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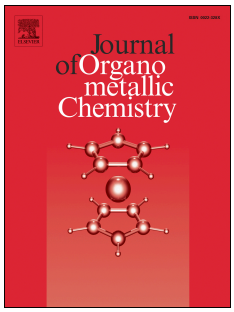

Novel cationic η^3-methallyl palladium complexes bearing pyridinyl-imine ligands: synthesis, characterization and X-ray study

Sana Dridi, Ali Mechria, Moncef Msaddek

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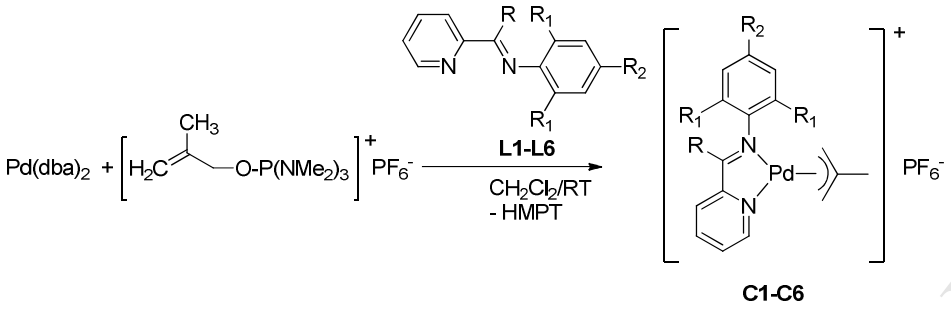
Oxidative addition of the methallyloxytris(dimethylamino) phosphonium hexafluorophosphate $[C_4H_7OP(NMe_2)_3]^+PF_6^-$ to the zerovalent $Pd(dba)_2$ in the presence of pyridinylimine ligands gives the corresponding monometallic cationic η^3-methallylpalladium complexes bearing pyridinylimine ligands in high yields.



C1-C6

Novel cationic η^3-methallyl palladium complexes bearing pyridinyl-imine ligands: synthesis, characterization and X-ray study

Sana Dridi[a] , Ali Mechria[a,] ∗ and Moncef Msaddek[a]

[a] *Laboratoire de chimie hétérocyclique, produits naturels et réactivité : L.C.H.P.N.R, Faculté des sciences de Monastir, Bd de l'environnement, 5000 Monastir, Tunisie*

Abstract

Ligands (pyridin-2-ylmethylene)anilines (**L1**-**L4**) and (1-(pyridin-2-yl)ethylidene)anilines (**L5-L6**) were obtained by condensation reactions. These ligands react with $Pd(dba)_2$ in the presence of methallyloxytris(dimethylamino)phosphonium hexafluorophosphate $[C_4H_7OP(NMe_2)_3]^+PF_6^-$ to give the corresponding monometallic cationic η^3-methallylpalladium complexes **C1**-**C6** in high yields. All new complexes **C1**-**C6** have been characterized by CHN analyses, ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy. Solid state and electronic structures of complex **C5** have been determined.

Key words: pyridinyl-imine; methallylpalladium; cationic; oxidative addition; X-ray structure.

1. Introduction

Late transition metal-catalyzed olefin polymerization has received greater prominence over the recent years as a result of Brookhart's report on Pd(II) and Ni(II) diimine catalyst systems, which were capable of polymerizing ethylene and other α-olefins to form high molecular weight polymers [1–3]. The key feature of their catalysts is the symmetrical presence of bulky ortho aryl substituents at the imino nitrogen atoms, which effectively block the axial coordination sites thus retarding the rate of chain termination. Reduced steric bulk results in a decrease in polymer molecular weight. For this class of catalysts, Pd(II)-based systems produce highly branched polymers from ethylene. Subsequent to Brookhart's initial work on Ni and Pd, he as well as Gibson discovered that iron and cobalt-based complexes bearing tridentate bis(imino)pyridine ligands with bulky aryl groups were also capable of converting olefins to high molecular weight polymers as well as co-polymers [4–8]. Other groups have also reported on Ni(II) and Pd(II) catalysts bearing asymmetrical bidentate aryl-substituted pyridylimines [9–11], it was found that only oligomerization of ethylene was possible with

∗ Corresponding author. Tel.: +216-73-500-276; fax: +216-73-500-278; e-mail: ali.mechria@fsm.rnu.tn

