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Synthesis and X-ray structure of cationic β-diimine palladium complexes containing π-methallyl ligand

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Abstract

High yield of cationic palladium β-diimine complexes [$(CH_2(MeCNAr)_2)Pd(\eta^3\text{-}C_4H_7)$][Y] (Ar = C_6H_5, Y = PF_6 (**8**); 2-Me-C_6H_4, Y = PF_6 (**9**); 2,6-Me_2-C_6H_3, Y = PF_6 (**10**); 2,6-*i*Pr_2-C_6H_3, Y = PF_6 (**11**), Y = B(3,5-$(CF_3)_2$-$C_6H_3)_4$ (**12**)) have been obtained by an oxidative addition of the methallyloxyphosphonium salts (**5, 6**) to a preformed complex $Pd(dba)_2$ (**7**) in the presence of the β-iminoamine ligands (**1**–**4**).

These complexes are thermally stable and have been characterized by ^1H and $^{13}C\{^1H\}$ NMR as well as IR spectroscopy. The structure of the cationic allyl palladium complex (**12**) has been solved by X-ray crystallography.

Keywords: Palladium; Cationic methallyl complexes; β-diimine ligands; Methallyloxyphosphonium salts

1. Introduction

Cationic, η^3-allyl complexes of palladium(II) prepared either in situ, or separately, have been reported to catalyse the dimerization of functionalized alkenes, the oligomerization of monoolefins [1,2], and the telomerization of olefins with alcohols [3]. In addition much attention has been paid to these compounds as a result of their importance as intermediate in palladium catalyzed allylic substitution reactions. Attack of a nucleophile moiety on a cationic palladium π-allyl complex is nowdays conventionally accepted as the crucial step in the catalytic cycle [4–6].

The lack of reactivity and non-nucleophilic character of $[PF_6]^-$ have led to its widespread use as non coordinating (or weakly coordinating) counterion supporting cationic organometallic complexes [7,8]. Sufficiently electrophilic complexes of $[PF_6]^-$ present reactivity limitation of this anion as non-reactive entity [9]. In addition to the recognized requirements for weakly coordinating anions, an effective counteranion must necessarily be chemically robust and exceptionally resistant to electrophilic attack. In regard to this, (fluoroaryl)borate are worthy of attention. However, as the preparation of such anion is costly and involves significant synthetic effort. New methallyloxyphosphonium salts with the bulky and weakly coordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl] borate have been investigated in the hope of generating electrophilic cationic species.

On the other hand, the use of anionic β-diiminate as supporting ligand systems in both main and transition metal coordination chemistry has recently attracted considerable attention [10–29]. These ligands have several attractive features, including the possible tunability in both the Ar and R groups as well as variable binding modes ranging from purely σ to a combination of σ and π donation and depending on the steric environment and the electron demand at the bound metal

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[15,30]. However complexes in which the ligand is bound as a neutral donor (β-iminoamine) still remain relatively unexplored.

Recently the β-diimine ligands became more popular since the discovery by Feldman and Co-workers [31] of "Brookhart type" Ni and Pd polymerization catalysts. They synthesized the first cationic β-diimine palladium complex by reaction between a "β-iminoamine" and $[Pd(MeCN)_4][BF_4]_2$. The species isolated was α-C metallated, a reflection of the "soft" character of the palladium centre. The C-palladated diimine was coordinated through its two nitrogen atoms to another palladium centre, and it was unclear as to which of these was the active centre (Scheme 1).

2. Results and discussion

Our interest in β-diimine ligands was sparkled by Brookhardt's group 10 alkene polymerization precatalysts [32,33], as well as a concurrent renewer interest in the coordination chemistry of diiminate ligands [10–30], we synthesized η^3-allylic β-diimine complexes of palladium **8**–**12** from "β-iminoamine" **1**–**4** in order to assess the relative merits of α and β-diimine in the polymerisation of alkenes.

