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Note

Bis(diphenylphosphino)methylamine as chelate ligand in pentamethylcyclopentadienylrhodium(III) and iridium(III) complexes. Crystal structure of $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,P'\text{-}(PPh_2)_2NMe\}]BF_4$

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Abstract

Reactions of the dimers $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (M = Rh, Ir) with the ligand $NMe(PPh_2)_2$ in 1:2 molar ratio afford the mononuclear cationic complexes $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]Cl$ (M = Rh **1**, Ir **2**). Similar iodide complexes, $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]I$ (M = Rh **3**, Ir **4**), can be prepared by N-functionalization of co-ordinated dppa ligand in complexes $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NH\}]BF_4$. The tetrafluoroborate derivatives, $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]BF_4$ (M = Rh **5**, Ir **6**) are prepared by reaction of complexes **1**–**4** with $AgBF_4$ in acetone. All the compounds described are characterised by microanalysis, IR and NMR (^1H, $^{31}P\{^1H\}$) spectroscopy. The crystal structure of complex **5** is determined by X-ray diffraction methods. The complex exhibits a pseudo-octahedral molecular structure with a C_5Me_5 group occupying three co-ordination positions and a bidentate chelate P,P'-bonded ligand and a chloride atom completing the co-ordination sphere.

Keywords: Rhodium; Iridium; Bis(diphenylphosphino)methylamine complexes; Diphosphazane complexes; Crystal structures

1. Introduction

Transition-metal chemistry of bis(diphenylphosphino)amine [dppa, $NH(PPh_2)_2$] has been the subject of increasing interest due to its versatile co-ordination behaviour [1]. In a similar form to the widely used ligand bis(diphenylphosphino)methane (dppm), dppa can bind to metal centres as monodentate [2], chelate bidentate [3] or bridging ligand [4].

Interestingly, the greater acidity of the NH proton of the co-ordinated dppa ligand than that of the CH_2 protons of dppm, may facilitate the N-functionalization reactions. Thus, it has been recently described the N-derivatization of the chelate or bridging dppa ligand in mononuclear complexes [2b,2c] or heterobinuclear clusters [4e,4f] affording the corresponding ethyl or methyl-dppa derivatives.

In contrast to the great interest on the ligand behaviour and reactivity of co-ordinated dppa, little attention has been paid to the co-ordination chemistry of alkyl or aryl-substituted phosphinoamines $NR(PPh_2)_2$ (R = Me, Ph, ^{i}Pr) [5]. Although some recent studies demonstrated that N-substitution increases the chelate behaviour of the ligand, probably by constraint of the PNP angle due to steric effects, we found some examples where the $NMe(PPh_2)_2$ ligand acts as bridging ligand [5b,6].

Following our interest in the co-ordination behaviour of short-bite bidentade phosphine ligands, we report in this paper the synthesis of cationic rhodium and iridium compounds containing $NMe(PPh_2)_2$ (dppma) as chelate ligand. The complexes were prepared by direct reaction of dppma with the dimer $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ or by N-functionalization of the co-ordinated dppa ligand. The crystal structure of $[(\eta^5\text{-}C_5Me_5)RhCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]BF_4$, determined by single-crystal X-ray diffraction, is also reported.

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2. Experimental

2.1. General

All reactions were carried out under purified nitrogen using Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting compounds $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (M = Rh, Ir) and $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NH\}]BF_4$ were prepared by published procedures [3b,7]. The ligands $NH(PPh_2)_2$ and $NMe(PPh_2)_2$ were prepared following the method of Wang et al. [8]. Elemental analyses (C, H, N) were carried out with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. The NMR spectra were recorded on a Bruker AC-200P spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P, positive shifts downfield) as internal and external standards, respectively.

