ELSEVIER

Inorganica Chimica Acta 334 (2002) 10–16

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Cationic half-sandwich complexes, $[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (M = Ni, Pd, Pt), containing a bidentate tri(1-cyclohepta-2,4,6-trienyl)phosphane ligand

Max Herberhold *, Thomas Schmalz, Wolfgang Milius, Bernd Wrackmeyer *

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

Received 22 June 2001; accepted 28 August 2001

Dedicated to Professor Andrew Wojcicki

Abstract

Displacement of η^4-cycloocta-1,5-diene (cod) from $[CpM(cod)]BF_4$ by the olefinic phosphane $P(C_7H_7)_3$ (**1**) leads to complexes $[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (M = Ni (**4**), Pd (**5**)) in which one of the cyclohepta-2,4,6-trienyl substituents is symmetrically η^2-coordinated to the metal in addition to phosphorus. The platinum analogue (M = Pt (**6**)) was obtained from $[PtCl_2(cod)]$ by consecutive reactions with **1**, TlCp and $AgBF_4$. The homologous series **4**–**6** was studied by multinuclear (^1H, ^{13}C, ^{31}P and ^{195}Pt) NMR spectroscopy, and related tetrafluoroborates such as the pentaphenyl-cyclopentadienyl analogue of **5** and the *tert*-butylisocyanide adduct of **4**, $[CpNi(CN^tBu)\{P(C_7H_7)_3\}]BF_4$ (**11**), were considered for comparison. An X-ray crystallographic structure determination of **4** has been carried out.

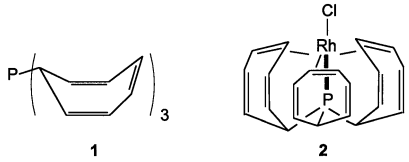
Keywords: Nickel; Palladium; Platinum; Phosphane complexes; Olefin complexes; NMR; X-ray crystallogaphy

1. Introduction

The tertiary phosphane tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ (**1**) [1], is a versatile ligand, which is able to use its olefinic cycloheptatrienyl side arms as coordinating centers in addition to the firmly bound phosphorus atom. If all three C_7H_7 substituents are attached to the metal as—in $[RhCl\{P(\eta^2\text{-}C_7H_7)_3\}]$ (**2**) [2,3] or in the corresponding iridium(I) complex [2]—a highly symmetrical (C_{3v}) molecule is formed in which **1** acts as an 8-electron ligand (Scheme 1).

In half-sandwich cyclopentadienyl complexes such as $[CpRh\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]$ (**3**) [3], the olefinic phosphane **1** plays the part of a 4-electron ligand, bearing only one η^2-coordinated and two free cyclohepta-2,4,6-trienyl substituents at the phosphorus atom. An analogous structure of type **3** is formed if substituted cyclopentadienyl rings ($\eta^5\text{-}C_5H_4^tBu$ (**3a**), $\eta^5\text{-}C_5Me_5$) or an indenyl ring ($\eta^5\text{-}C_9H_7$) are used to form the half-sandwich complex instead of the unsubstituted Cp ligand [3] (Scheme 2). The molecular structures in the solid state have been determined for **1**, **2**, **3** and **3a** by X-ray crystallography [1–3].

We now present a comparative study of the tetrafluoroborate salts **4**–**6** (Scheme 2), in which the half-sandwich cation is isoelectronic and isostructural with the neutral complex **3**. In a formal sense, the coordination number 5 can be assigned to these complexes, if the Cp ring occupies three and the 4-electron ligand $\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}$ two coordination sites. A similar 4-electron ligand is found in the osmium complex $[(mesitylene)OsCl\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]PF_6$ (**7**) [4],



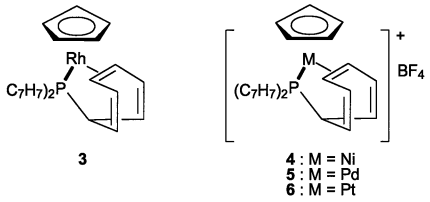
1 2

Scheme 1.

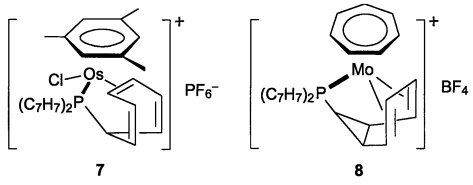
* Corresponding authors. Tel.: +49-921-552 540; fax: +49-921-552 157.

E-mail addresses: max.herberhold@uni-bayreuth.de (M. Herberhold), b.wrack@uni-bayreuth.de (B. Wrackmeyer).

0020-1693/02/$ - see front matter
PII: S0020-1693(02)00747-8



Scheme 2.



Scheme 3.

whereas the phosphane is a 6-electron system in $[(\eta^7\text{-}C_7H_7)Mo\{P(C_7H_7)_2(\eta^4\text{-}C_7H_7)\}]BF_4$ (**8**) [5] (Scheme 3).

