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CRYSTAL STRUCTURE OF CATIONIC η^3-METHALLYLPALLADIUM COMPLEXES BEARING ALIPHATIC IMINOPYRIDINE LIGANDS

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Three aliphatic ligands are synthesized and fully characterized by IR, ^{1}H and ^{13}C NMR spectroscopy. These ligands react with a zerovalent compound $Pd(dba)_2$ in the presence of methallyloxytris(dimethylamino) phosphonium hexafluorophosphate salt $[C_4H_7OP(NMe_2)_3]^+PF_6^-$ as an allylating agent for the synthesis of cationic η^3-methallylpalladium complexes to give three cationic mononuclear η^3-methallylpalladium complexes in high yields. These formed complexes are characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. One of them is characterized by X-ray diffraction. A DFT-optimized structure is also discussed.

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Keywords: methallylpalladium, cationic, aliphatic iminopyridine, crystal structure.

INTRODUCTION

Schiff bases with an imine moiety such as α- and β-diimines [1-8], 2,6-bis(imino)pyridines [9-16], pyridylimines, and N-substituted 2-iminoalkylpyridines have significant importance in chemistry, especially in the development of Schiff base complexes [17-43]. Many Schiff base complexes show an excellent catalytic activity in various reactions such as olefin polymerisation [2-4, 6-15, 31, 40], hydrogenation and hydrosilylation [44], olefin epoxidation [45], organic transformations [5, 16, 24, 25, 36, 37, 43], and aerobic oxidation reactions [46-48]. In addition, several complexes were described with various metal centers and different ligand structures, and many studies have reported the effects of ligand substitution patterns on the catalytic activity [49-53]. These structural variations include the increased presence of N-aryl substituted 2-iminomethylpyridine in these transition metal complexes. However, upon varying the steric and electronic properties of the ligands, no substantial change has been observed in the properties of the complexes [54, 55]. On the other hand, N-alkyl substituents in the iminopyridine ligands may adjust the steric and electronic interactions and tune the physical and chemical properties of iminopyridine complexes [56-60].

Despite our previous reports on cationic methallyl palladium(II) complexes with N-aryl substituted pyridylimine derivatives, little is known regarding cationic palladium complexes with bidentate N-substituted 2-iminoalkylpyridines ligands. As part of our ongoing research, we report the synthesis of new cationic methallyl palladium(II) complexes containing aliphatic iminopyridine ligands. The molecular structure of one of them was determined by X-ray crystallography.

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EXPERIMENTAL

Materials and instruments. All reactions were carried out under the dry argon atmosphere using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent and distilled prior to use. Heptylamine, isopentylamine, cyclohexylamine, and pyridine-2-carboxaldehyde were purchased from Sigma-Aldrich. Pyridylimine aliphatic ligands [61], $Pd(dba)_2$[62], and methallyloxytris(dimethylamino)phosphonium hexafluorophosphate [63] were prepared according to the literatures methods.

^1H NMR (600 MHz) and ^{13}C NMR (150.91 MHz) spectra were recorded on a Bruker AMX 600 spectrometers using CD_3CN as a solvent. H and C chemical shifts were given in ppm and referenced to the residual solvent resonance relative to TMS. Infrared (IR) spectra were measured on a Perkin-Elmer Spectrum two FT-IR instruments with the Universal ATR Sampling Accessory, while the elemental analyses (C, H, N) of the prepared complexes were performed on a Perkin-Elmer 2400 seriesII CHNS/O analyzer.