2.2. Preparation of complexes

2.2.1. Synthesis of $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]Cl$ (M = Rh **1**, Ir **2**)

To a solution of the binuclear complex $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (0.08 mmol; Rh, 50 mg; Ir, 64 mg) in $C_6H_5CH_3$ (10 ml) was added a solution of $NMe(PPh_2)_2$ (64 mg; 0.16 mmol) in $C_6H_5CH_3$ (10 ml). After stirring the mixture for 1 h at room temperature (r.t.) the solution was concentrated to a small volume. Yellow solids were obtained by addition of *n*-hexane. Complex **1**: Yield: 109 mg, 96%. Anal. Found: C, 59.0; H, 5.1; N, 2.0. $C_{35}H_{38}Cl_2NP_2Rh$ requires: C, 59.3; H, 5.4; N, 2.0%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.67 [t, 15H, C_5Me_5, $^4J(PH) = 4.2$ Hz], 2.91 [t, 3H, Me, $^3J(PH) = 9.7$ Hz], 7.25–7.80 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 66.9 [d, $^1J(PRh) = 120$ Hz]. FTIR (KBr, cm^{-1}): ν(CH, aliphatic) 2984 w, γ(N–CH_3) 841 vs. Complex **2**: Yield: 70 mg, 55%. Anal. Found: C, 52.8; H, 4.9; N, 1.8. $C_{35}H_{38}Cl_2IrNP_2$ requires: C, 52.7; H, 4.8; N, 1.8%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.70 [t, 15H, C_5Me_5, $^4J(PH) = 2.8$ Hz], 2.92 [t, 3H, Me, $^3J(PH) = 10.1$ Hz], 7.20–7.80 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 33.5 [s]. FTIR (KBr, cm^{-1}): ν(CH, aliphatic) 2914 w, γ(N–CH_3) 817 vs.

2.2.2. Synthesis of $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]I$ (M = Rh **3**, Ir **4**)

A mixture of complex $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NH\}]BF_4$ (0.18 mmol) and potassium *tert*-butoxide (20.2 mg; 0.18 mmol) in dry CH_2Cl_2 (20 ml) was stirred at r.t. for 1 h. The solution was evaporated to dryness and the solid residue extracted with $C_6H_5CH_3$.[1] To this solution, methyl iodide (1 ml; 16 mmol) was added and the mixture was heated under reflux for 1 h. The yellow solid formed was filtered, washed with Et_2O and dried under vacuum. Complex **3**: Yield: 70 mg, 46%. Anal. Found: C, 52.5; H, 4.7; N, 1.6. $C_{35}H_{38}ClINP_2Rh$ requires: C, 52.6; H, 4.8; N, 1.8%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.62 [t, 15H, C_5Me_5, $^4J(PH) = 4.2$ Hz], 2.9 [t, 3H, Me, $^3J(PH) = 9.7$ Hz], 7.3–7.8 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 66.7 [d, $^1J(PRh) = 121.9$ Hz]. FTIR (KBr, cm^{-1}): ν(CH, aliphatic) 2936 m, γ(N–CH_3) 839 vs. Complex **4**: Yield: 92 mg, 60%. Anal. Found: C, 47.8; H, 4.4; N, 1.7. $C_{35}H_{38}ClIIrNP_2$ requires: C, 47.3; H, 4.3; N, 1.6%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.70 [t, 15H, C_5Me_5, $^4J(PH) = 2.81$ Hz], 2.93 [t, 3H, Me, $^3J(PH) = 10.1$ Hz], 7.20–7.80 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 33.5 [s]. FTIR (KBr, cm^{-1}): ν (CH, aliphatic) 2912, 2983 w, γ(N–CH_3) 827 vs.

2.2.3. Synthesis of $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P'\text{-}(Ph_2P)_2NMe\}]BF_4$ (M = Rh **5**, Ir **6**)

The complexes could be prepared by either of the two methods described below.

a) A mixture of the binuclear complex $[\{(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)\}_2]$ (0.08 mmol; Rh, 50 mg; Ir, 64 mg), $NMe(PPh_2)_2$ (64 mg; 0.16 mmol) and $NaBF_4$ (18 mg; 0.16 mmol) in C_3H_6O (20 ml) was stirred for 1 h at r.t. The precipitated NaCl was removed by filtration and the solution was evaporated to a small volume. The complexes were crystallised by careful addition of Et_2O (**5**: yield: 109 mg, 90%; **6**: yield: 135 mg, 84%).

b) To a suspension of complex **3** or **4** (0.1 mmol) in C_3H_8O (15 ml) was added $AgBF_4$ (20 mg; 0.1 mmol). After stirring the mixture at r.t. for 1 h, the solid AgCl formed was filtered off and the solution evaporated to a small volume. The complexes were precipitated by addition of Et_2O (**5**: Yield 72 mg, 95%; **6**: Yield 78 mg, 92%).

