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New cationic palladium (II) and rhodium (I) complexes of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$

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Abstract

Treatment of the bulky iminophosphine ligand $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) with $[M(CH_3CN)_2(ligand)]^{+n}$, where for M = Pd(II): ligand = η^3-allyl, $n = 1$, and for M = Rh(I), ligand: $2(C_2H_4)$, 2(CO) or cod, $n = 0$, yields the mono-cationic iminophosphine complexes $[Pd(\eta^3\text{-}C_3H_5)(L)][BF_4]$ (**1**), $[Rh(cod)(L)][BF_4]$ (**2**), $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**), and *cis*-$[Rh(L)_2][BF_4]$ (**4**). All the new complexes have been characterised by NMR spectroscopy and X-ray diffraction. Complex **1** shows moderate activity in the copolymerisation of CO and ethene but is inactive towards Heck coupling of 4-bromoacetophenone and *n*-butyl acrylate.

Keywords: Rhodium(I); Pd(II)-allyl; Iminophosphines; CO ethylene copolymerisation; Heck reactions

1. Introduction

Cationic four-coordinate Pd(II) and Rh(I) complexes incorporating tertiary phosphines and olefins (such as allyl or 1,5-cod) are of widespread interest as catalysts precursors in organic synthesis and species such as $[Rh(L_2)_2]^+$ (where L_2 is a bidentate nitrogen–phosphorus ligand) [1–4] have been shown to catalyse decarbonylation of aldehydes. Furthermore, there is considerable current interest in hybrid P/N ligands and a search in the Cambridge Structure Database revealed that although a vast number of Groups 9–10 complexes with nitrogen and phosphorus ligands have been characterised structurally, only a relatively small number of Pd(II) cations [5–53] and Rh(I) cations [54–65] containing bidentate N(sp^2)–P(sp^3) donors are reported. Since bulky substituents at the aryl groups of N(sp^2) donors have been found to strongly influence the catalytic activity and selectivity of Group 10 complexes [66], it is surprising that no Rh(I) complexes of ligands combining tertiary phosphine donors and (sp^2)N-aryl donors with bulky *ortho* substituents have been structurally investigated. To date, no Rh(I) complexes of bulky iminophosphines such as $[Ph_2PCH_2C(Ph)=N(2,6\text{-}R_2C_6H_3)]$ (where R = H, alkyl, aryl) are known.

We have been interested in studying neutral and cationic group 10 complexes of hybrid hemi-labile ligands, and particularly featuring a bulky iminophosphine and a diphenylphosphino group. The present work continues our study on the synthesis, reactivity and catalysis of neutral Ni(II), Pd(II) and Pt(II) complexes of enolisable iminophosphine ligands with flexible backbone such as $[Ph_2PCH_2C(Ph)=N(2,6\text{-}R_2C_6H_3)]$ (where R = H, Me, iPr) [67]. Herein, we are reporting the synthesis and spectroscopic studies of new organometallic cationic Pd(II) and Rh(I) complexes of $[Ph_2PCH_2C(Ph)=N\text{-}(2,6\text{-}Me_2C_6H_3)]$ (**L**). The activity of a new Pd(II) η^3-allyl complex in typical C–C coupling reactions, such as CO/ethylene copolymerisation and the Heck coupling of an activated olefin with an aryl-bromide, was tested.

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2. Results and discussions

2.1. Syntheses

Bridge cleavage reactions of dimeric η^3-allyl complexes such as $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ are known to leave the palladium-π-allyl groups intact [68]. The cationic η^3-allyl complex $[Pd(\eta^3\text{-allyl})(L)][BF_4]$ (**1**) was obtained by the reaction between $[Pd(\eta^3\text{-allyl})(MeCN)_2][BF_4]$ (prepared in situ, after reacting $[Pd(\eta^3\text{-allyl})Cl]_2$ with one equivalent of $AgBF_4$ in CH_3CN) and one equivalent of the compound $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) (Scheme 1). Complex **1** is stable in the solid state and can be exposed to air for up to 2 h without any apparent decomposition. However, solutions in halogenated solvents at room temperature lead to slow decomposition but they are stable for weeks at −20 °C under N_2. The complexes $[Rh(cod)(L)][BF_4]$ (**2**), $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**) and $[Rh(L)_2][BF_4]$ (**4**) (Scheme 1) were made using a 1:2:2 ratio of Rh-precursor $[RhCl(cod)]_2$ (in case of **2**), $[RhCl(CO)_2]_2$ (in case of **3**) or $[RhCl(C_2H_4)_2]_2$ (in case of **4**), $AgBF_4$ and the ligand **L**, in CH_3CN solutions at room temperature. $[Rh(cod)(L)][BF_4]$ (**2**) was isolated in 75% yield. When the precursor $[RhCl(CO)_2]_2$ was used, the complex $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**) was isolated in 62% yield and not the expected compound $[Rh(CO)_2(L)][BF_4]$. If the complex $[Rh(CO)_2(L)][BF_4]$ formed initially as an intermediate, a *trans* effect of the PPh_2 ligand moiety in the metal complex would lead to the weakening of the corresponding M–CO bond. This could be responsible for the lability (in the CH_3CN solution) of the CO group. With $[RhCl(C_2H_4)_2]_2$, $AgBF_4$ and **L** in CH_3CN, a small amount of red crystals were obtained, together with an unidentifiable mixture of products. The red crystals were shown by ^1H NMR spectroscopy and X-ray diffraction to be *cis*-$[Rh(L)_2][BF_4]$ (**4**). There was no evidence for the expected products $[Rh(C_2H_4)_2(L)][BF_4]$ or $[Rh(CH_3CN)(C_2H_4)(L)][BF_4]$. The reaction was repeated using $[RhCl(C_2H_4)_2]_2$, $AgBF_4$ and **L** in a 1:2:4 ratio, and led to similar observation. Complex **4** was formed in 35% yield. Finally, reaction between $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**) and one equivalent of free **L** was performed in CH_2Cl_2, and again gave only the *cis* isomer of $[Rh(L)_2][BF_4]$ (**4**).

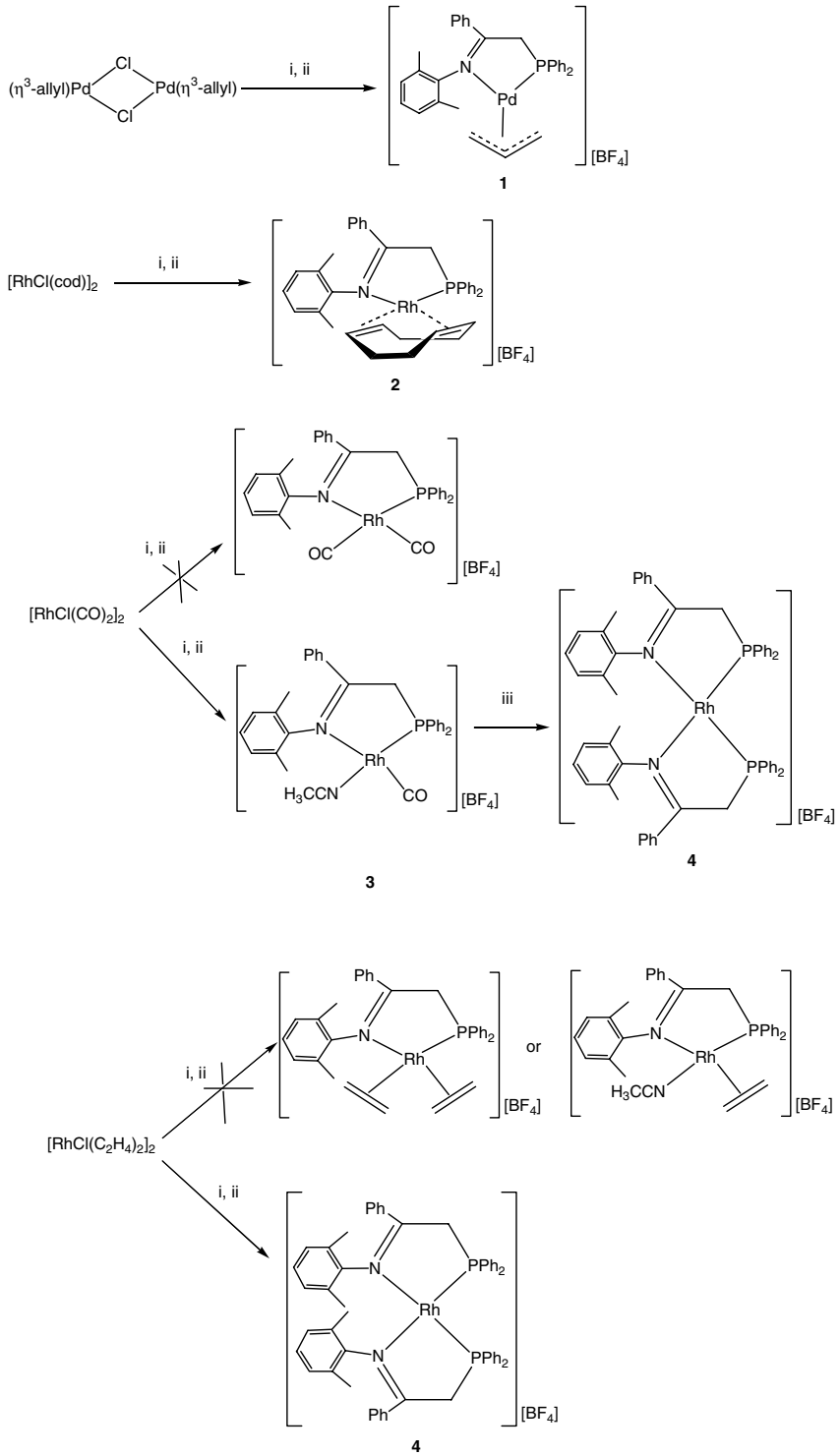
2.2. Spectroscopic investigations

The complexes **1**–**4** have been characterised by elemental analysis, mass spectrometry (FAB), infrared and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy (in CD_2Cl_2). Full assignments are given in Table 1.

