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Cationic derivatives of $RhCl[P(\eta^2\text{-}C_7H_7)_3]$. An intramolecular Diels–Alder rearrangement in the tripodal ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

Starting from the chloro-rhodium(I) complex, $RhCl[P(\eta^2\text{-}C_7H_7)_3]$ (**1**), several salts such as $\{Rh[P(\eta^2\text{-}C_7H_7)_3]\}^+X^-$ ($X^- = BF_4^-$ (**2**), CF_3COO^- (**5**), $CF_3SO_3^-$ (**7**)) and $\{Rh(L\text{–}L)[P(\eta^2\text{-}C_7H_7)_2(C_7H_7)]\}^+BF_4^-$ (L–L = 1,10-phenanthroline (**4a**) or 2,2'-bipyridine (**4b**)) have been prepared. The reaction of **1** with trimethylsilyl trifluoromethane sulfonate, $CF_3SO_2\text{–}OSiMe_3$, has been found to involve a stereospecific 4:2 Diels–Alder cycloaddition between two coordinated cyclohepta-2,4,6-trienyl substituents to give a dinuclear rhodium(III) complex, $\{Rh_2[P(\eta^3\text{-}C_{14}H_{15})(C_7H_7)]_2(\mu\text{-}Cl)_3\}^+(CF_3SO_3^-)$ (**8**), which has been characterized by NMR spectroscopy and an X-ray structure analysis.

Keywords: Rhodium; Olefinic phosphane complexes; Tripodal ligands; Diels–Alder cycloaddition; NMR; Crystal structure

1. Introduction

The rhodium(I) complex $RhCl[P(\eta^2\text{-}C_7H_7)_3]$ (**1**) which contains the metal as part of a ligand cage [1] is a versatile educt [2,3]. Displacement of the chloro ligand by anions such as acetylacetonate, allyl, cyclopentadienyl [2] or tris(3,5-dimethyl-1-pyrazolyl)borate (Tp*) [3] leads to neutral derivatives in which one, two or all three cyclohepta-2,4,6-trienyl substituents may be displaced from rhodium(I), although phosphorus always remains coordinated. The reversible decomplexation of olefinic ligands — combined with opening of a free coordination site at the metal — can be an important step in metal-catalyzed processes.

2. Results and discussion

Abstraction of the chloro ligand from $RhCl[P(\eta^2\text{-}C_7H_7)_3]$ (**1**) by $AgBF_4$ in acetonitrile solution formally leads to a salt, $\{Rh[P(\eta^2\text{-}C_7H_7)_3]\}^+BF_4^-$, the cation of which is apparently stabilized in the solution by the donor solvent [1]. This can be deduced from the ^{31}P-NMR data of the salts $\{Rh[P(\eta^2\text{-}C_7H_7)_3]\}^+X^-$ in CD_3CN solution, where the same chemical shift ($\delta(^{31}P)$ 330 ppm) and the same coupling constant ($^1J(Rh,P)$ 188 Hz) are observed, irrespective of the nature of the anion ($X^- = BF_4^-$ (**2**), CF_3COO^- (**5**) or $CF_3SO_3^-$ (**7**)). It is assumed that in all three cases an acetonitrile ligand occupies the position trans to phosphorus in solution, and that the cage formed by the tetradentate $P(C_7H_7)_3$ ligand is retained in the cations. The trigonal pyramidal structure of the $\{Rh[P(\eta^2\text{-}C_7H_7)_3]\}^+$ cation in the solid is similar to the molecular structures found in the cations $\{Ni[P(CH_2CH_2PPh_2)_3]\}^+$ [4] and $\{Co[N(CH_2CH_2PPh_2)_3]\}^+$ [5]. In CD_2Cl_2 solution the chemical shifts ($\delta(^{31}P)$ 314 ppm) observed for **5** and **7** are again very similar, although the coupling constants $J(Rh,P)$ are different (Table 1, Scheme 1).