Complex **5**: red–orange crystals. Anal. Found: C, 55.7; H, 5.1; N, 1.7. $C_{35}H_{38}BClF_4NP_2Rh$ requires: C, 55.3; H, 5.0; N, 1.8%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.63

[1] For the iridium compound, the intermediate neutral complex $[(\eta^5\text{-}C_5Me_5)MCl\{\eta^2\text{-}P,P\text{-}(Ph_2P)_2N\}]$ was obtained by evaporation of the $C_6H_5CH_3$ solution to a small volume and cooling to −20 °C [yield: 122 mg, 91%. Anal. Found: C, 53.8; H, 4.5; N, 1.8. $C_{34}H_{35}ClIrNP_2$ requires: C, 54.6; H, 4.7; N, 1.9%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.47 [t, 15H, C_5Me_5, $^4J(PH) = 2.5$ Hz], 7.20–7.80 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ −25.08 (s)].

[t, 15H, C_5Me_5, $^4J(PH) = 4.2$ Hz], 2.91 [t, 3H, Me, $^3J(PH) = 9.7$ Hz], 7.20–7.80 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 66.9 [d, $^1J(PRh) = 122$ Hz]. FTIR (KBr, cm^{-1}): ν(CH, aliphatic) 2919 w, γ(N–CH_3) 837 s, $\nu(BF_4)$ 1050 vs,br.

Complex **6**: yellow crystals. Anal. Found: C, 49.8; H, 4.7; N, 1.6. $C_{35}H_{38}BClF_4IrNP_2$ requires: C, 50.0; H, 4.5; N, 1.7%. ^{1}H-NMR ($CDCl_3$, 23 °C): δ 1.67 [t, 15H, C_5Me_5, $^4J(PH) = 2.8$ Hz], 2.9 [t, 3H, Me, $^3J(PH) = 10.1$ Hz], 7.20–7.70 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 23 °C): δ 33.7 [s]. FTIR (KBr, cm^{-1}): ν(CH, aliphatic) 2905 w, γ(N–CH_3) 831 s, $\nu(BF_4)$ 1050 vs,br.

2.3. X-ray crystallography of complex [(η^5-C_5Me_5)RhCl{η^2-*P*,*P*′-(Ph_2P)$_2$NMe}]BF_4 (**5**)

Suitable crystals for X-ray structure determination were obtained from a slow diffusion of diethyl ether into a solution of complex **5** in acetone. Intensity data were collected at room temperature on a Siemens R3m/V diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) in the θ–2θ scan mode. Semiempirical corrections based on ψ scans were applied for absorption. The structure was solved by Patterson and refined on F^2 by full-matrix least-squares calculations with SHELXL-97 [9]. A riding model was applied to H atoms, placed at calculated positions with C–H = 0.96 Å and isotropic $U = U_{eq}$ of attached atoms. Anion BF_4 was refined as a rigid group. The absolute structure of the compound could be determined with Flack parameter equal to −0.01(5). Relevant crystal data and refinement parameters are summarised in Table 1.

Table 1
Crystal data and structure refinement for complex [(η^5-C_5Me_5)RhCl{η^2-*P*,*P*′-(Ph_2P)$_2$NMe}]BF_4 (**5**)

Empirical formula	$C_{35}H_{38}BClF_4NP_2Rh$
Formula weight	759.77
Temperature (K)	297(2)
Wavelength (Å)	Mo–K_α (0.71073)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	12.045(2)
b (Å)	15.060(3)
c (Å)	18.815(3)
Volume (Å^3)	3413.0(10)
Z	4
D_{calc} (Mg m^{-3})	1.479
Absorption coefficient (mm^{-1})	0.720
F(000)	1552
Crystal size (mm)	0.30 × 0.14 × 0.07
θ Range for data collection (°)	1.73–27.57
Index ranges	$0 \le h \le 15$, $-19 \le k \le 8$, $0 \le l \le 24$
Reflections collected	4680
Independent reflections	4595 ($R_{int} = 0.0312$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4595/0/398
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.0781$
R indices (all data)	$R_1 = 0.1128$, $wR_2 = 0.0893$
Absolute structure parameter	−0.01(5)
Goodness-of-fit on F^2	0.815
Largest difference peak and hole (e Å^{-3})	0.452 and −0.507