The IR spectrum of **1** (in CD_2Cl_2) showed a $\nu_{C=N}$ band at 1572 cm^{-1}, which is significantly shifted from 1634 cm^{-1} for the free ligand [67], indicating that the iminophosphine is chelated to the metal centre. The IR spectra of complexes **2**–**4** (in CD_2Cl_2) showed bands at 1539 (**2**), 1538 (**3**) and 1559 cm^{-1} (**4**) assignable to $\nu_{C=N}$. For **3**, a broad band at 2304 cm^{-1} indicated the presence of coordinated CH_3CN and the band at 2004 cm^{-1} was assigned to theCO stretching vibration. The presence of CH_3CN and CO ligands was also confirmed by $^{13}C\{^1H\}$ NMR spectroscopy. In all cases, IR spectra (CD_2Cl_2) showed broad bands in the region 1220 cm^{-1} corresponding to $[BF_4]^-$.

The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of $[Pd(\eta^3\text{-allyl})(L)][BF_4]$ (**1**) exhibited a singlet at δ 37.5, consistent with the coordination of the phosphine group to the palladium (II) centre (^{31}P NMR resonance for the Z isomer of the free ligand is δ −19.8) [67]. The temperature dependence of the NMR spectra of η^3-allyl Pd(II) complexes both in the presence and absence of coordinating ligands has been described [68,69]. In accordance, the allyl complex $[Pd(\eta^3\text{-allyl})(L)][BF_4]$ (**1**) was found stereochemically non-rigid in CD_2Cl_2. The ^1H NMR spectrum of **1** (room temperature, CD_2Cl_2) showed diastereotopic methylene protons of the ligand as a pair of doublet of doublets at δ 4.57 and 4.34 (J_{HP} = 10.7 Hz, J_{HH} = 7.4 Hz). The two methyl groups of $Me_2C_6H_3$ are also inequivalent, and the corresponding resonances were observed as singlets at δ 2.10 and 2.02. The aromatic protons were found as complex multiplets between δ 7.77 and δ 6.98. The ^1H NMR spectrum, of ABCDX type, exhibited five resonances assigned to the η^3-allyl group between 30 and −80 °C (Table 1). The assignment of the ^1H NMR spectrum was assisted by ^1H –^1H COSY and nOe difference experiments Strong nOes of H_a^5 with H_2 and H_3, as well as with the *o*-P*Ph*$_2$ protons of the ligand were observed. Irradiating H_a^1 at room temperature and +30 °C, the exchange between H_a^1 and H_a^2 is observed (negative nOe) as well as nOe's and transferred nOe's with the P*Ph*$_2$ protons, H_a^5 and H_a^4. Exchange between H_1 and H_2 is observed at +30, +20 and + 10 °C. Between 0 and −80 °C, no H_a^1/H_a^2 exchange nOe is observed, however, the complete freezing of exchange processes could not be achieved even upon cooling to −80 °C. For square-planar allyl complexes of mixed hard and soft donor ligands, it is documented that the *syn–anti* interchange of the allyl protons takes place through the η^3-η^1-η^3 interconversion process (Scheme 2) [24,70,71]. The PPh_2 group weakens the *trans* Pd–CH_2 bond. Therefore, the opening of the allyl ring is promoted and the interchange of the *syn–anti* protons H_a^3 and H_a^4 occurs due to rotation about the σ bonds, as suggested by VT ROESY experiments.

The $^{13}C\{^1H\}$ NMR spectrum of **1** exhibited doublet resonances at δ 181.7 ($^2J_{PC}$ = 7.9 Hz) and δ 46.3 ($^1J_{PC}$ = 28 Hz), which were assigned to the *C*=N and methylene carbons of the iminophosphine ligand, respectively. The chemical shift of the C=N function is shifted compared to the chemical shift for the free ligand



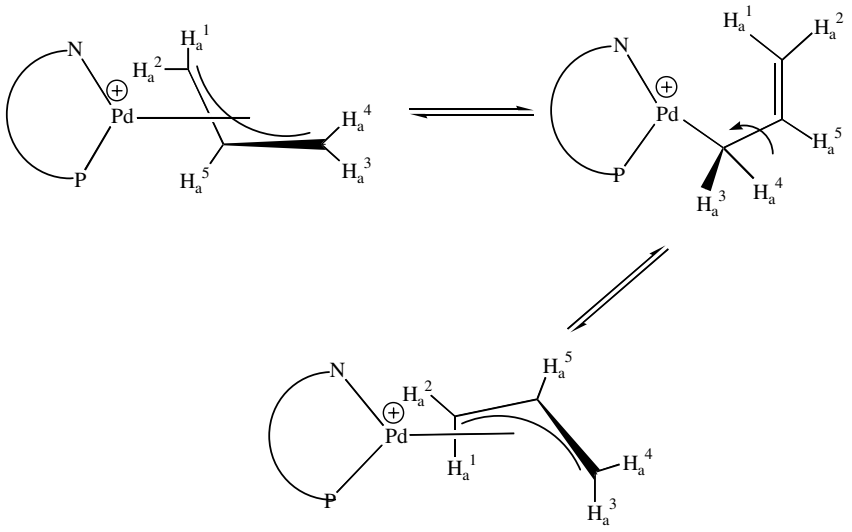
Scheme 1. Formation of compounds **1**–**4**. (i) $AgBF_4$, CH_3CN; (ii) $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**), CH_3CN; (ii) $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**), CH_2Cl_2.

(δ 167.2) and is consistent with coordination through the nitrogen. Peaks at δ 18.7 and 18.6 were assigned to the carbons of the $Me_2C_6H_3$ unit and peaks at δ 52.7 ($^2J_{PC}$ = 4 Hz), δ 84.1 ($^2J_{PC}$ = 30 Hz), and δ 122.9 ($^2J_{PC}$ = 6) to η^3-allyl ligands (terminal *trans* to PPh_2, terminal *cis* to PPh_2 and central, respectively).

The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of complex **2** showed a doublet at δ 46.9 with the Rh–P coupling $^1J_{RhP}$ = 154 Hz, which is typical for $[Rh(cod)(PR_3)_2]^+$ and $[Rh(cod)(N/P)_2]^+$ compounds [63,72,73]. ^1H NMR studies of **2** showed equivalent methylene protons of the ligand as a doublet at δ 4.50 (J_{HP} = 11.0 Hz). The