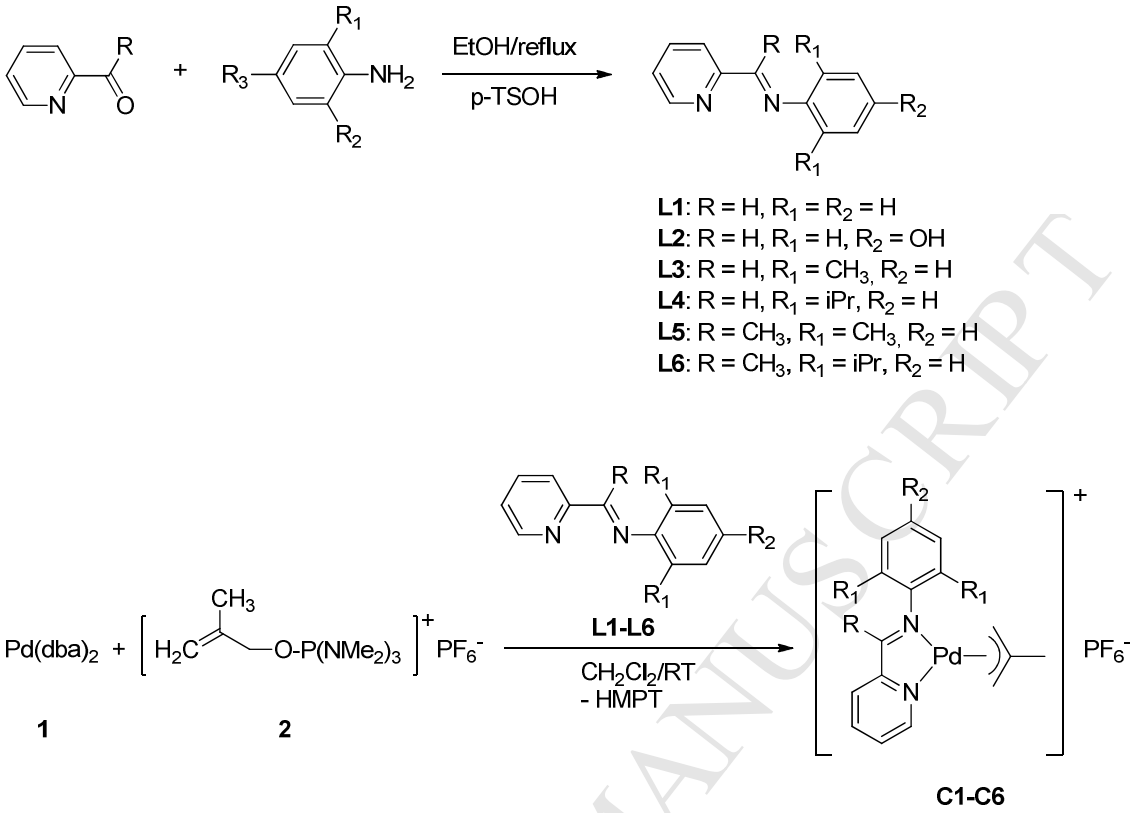
Ni(II) catalysts while Pd(II) analogues were found to be inactive. Structurally, in group 10 (Ni, Pd, Pt) pyridyl-imine complexes, Ni complexes exist as dimers or two ligand units coordinated to Ni, achieving a 5-coordinated trigonal–bipyramidal structure [12–15]. In contrast, Pd and Pt complexes with pyridinyl-imines appear as monomeric square-planar structures [14–26]. In our knowledge, the reaction of N,N-chelate ligands with allylpalladium(II) chloride dimer represents the standard synthetic approach to cationic allyl palladium complexes bearing N,N-chelate ligands [27-29].

As part of our ongoing research in the field of late transition metal complexes containing α- and β-diimines ligands [30-37], we describe herein the synthesis of a series of new cationic η^3-methallyl palladium(II) complexes bearing pyridinyl-imine ligands containing a bulky arylimino substituent on one side of the ligand and a relatively unhindered heterocyclic donor on the other. The molecular structure of a Pd(II) complex was determined by X-ray crystallography. A DFT optimized structure has been also discussed.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 shows the synthetic route of the ligands and cationic Pd(II) complexes. The addition of a primary amine to commercially available 2-pyridinecarboxaldehyde or 2-acetylpyridine to afford the corresponding pyridinyl-imine ligand is a well-known route to a versatile class of nitrogen bidentate ligands [17–26]. The reaction is an acid catalyzed condensation which is conducted in alcohols or ethers. Variation of the amine therefore allows for the facile design of ligands and subsequent metal complexes with different physical and chemical properties. The new cationic methallyl palladium complexes **C1–C6** were prepared via an oxidative addition of methallyloxyphosphonium salt to the zerovalent compound $Pd(dba)_2$ in the presence of pyridinyl-imine ligands (Scheme 1). The reaction is carried out in CH_2Cl_2 at room temperature and afford, in quantitative yields, the cationic methallyl Pd(II) complexes.