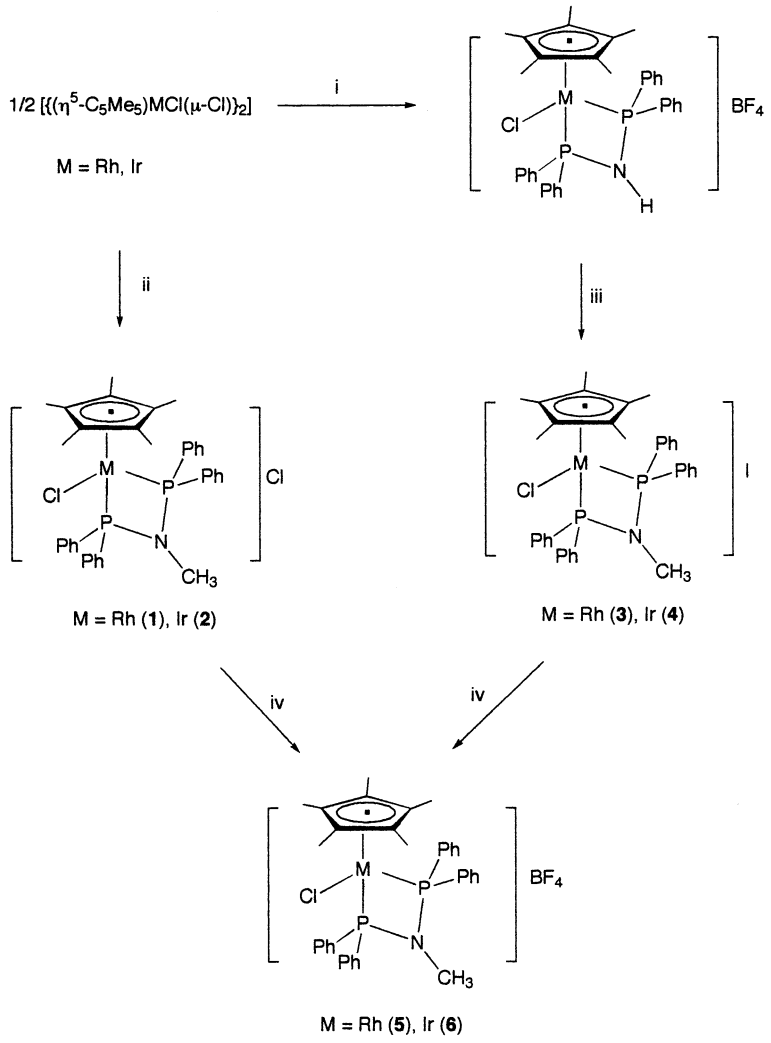
3. Results and discussion

The synthetic routes to the complexes are summarised in Scheme 1. The binuclear complex [{(η^5-C_5Me_5)MCl(μ-Cl)}$_2$] (M = Rh, Ir) reacts in toluene solution with bis(diphenylphosphino)methylamine [dppma, NMe(PPh_2)$_2$] in 1:2 molar ratio, by cleavage of the chloride bridges, to give cationic compounds of the type [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-(PPh_2)$_2$NMe}]Cl (M = Rh **1**, Ir **2**).

Similar compounds can be prepared by N-derivatization of the co-ordinated dppa ligand. Thus, the reaction of the cationic complexes [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-(PPh_2)$_2$NH}]BF_4 (M = Rh, Ir) [3b] with potassium *tert*-butoxide in dry dichloromethane causes the deprotonation of the co-ordinated dppa ligand. The neutral intermediate formed readily reacts with methyl iodide in toluene solution to give the cationic complexes [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-(Ph_2P)$_2$NMe}]I(M = Rh **3**, Ir **4**).

Complexes **1**–**4** were isolated as stable yellow solids and characterised by elemental analysis, IR and NMR spectroscopy. Their solid-state IR spectra in KBr pellets show the characteristic absorption's ν(CH, aliphatic) and γ(N–CH_3) of the co-ordinated dppma ligand [5b]. The ^{1}H-NMR spectra of rhodium complexes (**1**, **3**), in deuterated chloroform, exhibit two triplet resonances at δ 1.67 [$^4J(PH) = 4.2$ Hz] and 2.91 [$^3J(PH) = 9.7$ Hz] ppm attributed to the C_5Me_5 and Me groups, respectively. The $^{31}P\{^1H\}$-NMR spectra show a doublet resonance at δ 66.9 [$^1J(PRh) = 120$ Hz] ppm. On the other hand, the ^{1}H-NMR spectra of iridium complexes (**2**, **4**), exhibit two triplet resonances at δ 1.70 [$^4J(PH) = 2.8$ Hz] and 2.92 [$^3J(PH) = 10.1$ Hz] for the C_5Me_5 and Me groups. The $^{31}P\{^1H\}$ NMR spectra show a singlet resonance at δ 33.5 ppm.