Table 1
Data characterising compounds **1**–**4**

	Compound data	NMR data (CD_2Cl_2)
1	[Pd(η^3-allyl){$P_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}][BF_4], $C_{31}H_{31}BF_4NPPd$, Mw 641.79. Air and moisture sensitive yellow powder. E.A.% Found (Calc.) C 57.8 (58.0), H 4.5 (4.9), H 1.8 (2.2). FAB$^+$: *m/z* 554.2 (100) [M − BF_4]. IR (CsI): $\nu_{C=N}$ 1572–1596 cm^{-1} (broad) ν_{BF4} 1061 cm^{-1} (broad).	^{1}H NMR data (500 MHz): 2.02 (s, 3H, *Me*$_2$C$_6$H$_3$, 12H), 2.10 (s, 3H, *Me*$_2$C$_6$H$_3$, 12H), 4.34 (d, 1H, *H*CH–P, $^2J_{PH}$ = 10.7, $^2J_{HH}$ = 7.4), 4.57 (d, 1H, HC*H*–P, $^2J_{PH}$ = 10.7, $^2J_{HH}$ = 7.4), 5.83 (b, 1H, H^5_a, central allyl-H), 3.15 (b, 1H, H^1_a, *anti*-H^5_a, terminal allyl-H), 4.13 (b, 1H, H^2_a, *syn*-H^5_a, terminal allyl-H), 3.61 (b, 1H, H^3_a, *syn*-H^5_a, terminal allyl-H), 3.70 (b, 1H, H^4_a, *anti*-H^5_a, terminal allyl-H), 6.99 (m, 3H, *m* + *p*-H of $Me_2C_6H_3$), 7.10 (m, 2H, *o*-*H* of *Ph*), 7.26 (m, 2H, *m*-*H* of *Ph*), 7.43 (m, 1H, *p*-*H* of *Ph*), 7.62 (m, 6H, *p* + *m*-H of P*Ph*$_2$), 7.76 (m, 4H, *o*-*H* of P*Ph*$_2$); ^{31}P{^{1}H} NMR data (202.4 MHz): 37.5 (s); ^{11}B{^{1}H} NMR data (160.4 MHz): −0.6 (s); ^{19}F NMR data (282.45 MHz): −152.5 (s); ^{13}C{^{1}H} NMR data (125.7 MHz): 18.7 (s, *Me*$_2$C$_6$H$_3$N), 18.6 (s, *Me*$_2$C$_6$H$_3$N), 46.3 (d, *C*H$_2$P, $^1J_{PC}$ = 28), 52.7 (d, terminal allyl-*C*, *trans*-*P*Ph$_2$, $^2J_{PC}$ = 4), 84.1 (d, terminal allyl-*C*, *cis*-*P*Ph$_2$, $^2J_{PC}$ = 30), 122.9 (d, central allyl-*C*, $^2J_{PC}$ = 6), 128.8, 128.7 (s, *o*-, *o*′-*C* of Me$_2$C$_6$H$_3$N), 127.6 (s, *m*-*C* of Me$_2$C$_6$H$_3$N), 127.4 (s, *p*-*C* of Me$_2$C$_6$H$_3$N), 181.7 (d, N=*C*, $^2J_{PC}$ = 7.9), 132.2 (s, *o*-C of *Ph*), 132.5 (s, *m*-C of *Ph*), 127.3 (s, *p*-C of *Ph*), 133.3 (b, *i*-C of P*Ph*$_2$), 132.9 (d, *o*-C of P*Ph*$_2$, $^2J_{PC}$ = 12), 129.9 (d, *m*-C of P*Ph*$_2$, $^3J_{PC}$ = 11)
2	[Rh(cod){$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}][BF_4], $C_{36}H_{38}BF_4NPRh$, Mw 705.38. Air and moisture sensitive orange powder. E.A.% Found (Calc.) C 61.2 (61.3), H 5.5 (5.4), N 2.00 (1.9). FAB$^+$ 618.2 (100) [M − BF_4]$^+$, 510.4 (40) [M − BF_4–C_8H_{12}]$^+$. IR (CD_2Cl_2) $\nu_{C=N}$ 1539 cm^{-1}, ν_{BF4} 1000 cm^{-1} (broad).	^{1}H NMR data (500 MHz): 2.07 (m, 2H, cod-C*H*$_2$, vicinal to cod-C*H trans* to *P*Ph$_2$), 2.11 (s, 6H, *Me*$_2$C$_6$H$_3$, 2.23 (m, 2H, cod-C*H*$_2$, vicinal to cod-C*H cis* to *P*Ph$_2$), 2.32 (m, 2H, cod-CH$_2$, vicinal to cod-C*H trans* to *P*Ph$_2$), 2.43 (m, 2H, cod-CH$_2$, vicinal to cod-C*H cis* to *P*Ph$_2$), 4.19 (b, 2H, cod-(C*H*=C*H*) *trans* to *P*Ph$_2$), 4.34 (b, 2H, cod-(C*H*=C*H*) *cis* to *P*Ph$_2$), 4.50 (d, C*H*$_2$P, 2H, $^2J_{PH}$ = 11), 6.96 (m, 3H, m + *p*-H of $Me_2C_6H_3$), 7.2 (m, 4H, *o* + *m*-H of *Ph*), 7.4 (m, 1H, *p*-H of *Ph*), 7.75 (m, 4H, *o*-H of P*Ph*$_2$), 7.70 (m, 2H, *p*-H of P*Ph*$_2$), 7.58 (m, 4H, *m*-H of P*Ph*$_2$); ^{31}P{^{1}H} NMR data (202.4 MHz): 46.9 (d, $^1J_{RhP}$ = 154); ^{11}B{^{1}H} NMR data (160.4 MHz): 1.0 (s); ^{19}F NMR data (282.45 MHz): −151.4 (s); ^{13}C{^{1}H} NMR data (125.7 MHz): 19.1 (s, *Me*$_2$C$_6$H$_3$), 28.5, 32.1 (s, cod-CH$_2$, 45.7 (d, CH$_2$P, $^1J_{PC}$ = 24), 78.8 (b, cod-*C*H *trans* to *P*Ph$_2$), 109.7 (b, cod-*C*H *cis* to *P*Ph$_2$), 183.8 (d, N=*C*, $^2J_{PC}$ = 9), 145.2 (s, *i*-C of Me$_2$C$_6$H$_3$), 127.6 (s, *m*-C of Me$_2$*C*$_6$H$_3$N), 128.4, 128.2, 129.0 (s, *o*-*m*-, *p*-C of *Ph*), 133.1 (d, *o*-C of P*Ph*$_2$, $^2J_{PC}$ = 12), 129.8 (d, *m*-C of P*Ph*$_2$ $^3J_{PC}$ = 10), 134.2 (b, *i*-C of P*Ph*$_2$)
3	[Rh(CO)(CH_3CN){$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}][BF_4], $C_{31}H_{29}BF_4NPORh$, Mw 666.27. Air and moisture sensitive orange powder. % Found (Calc.) C 55.25 (55.9), H 4.99 (4.4), N 3.27 (4.2). FAB$^+$ *m/z* 582.1 (30) [M − BF_4]$^+$, 538.0 (100) [M − BF_4–CH_3CN]$^+$. IR (CD_2Cl_2) $\nu_{C=N}$ 1538 cm^{-1}, ν_{CO} 2004 cm^{-1}, ν_{CH_3CN} 2304 cm^{-1}, ν_{BF4} 1221 cm^{-1}.	^{1}H NMR data (500 MHz): 1.88 (b, 3H, *CH*$_3$CN, *trans*-P), 2.09 (s, 6H, *Me*$_2$C$_6$H$_3$), 4.47 (d, 2H, *CH*$_2$–P, $^2J_{PH}$ = 11.1), 7.07 (m, 2H, *m*-H of $Me_2C_6H_3$), 7.02 (m, 1H, *p*-H of $Me_2C_6H_3$), 7.14 (m, 2H, *o*-H of *Ph*), 7.27 (m, 2H, *m*-H of *Ph*), 7.41 (m, 1H, *p*-H of *Ph*), 7.60 (m, 4H, *m*-H of P*Ph*$_2$, $^4J_{PH}$ = 2.7), 7.66 (m, 2H, *p*-H of P*Ph*$_2$, $^5J_{PH}$ = 2.2), 7.81 (m, 4H, *o*-H of P*Ph*$_2$, $^3J_{PH}$ = 12.9); ^{31}P{^{1}H} NMR data (202.4 MHz): 60.1 (d, $^1J_{RhP}$ = 160 Hz); ^{11}B{^{1}H} NMR data (160.4 MHz): −1.0 (s); ^{19}F NMR data (282.45 MHz): −153.0 (s); ^{13}C{^{1}H} NMR data (125.7 MHz): 1.1 (d, *C*H$_3$CN *trans*-P, $^3J_{RhC}$ = 12), 18.2 (s, *Me*$_2$C$_6$H$_3$), 47.7 (d, *C*H$_2$–P, $^1J_{PC}$ = 29), 122.4 (b, CH$_3$*C*N), 129..35 (s, *o*-C of Me$_2$C$_6$H$_3$N), 130.5 (s, *p*-C of Me$_2$C$_6$H$_3$N), 130.3 (s, *m*-C of Me$_2$*C*$_6$H$_3$N), 186.4 (d, N=*C*, $^2J_{PC}$ = 13), 189.3 (dd, *C*O, $^2J_{PC}$ = 18, $^1J_{RhC}$ = 73), 129.1 (s, *i*-C of *Ph*), 134.1 (s, *o*-C of *Ph*), 134.3 (s, *m*-C of *Ph*), 130.8 (s, *p*-C of *Ph*), 129.7 (b, *i*-C of P*Ph*$_2$), 134.7 (d, *o*-C of P*Ph*$_2$,$^2J_{PC}$ = 20), 131.4 (d, *m*-C of P*Ph*$_2$, $^3J_{PC}$ = 12), 134.6 (b, *p*-C of P*Ph*$_2$)
4	[Rh{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}$_2$][BF_4], $C_{56}H_{52}BF_4N_2P_2Rh$, Mw 1004.70. Air and moisture sensitive red crystals. % Found (Calc.) C 66.7 (66.9), H 4.19 (5.2), N 2.2 (2.8). FAB$^+$m/z 917.6 (100) [M − BF_4]$^+$. IR (CD_2Cl_2) $\nu_{C=N}$ 1559 cm^{-1}.	^{1}H NMR data (500 MHz): 2.05 (s, 12 H, *Me*$_2$C$_6$H$_3$, 4.20 (d, 4H, C*H*$_2$P, $^2J_{PH}$ = 12.4), 6.50 (m, 6H, *m*-H of $Me_2C_6H_3$), 6.57 (m, 6H, *p*-*H* of $Me_2C_6H_3$), 6.84 (m, 4H, *p*-*H* of *Ph*), 7.05 (m, 8H, *m*-*H* of *Ph*), 7.30 (m, 8H, *o*-*H* of *Ph*), 7.42 (m, 8H, *o*-*H* of P*Ph*$_2$, $^3J_{PH}$ = 15.6), 7.19 (m, 8H, *m*-*H* of P*Ph*$_2$, $^4J_{PH}$ = 8.1), 7.27 (m, 4H, *p*-*H* of P*Ph*$_2$); ^{31}P{^{1}H} NMR data (202.4 MHz): 61.9 (d, $^1J_{RhP}$ = 176); ^{11}B{^{1}H} NMR data (160.4 MHz): −0.6 (s); ^{19}F NMR data (282.45 MHz): −155.7 (s); ^{13}C{^{1}H} NMR data (125.7 MHz): 20.1 (s, Me$_2$C$_6$H$_3$N), 48.2 (b, *C*$_2$ P), 129.2 (s, *p*-C of Me$_2$*C*$_6$H$_3$), 128.8 (s, *m*-C of Me$_2$*C*$_6$H$_3$N), 146.2 (s, *i*-C of Me$_2$*C*$_6$H$_3$N), 126.3 (s, *o*-C of Me$_2$*C*$_6$H$_3$N), 133.2 (d, *o*-C of P*Ph*$_2$,$^2J_{PC}$ = 12), 128.2 (d, *m*-C of P*Ph*$_2$,$^3J_{PC}$ = 10), 134.2 (b, *i*-C of PPh$_2$), 179.8 (b, *C*=N)