Synthesis of complex C1. $Pd(dba)_2$ (100 mg, 0.173 mmol), the ligand L1 (30 mg, 0.17 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 (64 mg, 0.17 mmol) was added and the stirring process was continued overnight. The resulting solution was then filtered through celite. The solvent was removed under vacuum and the solid residue was washed with Et_2O (3×20 mL) to give yellow solid complex C1. Recrystallization from a CH_2Cl_2:Et_2O mixture afforded single crystals suitable for the X-ray analysis. Yield: 71 mg (85%). Anal. calc. for $C_{15}H_{23}F_6N_2PPd$ (482.74): C 37.32, H 4.80, N 5.80. Found: C 37.31, H 4.76, N 5.80. IR (ν, cm^{-1}): 824 (PF_6^-); 1599, 1634 (C=N). ^1H NMR (600.13 MHz, CD_3CN): 0.82 (d, 6H, $2CH_3$); 1.50-1.53 (td, 2H, CH_2); 1.78 (m, 1H, CH); 2.00 (s, 3H, CH_3-allyl); 3.11 (s, 2H, H_{anti}); 3.76-3.78 (td, 2H, CH_2); 3.91 (s, 2H, H_{syn}); 7.57-7.59 (dd, 1H, H_{2py}); 7.79-7.80 (d, 1H, H_{4py}); 8.04-8.07 (td, 1H, H_{3py}); 8.42 (s, 1H, HC=N); 8.62-8.63 (d, 1H, H_{1py}). ^{13}C NMR (150.91 MHz, CD_3CN): 22.77, 23.69 (C_{15}); 26.59, 39.89, 61.83 ($C_{12,14}$); 62.73, 128.92, 130.31, 136.55 (C_{13}), 142.21, 154.79, 155.32; 168.91 (C=N).

Synthesis of complex C2. Complex C2 was prepared in a similar manner as used for the synthesis of complex C1 with $Pd(dba)_2$ (100 mg, 0.173 mmol), the ligand L2 (35 mg, 0.17 mmol), and salt 2 (64 mg, 0.17 mmol). Yield: 65 mg (74%). Anal. calc. for $C_{17}H_{27}F_6N_2PPd$ (510.79): C 39.97, H 5.32, N 5.48. Found: C 39.08, H 5.87, N 5.55. IR (ν, cm^{-1}): 828 (PF_6^-); 1599, 1639 (C=N). ^1H NMR (600.13 MHz, CD_3CN): 0.87-0.92 (t, 3H, CH_3); 1.31-1.37 (ddd, 8H, $4(CH_2)$); 1.76-1.81 (t, 2H, CH_2); 2.16 (s, 3H, CH_3-allyl); 3.27 (s, 2H, H_{anti}); 3.89-3.94 (td, 2H, CH_2); 4.08 (s, 2H, H_{syn}); 7.72-7.76 (ddd, 1H, H_{2py}); 7.94-7.97 (d, 1H, H_{4py}); 8.19-8.22 (td, 1H, H_{3py}); 8.56 (s, 1H, HC=N); 8.78-8.79 (d, 1H, H_{1py}). ^{13}C NMR (150.91 MHz, CD_3CN): 13.04 (CH_3), 22.01 (C_{15}); 22.35, 25.92, 28.33, 29.60, 31.14, 60.52, 63.11 ($C_{12,14}$); 127.62, 129.01, 135.27, 140.90, 153.49 (C_{13}), 154.01; 167.57 (C=N).

Synthesis of complex C3. Complex C3 was prepared in a similar manner as used for the synthesis of complex C1 with $Pd(dba)_2$ (100 mg, 0.173 mmol), the ligand L3 (32 mg, 0.17 mmol) and salt 2 (64 mg, 0.17 mmol). Yield: 59 mg (69%). Anal. calc. for $C_{16}H_{23}F_6N_2PPd$ (494.75): C 38.84, H 4.68, N 5.66. Found: C 38.13, H 4.34, N 5.42. IR (ν, cm^{-1}): 827 (PF_6^-); 1596, 1631 (C=N). ^1H NMR (600.13 MHz, CD_3CN): 1.07-1.15 (qt, 2H, amine ring); 1.24-1.32 (qt, 3H, amine ring); 1.33-1.40 (qt,3H, amine ring); 1.56-1.59 (dq, 2H, amine ring); 2.00 (s, 3H, CH_3-allyl); 3.14 (s, 2H, H_{anti}); 3.49-3.54 (tt, 1H, CH, amine ring); 4.01 (s, 2H, H_{syn}); 7.56-7.58 (ddd, 1H, H_{2py}); 7.79-7.80 (d, 1H, H_{4py}); 8.04-8.07 (td, 1H, H_{3py}); 8.48 (s, 1H, HC=N); 8.62-8.64 (d, 1H, H_{1py}). ^{13}C NMR (150.91 MHz, CD_3CN): 23.57 (C_{15}); 25.23, 25.90, 33.98, 62.52 ($C_{12,14}$); 71.32, 129.05, 130.23, 135.65, 142.23, 154.86 (C_{13}), 155.21; 166.90 (C=N).