Only in the deprotonation reaction of the iridium complex [(η^5-C_5Me_5)IrCl{η^2-*P*,*P*′-(PPh_2)$_2$NH}]BF_4 we could isolate the intermediate neutral complex [(η^5-C_5Me_5)IrCl{η^2-*P*,*P*′-(PPh_2)$_2$N}] as a dark-orange solid, by evaporation of the toluene solution and cooling to −20 °C. As expected, in the $^{31}P\{^1H\}$-NMR spectrum the singlet resonance of the equivalent phosphorus atoms of the anionic bidentate ligand is shifted to high field, δ −25.08 ppm, relative to the starting cationic complex (δ 16.8 ppm). In the case of the rhodium compound, the reaction with potassium *tert*-butoxide always gives a dark-red solution for which all the attempts to isolate a pure complex were unsuccessful.



Scheme 1. (i) dppa, $AgBF_4$; (ii) dppma; (iii) K^{t}BuO, MeI; (iv) $AgBF_4$.

When the deprotonation reaction was carried out in deuterated dichloromethane a doublet resonance centred at δ 9.1 ppm [^1J(PRh) = 100.0 Hz] was observed in the $^{31}P\{^1H\}$-NMR spectrum, demonstrating the formation of the corresponding neutral complex in solution (starting complex δ 49.8 ppm, ^1J(PRh) = 118.4 Hz).

Complexes **1**–**4** reacted with the stoichiometric amount of $AgBF_4$ in acetone solution to form the corresponding tetrafluoroborate derivatives [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-$(PPh_2)_2NMe$}]BF_4 (M = Rh **5**, Ir **6**). Alternatively, complexes **5** and **6** can be prepared by reaction of the dimeric complexes [{(η^5-C_5Me_5)MCl(μ-Cl)}$_2$] with the ligand dppma in acetone, in the presence of sodium tetrafluoroborate. These compounds were isolated as stable microcrystalline red–orange (**5**) or yellow (**6**) solids. Their IR spectra in KBr pellets show the characteristic bands of the co-ordinated dppma ligand together with a broad band at 1050 cm^{-1} corresponding to the uncoordinated BF_4 anion. The NMR spectra of these complexes are similar to those above described for complexes **1**–**4**. The ^{1}H-NMR spectra of complex **5** and **6** exhibit the expected triplet resonances assigned to the C_5Me_5 and MeN groups, and the $^{31}P\{^1H\}$-NMR spectra showed a doublet and a singlet resonance, respectively.

3.1. X-ray diffraction study of [(η^5-C_5Me_5)RhCl{η^2-*P*,*P*′-$(Ph_2P)_2NMe$}]BF_4 (5)

The molecular structure of the cation of complex **5**, including the atom numbering scheme, is shown in Fig. 1. The most relevant bond distances and angles are collected in Table 2. In this complex, the rhodium atom exhibits a distorted octahedral co-ordination sphere with the pentamethylcyclopentadienyl ligand formally occupying three octahedral sites. A chloride atom and a chelate bidentate ligand bonded to the metal centre through two phosphorus atoms complete the co-ordination sphere.

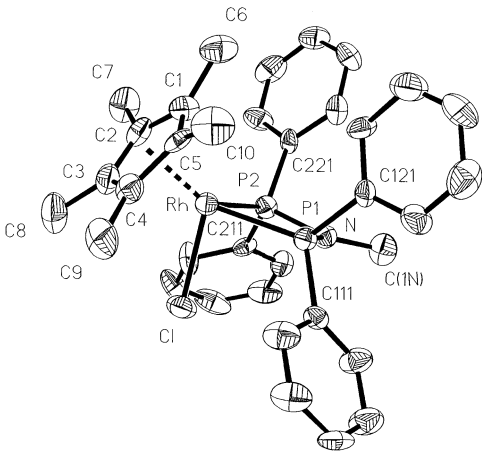


Fig. 1. ORTEP view of the structure of the complex cation **5** with atom numbering scheme (thermal ellipsoids at 40% probability level).