Scheme 2. η^3-η^1-η^3 interconversion process in Pd-allyl complexes with N/P ligands.

two methyl groups of $Me_2C_6H_3$ are also equivalent, and the corresponding resonances were observed as singlet at δ 2.10. The aromatic protons were found as complex multiplets between δ 7.75 and δ 6.96 and could be fully assigned with the help of integration and of a ^1H–^1H COSY experiment. NOe difference experiments allowed the assignment of the cod olefinic protons. The resonances belonging to olefinic protons *trans* to phosphorus overlap, e.g., broad multiplets at δ 4.34 (2H) were observed, while those *trans* relative to nitrogen (also coinciding) appeared at higher field as broad multiplets (δ 4.04, 2H). NOe difference experiments suggest a slow exchange of the four 1,5-cod olefinic protons, i.e., the protons at C(4) and C(3) with C(7) and C(6), at room temperature, at a time-scale estimated to be $<0.5\ s^{-1}$. NOe difference experiments indicate that $[Rh(cod)(L)]^+$ cation is 'dynamic', via a mechanism involving breaking of the Rh–N bond with the apparent rotation of the 1,5-cod, analogous with that described earlier [57].

The ^1H NMR spectrum (CD_2Cl_2) of **3** shows a broad signal at δ 1.80, assignable to the protons of the *Me*CN group *trans* to phosphorus. This resonance is in the expected ratio (by relative integration) to those corresponding to the ligand, which were found at δ 2.09 (singlet assigned to $Me_2C_6H_3$), δ 4.47 (a doublet, assigned to the CH_2 backbone, $^2J_{PH}$ 11.1 Hz) and in the range δ 7.84–6.99 (the aromatic proton resonances). $^{31}P\{^1H\}$ NMR spectroscopy (CD_2Cl_2) showed a single doublet at δ 60 with a coupling constant of $^1J_{RhP}$ 160 Hz.

The ^1H NMR spectrum of **4** showed no indication of Rh-coordinated C_2H_4 groups. We believe that the complex *cis*-$[Rh(L)_2][BF_4]$ (**4**) was formed in this process, and NMR confirmed complete conversion to a new species where **L** is chelated to Rh(I), with loss of both C_2H_4 groups. NMR studies show that the $Me_2C_6H_3$ methyl protons of the ligands are equivalent (δ 2.05) and the ligand backbone CH_2 proton resonances were found as a broad doublet, at δ 4.2 ($^2J_{PH}$ 12.5 Hz) and the aromatic protons as a complex multiplet between δ 7.85 and 6.46. Broadening can be indicative of fluxionality, but no convincing evidence was found for the presence of other isomers by VT ^1H and $^{31}P\{^1H\}$ NMR. The $^{31}P\{^1H\}$ NMR (CD_2Cl_2) resonance in **4** (doublet at $\delta = 61.9$, $^1J_{RhP} = 176$ Hz) is shifted downfield from that of the free ligand $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) (isomer Z, $\delta = -19.8$). A shift of this magnitude is typical for Rh(I) complexes incorporating chelating N/P ligands [74–77]. In addition, the magnitude of the Rh–P coupling constant is typical for square planar complexes with a *trans* N–Rh–P coordination [74].

2.3. X-ray data

Crystals suitable for single-crystal X-ray structural determination were grown for **1**–**4**, as detailed in Section 5. ORTEP diagrams for compounds are presented in Figs. 1–4 and relevant molecular parameters are listed in Table 2. In all cases, molecular structural determinations are consistent with the observations made by NMR spectroscopy. The cations, anions and solvent molecules are all well separated and there are no unusually short intermolecular contacts. X-ray structural determination confirmed the bidentate coordination of the ligand and the square planar geometry of the metal centre (but slightly distorted due to steric crowding). In complex $[Pd(\eta^3\text{-allyl})(L)][BF_4]$ (**1**), where $L = [Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$, the bite angle P(1)–Pd(1)–N(1) is 82.60(12)°, close to that found in $[Pd(\eta^3\text{-}C_3H_5)(L')][Br]$ (L′ = 2-(diisopropylphosphinomethyl)-1-methylimidazole), of 83.2(2)° [70]. When coordinated to an allyl ligand in the symmetric η^3 bonding

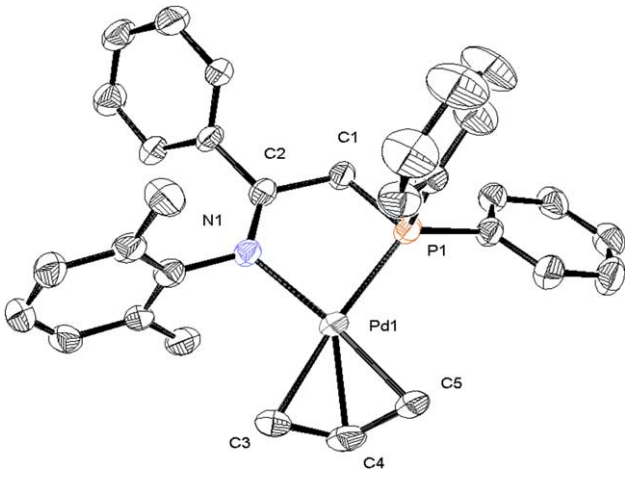


Fig. 1. Molecular structure of **1**. ORTEP diagram shows the cation of molecule 1 only. The asymmetric unit contains two independent molecules of [Pd(η^3-allyl)(L)][BF_4].

mode, the metal atom sits above the C_3 plane approximately equidistant from each carbon atom. In **1**, the torsion angle Pd(1)–C(5)–C(3)–N(1) is ca. 4°. Usually, a small *exo* or *endo* distortion of the central allyl carbon is observed in the solid state relative to the coordination plane which can be defined (for Molecule 1 of **1**) by P(1), N(1), C(3) and C(5). The deviation of the central carbon atom, C(4), of the allyl ligand from the coordination plane can be measured by the torsion angle C(4)–C(5)–P(1)–N(1) (ca. 26°). The torsion angle C(1)–P(1)–C(3)–C(5), of 20°, measures the deviation of the backbone carbon atom C(1) of the iminophosphine ligand, residing below this plane, on the same side as the central allyl carbon. The distances from the two terminal allyl carbon atoms to palladium

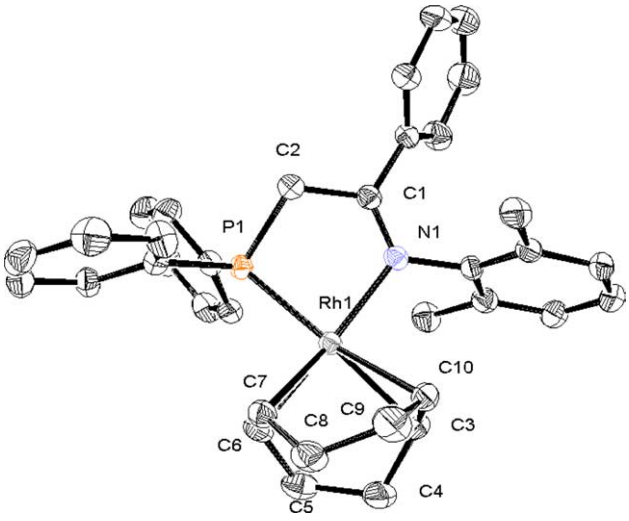


Fig. 2. Molecular structure of **2**. ORTEP diagram shows the cation of molecule 1 only. The asymmetric unit contains two independent molecules of [Rh(cod)(L)][BF_4] and two molecules of toluene.