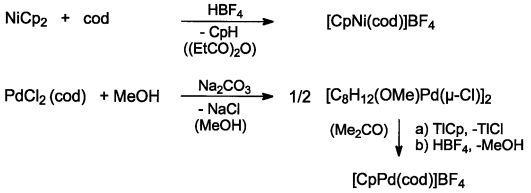
2. Results and discussion

2.1. Syntheses

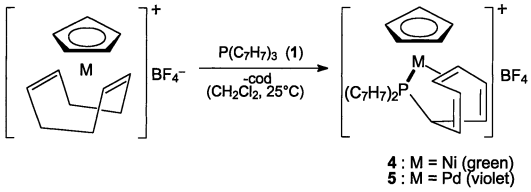
The general strategy for the introduction of $P(C_7H_7)_3$ (**1**) as a four-electron ligand is to displace a chelating cycloocta-1,5-diene (cod) chelate ligand by **1**. The synthetic routes to the tetrafluoroborate salts **4**,**5**, therefore, involve the initial formation of the cycloocta-1,5-diene precursors $[CpM(cod)]BF_4$. In the case of nickel, the 20e sandwich complex nickelocene ($NiCp_2$) can be easily converted into the 18e cation $[CpNi(cod)]^+$ [6]. In the cases of palladium and platinum, the 16e dichlorides, $[MCl_2(cod)]$, were used as starting materials [7]. Conversion of $[PdCl_2(cod)]$ into a dinuclear, chloro-bridged, methoxy-cyclooctenyl (16e) complex and subsequent reaction with thallium cyclopentadienide (TlCp) gave the 18e cation $[CpPd(cod)]^+$ [8] (Scheme 4).

The $[CpM(cod)]BF_4$ salts (M = Ni, Pd) were then treated with **1** to give $[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (**4**,**5**) (Scheme 5).

In the case of platinum, the ligand $P(C_7H_7)_3$ (**1**) was introduced first to give $[PtCl_2\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]$ (**9**), before the reaction with TlCp and $AgBF_4$ was applied



Scheme 4.



Scheme 5.

for the synthesis of the half-sandwich cation in **6** (Scheme 6).

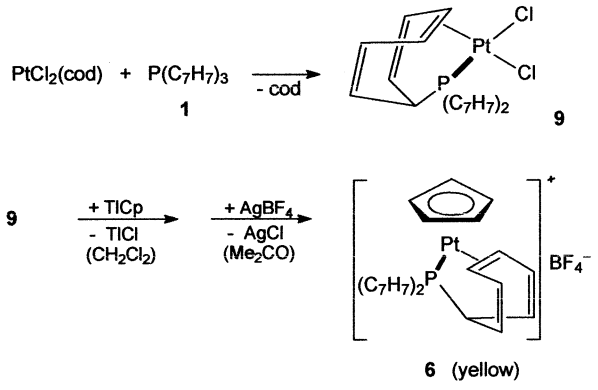
A palladium complex **10** which contains a voluminous η^5-pentaphenyl-cyclopentadienyl ring ligand (Scheme 7) instead of the unsubstituted Cp ring in **5**, was obtained through the known reaction sequence starting from palladium acetate and diphenylacetylene [9,10]. The intermediate $[(\eta^5\text{-}C_5Ph_5)_2Pd_2(\mu\text{-}C_2Ph_2)]$ [9] was converted into the salt $[(\eta^5\text{-}C_5Ph_5)Pd(cod)]BF_4$ [10] from which the cycloocta-1,5-diene chelate ligand could be eliminated by the action of $P(C_7H_7)_3$ (**1**) in the usual way.

The cations of the tetrafluoroborate salts **4**–**6** remain intact in the presence of an excess of $P(C_7H_7)_3$. Model experiments with $[CpNi\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (**4**) have shown that phosphanes and phosphites (such as PPh_3 or $P(OMe)_3$) do not open the chelate ring, although *tert*-butyl isocyanide reacts to give the adduct **11** (Scheme 7).

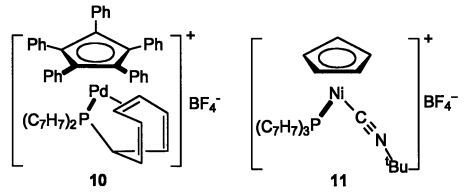
In **11**, the $P(C_7H_7)_3$ system acts as a simple two-electron phosphane ligand. The cations $[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]^+$ (M = Ni, Pd, Pt) in **4**–**6** are related to the cations $[CpM(L)(C_2H_4)]^+$ (M = Ni, L = $PPhMe_2$ [11]; M = Pd and Pt, L = PPh_3 [11–13]) which were studied by Kurosawa and coworkers.

2.2. NMR spectra

The ^1H, ^{13}C and ^{31}P NMR data obtained for the tetrafluoroborate salts **4**–**6**, **10** and **11** are collected in Table 1. The 18e cations $[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]^+$ (M = Ni, Pd, Pt) apparently possess rigid structures in



Scheme 6.



Scheme 7.

solution, which is in contrast to neutral 16e complexes such as $[PtCl_2\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]$ (**9**) [14].