Scheme 1. Synthesis of iminopyridine ligands and Pd(II) complexes

These new cationic methallyl complexes of palladium(II) (**C1-C6**) were isolated as a yellow to orange solids soluble in dichloromethane but sparingly soluble in diethyl ether and in n-hexane. ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy and elemental analyses were consistent with the palladium(II) complex formulation. The NMR spectra of complexes **C1-C6** show similar trends especially in the aromatic region. There is a distinct shift of the signals of the aromatic groups of the imine system including the pyridine ring on complexing of the ligand to the metal centre. A rearrangement of the aromatic signals as compared to the ligand spectra. In all cases, there is a shift of the doublet found around 8.50 ppm assigned to H-6 (see Fig. 1) and the singlet found around 8.25 ppm assigned to H-7 in the ligand spectra. These two signals shift to around 8.97 and 8.62 ppm, respectively, in the spectrum of the metal complex. Thus, these two signals also exhibit a greater separation between each other when complexation takes place.

Furthermore, the two triplets, which occur at 7.18 ppm (H-4) and 7.56 ppm (H-5) in the ligand spectrum and move significantly downfield to 7.87 and 8.35 ppm during complexation. The ^{1}H NMR peaks of the Pd(II) complexes were shifted to low field by approximately d 0.1–0.5 ppm as compared with the ligands, while the ^{13}C NMR peaks of the Pd(II) complexes

were shifted to low field by approximately 5 ppm as compared with the ligands. The presence of the non-coordinated PF_6^- counter-ions in complexes **C1-C6** was confirmed by the ^{31}P NMR spectra. In addition, IR spectra of the complexes showed typical lower absorption bands between 1620 and 1630 cm^{-1} compared to the respective ligands [38]. All IR spectra present the characteristic band of the PF_6^- counter-ion at around 832 cm^{-1}.

2.2. Molecular structure of complex **C5**

Single crystals of complex **C5** suitable for X-ray analyses were grown by slow diffusion of diethyl ether into a dichloromethane solution at room temperature. Crystallographic data and structural refinement parameters are given in Table 1 while selected bond lengths and angles are contained in Table 2. Molecular structure of complex **C5** is shown in Fig. 1. The single-crystal X-ray diffraction study of complex **C5** reveals a structure consisting of loosely associated $[(\eta^3\text{-}C_4H_7)Pd(L5)]^+$ cations and octahedral PF_6^- counteranions without direct interactions as appears from the large distance between the metal and the nearest fluorine atom (Pd-F5 = 4.171 Å). The geometry around the palladium atom in the complex **C5** could be described as distorted square planar consisting of two carbone atoms (C1 and C3) of the allyl group and two nitrogen atoms (N1 and N2) of the ligand. For instance, the relatively small N(1)-Pd(1)-N(2) bond angle in **C5** of 78.0(2)° is a result of chelating ligand steric constraints. The bond angles around the Pd atom which sum to 359.9(11)° are consistent with a planar geometry. The metal-chelate ring (Pd-N1-C10-C9-N2) in complex **C5** is almost flat as indicated by the torsion angles of -3.4(9)°, 6.1(8)° and -0.9(7)° for N2-C9-C10-N1, Pd-N1-C10-C9 and Pd-N2-C9-C10, respectively. The methyl on the allyl group is slightly tilted out of the allyl plane by approximately 15° as indicated by the torsion angle of 165.1(8)° for C4-C2-C3-C1. The allyl plane makes an angle of 112.2(4)° with the palldium coordinative plane which is normal for η^3-2-methylallyl complexes of palladium [31-32]. The average Pd–N1 bond length of 2.082(5) Å in **C5** compares well with bond lengths of 2.045(2) Å reported for the unconjugated diimine palladium complexes [39]. The Pd(1)–N(2) bond length of 2.089(6) Å in **C5** is significantly similar to the Pd–N bond length of square planar imine Pd(II) complexes [40]. The Pd–C bond lengths in **C5** was reported as 2.0366(18) Å, and compares well with the bond lengths of 2.005(12) Å observed in other related palladium complexes [31-32].