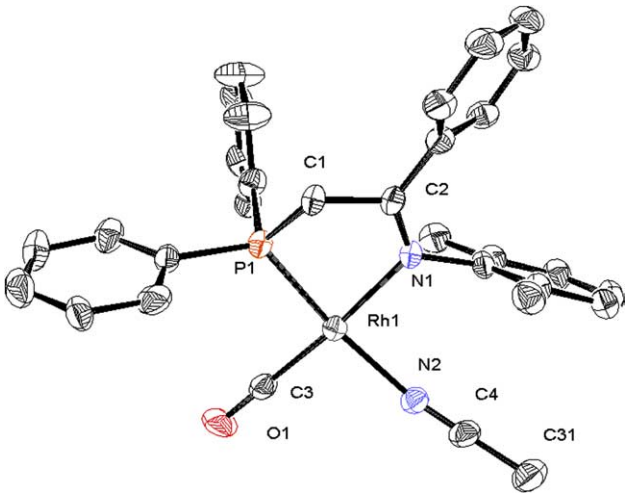


Fig. 3. Molecular structure of the complex **3**. ORTEP diagram of the cation of molecule 1 only. The asymmetric unit contains two independent molecules of [Rh(CO)(CH_3CN)(L)][BF_4], one molecule of benzene and one molecule of CH_2Cl_2.

are significantly different due to the different *trans* influences of the phosphorus and nitrogen atoms. These are 2.125(5) Å (Pd(1)–C(5)) and 2.214(5) Å (Pd(1)–C(3)) in molecule 1 and 2.208(5) Å (Pd(2)–C(34)) and 2.144(5) Å (Pd(2)–C(36)) in molecule 2. The Pd–P distances (2.2672(15) Å in molecule 1 and 2.2686(15) Å in molecule 2) are within the expected range and close to the values determined for complex [$PdMe_2$(L)] (2.273(3) Å) [67] and [Pd(η^3-C_3H_5)(L′)][Br] of 2.292(2) Å (L′ = 2-(diisopropylphosphinomethyl)-1-methylimidazole) [70]. This separation is considerably longer than the corresponding distance found in the

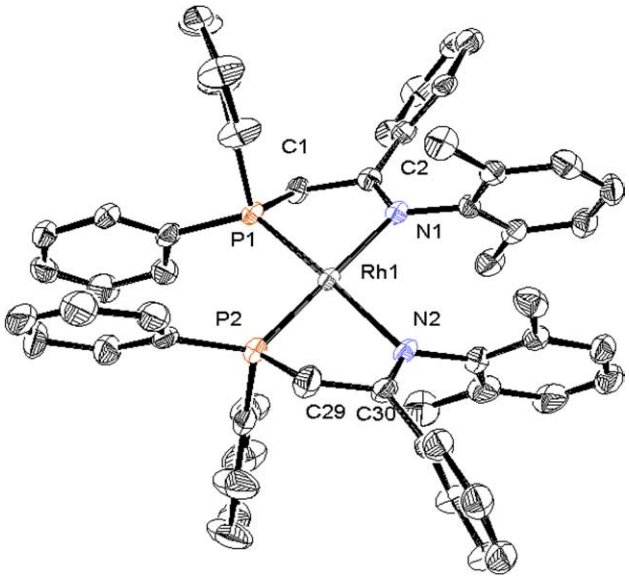


Fig. 4. Molecular structure of the complex **4**. ORTEP diagram of the cation of molecule 1 only. The asymmetric unit contains two independent molecules of [$Rh(L)_2$][BF_4] and three molecules of CH_2Cl_2.

Table 2
Selected bond lengths and angles for complexes **1**–**4**

Compound	Bond lengths (Å)		Bond angles (°)	
1				
Molecule 1	Pd(1)–N(1)	2.123(4)	N(1)–Pd(1)–P(1)	82.60(12)
	Pd(1)–P(1)	2.2672(15)	N(1)–Pd(1)–C(3)	104.82(18)
	Pd(1)–C(3)	2.214(5)	P(1)–Pd(1)–C(3)	168.52(15)
	Pd(1)–C(4)	2.162(5)	N(1)–Pd(1)–C(4)	137.6(2)
	Pd(1)–C(5)	2.125(5)	P(1)–Pd(1)–C(4)	138.58(17)
	N(1)–C(2)	1.290(6)	C(3)–Pd(1)–C(4)	37.0(2)
	N(1)–C(6)	1.448(7)	N(1)–Pd(1)–C(5)	170.4(2)
	P(1)–C(1)	1.840(5)	P(1)–Pd(1)–C(5)	103.67(16)
	P(1)–C(20)	1.820(5)	C(3)–Pd(1)–C(5)	67.9(2)
	P(1)–C(26)	1.803(5)	C(4)–Pd(1)–C(5)	38.4(2)
	C(1)–C(2)	1.517(7)	C(3)–C(4)–C(5)	120.0(5)
	C(3)–C(4)	1.388(8)		
	C(4)–C(5)	1.411(8)		
Molecule 2	Pd(2)–N(2)	2.139(4)	N(2)–Pd(2)–P(2)	82.46(12)
	Pd(2)–P(2)	2.2686(15)	N(2)–Pd(2)–C(34)	105.24(19)
	Pd(2)–C(34)	2.208(5)	P(2)–Pd(2)–C(34)	169.32(16)
	Pd(2)–C(35)	2.169(5)	N(2)–Pd(2)–C(35)	138.14(19)
	Pd(2)–C(36)	2.144(5)	P(2)–Pd(2)–C(35)	137.99(16)
	N(2)–C(32)	1.294(7)	C(34)–Pd(2)–C(35)	36.9(2)
	N(2)–C(37)	1.426(7)	N(2)–Pd(2)–C(36)	169.7(2)
	P(2)–C(33)	1.831(5)	P(2)–Pd(2)–C(36)	103.72(17)
	P(2)–C(51)	1.815(5)	C(34)–Pd(2)–C(36)	67.6(2)
	P(2)–C(57)	1.821(5)	C(35)–Pd(2)–C(36)	38.5(2)
	C(32)–C(33)	1.491(8)	C(34)–C(35)–C(36)	119.3(5)
	C(34)–C(35)	1.386(8)		
	C(35)–C(36)	1.421(8)		
2				
Molecule 1	Rh(1)–P(1)	2.2361(6)	P(1)–Rh(1)–N(1)	80.93(6)
	Rh(1)–N(1)	2.138(2)	P(1)–Rh(1)–C(3)	167.81(8)
	Rh(1)–C(3)	2.272(3)	N(1)–Rh(1)–C(3)	99.69(9)
	Rh(1)–C(6)	2.140(3)	P(1)–Rh(1)–C(6)	94.41(8)
	Rh(1)–C(7)	2.151(2)	N(1)–Rh(1)–C(6)	161.76(9)
	Rh(1)–C(10)	2.230(3)	C(3)–Rh(1)–C(6)	81.21(11)
	P(1)–C(2)	1.833(3)	P(1)–Rh(1)–C(7)	95.73(7)
	P(1)–C(30)	1.812(2)	N(1)–Rh(1)–C(7)	159.61(9)
	P(1)–C(31)	1.820(2)	C(3)–Rh(1)–C(7)	87.8(1)
	N(1)–C(1)	1.296(3)	C(6)–Rh(1)–C(7)	37.9(1)
	N(1)–C(11)	1.444(3)	P(1)–Rh(1)–C(10)	156.82(8)
	C(1)–C(2)	1.501(3)	N(1)–Rh(1)–C(10)	93.58(9)
	C(1)–C(19)	1.489(3)	C(3)–Rh(1)–C(10)	35.28(11)
	C(3)–C(4)	1.518(4)	C(6)–Rh(1)–C(10)	97.22(11)
	C(3)–C(10)	1.365(4)	C(7)–Rh(1)–C(10)	81.58(11)
	C(4)–C(5)	1.525(5)		
	C(5)–C(6)	1.511(4)		
	C(6)–C(7)	1.394(4)		
	C(7)–C(8)	1.522(4)		
	C(8)–C(9)	1.532(5)		
	C(9)–C(10)	1.511(4)		
Molecule 2	Rh(101)–P(101)	2.2335(6)	P(101)–Rh(101)–N(101)	80.79(6)
	Rh(101)–N(101)	2.145(2)	P(101)–Rh(101)–C(103)	161.21(8)
	Rh(101)–C(103)	2.252(3)	N(101)–Rh(101)–C(103)	100.69(9)
	Rh(101)–C(106)	2.146(3)	P(101)–Rh(101)–C(106)	91.90(8)
	Rh(101)–C(107)	2.150(2)	N(101)–Rh(101)–C(106)	162.59(9)
	Rh(101)–C(110)	2.240(3)	C(103)–Rh(101)–C(106)	81.3(1)
	P(101)–C(102)	1.828(3)	P(101)–Rh(101)–C(107)	97.35(8)
	P(101)–C(130)	1.811(3)	N(101)–Rh(101)–C(107)	158.19(9)
	P(101)–C(131)	1.814(3)	C(103)–Rh(101)–C(107)	88.1(1)
	N(101)–C(101)	1.298(3)	C(106)–Rh(101)–C(107)	38.1(1)
	N(101)–C(111)	1.447(3)	P(101)–Rh(101)–C(110)	163.47(8)

(*continued on next page*)

Table 2 (*continued*)