In general, acetone-d_6 served as the solvent for measuring the NMR spectra. Only in the case of the platinum complex **6** which was used for many NMR experiments, advantage was taken of the better solubility in CD_2Cl_2. The assignments of the various ^1H and ^{13}C signals are supported by two-dimensional (2D)

Table 1
NMR spectra [a] of the ligand $P(C_7H_7)_3$ (**1**) and of the half-sandwich cations in the tetrafluoroborate salts **4**–**6**, **10** and **11**

Compound [b]	$P(C_7H_7)_3$	$[CpM\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$			$[(C_5Ph_5)Pd\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$	$[CpNi(CN^tBu)\{P(C_7H_7)_3\}]BF_4$
	(**1**)	M = Ni (**4**)	M = Pd (**5**)	M = Pt (**6**) [a]	(**10**)	(**11**)
^1H NMR [c,e]						
H^1	2.34dt [7.1] (2.4)	2.24dt [8.2] (6.7)	2.35dt [9.0] (6.7)	2.18dt [9.6] {16.4} (6.9)	2.14dt [7.8] (6.9)	2.56dt [11.3] (6.0)
H^2,H^7	5.20m	5.37m/5.47m	5.10m/5.20m	4.92m/4.99m	4.72m/5.14m	5.42m
H^3,H^6	6.17m	6.37m	6.36m	6.34m	5.95m/6.25m	6.41m
H^4,H^5	6.52m	6.71m	6.62m	6.58m	6.69m	6.70m
$H^{1'}$		4.81dt [15.2] (8.2)	4.96dt [14.8] (8.5)	4.59dt [12.4] {65.6}, (8.6)	5.25dt [14.2] (8.5)	
$H^{2'}$,$H^{7'}$		6.33m	6.31m	6.04m	6.47m	
$H^{3'}$,$H^{6'}$		6.76m	6.67m	6.63m	7.05–7.15m	
$H^{4'}$,$H^{5'}$		6.69m	6.29m	5.34m {74.2}	5.84m	
Ph					[g]	
Cp		5.95s	6.25d [2.0]	6.07 [1.5] {16.0}	-	5.88s
CMe_3						1.42s
^{13}C NMR [d,e]						
C^1	36.7d [17.4]	37.9d [27.7]	36.7 [25.9]	35.2 [36.3] {52.8}	37.3d [24.3]	37.3d [31.6]
C^2,C^7	120.0d [12.3]	116.8s 117.3s	111.8s	112.0s {18.4} 112.6s {19.2}	113.7s 114.3s	116.2s
C^3,C^6	127.3d [7.4]	128.1d [12.1] 128.2d [10.4]	128.2d [11.3] 128.3d [10.3]	128.5d [16.0] 128.6d [15.3]	128.2d [10.2] 128.7d [12.5]	128.4d [11.6]
C^4,C^5	131.6s	131.8s 132.0s	131.1s 131.3s	131.35s 131.38s	131.1s 131.3s	131.9s
$C^{1'}$		35.1d [17.3]	35.3d [19.3]	30.0d [27.5] {11.4}	38.8d [19.8]	
$C^{2'}$,$C^{7'}$		133.3d [2.8]	133.5d [2.8]	132.2d [1.3] {76.6}	132.2s	
$C^{3'}$,$C^{6'}$		133.9d [12.0]	131.4d [10.8]	131.3d [11.4] {44.2}	131.4d [11.0]	
$C^{4'}$,$C^{5'}$		68.5s	77.1s	52.1s {190.2}	92.3s	
Ph					[g]	
Cp		97.8d [1.7]	102.1d [2.1]	96.6d [2.3]	121.9d [2.3] {16.3}	96.2s
CMe_3						29.6s; 61.0s
^{31}P NMR	−12.3s	153.6s	164.8s	120.8s {5149} [f]	127.0s	51.5s
^{195}Pt NMR				−1786.1d {5149} [f]		

[a] Measured at 25 °C; δ values (ppm); solvent acetone-d_6 (except CD_2Cl_2 in the case of **6**).
[b] The numbers of the H and C atoms (**1**–**7**) refer to the positions in the uncoordinated cyclohepta-2,4,6-trienyl substituents, the primed numbers (**1'**–**7'**) to the (via **4'**–**5'**) η^2-coordinated cyclohepta-2,4,6-trienyl substituent.
[c] Coupling constants ($^3J(^1H,^1H)$) and [$^nJ(^{31}P,^1H)$] in Hz.
[d] Coupling constants [$^nJ(^{31}P,^{13}C)$] in Hz.
[e] Coupling constants {$^nJ(^{195}Pt,^1H)$} and {$^nJ(^{195}Pt,^{13}C)$} in Hz.
[f] Coupling constant {$^1J(^{195}Pt,^{31}P)$} in Hz.
[g] The phenyl substituents of the η^5-C_5Ph_5 ring in **10** are observed at $\delta(^1H)$ 6.98 m (o), ca 7.10 m (m), 7.30m (p) and $\delta(^{13}C)$ 128.9 (m), 129.5 (p), 132.6 (o), 134.9 (i).