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Table 1
^{31}P-NMR data [a]

	Complex	$\delta(^{31}P)$	^1J(RhP)	Solvent
1	$RhCl[P(C_7H_7)_3]$ [b]	325.3	189.5	$CDCl_3$
		327.2	187.1	CD_3CN
2	$\{Rh[P(C_7H_7)_3]\}BF_4$ [b]	330.3	187.9	CD_3CN
3	$Rh(pz^{3Ph})[P(C_7H_7)_3]$	310.8	167.5	$CDCl_3$
4a	$\{Rh(ophen)[P(C_7H_7)_3]\}BF_4$	215.4 (263K)	181.7	$CDCl_3$
4b	$\{Rh(bipy)[P(C_7H_7)_3]\}BF_4$	214.8 (243K)	180.7	$CDCl_3$
5	$\{Rh[P(C_7H_7)_3]\}(CF_3COO)$	329.9	188.6	CD_3CN
		314.6	195.4	CD_2Cl_2
6	$Tp^*Rh[P(C_7H_7)_3]$ [3]	238.6	181.5	$CDCl_3$
7	$\{Rh[P(C_7H_7)_3]\}(CF_3SO_3)$	330.3	187.9	CD_3CN
		313.3	208.6	CD_2Cl_2
8	$\{Rh_2[P(\eta^3\text{-}C_{15}H_{14})(C_7H_7)]_2\text{-}(\mu\text{-}Cl)_3\}(CF_3SO_3)$	180.4	150.7	$CDCl_3$

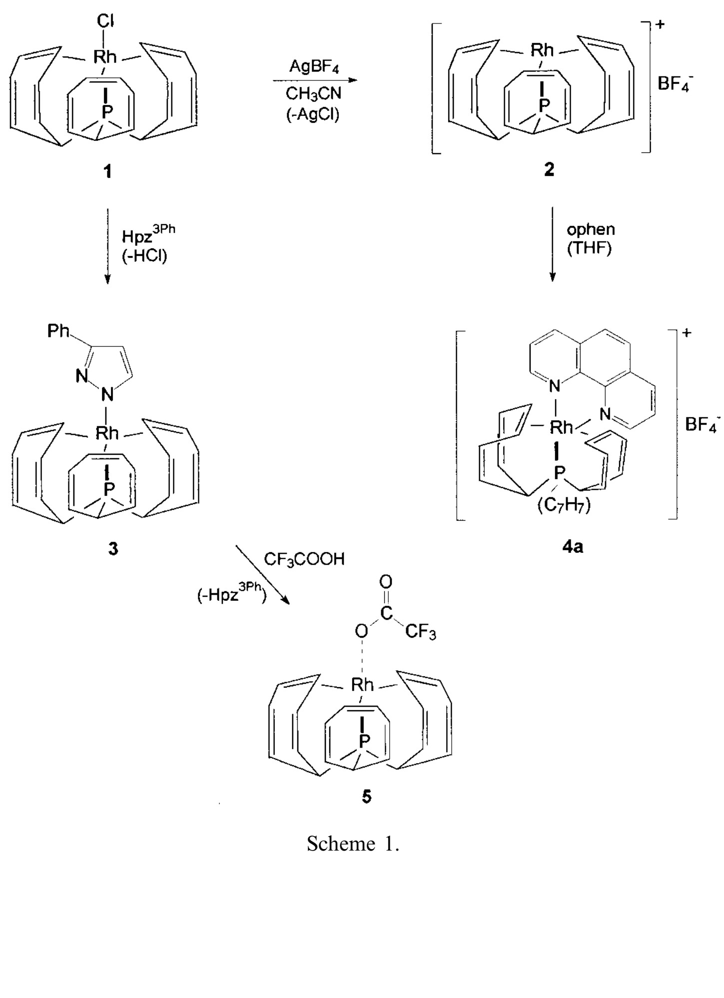
[a] Chemical shifts, $\delta(^{31}P)$, and coupling constants, $^1J(^{103}Rh,^{31}P)$ $\{\pm 1$ Hz$\}$; room temperature, unless noted otherwise (**4a** and **4b**). NMR spectrometer Bruker ARX 250.

[b] cf. Ref. [1] (NMR spectrometer Jeol FX 90Q); **1**, 322.7 {190.4} ($CDCl_3$); **2**, 327.7 {188.0} (CD_3CN).