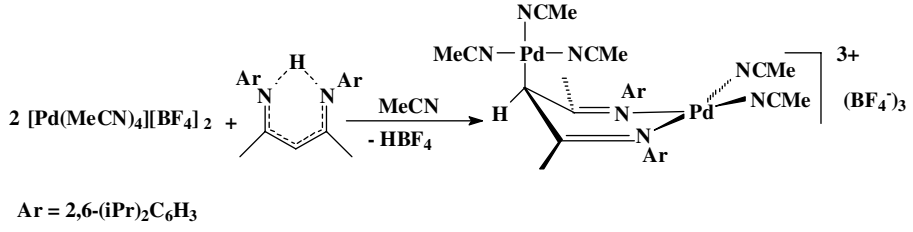
The present work is a continuation of our study in β-diimine allylic complexes [34]. We describe in this paper a one pot synthesis of new η^3-allyl cationic complexes of palladium (II) bearing variable *N*,*N*′-disubstituted β-diimine ligands which lead to coordination of palladium by two hard donor atoms.

These compounds $[(CH_2(MeCNAr)_2)Pd(\eta^3\text{-}C_4H_7)]^+$, which are isolated as stable $[PF_6]^-$ and $[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]^-$ salts, can be easily obtained in high yields by an oxidative addition of methallyloxyphosphonium salts [35,36] **5** and **6** to the zerovalent compound $Pd(dba)_2$ [37] **7** in methylene chloride in the presence of a β-iminoamine ligand [24,25,30] (Scheme 2).

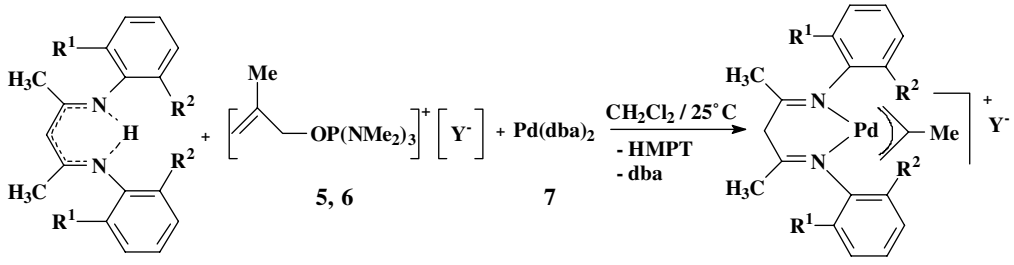
The new complexes **8**–**11** which are soluble in methylene chloride and sparingly soluble in chloroform and diethyl ether gave satisfactory analysis and were characterized by ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy. Special attention is given to the enhancement of the solubility and stability of the new cationic complex **12** in relatively apolar solvents through the use of the fluorine-substituted tetraarylborate anion $[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$.

The NMR data of ligands **1**–**4** are consistent with the symmetrical, hydrogen-bridged "β-iminoamine" structure shown in Scheme 2 [30], although complexes **8**–**12** incorporating neutral ligands of this type are coordinated to palladium as a β-diimine tautomer.

The ^1H NMR spectra of these compounds show two resonances signals for the allyl protons (H_{syn} and H_{anti}) besides of the methyl group. These signals were attributed considering that in allyl complexes the syn protons



Scheme 1. α-C palladated diimine complex.



8: $R^1 = R^2 = H$; $Y = PF_6^-$
9: $R^1 = H$; $R^2 = CH_3$; $Y = PF_6$
10: $R^1 = R^2 = CH_3$; $Y = PF_6$
11: $R^1 = R^2 = iPr$; $Y = PF_6$
12: $R^1 = R^2 = iPr$; $Y = B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4$
dba = dibenzylideneacetone.
HMPT = Hexamethylphosphotriamide.

Scheme 2. Synthesis of $[(\eta^3\text{-}C_4H_7)Pd(H_2C(MeCNAr)_2)]^+[PF_6]^-$ complexes.

resonate at higher frequencies than the anti protons [38]. Thus the two resonances are located, respectively, at 2.62, 2.48, 2.28, 2.52 and 2.48 ppm for H_{anti} and at 2.69, 2.53, 2.57, 2.58 and 2.52 ppm for H_{syn} for complexes **8**–**12**. In ^{13}C NMR spectra, the allylic carbon C(6) and C(8) appears at (62.51 and 64.78); (63.55 and 64.66); 63.86, 64.87 and 66.10 ppm, respectively, for complexes **8**–**12**. The C=N carbon resonates between 176.30 and 181.02 ppm.