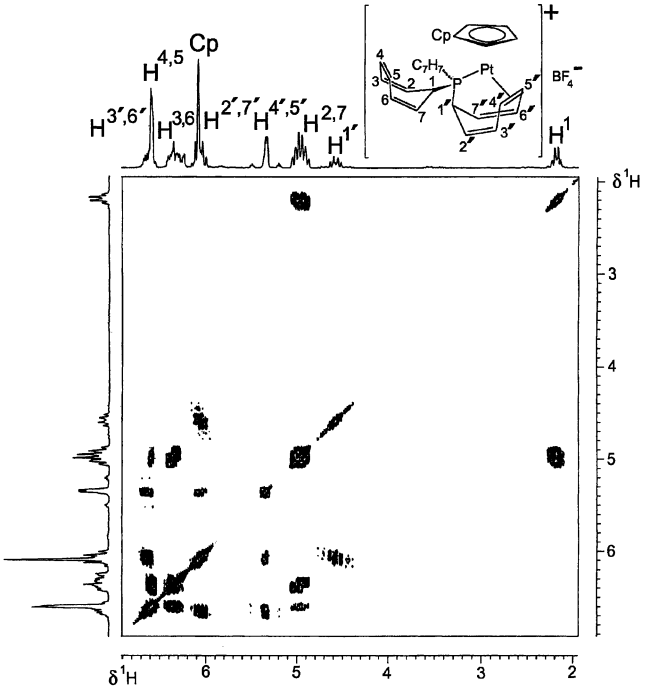


Fig. 1. Contour plot of the 250 MHz $^{1}H/^{1}H$ COSY NMR spectrum of $[CpPt\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (**6**), saturated solution in CD_2Cl_2. The negative tilt of the ^{195}Pt satellites for the cross peaks $H^{1'}/H^{2',7'}$, and for $H^{4',5'}/H^{3',6'}$ indicate opposite signs of the coupling constants $^{3}J(^{195}Pt,^{1}H^{1'})/^{4}J(^{195}Pt,^{1}H^{2',7'})$ and $^{2}J(^{195}Pt,^{1}H^{4',5'})/^{3}J(^{195}Pt,^{1}H^{3',6'})$.

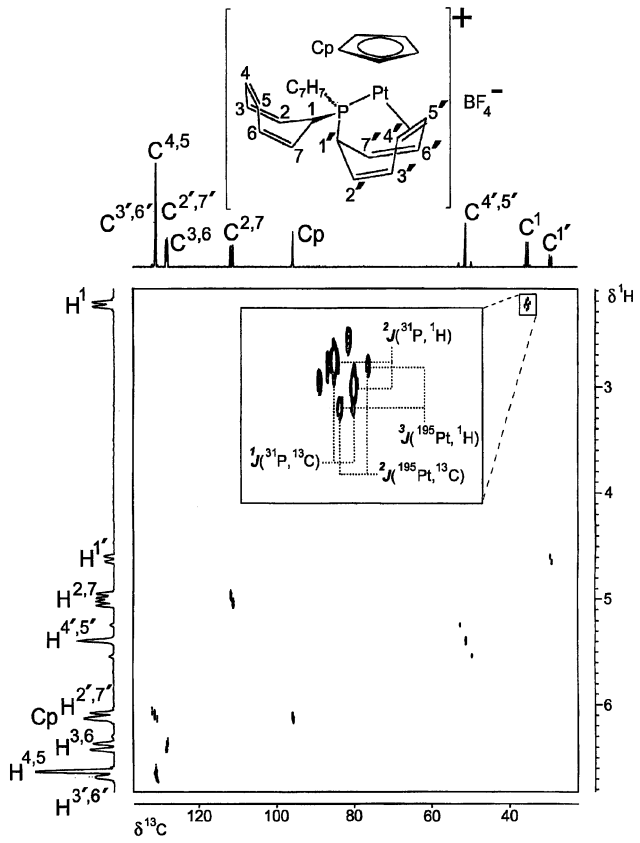
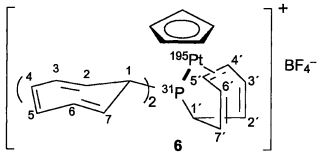


Fig. 2. Contour plot of the 62.8 MHz $^{13}C/^{1}H$ HETCOR NMR spectrum [based on $^{1}J(^{13}C,^{1}H)$] of $[CpPt\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (**6**), saturated solution in CD_2Cl_2. The expansion for C^1/H^1 clearly shows a negative tilt of the doublet owing to $^{1}J(^{31}P,^{13}C^1)$ and a positive tilt for the ^{195}Pt satellites owing to $^{2}J(^{195}Pt,^{13}C^1)$. Thus, the signs of $^{1}J(^{31}P,^{13}C^1)$ and $^{2}J(^{31}P,^{1}H^1)$ are opposite whereas the signs of $^{2}J(^{195}Pt,^{13}C^1)$ and $^{3}J(^{195}Pt,^{1}H^1)$ are alike. In the case of $C^{4',5'}$, the negative tilt of the ^{195}Pt satellites shows that $^{1}J(^{195}Pt,^{13}C^{4',5'})$ and $^{2}J(^{195}Pt,^{1}H^{4',5'})$ possess opposite signs.

$^{1}H/^{1}H$ and $^{13}C/^{1}H$ shift correlations, as shown for $[CpPt\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}]BF_4$ (**6**) in Fig. 1 and Fig. 2. The assignments agree well with our earlier studies [2,3,5].