The reaction of **1** with pyrazole or substituted pyrazoles (such as 3-phenyl-pyrazole, Hpz^{3Ph}) leads to pyrazolato complexes which contain a reactive Rh–N amide bond. The molecular geometry of the 3-phenyl-1-pyrazolato complex **3** has been determined by an X-ray structure analysis; important bond lengths and angles are given in the legend of Fig. 1. As in the chloro analogue (**1**), the tetradentate ligand $P(C_7H_7)_3$ forms a cage; and the three coordinated olefinic bonds (C(4)–C(5), C(11)–C(12) and C(18)–C(19); d(C=C) 140.4(6) pm av., angle C–Rh–C 35.68(15)° av.) define the equatorial plane (with an average deviation of C atoms by only 2.9 pm). The analogous parameters described for **1** are d(C=C) 140.7(3) pm av. and angle C–Rh–C 35.9(1)° av. [1]. The rhodium atom is coplanar with the six coordinated olefinic carbon atoms, the pyrazole ring plane is nearly perpendicular to the equatorial plane $[Rh(C{=}C)_3]$ (dihedral angle 96,8°), and the phenyl ring plane includes only a small dihedral angle (16.8°) with the pyrazole plane.

When $Rh(pz^{3Ph})[P(C_7H_7)_3]$ (**3**) is treated with excess trifluoroacetic acid, the Rh–N bond is cleaved to give 3-phenyl-1-pyrazole and the trifluoroacetate salt **5**. Although the CF_3COO^- anion is certainly displaced from Rh in CD_3CN solution (cf. Table 1), it is probably coordinated in the solid state. Thus, the molecular ion $M^+ = \{Rh[P(C_7H_7)_3](CF_3COO)\}^+$ ($m/e = 550$) and a fragment $M^+ - C_7H_7$ ($m/e = 459$) are clearly observed in the electron-impact (EI) mass spectra of solid samples.

The solvent-free salt $\{Rh[P(\eta^2\text{-}C_7H_7)_3]\}^+BF_4^-$ (**2**) is able to incorporate chelating ligands such as 1,10-phenanthroline (ophen) and 2,2′-bipyridine (bipy) into the coordinated sphere to give and $\{Rh(L–L)[P(\eta^2\text{-}C_7H_7)_2(C_7H_7)]\}^+BF_4^-$ (L–L = ophen (**4a**) or bipy (**4b**)).



Scheme 1.

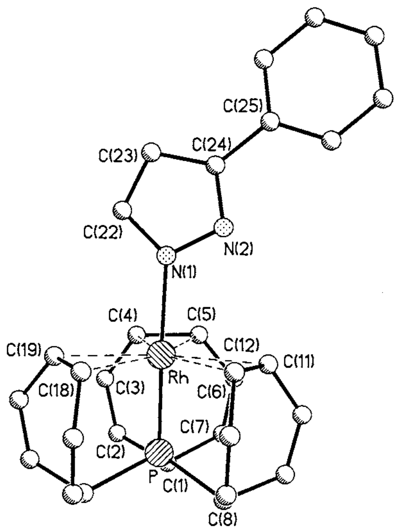


Fig. 1. Molecular structure of Rh(pz^{3Ph})[P(η^2-C_7H_7)$_3$], (**3**·$CHCl_3$), in the crystal. Selected bond distances (pm) and bond angles (°): Rh–P 217.15(9), Rh–N(1) 214.8(3), Rh–C(4) 230.7(4), Rh–C(5) 229.7(4), Rh–C(11) 231.2(3), Rh–C(12) 228.6(4), Rh–C(18) 227.7(4), Rh–C(19) 226.7(4); C(4)–C(5) 140.7(5); C(11)–C(12) 139.8(6), C(18)–C(19) 140.6(6); N(1)–N(2) 135.0(4), N(1)–C(22) 134.1(5), C(22)–C(23) 137.9(6), C(23)–C(24) 138.4(6), C(24)–C(25) 147.3(5); N(1)–Rh–P(1) 178.20(9), P–Rh–C(4) 89.45(10), P–Rh–C(5) 90.60(10), N(1)–Rh–C(4) 90.11(13), N(1)–Rh–C(5) 88.03(13), C(4)–Rh–C(5) 35.60(13); Rh–N(1)–N(2) 119.7(2), Rh–N(1)–C(22) 132.5(3), N(2)–N(1)–C(22) 107.5(3).

In the cations, the P(C_7H_7)$_3$ ligand behaves as a tridentate six-electron ligand with one uncoordinated cyclohepta-2,4,6-trienyl substituent, thus opening one equatorial position for the bidentate four-electron ligand L–L. The complexes **4a** and **4b** are fluxional in solution at room temperature, but become rigid at −10°C (**4a**) or −30°C (**4b**), respectively. The fully assigned ^{1}H- and ^{13}C-NMR data of **4a** and **4b** are given in Table 2.