Compound	Bond lengths (Å)		Bond angles (°)	
	C(101)–C(102)	1.504(3)	N(101)–Rh(101)–C(110)	94.1(1)
	C(101)–C(119)	1.485(4)	C(103)–Rh(101)–C(110)	35.16(11)
	C(103)–C(104)	1.508(4)	C(106)–Rh(101)–C(110)	97.03(11)
	C(103)–C(110)	1.357(4)	C(107)–Rh(101)–C(110)	81.53(11)
	C(104)–C(105)	1.527(4)		
	C(105)–C(106)	1.512(4)		
	C(106)–C(107)	1.402(4)		
	C(107)–C(108)	1.523(4)		
	C(108)–C(109)	1.529(5)		
	C(109)–C(110)	1.514(4)		
3				
Molecule 1	Rh(1)–P(1)	2.2149(15)	P(1)–Rh(1)–N(1)	80.60(13)
	Rh(1)–N(1)	2.109(5)	P(1)–Rh(1)–N(2)	168.12(19)
	Rh(1)–N(2)	2.087(5)	N(1)–Rh(1)–N(2)	90.44(19)
	Rh(1)–C(3)	1.836(9)	P(1)–Rh(1)–C(3)	94.57(18)
	P(1)–C(1)	1.844(8)	N(1)–Rh(1)–C(3)	174.9(2)
	P(1)–C(19)	1.819(6)	N(2)–Rh(2)–C(3)	94.1(2)
	P(1)–C(25)	1.818(6)		
	O(1)–C(3)	1.140(9)		
	N(1)–C(2)	1.302(7)		
	N(1)–C(5)	1.453(6)		
	N(2)–C(4)	1.139(7)		
	C(1)–C((2)	1.515(7)		
Molecule 2	Rh(101)–P(101)	2.2074(16)	P(101)–Rh(101)–N(101)	81.63(13)
	Rh(101)–N(101)	2.115(5)	P(101)–Rh(101)–N(102)	173.48(17)
	Rh(101)–N(102)	2.086(5)	N(101)–Rh(101)–N(102)	92.10(19)
	Rh(101)–C(103)	1.820(9)	P(101)–Rh(101)–C(103)	92.06(19)
	P(101)–C(101)	1.826(8)	N(101)–Rh(101)–C(103)	173.0(2)
	P(101)–C(119)	1.804(9)	N(102)–Rh(101)–C(103)	94.3(2)
	P(101)–C(125)	1.807(6)		
	O(101)–C(103)	1.138(9)		
	N(101)–C(102)	1.296(7)		
	N(101)–C(105)	1.460(6)		
	N(102)–C(104)	1.139(7)		
	C(101)–C(102)	1.526(7)		
4				
Molecule 1	Rh(1)–P(1)	2.1934(11)	P(1)–Rh(1)–P(2)	98.62(4)
	Rh(1)–P(2)	2.1957(13)	P(1)–Rh(1)–N(1)	79.64(9)
	Rh(1)–N(1)	2.209(4)	P(2)–Rh(1)–N(1)	176.2(1)
	Rh(1)–N(2)	2.229(3)	P(1)–Rh(1)–N(2)	177.7(1)
	P(1)–C(1)	1.825(5)	P(2)–Rh(1)–N(2)	79.1(1)
	P(1)–C(9)	1.821(5)	N(1)–Rh(1)–N(2)	102.69(13)
	P(1)–C(15)	1.825(5)		
	N(1)–C(2)	1.296(5)		
	N(1)–C(21)	1.442(5)		
	N(2)–C(30)	1.292(6)		
	N(2)–C(49)	1.444(6)		
	C(1)–C(2)	1.504(6)		
	C(29)–C(30)	1.514(6)		
Molecule 2	Rh(2)–P(3)	2.2018(11)	P(3)–Rh(2)–P(4)	98.71(4)
	Rh(2)–P(4)	2.1938(11)	P(3)–Rh(2)–N(3)	80.87(9)
	Rh(2)–N(3)	2.200(3)	P(4)–Rh(2)–N(3)	167.80(9)
	Rh(2)–N(4)	2.176(3)	P(3)–Rh(2)–N(4)	170.5(1)
	P(3)–C(57)	1.841(4)	P(4)–Rh(2)–N(4)	81.4(1)
	P(3)–C(65)	1.817(4)	N(3)–Rh(2)–N(4)	101.07(13)
	P(3)–C(71)	1.831(5)		
	P(4)–C(85)	1.850(4)		
	P(4)–C(93)	1.818(5)		
	P(4)–C(99)	1.826(4)		
	N(3)–C(58)	1.292(5)		
	N(3)–C(77)	1.442(5)		

Table 2 (*continued*)

Compound	Bond lengths (Å)		Bond angles (°)
	N(4)–C(86)	1.303(5)	
	N(4)–C(105)	1.445(5)	
	C(57)–C(58)	1.496(6)	
	C(85)–C(86)	1.508(6)	

monohalide complex [PdMeCl(L)] (2.1925(9) Å) and in the dihalide complexes of the same ligand studied by us earlier [67]. The Pd–N distances (2.123(4) and 2.139(4) Å) are similar to those found for Pd(II) complexes in the same series. The C–C bond lengths within the allyl groups of **1** are: 1.388(8) Å (C(3)–C(4)) and 1.411(8) Å (C(4)–C(5)) (molecule 1) and 1.386(8) Å (C(34)–C(35)) and 1.421(8) Å (C(35)–C(36)). The C(3)–C(4) (molecule 1) and C(34)–C(35) distances show somewhat more double-bond character, probably again as a consequence of different donor properties of the P–N ligand.

For complexes **2**–**4**, the chelating ligand N–Rh–P bite angles are 80.93(6)° and 80.79(6) (for **2**, molecules 1 and 2, respectively), 80.60(13)° and 81.63(13)° (for **3**, molecules 1 and 2, respectively), 79.64(9)° and 79.1(1)° (molecule 1 of **4**) and 80.87(9)° and 81.4(1)° (molecule 2 of **4**). These values indicate slight deviations from ideal square planar geometry. The lengths of the carbon–nitrogen double bonds are all within the expected range, and are shown in Table 2. These values average 1.297 Å, and are slightly longer than that of the free ligand [$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$] (**L**) (1.273(2) Å). The Schiff-base character of the coordinated ligand is thus confirmed. As with other Group 10 complexes of this ligand the carbon–carbon backbone distances for complexes **2**–**4** are comparable with that of the free ligand (1.504(2) Å) (Table 2).

For all Rh(I) complexes, the puckering of the chelates (measured as the deviation of the methylene group of the ligand backbone from the best nitrogen–rhodium–phosphorus plane) ranges 20–31°, differing significantly for the two molecules within the same asymmetric unit (by ca. 10°). For complex **4**, the rhodium–phosphorus distances are 2.1934(11) Å and 2.1957(13) Å (molecule 1) and 2.2018(11) and 2.1938(11) Å (molecule 2), which are shorter than those of the literature N/P complexes with the P-atoms mutually *trans* (typical values 2.30–2.34 Å) [78]. The Rh–P distances in complex **4** are short due to the weak *trans* influence of nitrogen compared with that of phosphorus. The rhodium–phosphorus distances in **2** are 2.2361(6) Å (molecule 1) and 2.2335(6) Å (molecule 2), whereas in **3** these distances are 2.2149(15) and 2.2074(16) Å. These values reflect the relative *trans* influences of phosphines, nitriles and olefins. The rhodium–nitrogen bond lengths are all within the same range, for example: 2.138(2) Å (in **2**), 2.109(5) Å (in **3**), 2.209(4) and 2.229(3) Å (in **4**). In **3**, the observed Rh–CO bond lengths are 1.836(9) and 1.820(9) Å (molecules 1 and 2, respectively), which are slightly shorter than the average value of 1.847 Å, and similar to those found in N/P complexes of the type [RhCl(CO)(L″)], where L″ = chiral ferrocenyl chelating ligands, containing a tertiary phosphine and a pyrazole moiety [56,62,79–81]. The CO group of [$Rh(CH_3CN)(CO)(L)$][BF_4] (**3**) was shown to be coordinated *cis* to the phosphine group of the ligand. These observations are in agreement with previous findings whereby the complexes [$PdMe(PPh_3)(L)$] have been shown to exhibit a mutual *cis*-arrangement of the phosphine ligands [67]. The relative *cis*-arrangement of the phosphines was found in [$Rh(L)_2$][BF_4] (**4**). These observations are also consistent with previous literature reports, which suggested that the mutual *trans* positioning (in square planar complexes) of two phosphorous ligands, or of a phosphorus and a carbon ligand, would lead to the weakening of the corresponding M–P bonds [71,82].