Due to the additional coupling with ^{195}Pt, many of the ^{1}H and ^{13}C nuclei in **6** can be easily identified by their ^{195}Pt satellites. Thus, spin–spin coupling with ^{195}Pt ($I = 1/2$, natural abundance 33.8%) is observed for the protons H^1 and $H^{1'}$–$H^{7'}$, for the carbon atoms ($C^{2'}$–$C^{7'}$) of the η^2-coordinated cycloheptatrienyl substituent, and also for C^1 and C^2/C^7 of the free C_7H_7 groups, as well as for the ^{1}H and ^{13}C nuclei of the η^5-cyclopentadienyl ring. It is remarkable that the magnitude of the coupling constant $^{1}J(^{195}Pt,^{31}P)$ (5149 Hz) is considerably larger than the corresponding value in the related cation $[CpPt(PPh_3)(C_2H_4)]^+$ (4343 Hz) [13] or in the neutral precursor complex $[PtCl_2\{P(C_7H_7)_3\}]$ (**9**) (3932 Hz) [14]. In the 2D $^{13}C/^{1}H$ experiments based on $^{1}J(^{13}C,^{1}H)$, the tilt of the respective cross peaks [15,16] reveals the relative signs of coupling constants $^{n}J(^{31}P,^{13}C)$ and $^{n+1}J(^{31}P,^{1}H)$ and of $^{n}J(^{195}Pt,^{13}C)$ and $^{n+1}J(^{195}Pt,^{1}H)$ (Fig. 2). Scheme 8 shows the isotopomers and some experiments relevant to the determination of absolute coupling signs. The absolute signs are based on the positive signs of $^{1}J(^{195}Pt,^{13}C)$ [16] and $^{1}J(^{195}Pt,^{31}P)$ [17]. An interesting case is the observation that the signs of $^{2}J(^{195}Pt,^{13}C^1)$ and $^{3}J(^{195}Pt,^{1}H^1)$ are alike (see Fig. 2) which is unexpected, since alternating



Experiment	Coupling signs compared	Res
$^{13}C^1$ / $^{1}H^1$	$^{1}J(P,C^1)$ / $^{2}J(P,H^1)$	< 0
	$^{2}J(Pt,C^1)$ / $^{3}J(Pt,H^1)$	> 0
^{31}P / $^{1}H^1$	$^{1}J(Pt,P)$ / $^{3}J(Pt,H^1)$	> 0
$^{1}H^{1'}$ / $^{1}H^{2',7'}$	$^{3}J(Pt,H^{1'})$ / $^{4}J(Pt,H^{2',7'})$	< 0
$^{1}H^{4',5'}$ / $^{1}H^{3',6'}$	$^{2}J(Pt,H^{4',5'})$ / $^{3}J(Pt,H^{3',6'})$	< 0

Scheme 8. Some 2D shift correlations (experiments) allow for comparison of coupling signs; the result > 0 indicates a positive tilt of the relevant cross peaks (alike signs), and < 0 indicates a negative tilt of the cross peaks (opposite signs).

signs are in general expected for two- and three-bond couplings in the absence of lone pairs of electrons at the intervening nuclei or at the coupled nuclei. Therefore, a 2D $^{31}P/^{1}H$ shift correlation was carried out in order to obtain the absolute sign of $^{3}J(^{195}Pt,^{1}H^1)$ by comparison with $^{1}J(^{195}Pt,^{31}P)$ (known to be positive [17]). This shows that the sign of $^{3}J(^{195}Pt,^{1}H^1)$ is positive, and, therefore, $^{2}J(^{195}Pt,^{13}C^1)$ must also be > 0.

The ^{31}P chemical shifts of **4**–**6** and **10** are all observed in the range between $\delta(^{31}P)$ 120 and 170, typical of tri(cyclohepta-2,4,6-trienyl)phosphane complexes containing one (and only one) η^2-cyclohepta-2,4,6-trienyl substituent [cf. [3,5,18]. For **11** the $\delta(^{31}P)$ value (51.5) indicates that all three cyclopentadienyl substituents are freely pending side-arms in solution.

In the ^1H NMR spectra of **4**–**6** and **10**, generally two multiplets are observed for the protons H^2/H^7 of the uncoordinated cyclohepta-2,4,6-trienyl substituents: the shift difference ($\Delta\delta$) is particularly large in the case of the pentaphenyl cyclopentadienyl complex **10** (Fig. 3). In the ^{13}C NMR spectra, two slightly separated signals are recorded for the diastereotopic pairs C^2/C^7, C^3/C^6 and C^4/C^5 of the two free C_7H_7 substituents; only the $^{13}C(C^3/C^6)$ signals show significant splitting into doublets due to ^{31}P-^{13}C spin–spin-coupling.

^{11}B NMR spectra show the ^{11}B NMR signal at δ −0.8 typical of the $[BF_4]^-$ anion [19]. These signals are sharp and do not show resolved coupling $^1J(^{19}F,^{11}B)$. In the case of **4**, the line width is less than 0.4 Hz, indicating a perfect tetrahedral symmetry at the site of the quadrupolar ^{11}B nucleus in solution. Therefore, the ions must be separated by the solvent, and there are no appreciable cation–anion interactions in solution.