The trifluoromethane sulfonate salt, {Rh[P(η^2-C_7H_7)$_3$]}$^+$$CF_3SO_3^-$ (**7**), was prepared using the trimethylsilyl ester, CF_3SO_2–OSiMe$_3$ (Scheme 2). With Cl-free precursors such as the 3-phenyl-pyrazolate complex **3** or the tris(3,5-dimethyl-1-pyrazolyl)borate complex **6**, the yellow salt **7** is formed as expected if an excess of CF_3SO_2–OSiMe$_3$ is applied. If, however, the trimethylsilyl ester was added slowly in small concentrations and moist THF was used, an orange dinuclear complex (**8**) became the main product.

According to the X-ray crystallographic structure determination, complex **8** contains a triply chloro-bridged rhodium(III) cation with a modified olefinic phosphane ligand which has apparently been formally reduced during the redox process (Fig. 2). The rearranged phosphane is formally a five-electron ligand, attached to rhodium(III) through a Rh–CH σ-bond, a π-coordinated olefinic double bond and the phosphorus atom; one cyclohepta-2,4,6-trienyl substituent is uncoordinated. A stereoselective 4:2 Diels–Alder cycloaddition between the two other C_7H_7 substituents has taken place to give a rigid cyclohexene ring. It should be noted that cycloadditions involving cycloheptatrienes are, in general, difficult to control [6,7], although intramolecular Diels–Alder reactions in 1-cyclohepta-2,4,6-trienyl derivatives have been used synthetically in special cases [8,9].

The molecular geometry of the cation in **8** could not have been understood without an X-ray structure analysis (Fig. 2, Table 3). However, on the basis of this structure, the ^{1}H- and ^{13}C-NMR data could unambiguously be assigned using two-dimensional ^{1}H/^{1}H-COSY and ^{13}C/^{1}H-HETCOR correlation spectra; in particular, the unique CH_2 group (C14 and C35, respectively) was clearly identified by a ^{13}C J-modulated spin-echo NMR experiment. The cation of complex **8** is rigid in $CDCl_3$ solution at room temperature.

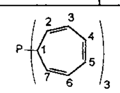
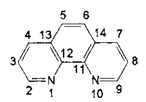
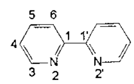
The dinuclear structure of the cation in **8** (Fig. 2) contains three chloro bridges, but only one (Cl(3)) is symmetrical. The tridentate phosphane ligand [P(η^3-$C_{14}H_{15}$)(C_7H_7)] behaves formally as an anionic five-electron system, i.e. **8** is an analogue of the pentamethylcyclopentadienyl complexes {Cp$^*_2$Rh$_2$(μ-Cl)$_3$}ClO$_4$ and {Cp$^*_2$Ir$_2$(μ-Cl)$_3$}ClO$_4$ [10]. In contrast to **8**, the three chloro bridges are symmetrical in the salts Cs$_3$[Cl$_3$Rh(μ-Cl)$_3$RhCl$_3$] (Rh–Cl(bridge) 252.4(1) pm, Rh–Cl(terminal) 229,3(1) pm) [11] and {Cp$^*_2$Ir$_2$(μ-Cl)$_3$}ClO$_4$ (Ir–Cl 244.9 pm av.) [10]. The distance between the two metals (327.9(1) pm in **8** and 332.2(2) pm in {Cp$^*_2$Ir$_2$(μ-Cl)$_3$}ClO$_4$ [10], respectively) indicates that direct interactions are absent, although the bridge system is contracted in Cs$_3$[Rh$_2$Cl$_9$] and Cs$_3$[Rh$_2$Br$_9$] (Rh–Rh distances of 306.6(1) pm and 298.9(1) pm, respectively [11]). Each phosphorus atom carries an uncoordinated cyclohepta-2,4,6-trienyl substituent, one of them (C(15)–C(21)) is disordered in the C(18)–C(21) part.

3. Experimental

The synthesis of the ligand P(C_7H_7)$_3$ [12] and of the rhodium(I) educts [RhCl(η^4-C_8H_{12})]$_2$ [13], [RhCl-[P(C_7H_7)$_3$] (**1**) [1], [Rh(Cp)[P(C_7H_7)$_3$] [2] and Tp*Rh[P(C_7H_7)$_3$] (**6**) [3] has been documented in the literature.