The IR spectra of both ligands **1**–**4** exhibit (NH) absorption bands at 3400–3300 cm^{-1} which were not present in the coordinated ligand. The absence of the ν(H–N) stretching frequencies detected in β-iminoamine ligands confirm that they are indeed β-diimine tautomer. Moreover, complexes **8**–**12** exhibit the frequencies of the corresponding counterions at 827, 832, 831 and (830 and 838 cm^{-1}) for [PF_6] and 1162 and 1121 cm^{-1} for [B(3,5-$(CF_3)_2$-$C_6H_3)_4$)]. The ν(C=N) stretching frequencies of the free ligands (1643, 1620, 1631 and 1626 cm^{-1} respectively for ligands **1**–**4**) are different from those coordinated (1652, 1660, 1667, 1663 and 1663 cm^{-1}, respectively, for complexes **8**–**12**).

X-ray single-crystal analysis reveals that compound **12** exhibit some interesting features. Suitable prismatic and yellow single crystals of **12** were obtained by crystallization from CH_2Cl_2/*n*-hexane. The complex **12** crystallizes in the triclinic unit cell $P\bar{1}$ group (Table 1).

An ORTEP-plot shown in Fig. 1 confirms the identity of complex **12**. The structure of the complex **12** consists of loosely associated [(η^3-C_4H_7)Pd(NN)] cation and tetrahedral [B(3,5-$(CF_3)_2$-$C_6H_3)_4$] counteranion (Fig. 1(a)). The anion [B(3,5-$(CF_3)_2$-$C_6H_3)_4$] adopts a structure in which the four fluoroaryl groups are tetrahedrally bonded to the central boron atom. The [(η^3-C_4H_7)Pd(NN)]$^+$ cation of **12** adopts the usual slightly distorted square planar arrangement and this distortion is illustrated by the N(1)–Pd–N(2) bond angle equal to 90.61(10)° (Fig. 1(b)). The allyl ligand is bonded almost symmetrically to the palladium centre (Pd–C(6) = 2.129(4) Å and Pd–C(8) = 2.115(4) Å. We note that the Pd–C(allyl) distances are reasonable for an allyl *trans* to a ligand of moderate *trans* influences. Selected bond lengths and angles are listed in Table 2.

The β-iminoamine ligand is bounded in a symmetric fashion as the β-diimine tautomer, which acts as a chelating ligand through its two N atoms. This ligand forms a six-membered ring with the palladium atom with Pd–N(sp^2) bond length of 2.106(3) Å in agreement with known values in the literature for related complexes [33,35,39]. Bond distances within the six-member chelate ring are consistent with the localized β-diimine structure drawn in Fig. 1 while the ring itself adopts a boat conformation as indicated in Fig. 1(b).

The methyl on the allyl group is slightly tilted out of the allyl plane by about 12° as indicated by the torsion angle of 167.6° of C(7)–C(6)–C(8)–C(9). The allyl plane (C(6),C(7),C(8)) makes an angle of 63.5(3)° with the palladium coordinative least-squares plane (N(1),N(2), C(6),C(8)). The aryl rings C(10–15) and C(22–27) are tilted out of the (N(1),C(2),C(4),N(2)) least-squares plane by 72.3(1)° and 86.1(2)°, respectively.

Table 1
Crystallographic data and structure refinement for **12**

Empirical formula	$C_{33}H_{49}N_2Pd \cdot BC_{32}H_{12}F_{24} \cdot CH_2Cl_2$
Formula weight	1528.29
Temperature (K)	110(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.7937(4)
b (Å)	13.0162(3)
c (Å)	21.1177(6)
α (°)	96.409(1)
β (°)	92.190(1)
γ (°)	102.961(1)
Volume (Å^3)	3398.35(16)
Z	2
F(000)	1539
$D_{(calc)}$ (g cm^{-3})	1.484
Diffractometer	Enraf–Nonius Kappa CCD
Scan type	Mixture of ϕ rotation and ω scans
Wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	0.459
Crystal size (mm^3)	$0.3 \times 0.25 \times 0.15$
$\sin(\theta)/\lambda_{max}$ (Å^{-1})	0.65
Index ranges	$-16 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 16$, $-27 \leqslant l \leqslant 27$
Absorption correction	SCALEPACK
RC = Reflections collected	25,131
IRC = Independent RC	15,208 [R_{int} = 0.0612]
IRCGT = IRC and [$I > 2\sigma(I)$]	8643
Refinement method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	15,208/0/891
R for IRCGT	R_1[a] = 0.0551, wR_2[b] = 0.0966
R for IRC	R_1[a] = 0.1306, wR_2[b] = 0.1168
Goodness-of-fit[c]	0.972
Largest difference peak and hole (e Å^{-3})	0.58 and −0.64

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$, where $P = (\mathrm{Max}(F_o^2, 0) + 2^*F_c^2)/3$.
[c] Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2/(N_0 - N_v)]^{1/2}$.

