z. Otwinowski, W. Minor, in: *Methods in Enzymology*, C. W. Carter, R. M. Sweet (eds), Academic Press, New York. 1996, vol. 276, p. 307; (b) Sir-97: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giocavazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst*. **1999**, *32*, 115. (c) Dirdiff-99: P. T. Beurskens, G. Peurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, University of Nijmegen, Netherlands, 1996; (d) G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; (e) Sortav: R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33.