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New cationic palladium (II) and rhodium (I) complexes of [Ph2PCH2C(Ph)=N(2,6-Me2C6H3)]

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Abstract

Treatment of the bulky iminophosphine ligand [Ph2PCH2C(Ph)=N(2,6-Me2C6H3)] (L) with [M(CH3CN)2(ligand)]$^{+n}$, where for M = Pd(II): ligand = η^3-allyl, n = 1, and for M = Rh(I), ligand: 2(C2H4), 2(CO) or cod, n = 0, yields the mono-cationic iminophosphine complexes [Pd(η^3-C3H5)(L)][BF4] (1), [Rh(cod)(L)][BF4] (2), [Rh(CO)(CH3CN)(L)][BF4] (3), and cis-[Rh(L)2][BF4] (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.
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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(L2)2]$^+$ (where L2 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 [Ph2PCH2C(Ph)=N(2,6-R2C6H3)] (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 [Ph2PCH2C(Ph)=N(2,6-R2C6H3)] (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 [Ph2PCH2C(Ph)=N-(2,6-Me2C6H3)] (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(η^3-allyl)(μ-Cl)]$_2$ are known to leave the palladium-π-allyl groups intact [68]. The cationic η^3-allyl complex [Pd(η^3-allyl)(L)][BF$_4$] (**1**) was obtained by the reaction between [Pd(η^3-allyl)(MeCN)$_2$][BF$_4$] (prepared in situ, after reacting [Pd(η^3-allyl)Cl]$_2$ with one equivalent of AgBF$_4$ in CH$_3$CN) and one equivalent of the compound [Ph$_2$PCH$_2$C(Ph)=N(2,6-Me$_2$C$_6$H$_3$)] (**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$_3$CN)(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$_2$H$_4$)$_2$]$_2$ (in case of **4**), AgBF$_4$ and the ligand **L**, in CH$_3$CN 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$_3$CN)(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$_3$CN solution) of the CO group. With [RhCl(C$_2$H$_4$)$_2$]$_2$, AgBF$_4$ and **L** in CH$_3$CN, a small amount of red crystals were obtained, together with an unidentifiable mixture of products. The red crystals were shown by ^{1}H 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$_2$H$_4$)$_2$(L)][BF$_4$] or [Rh(CH$_3$CN)(C$_2$H$_4$)(L)][BF$_4$]. The reaction was repeated using [RhCl(C$_2$H$_4$)$_2$]$_2$, 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$_3$CN)(L)][BF$_4$] (**3**) and one equivalent of free **L** was performed in CH$_2$Cl$_2$, 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 ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy (in CD$_2$Cl$_2$). Full assignments are given in Table 1.

The IR spectrum of **1** (in CD$_2$Cl$_2$) showed a $v_{C=N}$ 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$_2$Cl$_2$) showed bands at 1539 (**2**), 1538 (**3**) and 1559 cm^{-1} (**4**) assignable to $v_{C=N}$. For **3**, a broad band at 2304 cm^{-1} indicated the presence of coordinated CH$_3$CN and the band at 2004 cm^{-1} was assigned to the CO stretching vibration. The presence of CH$_3$CN and CO ligands was also confirmed by ^{13}C{^{1}H} NMR spectroscopy. In all cases, IR spectra (CD$_2$Cl$_2$) showed broad bands in the region 1220 cm^{-1} corresponding to [BF$_4$]$^-$.

The ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$) of [Pd(η^3-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(η^3-allyl)(L)][BF$_4$] (**1**) was found stereochemically non-rigid in CD$_2$Cl$_2$. The ^{1}H NMR spectrum of **1** (room temperature, CD$_2$Cl$_2$) 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$_2$C$_6$H$_3$ 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 ^{1}H 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 ^{1}H NMR spectrum was assisted by ^{1}H –^{1}H 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 P*Ph*$_2$ 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{^{1}H} 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