3. Conclusions

The coordination chemistry of β-diimines has been found to be markedly different from otherwise identical α-diimines, as it is significantly more difficult to prepare stable complexes of a variety of transition metal species.

We have described in the present work a convenient synthetic procedure for the preparation of a new cationic methallylpalladium complexes supported by β-diimine ligand with different anion such as [PF_6] and [B(3,5-$(CF_3)_2$-$C_6H_3)_4$]. The application of these compounds in catalytic reactions such as oligomerization and polymerization of alkenes (ethylene, styrene,

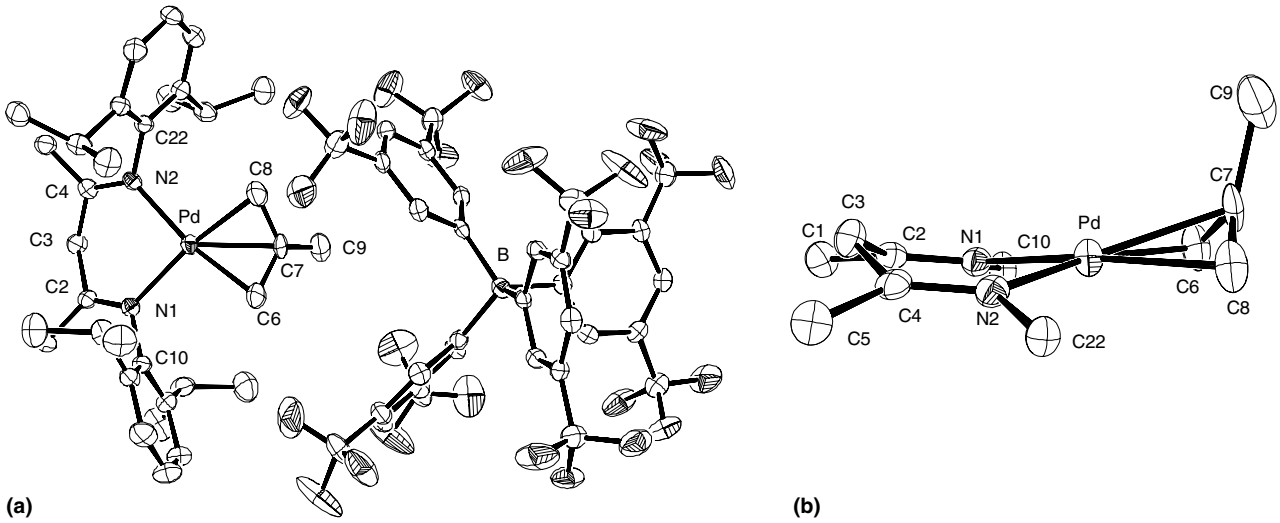


Fig. 1. (a) Perspective ORTEP diagram of **12**. Thermal ellipsoids are at 50% probability. Methylene chloride of crystallization and hydrogen atoms are omitted for clarity. (b) View of the chelate ring in **12**. $[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ anion, hydrogen atoms and aryl ring are omitted for clarity.

Table 2
Bond lengths [Å] and angles [°] for **12**

Pd–N(1)	2.105(3)	Pd–N(2)	2.106(3)
Pd–C(6)	2.129(4)	Pd–C(7)	2.153(3)
Pd–C(8)	2.115(4)		
N(1)–C(2)	1.284(4)	N(2)–C(4)	1.283(4)
N(1)–C(10)	1.458(4)	N(2)–C(22)	1.462(4)
N(1)–Pd–N(2)	90.61(10)		
N(1)–Pd–C(8)	167.12(14)	N(2)–Pd–C(6)	166.31(14)
N(1)–Pd–C(6)	100.58(13)	N(2)–Pd–C(8)	100.11(14)
N(1)–Pd–C(7)	133.73(13)	N(2)–Pd–C(7)	134.10(13)
C(7)–Pd–C(8)	38.34(15)	C(6)–Pd–C(7)	37.88(14)
C(6)–Pd–C(8)	67.87(16)		
C(2)–N(1)–C(10)	118.7(3)	C(4)–N(2)–C(22)	119.0(3)
C(2)–N(1)–Pd	125.6(2)	C(4)–N(2)–Pd	125.6(2)
C(10)–N(1)–Pd	115.7(2)	C(22)–N(2)–Pd	115.3(2)