Table 1

Crystal data and structure refinement for complex **C5**

Chemical formula	$C_{19}H_{23}N_2PdPF_6$
Crystal size (mm^3)	0.2 x 0.1 x 0.1
Formula weight	530.76
Crystal system	Triclinic
Space group	P-1
a (Å)	7.511(5)
b (Å)	10.346(5)
c (Å)	14.773(5)
α (°)	89.797(5)
B (°)	94.519(5)
γ (°)	109.635(5)
V ($Å^3$)	1077.5(10)
Z	2
T (K)	293(2)
ρ_{calc} ($g.cm^{-3}$)	1.636
Total reflections	3746
Unique reflections	2314
R(int)	0.0743
$2\theta_{max}$ (°)	59.92
λ (Å)	0.71073
μ (mm^{-1})	0.99
F(000)	532
Goodness-of-fit	1.001
R_1 ($I > 2\sigma(I)$)	0.0523
wR_2	0.1321

Experimental and theoretical bond distances of $[(\eta^3\text{-}C_4H_7)Pd(L5)]^+PF_6^-$

Bond lengths	Experimental	Theoretical
Pd-N1	2.082(5)	2.111
Pd-N2	2.089(6)	2.143
Pd-C1	2.110(7)	2.120
Pd-C2	2.136(7)	2.155

Pd-C3	2.111(8)	2.106
N1-C10	1.283(8)	1.279
N1-C12	1.450(8)	1.431
N2-C5	1.354(8)	1.331
N2-C9	1.349(8)	1.350

Table 2: Experimental and theoretical bond angles of $[(\eta^3\text{-}C_4H_7)Pd(L5)]^+PF_6^-$

Bond lengths	Experimental	Theoretical
N1-Pd-N2	78.0(2)	76.88
N1-Pd-C1	174.4(3)	172.56
N2-Pd-C1	107.2(3)	109.97
N1-Pd-C3	106.0(3)	104.51
N2-Pd-C3	175.0(3)	175.01
C1-Pd-C3	68.7(3)	68.39
N1-Pd-C2	137.8(3)	136.31
N2-Pd-C2	139.0(3)	142.22
C1-Pd-C2	38.4(3)	38.59
C3-Pd-C2	38.7(3)	38.69

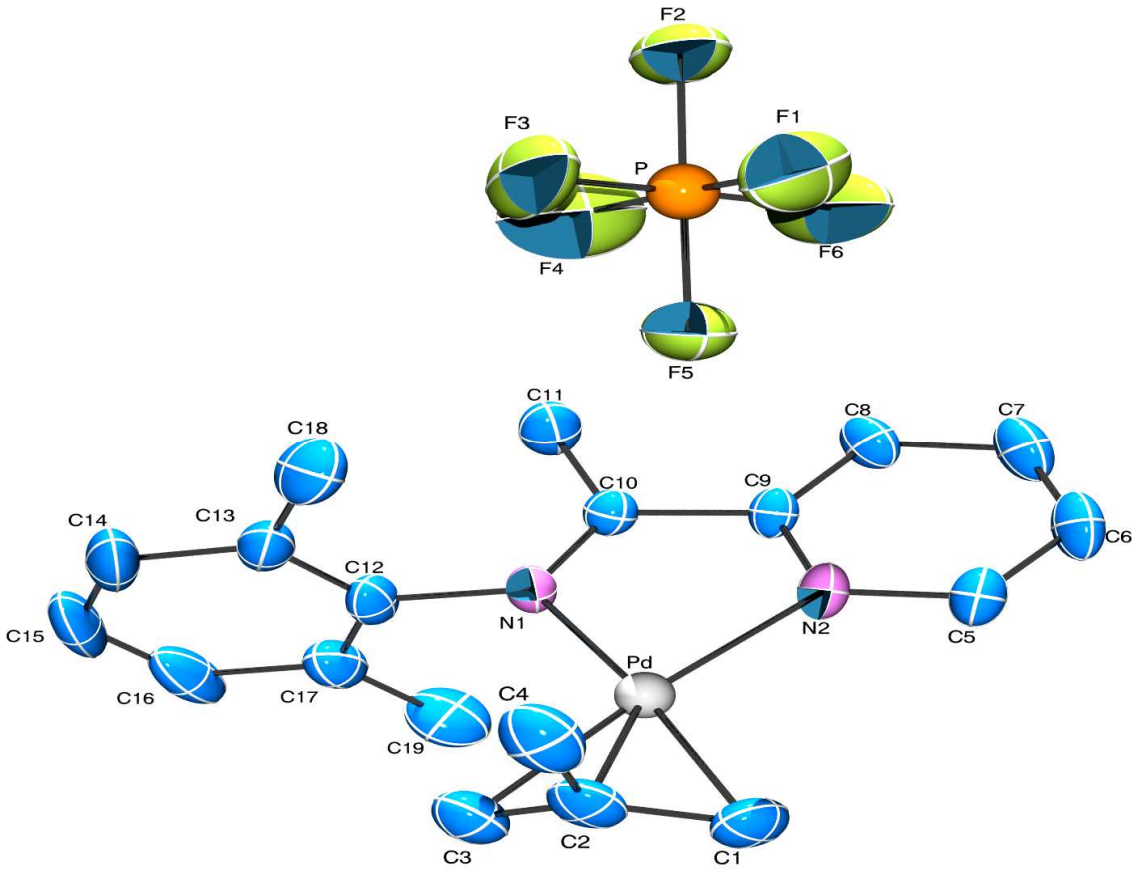


Fig. 1. ORTEP representation of the molecular structure of **C5** with atom labeling scheme and anisotropic displacement ellipsoid depicted at 30% probability. Hydrogen atoms are omitted for clarity.