Instrumentation: IR spectra: Perkin–Elmer, 983G. NMR spectrometer: Bruker ARX 250 (^{1}H, ^{13}C, ^{31}P) and AM 500 (^{1}H, ^{13}C). EI-MS: Finnigan MAT 8500 (Ionisation energy 70 eV); FD-MS: Varian MAT 311A.

Table 2
^{1}H- and ^{13}C-NMR spectra [a] of the cations in $\{Rh(L\text{–}L)[P(C_7H_7)_3]\}BF_4$

4a (L-L = 1,10-phenanthroline)				4b (L-L = 2,2'-bipyridine)			
^{1}H NMR [b)]		^{13}C NMR [c)]		^{1}H NMR [b)]		^{13}C NMR [c)]	
Uncoordinated C_7H_7 ring							
H^1	1.57dt	C^1	31.2d [26.1]	1.59dt		30.0d [25.7]	
H^2/H^7	4.97m	C^2/C^7	103.8s	5.29m		103.9s	
H^3/H^6	6.43m	C^3/C^6	126.7d [8.4]	6.28m		127.2d [8.4]	
H^4/H^5	6.82m	C^4/C^5	130.6s	6.70m		130.1s	
Coordinated C_7H_7 rings [d)]							
$H^{1'}$	3.52dt [12.2] (8.7)	$C^{1'}$	33.8d [17.4]	3.43dt [12.6] (8.7)		34.0d [17.3]	
$H^{2'}/H^{7'}$	5.44m, 6.21m	$C^{2'}/C^{7'}$	122.4s 120.0s	5.39m, 6.28m		122.6s, 121.4s	
$H^{3'}/H^{6'}$	6.10m	$C^{3'}/C^{6'}$	131.8d 132.6d [12.2] [11.0]	6.12m		130.0d 133.5d [12.0] [10.6]	
$H^{4'}/H^{5'}$	3.70m, 4.87m	$C^{4'}/C^{5'}$	73.1d 65.1d {8.6} {7.9}	3.52m, 4.63m		72.2d 64.3 {9.3} {7.0}	
Ligand L-L							
H^2/H^9	9.17m	C^2/C^9	150.4s	$H^3/H^{3'}$	9.10m	$C^3/C^{3'}$	150.6s
H^3/H^8	8.72m	C^3/C^8	136.5s	$H^4/H^{4'}$	7.61m	$C^4/C^{4'}$	137.2s
H^4/H^7	8.07m	C^4/C^7	127.1s	$H^5/H^{5'}$	8.05m	$C^5/C^{5'}$	123.4s
H^5/H^6	7.76m	C^5/C^6	123.2s	$H^6/H^{6'}$	8.61m	$C^6/C^{6'}$	125.8s
		C^{11}/C^{12}	146.2s			$C^1/C^{1'}$	148.3s
		C^{13}/C^{14}	128.7s				

a) $CDCl_3$ Solutions, Bruker ARX 250; measured at 263K (**4a**) or 243K (**4b**).
b) Coupling Constants : (^3J(H,H)) and {^2J(P,H)} in Hz.
c) Coupling Constants : [^nJ(P,C)] and {^1J(Rh,C)} in Hz.
d) The positions in the (via $C^{4'}/C^{5'}$) η^2-coordinated cycloheptatrienyl rings are primed.

3.1. Syntheses

3.1.1. *Tri(1-cyclohepta-2,4,6-trienyl)phosphane-rhodium tetrafluoroborate (**2**) [cf. 1]*

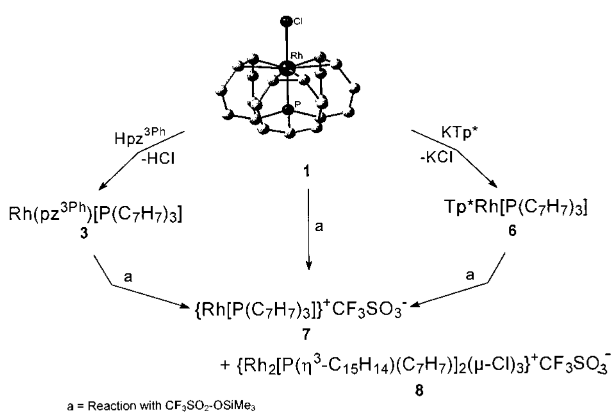
A solution of 195 mg (1 mmol) $AgBF_4$ in 20 ml of acetonitrile was added dropwise to an acetonitrile solution (30 ml) of 443 mg (1 mmol) $RhCl[P(C_7H_7)_3]$ (**1**). The precipitate (AgCl) was removed and the solution brought to dryness. The yellow product was washed with hexane and dried under high vacuum at 40°C. Yield 450 mg (91%), light-yellow powder, dec. above 250°C. The IR and ^{1}H-NMR spectra confirmed the absence of acetonitrile.