2.3. X-ray structure analysis of [CpNi{P(C_7H_7)$_2$(η^2-C_7H_7)}]BF_4 (4)

The molecular geometry of the cation of the tetrafluoroborate salt **4** is depicted in Fig. 4. The structure is similar to that of the neutral analogues [CpRh{P}] (**3**) [3] and [CpMn(CO){P}] (**12**) [20] ({P} = {P(C_7H_7)$_2$-(η^2(C_7H_7)}). Relevant distances and angles of the three related complexes **3**,**4** and **12** are compared in Table 2.

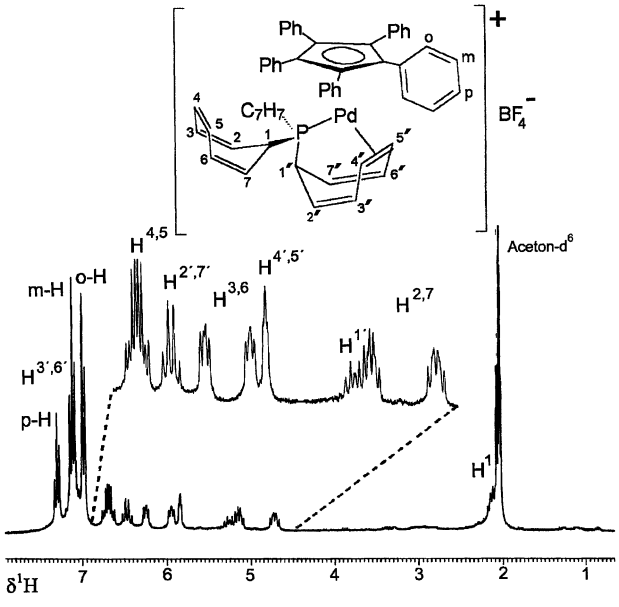


Fig. 3. 250 MHz ^1H NMR spectrum of [(η^5-C_5Ph_5)Pd{P(C_7H_7)$_2$(η^2-C_7H_7)}]BF_4 (**10**), saturated solution in acetone-d_6.

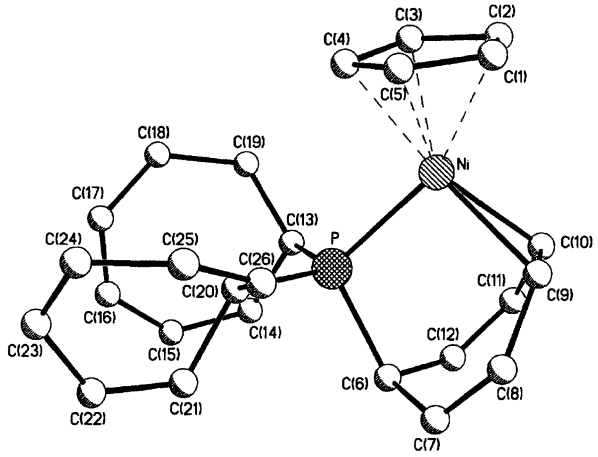


Fig. 4. Molecular structure of [CpNi{P(C_7H_7)$_2$(η^2-C_7H_7)}]BF_4 (**4**) in the crystal. Selected bond distances (pm) and bond angles (°): Ni–P 216.28(11), P–C(6) 185.5(5), P–C(13) 187.6(5), P–C(20) 183.1(4), B–F 137.0±0.1; Ni–P–C(6) 107.42(17), Ni–P–C(13) 113.91(18), Ni–P–C(20) 113.47(15), C(6)–P–C(13) 101.8(3), C(13)–P–C(20) 111.2(2), C(6)–P–C(20) 108.1(2), F–B–F 109.5±0.1. See also Table 2.

In the rhodium and nickel complexes **3** and **4**, respectively, the metal is coplanar with the P atom, the midpoint of the coordinated double bond (olefin(m)) and the centre of the cyclopentadienyl ring (Cp(Z)). As expected, the distances between the metal and the ligand centres (P, olefin(m) and Cp(Z)) in the coordination sphere are significantly shorter in the cation than in the neutral compounds **3** and **12** (cf. Table 2).

The cyclopentadienyl ligand is unsymmetrically attached to the central metal in all three complexes. In the case of **4**, the shortest distance Ni–C(4) (204.2(7) pm) is opposite to the coordinated double bond, whereas the longer bond distances (Ni–C(1) 212.8(6) and Ni–C(2) 212.2(7) pm) are those opposite to the phosphorus atom. Analogous differences in the M–C(Cp) bond lengths have been observed for **3** and **12**.

3. Experimental

All reactions were carried out under argon in carefully dried solvents. The starting compounds $P(C_7H_7)_3$ (**1**) [1], [CpNi(cod)]BF_4 [6], [CpPd(cod)]BF_4 [8], [(C_5Ph_5)Pd(cod)]BF_4 [10] and [$PtCl_2$(cod)] [7] were synthesized according to the literature.