2.3. Density functional theory (DFT) calculations

To obtain an insight in the electronic structures and bonding properties of the complex, calculations using the density functional theory (DFT) method with the wB97XD functional of GAUSSIAN-09 were carried out. Before the calculations, their geometry was optimized in singlet states using the DFT method with the wB97XD functional.

The cation $[(\eta^3\text{-}C_4H_7)Pd(L5)]^+$ attained a distorted square planar arrangement around the Pd atom as shown in Fig. 2. Experimental and theoretical geometric parameters are summarized in Tables 2 and 3. In general, the predicted bond lengths and angles are in very good agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations as one can see from the data given in Tables 2 and 3. It can be seen from the data collected in Tables 2

and 3 the bond lengths are maximally elongated by 0.05 Å in the calculated gas phase structure, while the bond angles changed maximally by 3°. The formal charge of palladium is +2 in the complex **C5**. The calculated charge on the palladium atom, obtained from natural population analysis, is 0.40. This is may be a result of charge donation from the ligand to the metal center and also shows the strong σ-donor character of the ligand.

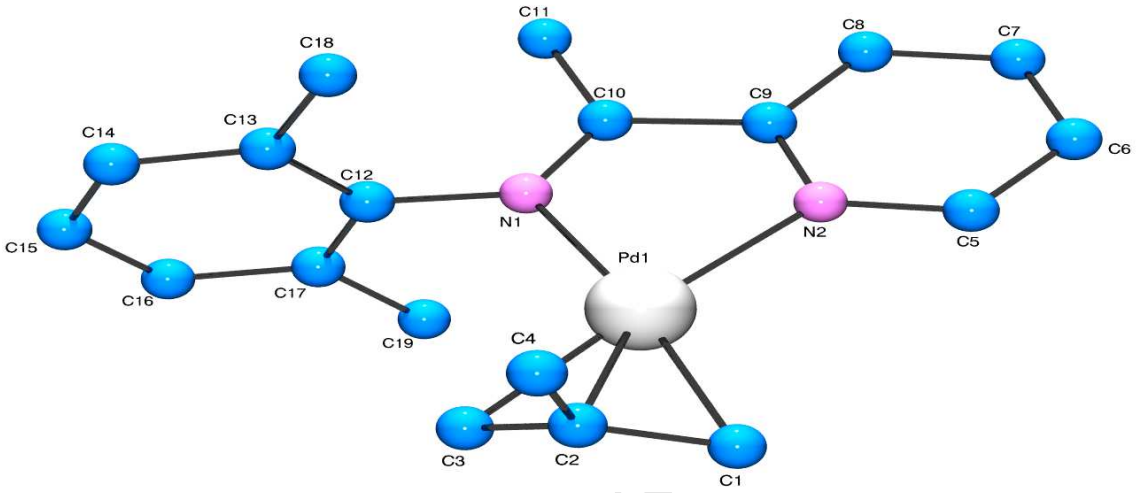


Fig. 2. DFT optimized structure of $[(\eta^3\text{-}C_4H_7)Pd(L5)]^+$ cation using the same atom labeling scheme as ORTEP representation. Hydrogen atoms are omitted for clarity.

3. Conclusion

The oxidative addition of methallyloxytris(dimethylamino)phosphonium hexafluorophosphate to the zerovalent $Pd(dba)_2$ in the presence of pyridinyl-imine compounds produces new monometallic cationic methallylpalladium(II) complexes in which the ligands coordinate via the pyridine and imine nitrogen atoms. Solid state structure and theoretical optimized structure (DFT) both indicate a distorted square planar arrangement around the palladium center.

4. Experimental

4.1. Materials and methods

All reactions were carried out under dry argon atmosphere using standard Schlenk techniques. Dichloromethane and hexane were refluxed and distilled from phosphorus pentoxyde (P_2O_5) while diethyl ether was dried over sodium wire and benzophenone. Aniline, 2,6-dimethylaniline and 2,6-diisopropylaniline were distilled from potassium hydroxide prior

to use. Pyridinylimine ligands [18,19], methallyloxyphosphonium hexafluorophosphate [41], $Pd(dba)_2$ [42] were prepared according to literature methods. NMR spectra were recorded on a Bruker AMX 300 spectrometer. H and C chemical shifts were given in ppm and referenced to the residual solvent resonance relative to TMS Starting materials. ^{31}P chemical shifts are given in ppm relative to an 85% H_3PO_4 external reference. IR spectra were recorded on a Perkin–Elmer Spectrum two FT-IR instrument with the Universal ATR Sampling Accessory. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer.