3.1.2. *(3-Phenyl-1-pyrazolato)-tri(1-cyclohepta-2,4,6-trienyl)phosphane-rhodium (**3**)*

50 mg (0.35 mmol) 3-phenyl-pyrazol and 80 mg (0.18 mmol) $RhCl[P(C_7H_7)_3]$ (**1**) were dissolved in acetonitrile (30 ml), and the solution was stirred at room temperature. After 2h a light-yellow powder started to precipitate which was collected, washed with pentane and dried. Yield: 59 mg (60%), dec. 278°C. EI-MS: (*m*/*e*, $I_{rel.}$): 550 (M^+, 30%), 459 ($M^+ - C_7H_7$, 12%), 144 ($Hpz - Ph^+$, 100%), 91 ($C_7H_7^+$, 100%).

3.1.3. *(1,10-Phenanthroline)-tri(1-cyclohepta-2,4,6-trienyl)phosphane-rhodium tetrafluoroborate (**4a**)*

A tetrahydrofuran solution (20 ml) containing both 100 mg (0.20 mmol) $Rh[P(C_7H_7)_3]BF_4$ (**2**) and 36 mg



Scheme 2.

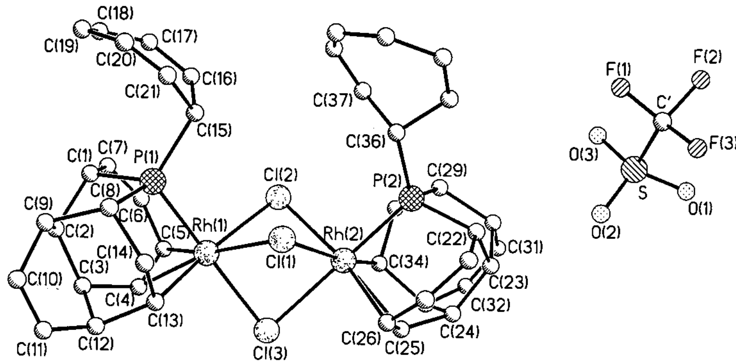


Fig. 2. Molecular structure of $\{Rh_2[P(\eta^3\text{-}C_{14}H_{15})(C_7H_7)]_2(\mu\text{-}Cl)_3\}^+(CF_3SO_3^-)$ (**8**) in the crystal. Selected bond distances (pm) and bond angles (°): Rh(1)–Cl(1) 242.40 (16), Rh(1)–Cl(2) 259.57(16), Rh(1)–Cl(3) 250.74(16); Rh(2)–Cl(1) 259.73(15), Rh(2)–Cl(2) 240.72(16), Rh(2)–Cl(3) 252.31(18); Rh(1)–P(1) 221.08(17), Rh(1)–C(13) 214.1(6), Rh(1)–C(4) 216.3(6), Rh(1)–C(5) 227.5(6); Rh(2)–P(2) 221.89(18), Rh(2)–C(34) 215.1(6), Rh(2)–C(25) 216.3(6), Rh(2)–C(26) 227.0(6); P(1)–C(1) 183.4(6), P(1)–C(8) 183.7(6), P(1)–C(15) 187.3(7), P(2)–C(22) 183.2(6), P(2)–C(29) 183.2(7), P(2)–C(36) 182.8(6); C(4)–C(5) 138.6(9), C(25)–C(26) 137.6(10), C(10)–C(11) 131.6(11), C(31)–C(32) 132.7(11); Rh(1)–Cl(1)–Rh(2) 81.50(5), Rh(1)–Cl(2)–Rh(2) 81.85(5), Rh(1)–Cl(3)–Rh(2) 81.40(5), C(4)–Rh(1)–C(5) 36.3(2), C(25)–Rh(2)–C(26) 36.1(2).