3. Catalysis

3.1. CO–ethylene copolymerisation test

The ability of [Pd(η^3-allyl)(L)] (**1**) to catalyse the copolymerisation of ethylene and CO was tested in the absence of additional Lewis acid activators or transferable alkyl groups such as MoOH. Complex **1** was found inactive in the CO/ethylene copolymerisation reaction performed under mild conditions (room temperature, 2 bar 1:1 ethylene). Braunstein et al. [83] found that in CH_2Cl_2, temperatures as high as 60–90 °C and pressures of ca. 40 bar CO/ethylene mixture are needed when methyl-Pd(II) complexes incorporating chelating phosphinemethyl–oxazoline ligands are used as pre-catalysts. Therefore, the compound **1** was also tested under these less mild conditions. A solution of [Pd(η^3-allyl)(L)][BF_4] (**1**) was stirred for 12 h in CH_2Cl_2 at 90 °C in the presence of 40 bar 1:1 ethylene:CO in a sealed Parr autoclave. No significant reduction in the pressure of the autoclave was observed. Subsequently, the autoclave was allowed to cool to room temperature before the remaining C_2H_4/CO mixture was vented. A sample from the solution was collected for GC–MS analysis that indicated the formation of a mixture of oligomers, –[CO–C_2H_4]$_n$– with n = 2–8. After quenching, a small amount of grey solid obtained was separated by filtration,

washed with methanol and dried in vacuum, to yield CO/ethylene copolymer with a productivity of 110 g polymerx mol $Pd^{-1} \times h^{-1}$(0.03 g yield). The resultant product was characterised by solution IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopies in a 1:1 mixture of 1,1,1,3,3,3-hexafluoro-isopropanol and C_6D_6. The ^{1}H NMR spectra of the copolymer contained a single band of resonances in the region δ 2.39–2.41, which can be assigned to the methylene protons $-[CH_2CH_2CO]_n-$. The $^{13}C\{^{1}H\}$ NMR spectra showed singlet resonances for the methylene and carbonyl carbons at δ 35.3 and 212, respectively. The presence of end-groups could not be unambiguously detected by ^{1}H or $^{13}C\{^{1}H\}$ NMR. Spectroscopic data suggest the formation of a perfectly alternating copolymer, probably with the formula $[CH_2{=}CHCH_2(O)[CH_2CH_2C(O)]_nH]$. Simple melting point determinations for the resulting copolymers were in the range 249–259 °C, suggesting that $n > 400$ [84,85]. For more accurate T_m results, differential scanning calorimetry (DSC) data of the copolymer were performed by Chisso Petrochemical Corporation (Japan). In order to obtain reproducible T_m, the polymers were first melted and cooled before the actual measurement. DSC spectra for copolymer showed a major peak at 241 °C. These indicate that the sample consisted mainly of alternating CO/ethylene copolymers. This is in accord with the NMR spectra of the copolymer, which showed no detectable signals in the region expected for a double insertion fault of ethylene into the copolymer structures. However, a further minor peak in the DSC spectra was observed at 150 °C, suggesting that the sample also contained a small amount of homo-polyethylene. Accurate molecular weight determinations were not obtained due to the poor solubility of the copolymers in common organic solvents. In addition, GS–MS analysis of the yellow solution prior to quenching showed the presence of oligomers of the type $[CH_2{=}CHCH_2C(O)\{CH_2CH_2C(O)\}_nH]$, where $n = 1$ (retention time 0.5–3.5 min), 2 (retention time 15–20 min) and 3 (retention time 29 min). In situ formation of active cationic species was shown by mass spectrometry (ES) of the liquid phase, which exhibited peaks with $m/z = 624$ (5% intensity) and the isotopic pattern indicative for the $[Pd\{(C_2H_4)_2(CO)_2\}(L)]^+$ ion, where L = $[Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]$. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy of the oligomer solutions also showed a mixture of species, among which metal-coordinated iminophosphine species was observed. Formation of a metal-bound polymer along with Pd-oligomers [59,86] has been reported. Although the structure of the catalyst resting state could not be assigned these observations are indicative of a 'living' copolymerisation process.

During this study, Liu and co-workers [6] reported several five-membered chelate complexes, incorporating phosphorus and nitrogen donor ligands with rigid backbones, which are active towards ethylene/CO copolymerisation and our results on catalyst activity are within the same range.

3.2. Heck coupling test

The compound $[Pd(\eta^3\text{-allyl})(L)][BF_4]$ (**1**) was tested as a pre-catalyst for the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate. A mixture of 4-bromoacetophenone and 1.4 equivalents *n*-butyl acrylate was heated at 130 °C for 20 h, under N_2 and in the absence of air and moisture in dry *N*,*N*-dimethylacetamide, in the presence of a base (sodium acetate) and 0.5 mol% pre-catalyst. $[^{n}Bu_4N][OAc]$ was also added to the reaction mixture, since it has been shown that the presence of a soluble base such as tetrabutylammonium acetate significantly reduced the induction time required to form the catalytically active species [87]. Although no Heck coupled product was observed by GC–MS, surprisingly, peaks at much higher retention times indicated the formation of di- and tri-*N*-butyl acrylate oligomers with *m*/*z* 254 and *m*/*z* 382, respectively.

4. Conclusions

Studies of the synthesis of cationic Pd(II) and Rh(I) complexes have led to the isolation and characterisation of the new mono-cationic complexes $[Pd(^3\text{-allyl})(L)][BF_4]$ (**1**), $[Rh(cod)(L)][BF_4]$ (**2**), $[Rh(CH_3CN)(CO)(L)][BF_4]$ (**3**) and $[Rh(L\}_2][BF_4]$ (**4**), where L = $[Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]$. These have been characterised spectroscopically and structures confirmed by X-ray diffraction. Complex **1** exhibits moderate activity towards CO/ethylene copolymerisation and no activity in the Heck coupling reaction between 4-bromoacetophenone and *n*-butyl acrylate.

5. Experimental details

5.1. General

All manipulations of air and/or moisture sensitive materials were performed under an inert atmosphere of pure Ar or dry N_2 using standard Schlenk line techniques or in an inert atmosphere dry box. Inert gases were purified firstly by passage through columns filled with activated molecular sieves (4 A) and then either manganese (II) oxide suspended on vermiculite, for the Schlenk line, or BASF catalyst, for the dry box. Celite filtration aid was purchased from Fluka Chemie and oven-dried at 150 °C prior to use. Solvents were predried over activated 4 A molecular sieves and then distilled under N_2 from Na/K alloy (light petroleum ether b.p. 40–60 °C, diethyl ether, pentane), from sodium (toluene), from potassium (THF), or from calcium hydride

(dichloromethane). Deuterated NMR solvents (Aldrich, Goss Scientific) were refluxed and distilled from potassium metal (d^8-toluene) or stirred overnight with calcium hydride (CD_2Cl_2) prior to use. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford and FAB^+ mass-spectra by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, UK.

NMR spectra were recorded using either a Varian Mercury-vx 300 (^1H 300 MHz, ^{13}C 75.5 MHz, ^{19}F 282.3 MHz, ^{31}P 121.6 MHz) or a Varian UNITY*plus* (^1H 500 MHz, ^{11}B 160.4 MHz, ^{13}C 125.7 MHz, ^{31}P 202.4 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (^1H, ^{13}C, $\delta = 0$) or externally to $BF_3 \cdot Et_2O$ (^{11}B, $\delta = 0$); H_3PO_4 (^{31}P, $\delta = 0$) or $CFCl_3$ (^{19}F, $\delta = 0$). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

GC–MS chromatographs and spectra were recorded using a Hewlett–Packard 5890 Gas Chromatograph fitted with a non-polar column connected to a Trio-1000 Mass Spectrometer operating Electron Impact (70 eV) and Chemical Ionisation (CI) mode (NH_3) and detecting positively charged species. The temperature profile for the GC is: 100 °C (3 min), then 10 °C/min ramp until 280 °C (held for 10 min).

The compounds $[RhCl(C_2H_4)_2]_2$ [88,89], $[RhCl(CO)_2]_2$ [88,89], and $[RhCl(cod)]_2$ [90], were prepared according to the literature methods, $[Pd(allyl)Cl]_2$ was purchased from Aldrich and used as received. The ligand **L** was prepared as described by us elsewhere [67].

5.2. Preparations

5.2.1. *[Pd(η³-allyl)(L)][BF₄] (1)*

The solids $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.10 g, 0.273 mmol) and $AgBF_4$ (145 mg, 0.547 mmol) were mixed in a Schlenk tube and 50 mL CH_3CN was added. The mixture was stirred at room temperature for 30 min and formation of a white precipitate was observed. A solution of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3]$ (**L**) in 50 mL CH_3CN was added to the reaction mixture whilst stirring. Subsequently, the reaction mixture was left stirring in darkness for 10 h and then the solids removed by filtration. The filtrate was concentrated to 5 mL, layered with pentane and stored at −20 °C. Light-yellow crystals of $[Pd(\eta^3allyl)(L)][BF_4]$ (**1**) were formed, isolated by filtration and dried under reduced pressure. Yield: 0.27 g, 69.5%.

5.2.2. *[Rh(cod)(L)][BF₄] (2)*

$AgBF_4$ (0.08 g, 0.41 mmol) was added to a CH_3CN (50 mL) solution of $[RhCl(cod)]_2$ (0.07 g, 0.203 mmol). The mixture was stirred at room temperature and the colourless precipitate formed was removed by filtration. To the filtrate, a CH_3CN (50 mL) solution of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) (0.12 g, 0.285 mmol) was added whilst stirring. The mixture was left stirring in darkness for 10 h at room temperature. The volatiles were removed under reduced pressure, and the residue washed with a cold mixture of toluene and pentane (30 mL, 1:4 ratio). The resulting orange solid was recrystallised from a 1:4 mixture of CH_2Cl_2 and pentane to afford orange crystals of $[Rh(cod)(L)\}][BF_4]$ (**2**). Yield: 0.15 g, 75%.

(NB. Elemental analysis given in Table 1 has been performed on the crushed, high vacuum dried crystals).

5.2.3. *[Rh(CO)(CH₃CN)(L)][BF₄] (3)*

$AgBF_4$ (0.04 g, 0.205 mmol) was added to a CH_3CN (50 mL) solution of $[RhCl(CO)]_2$ (0.05 g, 0.102 mmol). The mixture was stirred at room temperature and the colourless precipitate formed was removed by filtration. To the filtrate, a CH_3CN (50 mL) solution of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) (0.08 g, 0.0205 mmol) was added whilst stirring. The mixture was left stirring for 10 h at room temperature in darkness. The solvent was removed under reduced pressure and the residue washed with a cold mixture of benzene and pentane (20 mL, 1:4 ratio). The resulting orange solid was recrystallised from a 1:4 mixture of CH_2Cl_2 and pentane to afford orange crystals of $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**). Yield 0.84 g, 62%.