4.2. Synthesis of methallyloxytris(dimethylamino)phosphonium hexafluorophosphate **2**

Tris(dimethylamino)phosphine (2.29 g, 14 mmol) was added drop-wise to a stirred solution of 2-methylprop-2-en-1-ol (1 g, 14 mmol) and CCl_4 (2.46 g, 16 mmol) in dry CH_2Cl_2 (30 mL) cooled at -30°C. Then, 15 mL of distilled water was added and the reaction mixture was allowed to proceed at room temperature for 2 h. Organic phase was decanted and extracted with water (2 x 40 mL). Aqueous phases were collected, washed with Et_2O and decanted to give an aqueous solution of methallyloxyphosphonium chloride. After the addition of KPF_6 (3.68 g, 20 mmol) in 10 mL of water, an immediate precipitate was formed. The mixture was filtered and the crude product was washed with Et_2O and dried under vacuum. Recrystallization from a mixture of chloroform: Et_2O solution afforded salt **2** as a white solid. Yield: 4.15 g (78%). IR [ν cm^{-1}]: 836 (PF_6^-). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.78 (s, 3H, C*H*$_3$-allyl); 2.76 (d, 18H, (C*H*$_3$)$_2$N); 4.54 (d, 2H, C*H*$_2$-O); 5.01 (s, 1H, C*H*$_2$); 5.08 (s, 1H, C*H*$_2$). ^{13}C-NMR (75.47 MHz, $CDCl_3$): 18.7 (CH_3-allyl); 36.7 (C*H*$_3$-N); 71.9 (CH_2-O); 114.3 (CH_2); 137.7 (C).

4.3. Synthesis of Pd(II) complexes

4.3.1. Synthesis of complex **C1**

$Pd(dba)_2$ (150 mg, 0.26 mmol), the ligand **L1** (51 mg, 0.30 mmol) and CH_2Cl_2 (20 ml) were combined in a Schlenk tube and stirred at room temperature. After 15 min, methallyloxytris(dimethylamino)phosphonium hexafluorophosphate (98.6 mg, 0.26 mmol) was added and stirring continue overnight. The resulting solution was filtered through celite, the solvent was removed under vacuum and the solid residue was washed with Et_2O (3 x 20 ml) to give complex **C1** as an orange solid. Recrystallization from a mixture of CH_2Cl_2: Et_2O solution afforded single crystals suitable for X-ray analysis. Yield: 0.11 g (86%). Anal. Calc. for $C_{16}H_{17}F_6N_2PPd$ (488.70): C, 39.32; H, 3.51; N, 5.73. Found: C, 39.32; H, 3.51; N, 5.73.

IR [ν cm^{-1}]: 827 (PF_6^-); 1485; 1582 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.13 (s, 3H, C*H*$_3$-allyl); 3.23 (s, 1H, H_{anti}); 3.37 (s, 1H, H_{anti}); 3.68 (s, 1H, H_{syn}); 4.05 (s, 1H, H_{syn}), 7.34-7.48 (m, 5H, H_{ar}); 7.69-7.74 (td, 1H, H_{4py}); 8.06-8.09 (dd, 1H, H_{3py}); 8.14-8.20 (td, 1H, H_{5py}); 8.61 (s, 1H, *H*-C=N); 8.72-8.74 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 23.69 (C4); 62.42, 64,02 ($C_{1,3}$); 122.35, 129.80, 130.13, 130.19; 130.38; 136.82 (C_2); 141.61, 149.68, 153.82, 154.48; 166.58 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.39 (sept, PF_6^-).

4.3.2. Complex **C2**

Complex **C2** was prepared in a similar manner to complex **C1**. $Pd(dba)_2$ (150 mg, 0.26 mmol), the ligand **L2** (60 mg, 0.30 mmol) and salt **2** (98 mg, 0.26 mmol). Yield: 0.12 g (91%). Anal. Calc. for $C_{16}H_{17}F_6N_2OPPd$ (504.70): C, 38.08; H, 3.40; N, 5.55. Found: C, 38.08; H, 3.40; N, 5.55. IR [ν cm^{-1}] : 826 (PF_6^-); 1509, 1631 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ (ppm) 2.72 (s, 3H, C*H*$_3$-allyl); 3.40-3.43 (d, 2H, H_{anti}); 3.99 (s, 2H, H_{syn}); 7.43-7.47 (d, 2H, H_{ar});8.01-8.03 (d, 2H, H_{ar}); 8.36-8.41 (td, 1H, H_{4py}); 8.76-8.79 (dd, 1H, H_{5py}); 8.85-8.91 (td, 1H, H_{3py}); 9.45 (s, 1H, *H*-C=N); 9.50 (s, 1H, OH) ; 9.51-9.53 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 23.45 (CH_3-allyl); 63.52-66.08 ($C_{1,3}$); 116.90, 125.18, 129.86, 130.34, 137.01 (C_2);142.20, 142.80, 155.22, 155.32, 159.85; 165.74 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.23 (sept, PF_6^-).