Table 3
^{1}H- and ^{13}C-NMR spectra [a,b] of the cation $\{Rh_2[P(\eta^3\text{-}C_{14}H_{15})(C_7H_7)]_2(\mu\text{-}Cl)_3\}^+(CF_3SO_3^-)$ (**8**)

^{1}H-NMR [c]			^{13}C-NMR [d]		
Coordinated ring systems (η^3-$C_{14}C_{15}$)					
H^1	H^{22}	3.46	C^1	C^{22}	42.5 d [12.3]
H^2	H^{23}	2.40	C^2	C^{23}	45.4 d [8.9]
H^3	H^{24}	2.88	C^3	C^{24}	44.5 d [14.2] 44.6 d [14.2]
H^4	H^{25}	5.08	C^4	C^{25}	90.9 br
H^5	H^{26}	6.00	C^5	C^{26}	96.3 br
H^6	H^{27}	6.31	C^6	C^{27}	128.6 s 128.7 s
H^7	H^{28}	6.57	C^7	C^{28}	134.7 s
H^8	H^{29}	2.54	C^8	C^{29}	37.6 d [24.1]
H^9	H^{30}	2.88	C^9	C^{30}	44.5 d [14.5] 44.6 d [14.2]
H^{10}	H^{31}	6.00	C^{10}	C^{31}	128.5 s 128.6 s
H^{11}	H^{32}	6.15	C^{11}	C^{32}	131.9 br
H^{12}	H^{33}	3.62	C^{12}	C^{33}	55.9 s
H^{13}	H^{34}	5.75	C^{13}	C^{34}	71.2 d {8.3}
H^{14}	H^{35}	1.00 [e]	C^{14}	C^{35}	39.6 d [10.3]
Uncoordinated rings (C_7H_7)					
H^{15}	H^{36}	3.62	C^{15}	C^{36}	38.7 d [22.4]
H^{16}/H^{21}	H^{37}/H^{42}	5.35	C^{16}/C^{21}	C^{37}/C^{42}	118.2 s 119.4 s
H^{17}/H^{20}	H^{38}/H^{41}	6.31	C^{17}/C^{20}	C^{38}/C^{41}	129.0 d [8.8] 129.5 d [8.9]
H^{18}/H^{19}	H^{39}/H^{40}	6.51	C^{18}/C^{19}	C^{39}/C^{40}	131.5 s 131.9 s

[a] $CDCl_3$ solutions, room temperature; Bruker AM 500.
[b] The numbering system corresponds to that of the X-ray structure analysis (Fig. 2).
[c] All ^{1}H-NMR signals are multiplets (which may overlap).
[d] Coupling constants $[^nJ(^{31}P,^{13}C)]$ and $\{^1J(^{103}Rh,^{13}C)\}$ in Hz.
[e] CH_2 group.

(0.20 mmol) ortho-phenanthroline was stirred at room temperature for 3h. During the first hour, the yellow solution became orange-red, and an orange solid precipitated. More precipitate was formed by addition of pentane. The product **4a** was dried under high vacuum. Yield 110 mg (93%), dec. above 204°C. FD-MS (m/e, $I_{rel.}$): 587 (M^+, 8%), 496 ($M^+ - C_7H_7$, 3%).

The analogous addition reaction (1:1) of **2** with 2,2′-bipyridine (bipy) can be similarly carried out in THF solution.

*3.1.4. Tri(1-cyclohepta-2,4,6-trienyl)phosphane-rhodium trifluoroacetate (**5**)*

A tetrahydrofuran (THF) solution (10 ml) containing 82 mg (0.17 mmol) $Rh(Cp)[P(C_7H_7)_3]$ was treated with 1 ml ($\rho = 1.49$ g/ml, ca 13 mmol) of trifluoro acetic acid. A yellow precipitate was formed which was collected, washed with THF and dried under high vacuum. Yield 93 mg (98%), dec. 238°C.

EI-MS: (m/e, $I_{rel.}$): 520 (M^+, 18%), 429 ($M^+ - C_7H_7$, 8%), 407 ($M^+ - CF_3COO$, 5%), 316 $(Rh[P(C_7H_7)_2]^+$, 5%), 307 ($Rh(C_7H_7)(CF_3COO)^+$, 6%), 285 ($Rh(C_7H_7)_2^+$, 5%), 238 ($Rh(C_7H_7)(CO_2)^+$, 6%), 91 ($C_7H_7^+$, 100%). IR (cm^{-1}): ν(C=O) 1684 vs, ν(C=C) 1607 w, br.