Crystal structure determination and refinement. X-ray quality crystals of C1 were grown from a CH_2Cl_2/Et_2O solution which was kept standing at ambient temperature. Data were collected on a Bruker-Nonius Kappa-CCD diffractometer using graphite monochromated MoK_α radiation ($\lambda == 0.71073$ Å) at ambient temperature. Absorption correction was applied using the multi-scan method [64]. The structure was solved by direct methods [65] and refined by the full matrix least squares method [66] on F^2 against all reflections, using anisotropic displacement parameters for non-H

TABLE 1. Crystal, Collection, and Refinement Data

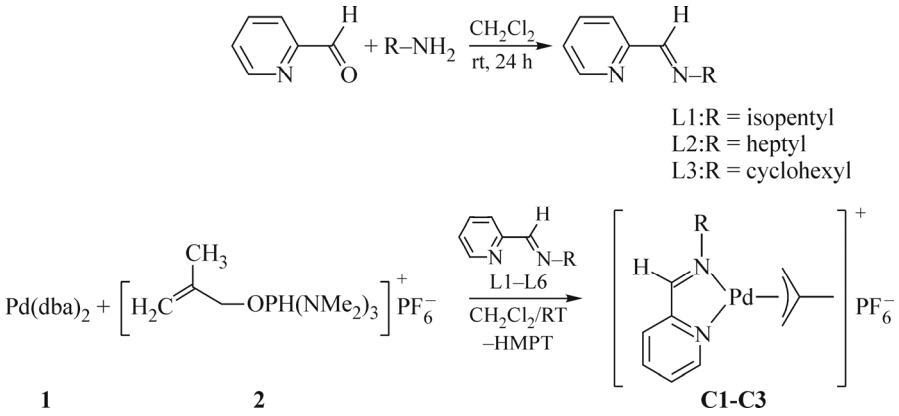
Chemical formula	$C_{15}\ H_{23}\ F_6\ N_2\ P\ Pd$
Formula weight	482.72
T, K	293(2)
Crystal system	Triclinic
Space group	P-1
a, b, c, Å	10.2530(9), 10.4100(10), 11.3460(17)
α, β, γ, deg.	101.418(9), 104.697(11), 117.269(8)
V, Å^3	969.18(19)
Z	2
Density, g/cm^3	1.654
μ, mm^{-1}	1.095
Refl. coll.	9594
Max. θ, deg.	27.5
Indep. refl.	4315
R_{int}	0.0265
Data / restraints / param.	4315 / 101 / 336
R, wR ($I > 2\sigma(I)$)	0.0387, 0.0974
R, wR (all data)	0.0508, 0.1109
Max. peak and hole, e/Å^3	0.800, –0.679

atoms, with the aid of the WinGX program [67]. H atoms of phenyl, alkyl, and imino groups were determined stereochemically and refined by employing the riding model. H atoms of the allyl group were found in Fourier difference maps and their coordinates were refined. For all H atoms, U_{iso} was fixed at 1.2 times U_{eq} of the carrier atom (1.5 in the case of H atoms of the methyl group). On analyzing the Fourier maps, a static disorder was found in the alkyl tail and the hexafluorophosphate ion. The two split positions were refined with some restraints on bond lengths and thermal parameters. A summary of crystal, collection, and refinement data is shown in Table 1. This analysis of the crystal packing was performed using the Mercury program [68].