NMR Instrumentation: Bruker ARX 250 (^1H: 250 MHz; ^{11}B: 80.3 MHz; ^{13}C: 62.8 MHz; ^{31}P: 101.3 MHz; ^{195}Pt: 53.5 MHz). Solvents for NMR measurements and chemical shift references: $CHCl_3/CDCl_3$: $\delta(^1H)$ 7.24, $\delta(^{13}C)$ 77.0; CD_2Cl_2: $\delta(^1H)$ 5.32, $\delta(^{13}C)$ 55.8; $(CD_3)_2CO$: $\delta(^1H)$ 2.04, $\delta(^{13}C)$ 29.8; $\delta(^{11}B) = 0$ for external Et_2O–BF_3 with Ξ (^{11}B) = 32.083971 MHz,

$\delta(^{31}P) = 0$ for external (85% aq) H_3PO_4 with $\Xi(^{31}P) = 40.480747$ MHz, and $\delta(^{195}Pt) = 0$ for Ξ (^{195}Pt) = 21.400000 MHz.

3.1. Syntheses

3.1.1. [CpNi{P(C7H7)2(η2-C7H7)}]BF4 (4)

A solution of 155 mg (0.51 mmol) $P(C_7H_7)_3$ (**1**) in 20 ml of dichloromethane was added dropwise during 15 min to a solution of 160 mg (0.50 mmol) [CpNi(cod)]BF_4 in 30 ml of dichloromethane. The reaction mixture was stirred at room temperature (r.t.) for 5 h and then brought to dryness. The remaining green solid was dissolved in a small amount of CH_2Cl_2. Addition of diethylether produced a dark-green precipitate which was filtered off and dried. Recrystallisation from acetone–ether mixtures gave 210 mg (83%) of a green powder, dec. 178 °C. EI–MS: *m/e* = 428 (1%, M^+ cation), 363 (1%, M^+–Cp), 337 (2%, M^+–C_7H_7), 304 (2%, $P(C_7H_7)_3^+$), 91 (100%, $C_7H_7^+$).

3.1.2. [CpPd{P(C7H7)2(η2-C7H7)}]BF4 (5)

In analogy to the preparation of **4**, two equimolar solutions of $P(C_7H_7)_3$ (**1**) (95 mg, 0.31 mmol, in 10 ml of CH_2Cl_2) and [CpPd(cod)]BF_4 (110 mg, 0.30 mmol, in 20 ml of CH_2Cl_2) were slowly combined, and the mixture stirred for 2 h under ambient conditions. Recrystallisation of the violet product **5** from acetone–ether gave 123 mg (74%) as a violet powder, dec. 165 °C.

3.1.3. [CpPt{P(C7H7)2(η2-C7H7)}]BF4 (6)

A solution containing the phosphane $P(C_7H_7)_3$ **1** (304 mg; 1 mmol) and [$PtCl_2$(cod)] (374 mg; 1 mmol) in CH_2Cl_2 (100 ml) was stirred for 1 h. The complex [$PtCl_2${$P(C_7H_7)_2(\eta^2$-$C_7H_7)$}] (**9**) was formed in almost quantitative yield. The product was recrystallised from CH_2Cl_2–hexane to give 520 mg (91%) of **9** (dec. 272 °C). EI–MS: *m/e* = 569 (1%, M^+), 534 (2%, M^+–Cl), 91 (100%, $C_7H_7^+$).

A solution of **9** (170 mg; 0.30 mmol) in CH_2Cl_2 (20 ml) was first treated with 80 mg (0.30 mmol) TlCp. After stirring for 1 h at 0 °C, a solution of $AgBF_4$ (60 mg; 0.31 mmol) in acetone (5 ml) was added, and the reaction mixture was stirred for additional 20 min at r.t. Insoluble material was filtered off, and the yellow filtrate was brought to dryness. The residue was dissolved in CH_2Cl_2 (2–3 ml). Addition of diethylether to the cooled (0 °C) solution gave 155 mg (80%) of **6** as a yellow powder which was dried in a high vacuum (dec. 183 °C).

3.1.4. [(η5-C5Ph5)Pd{P(C7H7)2(η2-C7H7)}]BF4 (10)

The phosphane $P(C_7H_7)_3$ **1** (100 mg; 0.33 mmol), dissolved in CH_2Cl_2 (10 ml), was added to a solution of [(η^5-C_5Ph_5)Pd(cod)]BF_4 (225 mg; 0.30 mmol) in CH_2Cl_2 (30 ml). The mixture was heated under reflux (40 °C) for 20 h. Then the solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (2–3 ml). Addition of hexane led to the precipitation of **10** as a dark green powder which was recrystallised from acetone–ether. Yield 210 mg (74%); dec. 163 °C.