3.1.5. Tri(1-cyclohepta-2,4,6-trienyl)phosphane-rhodium trifluormethane sulfonate (7)

0.1 ml (0.55 mmol) Trimethylsilyl trifluoromethane sulfonate ($\rho = 1.23$ g/ml) were added to an orange solution of 70 mg (0.10 mmol) Tp*Rh[$PC_7H_7)_3$ in 10 ml of acetonitrile. The colour of the solution turned to light-yellow. After 15 min the solvent was distilled off, and the light yellow residue was washed with hexane and dried. Yield: 48 mg (87%), dec. 278°C.

3.1.6. Synthesis of $\{Rh_2[P(\eta^3\text{-}C_{14}H_{15})(C_7H_7)]_2(\mu\text{-}Cl)_3\}^+CF_3SO_3^-$ (8)

Trimethylsilyl trifluoromethane sulfonate was slowly added to a solution of 90 mg (0.20 mmol) $RhCl[P(C_7H_7)_3]$ (**1**) in 30 ml of technical (i.e. moist) tetrahydrofuran. (Note: pure and dry THF may be polymerized in the presence of the cation $Rh[P(C_7H_7)_3]^+$.) The colour changed immediately from yellow to orange, indicating the formation of **8**. The orange solution was stirred for 5 h, then THF was evaporated at room temperature and the orange residue extracted with 20 ml of Et_2O in which **1** and salts of the $Rh[P(C_7H_7)_3]^+$ cation are almost insoluble.

The combined Et_2O extracts were brought to dryness and the product **8** crystallized from THF. Yield 32 mg (32%), dec. above 237°C.

3.2. Crystal data and structure determinations

The reflection intensities were collected on a Siemens P4 diffractometer (Mo–K_α radiation, $\lambda = 71.073$ pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. Measuring temperature for all structure determinations was 296 K.

All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms are on calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

3.2.1. Crystal structure of 3

$C_{30}H_{29}N_2PRh \cdot CHCl_3$, pale yellow prism of dimensions $0.18 \times 0.15 \times 0.12$ mm crystallizes in the monoclinic space group $P2_1/n$ with the lattice parameters $a = 892.91(5)$, $b = 2044.43(19)$, $c = 1481.90(9)$ pm, $\beta = 90.612(5)°$, $V = 2705.0(3) \cdot 10^6$ pm^3, $Z = 4$, $\mu = 0.913$ mm^{-1}; 6087 reflections collected in the range $3° \leq 2\vartheta \leq 50°$, 4761 reflections independent, 3929 assigned to be observed [$I > 2\sigma(I)$], full-matrix least squares refinement against F^2 with 335 parameters converged at R_1/wR_2-values of 0.034/0.090; empirical absorption correction (Ψ-scans) yielded min./max. transmission factors of 0.2402/0.2602, the max./min. residual electron density was $0.492/-0.532 \cdot 10^{-6}$ e pm^{-3}.

3.2.2. Crystal structure of 8

$[C_{42}H_{86}P_2Cl_3Rh_2] \cdot [CF_3SO_3]$, orange platelet with dimensions $0.40 \times 0.35 \times 0.08$ mm crystallizes in the triclinic space group $P\bar{1}$ with the lattice parameters $a = 1046.2(2)$, $b = 1410.5(3)$, $c = 11436.0(3)$ pm, $\alpha = 106.78(3)$, $\beta = 97.70(3)$, $\gamma = 90.28(3)°$, $V = 2008.4(7) \cdot 10^6$ pm^3, $Z = 2$, $\mu = 1.212$ mm^{-1}; 8166 reflections collected in the range $3° \leq 2\vartheta \leq 50°$, 6939 reflections independent, 6012 assigned to be observed [$I > 2\sigma(I)$], full-matrix least squares refinement against F^2 with 500 parameters converged at R_1/wR_2-values of 0.058/0.156, empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.3573/0.5299, the max./min. residual electron density was $1.93/-1.66$ 10^{-6} e pm^{-3}.

4. Supplementary information

Crystallographic data (excluding structure factors) for the structures of **3** and **8** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos CCDC 154038 and 154039. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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