4.3.3. Complex **C3**

Complex **C3** was prepared in a similar manner to complex **C1**. $Pd(dba)_2$ (150 mg, 0.26 mmol), the ligand **L3** (63 mg, 0.30 mmol) and salt **2** (98 mg, 0.26 mmol). Yield: 125 mg (93%). Anal. Calc. for $C_{18}H_{21}F_6N_2PPd$ (516,76): C, 41.84; H, 4.10; N, 5.42. Found: C, 42.80; H, 4.35; N, 5.80. IR [ν cm^{-1}]: 829 (PF_6^-); 1598, 1632 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.08 (s, 3H, o-CH_3); 2.13 (s, 3H, o-CH_3); 2.24 (s, 3H, C*H*$_3$-allyl); 2.94 (s, 1H, H_{anti}); 3.14 (s, 1H, H_{anti}); 3.30 (s, 1H, H_{syn}); 4.05 (s, 1H, H_{syn}); 7.04-7.17 (m, 3H, H_{ar}); 7.76-7.80 (td, 1H, H_{4py}); 8.04-8.07 (dd, 1H, H_{3py}); 8.18-8.23 (td, 1H, H_{5py}); 8.40 (s, 1H, *H*-C=N); 8.78-8.80 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 18.40, 18.74 (o-*C*H_3); 23.74 (C_4); 62.38-62.53 ($C_{1,3}$); 127.82, 128.04, 129.07, 129.18, 129.82, 130.95; 137.19 (C_2); 141.77, 148.88, 153.04, 154.84; 170.41 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.46 (sept, PF_6^-).

4.3.4. Complex **C4**

Complex **C4** was prepared in a similar manner to complex **C1**. $Pd(dba)_2$ (150 mg, 0.26 mmol), the ligand **L4** (80 mg, 0.30 mmol) and salt **2** (98 mg, 0.26 mmol). Yield: 141 mg

(94%). Anal. Calc. for $C_{22}H_{29}F_6N_2PPd$ (572,86): C, 46.13; H, 5.10; N, 4.89. Found: C, 46.14; H, 4.65; N, 5.24. IR [ν cm^{-1}]: 829 (PF_6^-); 1597; 1623 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): 1.06-1.09 (d, 6H, C*H*$_3$-iPr); 1.13-1.21 (d, 6H, C*H*$_3$-iPr); 2.06 (s, 3H, C*H*$_3$-allyl); 2.92-2.98(sept, 2H, C*H*-iPr); 3.09-3.16 (quintuplet, 1H, H_{anti}); 3.20-3.22 (d, 1H, H_{anti}); 3.32 (s, 1H, H_{syn}); 4.05-4.12 (d, 1H, H_{syn}), 7.17-7.29 (m, 3H, H_{ar}); 7.79-7.83 (td, 1H, H_{4py}); 8.06-8.08 (d, 1H, H_{3py}); 8.19-8.25 (td, 1H, H_{5py}); 8.35 (s, 1H, *H*-C=N); 8.82-8.84 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 22.77, 24.24 (CH_3-iPr); 24.44 (C_4); 28.68, 28.86 (CH-iPr); 62.26, 63,14 ($C_{1,3}$); 124.36, 128.59, 129.87, 131.15; 137.55 (C_2); 138.69, 138,97, 141.85, 146.36, 152.74, 155.14; 169.71 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.41 (sept, PF_6^-).