(NB. Elemental analysis given in Table 1 has been performed on the crushed, high vacuum dried crystals).

5.2.4. *[Rh(L)₂][BF₄] (4)*

$AgBF_4$ (0.08 g, 0.41 mmol) was added to a CH_3CN (50 mL) solution of $[RhCl(C_2H_4)]_2$ (0.10 g, 0.202 mmol). The mixture was stirred at room temperature and the colourless precipitate formed was removed by filtration. To the filtrate, a CH_3CN (50 mL) solution of $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$ (**L**) (0.17 g, 0.405 mmol) was added whilst stirring. The mixture was left stirring for 10 h at room temperature in darkness. The solvent was removed under reduced pressure and the residue washed with 20 mL cold pentane. The resulting red solid was recrystallised from a 1:4 mixture of CH_2Cl_2 and pentane to afford red crystals characterised as *cis*-$[Rh(L)_2][BF_4]$ (**4**) by X-ray diffraction.

The reaction was subsequently repeated using $[RhCl(C_2H_4)]_2$ (0.10 g, 0.20 mmol), $AgBF_4$ (0.08 g, 0.40 mmol) and **L** (0.33 g, 0.81 mmol) in a 1:2:4 ratio. Yield *cis*-$[Rh(L)_2][BF_4]$ (**4**): 0.04 g, 35%.

5.2.5. *Reaction between [Rh(CO)(CH₃CN)(L)][BF₄] (3) and L*

The solids $[Rh(CO)(CH_3CN)(L)][BF_4]$ (**3**) (0.03 g, 0.075 mmol) and $[Ph_2PCH_2C(Ph)=N(2,6\text{-}Me_2C_6H_3)]$

(L) (0.05 g, 0.075 mmol) were mixed in a Schlenk tube and 50 mL CH_2Cl_2 added dropwise. The mixture was stirred for 10 h. The volatiles were removed under reduced pressure, and a red-brown solid was isolated and recrystallised from a 1:4 mixture of CH_2Cl_2 and pentane at −20 °C to afford *cis*-[Rh(L)$_2$][BF_4] (**4**). Yield: 0.05 g, 69%.

5.3. Copolymerisation test

The Pd pre-catalyst compound **1** in 50 mL CH_2Cl_2 was transferred using a glove-box into a dried 200 mL Parr autoclave fitted with a Teflon liner and equipped with a stirrer bar. The autoclave was charged with 40 bar 1:1 C_2H_4:CO mixture, sealed, and allowed to reach 90 °C. The mixture was stirred at this temperature for a further 12 h. Subsequently, the autoclave was allowed to cool to room temperature before the remaining C_2H_4/CO mixture was vented. The grey precipitate obtained was separated by filtration, washed with methanol and dried in vacuum (yield 30 mg, 110 g polymerx mol $Pd^{-1} \times h^{-1}$). Infrared spectroscopy of the products showed the characteristic carbonyl stretch of poly(C_2H_4-alt-CO) at 1692 cm^{-1}. GS–MS analysis of the filtrate (a yellow coloured solution) prior to quenching showed the presence of a mixture of oligomers.

5.4. Heck coupling of 4-bromo-acetophenone and n-butyl acrylate using complexes *1* as a catalyst

Sodium acetate (2.25 g, 27.4 mmol), 4-bromo-acetophenone (4.97 g, 25.0 mmol), di-ethyleneglycol di-*n*-butylether (0.50 g, 2.9 mmol, G.C. standard), *n*-butyl acrylate (4.486 g, 35.0 mmol) and a *N*,*N*-dimethylacetamide solution (10 mL) of the pre-catalyst (0.5 mol%, based on 4-bromo-acetophenone) were added to *N*,*N*-dimethylacetamide (20 mL) in a 100-mL 3-necked flask equipped with a thermometer and reflux condenser, against a counterflow of nitrogen. Tetrabutylammonium acetate (2.26 g, 7.5 mmol) was also added to the reaction mixture, as a completely soluble base. The mixture was degassed and purged with nitrogen to ensure an inert reaction atmosphere, then refluxed at the appropriate reaction temperature for 20 h. The reaction mixture was added at room temperature to an excess of water, extracted with diethyl ether and dried with magnesium sulphate. The extraction was analysed by GC–MS. Complex **1** does not show significant activity as a catalyst in this process as shown by integration of the

Table 3
Crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{62}H_{62}B_2F_8N_2P_2Pd_2$	$C_{100}H_{108}B_2F_8N_2P_2Rh_2$	$C_{68}H_{64}B_2F_8N_4O_2P_2Rh_2$	$C_{115}H_{110}B_2C1_6F_8N_4P_4Rh_2$
Formula weight	1283.55	1779.4	1410.61	2264.09
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	19.4136(7)	12.3670(3)	12.1572(4)	13.3345(1)
b (Å)	9.5339(3)	18.9460(3)	16.6137(6)	20.1143(2)
c (Å)	31.8889(11)	19.3170(5)	16.6600(6)	20.6864(2)
α (°)	90	79.3020(10)	81.3903(12)	102.1839(6)
β (°)	101.0869(13)	80.1090(10)	79.7375(14)	90.8488(4)
γ (°)	90	87.1860(10)	78.699(2)	101.8863(5)
Volume (Å^3)	5792.1(3)	4380.61(7)	3223.8(2)	52926.9
Z	4	2	4	4
Density (calculated) (Mg/m^3)	1.472	1.35	1.45	1.419
Absorption coefficient (mm^{-1})	0.743	0.48	0.63	0.588
$F(000)$	2608	1848	1436	2324
Crystal size (mm^3)	0.20 × 0.20 × 0.20	0.3 × 0.3× 0.3	0.20 × 0.30 × 0.40	0.20 × 0.20 × 0.40
θ Range for data collection	5–23.5	0–26.5	1–27	4–28.4
Index ranges	$0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 9$, $-35 \leqslant l \leqslant 34$	$0 \leqslant h \leqslant 15$, $-23 \leqslant k \leqslant 23$, $-23 \leqslant l \leqslant 24$	$-6 \leqslant h \leqslant 6$, $-21 \leqslant k \leqslant 21$, $-21 \leqslant l \leqslant 21$	$-17 \leqslant h \leqslant 17$, $-26 \leqslant k \leqslant 26$, $-27 \leqslant k \leqslant 26$
Reflections collected	8560	23643	8022	46486
Independent reflections	8011 [R_{int} = 0.04]	16715 [R_{int} = 0.02]	4345 [R_{int} = 0.03]	25647 [R_{int} = 0.04]
Maximum and minimum transmission	0.86 and 0.86	0.87, 0.87	0.88 and 0.83	0.89 and 0.89
Parameters	703	1045	793	1271
Goodness-of-fit	1.0625	0.9808	1.1616	1.0688
Final R indices	R_1 = 0.0456	R_1 = 0.0460	R_1 = 0.0401	R_1 = 0.0540
[I>3σ(I)]	wR_2 = 0.0503	wR_2 = 0.0508	wR_2 = 0.0471	wR_2 = 0.0601
Largest difference peak and hole (e Å^{-3})	−0.75 and +0.90	−0.89, 1.26	−0.40 and 0.61	−0.92 and 3.28

chromatograph peak for the product against the 4-bromo-acetophenone and against the GC standard peak for the di-ethyleneglycol di-*n*-butylether.

6. X-ray crystallography

In each case, a single crystal was selected under an inert atmosphere, encased in perfluoro-polyether oil, and mounted on the end of a glass fibre. The fibre, secured in a goniometer head, was then placed under a stream of cold nitrogen maintained at 150 K and data collected on an Enraf–Nonius DIP2000 image plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The images were processed with the DENZO and SCALEPACK programs [91] and corrections for Lorentz and polarisation effects were performed. All solution, refinement, and graphical calculations were performed using the CRYSTALS [92] and CAMERON [92] software packages.

For **2**, attempts to solve the structure by direct methods failed to give a model suitable for further development. Examination of the intensity data showed clear evidence of a *pseudo C*-centering of the lattice. The structure was therefore solved in the non-standard space group $C\bar{1}$ using the direct-methods program SIR92[2]. The resulting model was then transformed to give a structure in which the space group was $P\bar{1}$, with two rhodium complexes in the asymmetric unit. An observed Fourier map showed a number of additional peaks, identified as four molecules of toluene and two tetrafluoroborate counterions. Selection of groups of peaks, which corresponded to geometrically reasonable solvent molecules, and subsequent Fourier refinement of these and the tetrafluoroborate anions lead to a model which could be successfully refined by conventional full-matrix least-squares methods. Refinement converged satisfactorily to give $R = 0.0460$, $wR = 0.0508$ (Table 3).

The structures of **1**, **3** and **4** were solved by direct methods using the SIR92 [93] program and refined by full-matrix least squares procedure on *F*. The crystallographic data are summarised in Table 3. In each case, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. Empirical absorption corrections were applied, as well as the 3-term Chebychev polynomial weighting scheme [94].

Appendix A. Supplementary data

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 257693–257696. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.01.016.

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