propylene…) and functional alkenes (methyl acrylate) is in currently under study.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Diethyl ether was distilled from sodium benzophenone; methylene chloride and hexane were distilled over P_2O_5. Aniline, 2-methylaniline, 2,6-diisopropylaniline and 2,6-dimethylaniline were distilled from potassium hydroxide prior to use. $Pd(dba)_2$ methallyloxyphosphonium salts and β-iminoamine ligands were prepared according to literature methods. All other reagents were obtained from standard commercial vendors and used as received. NMR spectra were recorded on a Bruker AC-300 spectrometer. H and C chemical shifts are given in ppm and referenced to the residual solvent resonance relative to TMS. Infrared spectra were recorded on a Bruker Victor 22 (Golden Gate Technique).

4.2. General procedure for the preparation of $[(\beta\text{-diimine})Pd(\eta^3\text{-}C_4H_7)]^+\ Y^-$ complexes

In an inert atmosphere, $Pd(dba)_2$ complex (1equiv.) was dissolved in anhydrous CH_2Cl_2. Methallyloxyphosphonium ($C_4H_7OP^+(NMe_2)_3Y^-$) and β-iminoamine ligands were added (1 equvi.). The black-red solution was stirred at room temperature for 24 h. The supernatant was separated by filtration through a Celite filter, and the solvent was removed under vacuum to afford the oil compound. This was washed with *n*-hexane (3×15 mL) and dried in vacuum. The solid was crystallized from methylene chloride/diethyl ether solution at −20 °C. Yields ranged from 83% and 94%.

4.2.1. Example: Synthesis of $[(PhNC(Me)CH_2C(Me)\text{-}NPh)Pd(\eta^3\text{-}C_4H_7)]^+PF_6^-$ (**8**)

Following the general procedure, from (PhNC(Me)CHC(Me)NHPh), (0.4 mmol, 0.1 g). $Pd(dba)_2$ (0.3 g, 0.4 mmol) and 2-methylallyloxyphosphonium (0.4 mmol, 0.15 g) was obtained 0.135 g of **7** as a pale yellow solid after crystallization from a mixture (diethyl ether/CH_2Cl_2: 1/1).

Yield 83%. $C_{21}H_{25}N_2PF_6Pd$. CH_2Cl_2 (641.76): Calc. C, 41.170; H, 4.242; N, 4.373. Found: C, 42.081; H, 4.762; N, 3.973%. IR (Golden Gate): $\nu_{C=N} = 1652$ cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): $\delta = 1.52$ (s, 3H, Me (allyl)); 2.41–2.45 (m, 6H, ligand-Me); 2.62 (s, 2H, H^6_{anti} and H^8_{anti}); 2.69 (s, 2H, H^6_{syn} and H^8_{syn}); 3.93 (m, 2H, ligand-CH_2); 6.84–7.44 (m, 10H, ArH). ^{13}C-NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): $\delta = 22.8$ (Me (allyl)); 24.98–25.93 (Me on

ligand); 43.55 and 49.61 (CH_2 on ligand); 62.51 and 64.78 (C(6) and C(8), CH_2 (allyl)); 120.57–143.18 (C_{aro} and C(7)-allyl); 151.08 (C–N on C_6H_5); 180.33 and 181.02 (C=N on ligand).

Yields, physical and spectral data of compounds **9**–**12** are reported below.