3.1.5. [CpNi(CN-tBu){P(C7H7)3}]BF4 (11)

Tert-Butylisocyanide (0.02 ml; 0.2 mmol) was added to a solution containing **4** (60 mg; 0.12 mmol) in CH_2Cl_2 (10 ml). While the solution was stirred for 4 h at 25 °C, its colour gradually changed from green to dark red. The solution was concentrated to a volume of 2–3 ml, pentane was added and the mixture kept at −78 °C over night. The brownish red precipitate was collected, recrystallised from acetone–ether and dried in a high

Table 2
Structural data of η^5-cyclopentadienyl halfsandwich complexes containing a {$P(C_7H_7)_2(\eta^2$-$C_7H_7)$} (= {P}) chelate ligand

	[CpNi{P}]BF_4 **4**	[CpRh{P}] [3] **3**	[CpMn(CO){P}] [20] **12**
Unit cell	monoclinic	orthorhombic	triclinic
Space group; *Z*	$P2_1$; *Z* = 2	$P2_12_12_1$; *Z* = 4	$P\bar{1}$; *Z* = 2
Distances (*pm*)			
M–P	216.28(11)	220.1(1)	221.49(6)
M–C (olefin)	208.1(5); 208.7(5)	213.4(3); 213.6(3)	220.0(2); 221.2(2)
M–C (olefin(m))	196.5	200.7	208.8
M–Cp(Z)	173.9	191.9	178.9
C=C	138.8(10)	145.5(4)	142.1(3)
Angles (°)			
C–M–C (olefin)	38.9(3)	39.9(1)	37.58(9)
P–M–C (olefin)	95.56(17); 94.98(16)	89.5(1); 90.7(1)	88.22(6); 91.69(7)
P–M–Cp(Z)	131.0	136.4	128.5
Cp(Z)–M–(olefin(m))	133.4	133.4	126.5

Abbreviations: Cp, η^5-cyclopentadienyl, C_5H_5, {P}, tri(1-cyclohepta-2,4,6-trienyl)phosphane, {$P(C_7H_7)_2(\eta^2$-$C_7H_7)$}; Cp(Z), center of the Cp ring; olefin(m), midpoint of the η^2-coordinated olefinic double bond ($C^{4'}$=$C^{5'}$).

vacuum to give **11** as a dark red powder (65 mg, 93%), dec. 151 °C. IR (CsI): 2197 cm^{-1}, ν(N≡C).

3.2. Crystal structure of [CpNi{P(C_7H_7)$_2$(η^2-C_7H_7)}]BF_4 (**4**)

The intensity data were collected on a Siemens P4 diffractometer with Mo Kα radiation ($\lambda = 71.073$ pm, graphite monochromator) at r.t. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

4, $[C_{26}H_{26}NiP]^+BF_4^-$, green prism of dimensions $0.18 \times 0.15 \times 0.12$ mm, crystallises in the monoclinic space group $P2_1$; $a = 906.31(8)$, $b = 1095.48(12)$, $c = 1170.77(11)$ pm, $\beta = 91.586(5)^\circ$, $Z = 2$, $\mu = 1.472$ mm^{-1}; 6749 reflections collected in the range 2–27.50° in ϑ, 5311 reflections independent, 5055 reflections assigned to be observed ($I > 2\sigma(I)$); full matrix least squares refinement with 270 parameters, $R_1/\omega R_2$-values 0.068/0.199, absorption correction (ψ-scans), min./max. transmission factors 0.3183/0.3417; max./min. residual electron density 1.23/−0.702 e 10^{-6} pm^{-3}.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165484 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] M. Herberhold, K. Bauer, W. Milius, Z. Anorg. Allg. Chem. 620 (1994) 2108.
[2] M. Herberhold, K. Bauer, W. Milius, J. Organomet. Chem. 502 (1995) C1.
[3] M. Herberhold, W. Milius, S. Eibl, Z. Anorg. Allg. Chem. 625 (1999) 341.
[4] M. Herberhold, M. Müller, Th. Daniel, W. Milius, to be published.
[5] M. Herberhold, K. Bauer, W. Milius, J. Organomet. Chem. 545/546 (1997) 267.
[6] A. Salzer, T.L. Court, H. Werner, J. Organomet. Chem. 54 (1973) 325.
[7] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 47–55.
[8] D.A. White, Inorg. Synth. 13 (1972) 55.
[9] T.R. Jack, C.J. May, J. Powell, J. Am. Chem. Soc. 99 (1977) 4707.
[10] K. Broadley, N.G. Connelly, G.A. Lane, W.E. Geiger, J. Chem. Soc., Dalton Trans. (1986) 373.
[11] T. Majima, H. Kurosawa, J. Organomet. Chem. 134 (1977) C45.
[12] H. Kurosawa, T. Majima, N. Asada, J. Am. Chem. Soc. 102 (1980) 6996.
[13] H. Kurosawa, N. Asada, A. Urabe, M. Emoto, J. Organomet. Chem. 272 (1984) 321.
[14] M. Herberhold, Th. Schmalz, W. Milius, B. Wrackmeyer, Z. Anorg. Allg. Chem. 628 (2002) 437.
[15] A. Bax, R. Freeman, J. Magn. Reson. 45 (1981) 177.
[16] B. Wrackmeyer, Z. Naturforsch. Teil. B 52 (1997) 1019.
[17] M. Herberhold, K. Bauer, W. Milius, J. Organomet. Chem. 563 (1998) 227–233.
[18] W. McFarlane, J. Chem. Soc. (A) (1967) 1922.
[19] H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR-Basic Principles and Progress, vol. 14, Springer–Verlag, Berlin, 1978, pp. 387–388.
[20] W. Milius, A. Pfeifer, M. Herberhold, to be published.