Table 2
Selected bond lengths (Å) and angles (°) for complex [(η^5-C_5Me_5)RhCl{η^2-*P*,*P*′-$(Ph_2P)_2NMe$}]BF_4 (**5**)

Bond lengths			
Rh–Cl	2.376(2)	Rh–C(1)	2.183(10)
Rh–P(1)	2.297(2)	Rh–C(2)	2.216(8)
Rh–P(2)	2.303(2)	Rh–C(3)	2.196(9)
P(1)–N	1.679(7)	Rh–C(4)	2.208(9)
P(2)–N	1.682(7)	Rh–C(5)	2.239(9)
N–C(1N)	1.469(9)	P(2)–C(211)	1.810(9)
P(1)–C(111)	1.801(9)	P(2)–C(221)	1.816(8)
P(1)–C(121)	1.815(9)		
Bond angles			
Cl–Rh–P(1)	86.05(8)	Cl–Rh–P(2)	88.85(9)
P(1)–Rh–P(2)	69.55(9)	P(1)–N–P(2)	102.6(4)
Rh–P(1)–C(111)	119.3(3)	Rh–P(2)–C(211)	121.6(3)
Rh–P(1)–C(121)	122.5(3)	Rh–P(2)–C(221)	118.6(3)
Rh–P(1)–N	93.9(3)	Rh–P(2)–N	93.6(3)
P(1)–N–C(1N)	129.1(6)	P(2)–N–C(1N)	127.6(6)
N–P(1)–C(111)	111.1(4)	N–P(2)–C(211)	112.6(4)
N–P(1)–C(121)	106.7(4)	N–P(2)–C(221)	107.6(4)
C(111)–P(1)–C(121)	102.4(4)	C(211)–P(2)–C(221)	102.3(4)

The Rh–C(ring) distances span the range 2.183(10)–2.239(9) Å and compare well with those found in other pentamethylcyclopentadienylrhodium(III) complexes, [(η^5-C_5Me_5)RhCl{η^2-*P*,*O*-$Ph_2PCH_2CHMeCH_2OH$}]-BF_4 [2.114(4)–2.229(4) Å] [10], [(η^5-C_5Me_5)RhCl{η^2-P,Se-$Ph_2PNP(Se)Ph_2$}] [2.171(4)–2.2230(4) Å] [2a] and [(η^5-C_5Me_5)Rh(OH_2)(prophos)]SbF_6 [1.650(9)–2.232(9) Å] [11]. The Rh–P [2.297(2) and 2.303(2) Å] and Rh–Cl [2.376(2) Å] distances are similar to those found in related rhodium(III) complexes, such as and [(η^5-C_5Me_5)RhCl(prophos)]BF_4 [Rh–P = 2.314(1) and 2.335(1), Rh–Cl = 2.393(1) Å] [12] and [(η^5-C_5Me_5)RhCl{η^2-P,S-$Ph_2PNHP(S)Ph_2$}]BF_4 [Rh–P = 2.293(4) and Rh–Cl = 2.389(3) Å] [13].

The P–N bond lengths of the co-ordinated chelate ligand [average 1.680(7) Å] are slightly smaller than the values 1.711(3) and 1.702(3) Å reported for the free dppma ligand [4h]. However, the P–N bond distances are comparable to those found in some palladium and platinum complexes, [$PdCl_2$(dppma)] [average 1.688(4) Å], [$Pt(CN)_2$(dppma)] [average 1.690(1) Å] and [$PtCl_2$(dppma)] [average 1.6845(6) Å] [5e]. On the other hand, the P(1)–N–P(2) angle [102.6(4)°] is smaller than the P–N–P angle of the free dppma ligand [114. 58(14)°] [4h] and is similar to those found in the related complexes [$PdCl_2$(dppma)] [100.4(2)°], [$Pt(CN)_2$-(dppma)] [100.0(6)°] and [$PtCl_2$(dppma)] [102.4(3)°] [5e]. Angles involving the P atoms reflect a tetrahedral geometry, and it is noteworthy that the P(1)–N– P(2) and Rh–P–N are smaller than the Rh–P–C and N–P–C angles.

4. Conclusions

In this communication we have described the synthesis of compounds [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-$(Ph_2P)_2NMe$}]BF_4 (M = Rh **5**, Ir **6**). We have shown that in the complexes [(η^5-C_5Me_5)MCl{η^2-*P*,*P*′-$(PPh_2)_2NH$}]BF_4 (M = Rh, Ir), the amine proton of the co-ordinated dppa ligand is easily removed by bases to form neutral complexes, in which the N-atom possesses a sufficient electron density to form N-methyl derivatives (**3**, **4**) by reaction with methyl iodide.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 193540 for compound **5**. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk. or www: http://www.ccd.cam.ac.uk).

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