*4.2.2. [(o − CH_3-C_6H_4NC(Me)CH_2C(Me)NC_6H_4-o-CH_3)-Pd(η^3-C_4H_7)]$^+PF_6^-$ (**9**)*

Yield = 89%. $C_{23}H_{29}N_2PF_6Pd$. (584.88): Calc. C, 47.230; H, 5.101; N, 4.790. Found: C, 47.247; H, 5.303; N, 4.139%. IR (Golden Gate): $\nu_{C=N}$ = 1660 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 1.74 (s, 3H, Me (allyl)); 1.98–2.24 (m, 12H, Me on ligand and o-CH_3 on C_6H_4); 2.48 (s, 2H, H^6_{anti} and H^8_{anti}); 2.53 (s, 2H, H^6_{syn} and H^8_{syn}); 3.88–4.11 (m, 2H, ligand-CH_2); 6.84–7.18 (m, 8H, ArH). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 18.21–18.55 (Me (allyl)); 23.18 and 24.15 (Me on ligand); 24.36 and 24.46 (o-C on C_6H_4); 49.73 and 50.12 (CH_2 on ligand); 63.55 and 64.66 (C(6) and C(8), CH_2 (allyl)); 120.51 and 120.84 (p-C on C_6H_4); 127.35–129.71 (o′-C and o′-C on C_6H_4); 131.87–132.06 (m-C and m′-C on C_6H_4); 137.33 and 137.79 (C(7)-allyl); 151.02 and 151.67 (C–N on C_6H_4); 177.07 and 177.21 (C=N on ligand).

*4.2.3. [(2,6-CH_3)$_2$-C_6H_3NC(Me)CH_2C(Me)NC_6H_3-2,6-(CH_3)$_2$)Pd(η^3-C_4H_7)]$^+PF_6^-$ (**10**)*

Yield = 92%. $C_{25}H_{33}N_2PF_6Pd$. (612.93): Calc. C, 48.880; H, 5.430; N, 4.570. Found: C, 49.140; H, 5.100; N, 4.847%. IR (Golden Gate): $\nu_{C=N}$ = 1667 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 1.91 (s, 3H, H^9, Me (allyl); 2.02 (s, 6H, o-CH_3); 2.18 (s, 6H, o′-CH_3); 2.28 (s, 2H, H^6_{anti} and H^8_{anti}); 2.31 (s, 6H, Me on ligand); 2.57 (s, 2H, H^6_{syn} and H^8_{syn}); 4.3 (dd, 2H, J = 13.8 Hz, CH_2 on ligand); 7.07–7.118 (s, 6H, H_{aro}). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 17.86 (Me (allyl)); 18.06 (Me on ligand); 22.49 (o-Me on C_6H_3); 23.106 (o′-Me on C_6H_3); 48.11 (CH_2 on ligand); 63.86 (C(6) and C(8), CH_2 (allyl)); 126.32 (p-C on C_6H_3); 126.49 (o-C on C_6H_3); 126.91 (o′-C on C_6H_2); 128.78 (m-C on C_6H_3); 129.93 (m′-C on C_6H_3); 137.26 (C(7)-allyl); 150.16 (C–N on C_6H_3); 176.30 (C=N on ligand).

*4.2.4. [(2,6-(iPr)$_2$-C_6H_3NC(Me)CH_2C(Me)NC_6H_3-2,6-(iPr)$_2$)Pd(η^3-C_4H_7)]$^+PF_6^-$ (**11**)*

Yield = 94%; $C_{33}H_{49}N_2PF_6Pd$. (725.15): Calc. C, 54.660; H, 6.810; N, 3.861. Found: C, 54.699; H, 6.471; N, 4.021%. IR (Golden Gate): $\nu_{C=N}$ = 1663 and 1640 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 1.2 (d, 6H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$); 1.23 (d, 6H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$); 1.32 (d, 6H, J_{HH} = 6.6Hz, $CH(CH_3)_2$); 1.36 (d, 6H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$); 1.94 (s, 3H, Me-allyl); 2.11 (s, 6H, CH_3 on ligand); 2.52 (s, 2H, H^6_{anti} and H^8_{anti}); 2.58 (s, 2H, H^6_{syn} and H^8_{syn}); 2.85 (sept, 2H, C*H*-CH_3, J_{HH} = 6.9 Hz); 3.19 (sept, 2H, C*H*-CH_3, J_{HH} = 6.9 Hz); 4.17 (dd, 2H, J = 13.8 Hz, CH_2 on ligand); 7.28 (s, 6H, H_{aro}, Aromatic H of Ar group); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 22.28 (Me-allyl); 23.37 (Me on *i*Pr group); 23.58 (Me on *i*Pr group); 23.78 (Me on *i*Pr group); 24.18 (Me on *i*Pr group); 24.87 (Me on ligand); 28.34 (CH on *i*Pr group); 28.73 (CH on *i*Pr group); 48.20 (CH_2 on ligand); 64.87 (C(6) and C(8), CH_2 (allyl)); 124.409 (p-C on C_6H_3); 127.37 (o-C on C_6H_3); 137.04 (m-C on C_6H_3);137.38 (m′-C on C_6H_3); 138.35 (C_7(allyl)); 147.62 (C–N); 177.08 (C=N on ligand).