4.3.5. Complex **C5**

Complex **C5** was prepared in a similar manner to complex **C1**. $Pd(dba)_2$ (115 mg, 0.20 mmol), the ligand **L5** (52 mg, 0.23 mmol) and salt **2** (76 mg, 0.20 mmol). Yield: 98 mg (92%). Anal. Calc. for $C_{19}H_{23}F_6N_2PPd$ (530.78): C, 42.99; H, 4.37; N, 5.28. Found: C, 43.79; H, 4.71; N, 5.86. IR [ν cm^{-1}]: 831 (PF_6^-); 1595; 1618 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.03-2.04 (s, 6H, o-C*H*$_3$); 2.14 (s, 3H, C*H*$_3$-C=N); 2.21 (s, 3H, C*H*$_3$-allyl); 2.82 (s, 2H, H_{anti}); 3.23 (s, 1H, H_{syn}); 3.95-3.96 (d, 1H, H_{syn}), 7.09-7.19 (m, 3H, H_{ar}); 7.77-7.79 (td, 1H, H_{4py}); 8.07-8.15 (dd, 1H, H_{3py}); 8.23-8.29 (td, 1H, H_{5py}); 8.79-8.81 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 16.93 (C*H*$_3$-C=N); 18.08-18.16 (o-CH_3); 23.84 (C_4); 61.91-62.30 ($C_{1,3}$); 127.19, 127.36, 127.43, 127.78, 129.16, 129.27, 130.56; 137.04 (C_2); 141.68, 146.98, 154.04, 154.78; 176.62 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.47 (sept, PF_6^-).

4.3.6. Complex **C6**

Complex **C6** was prepared in a similar manner to complex **C1**. $Pd(dba)_2$ (115 mg, 0.20 mmol), the ligand **L6** (65 mg, 0.23 mmol) and salt **2** (76 mg, 0.20 mmol). Yield: 106 mg (90%). Anal. Calc. for $C_{23}H_{31}F_6N_2PPd$ (586.89): C, 47.07; H, 5.32; N, 4.77. Found: C, 46.86; H, 5.17; N, 5.54. IR [ν cm^{-1}]: 832 (PF_6^-); 1597; 1618 (C=N). ^{1}H-NMR (300 MHz, CD_2Cl_2): 1.02-1.04 (d, 6H, C*H*$_3$-iPr); 1.07-1.20 (d, 6H, C*H*$_3$-iPr); 2.04 (s, 3H, C*H*$_3$-allyl); 2.25 (s,3H, C*H*$_3$-C=N); 2.77-2.85 (sept, 2H, C*H*-iPr); 2.95-2.98 (d, 2H, H_{anti}); 3.28 (s, 1H, H_{syn}); 3.96-3.97 (d, 1H, H_{syn}), 7.21-7.26 (m, 3H, H_{ar}); 7.77-7.83 (td, 1H, H_{4py}); 8.08-8.11 (dd, 1H, H_{3py}); 8.22-8.28 (td, 1H, H_{5py}); 8.81-8.83 (dd, 1H, H_{6py}). ^{13}C-NMR (75.47 MHz, CD_2Cl_2): 18.20 (CH_3-C=N); 23.44, 23.51, 23.81, 23.94 (CH_3-iPr); 23.65 (C_4); 28.84, 29.02 (CH-iPr); 62.03, 62,81 ($C_{1,3}$); 124.55, 124.71, 127.91, 128.34, 130.64; 137.59, 137.98, 138.25, 141.75; 144.41 5(C_2), 153.94, 154.84; 176.77 (C=N). ^{31}P-NMR (121.48 MHz, CD_2Cl_2): -144.48 (sept, PF_6^-).

4.4. Crystal structure determination and refinement

X-ray quality crystals of **C5** were grown from a mixture of CH_2Cl_2/n-hexane solution upon standing at ambient temperature. An orange prism, was chosen by size, habit, and polarized light microscopy and mounted on a glass fiber. Intensity data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromated Mo K_α radiation. Reflection data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by direct methods and subsequent difference Fourier techniques (SIR-92) [43] and refined with SHELXL-2013 [44]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions on parent atoms in the final refinement. Details of the crystal parameters, data collection, and structure refinement are given in Table 1.

4.5. Density functional theory (DFT) calculations

Geometry optimization reported in this article was done with the Gaussian09 [45] program package supported by GaussView 5.0.8. The DFT [46-47] calculations have been performed with the Long-range corrected hybrid density meta-GGA functional wB97XD [48-50] with dispersion corrections. The initial geometry has been taken from crystal structure. The geometry of **C5** in the gas phase has been optimized using tight convergent SCF procedure ignoring symmetry using S=0 spin state. In the calculation, the recently reported basis LANL2TZ(f) was used for Pd atom [51]. It contains the LANL2 relativistic ECP of Hay and Wadt [52] and a flexible triple-zeta basis set augmented with one set of 4*f* polarization functions. For C, H and N, a valence triple zeta basis set with polarization functions on all atoms 6-311G(d,p) [53] was employed for the calculation. The frequency calculation was carried out, verifying if the optimized molecular structure corresponds to energy minimum, thus only positive frequencies were expected.

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- This work represents a new way to access methallyl palladium complexes.
- These new complexes were prepared via an oxidative addition reaction.
- Distorted square planar arrangement around the palladium center.
- Novel cationic palladium precursors can be useful as catalysts.