*4.2.5. [(2,6-(iPr)$_2$-C_6H_3NC(Me)CH_2C(Me)NC_6H_3-2,6-(iPr)$_2$)Pd(η^3-C_4H_7)]$^+$ [B(3,5-(CF_3)$_2$$C_6H_3$)$_4$]$^-$ (**12**)*

Yield = 91%. $C_{33}H_{49}N_2Pd \cdot BC_{32}H_{12}F_{24} \cdot CH_2Cl_2$ (1528.34): Calc. C, 51.87; H, 4.15; N, 1.83. Found: C, 51.37; H, 3.861; N, 1.88%. IR (Golden Gate): $\nu_{C=N}$ = 1663 cm^{-1}). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 1.05 (d, 6H, J_{HH} = 3.3 Hz, $CH(CH_3)_2$); 1.10 (d, 6H, J_{HH} = 3.6 Hz, $CH(CH_3)_2$); 1.20 (d, 6H, J_{HH} = 3.3 Hz, $CH(CH_3)_2$); 1.25 (d, 6H, J_{HH} = 3.6 Hz, $CH(CH_3)_2$); 1.84 (s, 3H, Me-allyl); 1.96 (s, 6H, CH_3 on ligand); 2.48 (s, 2H, H^6_{anti} and H^8_{anti}); 2.52 (s, 2H, H^6_{syn} and H^8_{syn}); 2.71 (sept, 2H, C*H*-CH_3, J_{HH} = 3.9 Hz); 3.06 (sept, 2H, C*H*-CH_3, J_{HH} = 3.9 Hz); 3.97 (s, 2H, CH_2 on ligand); 7.20–7.64 (s, 6H, H_{aro}, Aromatic H of Ar group). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C, δ [ppm]): δ = 23.02 (Me-allyl); 23.37 (Me on *i*Pr group); 23.58 (Me on *i*Pr group); 23.78 (Me on *i*Pr group); 24.18 (Me on *i*Pr group); 24.87 (Me on ligand); 28.34 (CH on *i*Pr group); 28.73 (CH on *i*Pr group); 49.19 (CH_2 on ligand); 66.10 (C(6) and C(8), CH_2 (allyl)); 125.39 and 125.49 (p-C on C_6H_3); 127.17 (o-C on C_6H_3); 137.37 (m-C on C_6H_3);137.70 (m′-C on C_6H_3); 139.71 (C_7(allyl)); 147.86 (C–N); 176.33 (C=N on ligand) · [B(3,5-(CF_3)$_2$-C_6H_3)$_4$]$^-$: 118.17–119.94 (C_p); 127.161 (q, $^1J_{CF}$ = 104.9 Hz, CF_3); 129.39 (q, $^1J_{CF}$ = 32.52 Hz, CF_3); 161.5 (q, $^1J_{CB}$ = 49.8 Hz, C_{ipso}). ^{19}F NMR (282 MHz, CD_2Cl_2): δ (referenced to external C_6F_6) 63.27 (s, CF_3).

4.3. X-ray crystallographic study

The X-ray crystallographic study of complex **12** was carried out on an Enraf–Nonius Kappa CCD diffractometer (Mo Kα). Data were collected at 110 K for a range of θ up to 27.5° and this, gave a total of 25,131 reflections, yielding 15,208 independent values (R_{int} = 0.0612). The structure was solved by direct method and difference Fourier techniques and were refined by full-matrix last-squares analysis. Refinements were based on F^2 and were carried out using all the data (SHELXL-97). All of the non-hydrogen atoms were refined anisotropically. One CF_3 group of the anion was

found to be disordered over two positions with occupancies of 0.91:0.09. The *F* atoms of the disordered minor component were included with a torsional refinement with $U_{iso_o} = 1.5U_{eq}$ of the carrier carbon atom (C–F = 1.33 Å). The hydrogen atoms were included in the model with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups and refined either freely or with a riding mode. Pertinent crystallographic data are summarized in Table 1.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no.234943. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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