Density functional theory (DFT) details. Calculations using the DFT method were carried out to obtain an overview of the electronic structures and bonding properties of complex C1. The DFT [69-70] calculations were performed with the long-range corrected hybrid density meta-GGA functional wB97XD [71-73] with dispersion corrections. In this study, the double-zeta Pople-type 6-31G(*d*,*p*) basis set [74] was chosen for all atoms except palladium which was described by the widely used double zeta Los Alamos National Laboratory 2 basis set LANL2DZ [75-77] along with the corresponding effective core potentials (ECPs). This mixed basis set was created through the use of the GEN keyword in Gaussian 09.

RESULTS AND DISCUSSION

The synthesis routes of ligands and cationic methallyl Pd(II) complexes are shown in Scheme 1. The ligands were obtained in good yields of 98% (L1), 96% (L2), 98% (L3) from the condensation reaction between pyridine-2-carboxaldehyde and appropriate X-amine (X = isopentyl, heptyl, cyclohexyl) in dichloromethane [61]. These ligands containing N-alkyl imine groups showed a higher solubility than N-aryl imine groups. New cationic methallyl complexes C1–C3 of palladium(II) were obtained in high yields by the addition of methallyloxyphosphonium salt to zerovalent $Pd(dba)_2$ in the presence of the iminopyridine aliphatic ligand. The reaction was carried out in methylene chloride at room temperature (Scheme 1).



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

These diamagnetic Pd(II) complexes C1–C3 were isolated as yellow solids. The solubility of these new aliphatic pyridinylimine complexes has grown considerably in common solvents compared to N-aryl substituted ones.

The variation of the steric and electronic proprieties of iminopyridine ligands was insured by changing the aliphatic substituent at the imine N atom.

The FT-IR spectra of C1–C3 complexes showed typical lower absorption bands between 1631 cm^{-1} and 1639 cm^{-1} compared to their respective pyridylimine aliphatic ligands [61]. IR spectra of cationic complexes showed the characteristic band of the PF_6^- counterion between 824 cm^{-1} and 828 cm^{-1}. However, the NMR spectra of C1–C3 were recorded in CD_3CN; the proton numbering is shown in Scheme 1. The ^1H NMR spectra of all complexes showed similar trends, especially in the allyl groups, which were observed as singlet signals found to be around 4 ppm assigned to H_{syn} and another singlet found to be around 3.14 ppm assigned to H_{anti}, while the methyl protons resonatedat 2 ppm.

In addition to the corresponding, the aromatic region of the pyridine ring (δ range 7.56-8.63 ppm) shifted downfield by approximately δ 0.3-0.6 ppm in complexes (C1–C3) in comparison to those of the free ligands L1–L3. The change in the chemical shift of the aldimine (CH=N) protons in all the complexes confirmed the coordination of the ligand to the metal.

The ^{13}C NMR peaks of the cationic palladium complexes were shifted to a low field by approximately δ 6-8 ppm compared to their free ligands.

The IR and NMR spectroscopy confirmed the coordination of iminopyridine aliphatic and methallyl ligands to the zerovalent compound $Pd(dba)_2$.

Crystal growth. A single crystal of the C1 complex (Fig. 1) suitable for the X-ray analysis was grown by slow evaporation of a dichloromethane/diethyl ether solution at room temperature. The single crystal X-ray structural analysis of complex C1 showed a distorted square planar geometry around the palladium atom consisting of two N atoms (N1 and N2) of the ligand and two carbon atoms (C12 and C14) of the allyl group.

Crystallographic data and structural refinement parameters are shown in Table 1 while selected bond lengths and angles are presented in Tables 2 and 3. Complex C1 showed a structure consisting of two entities of a freely associated $[(\eta^3\text{-}C_4H_7)Pd(L1)]^+$ cation and a PF_6^- counter anion without direct interactions, which is evident from the large distance between metal and the nearby fluorine atom (Pd–F3a = 4.395 Å).

In complex C1, the Pd(1)–N_{imine} bond length (Pd(1)–N2 = 2.091(3) Å) is shorter than that of the Pd–$N_{pyridine}$ bond length (Pd(1)–N1 = 2.100(3) Å) due to different basicities of the imine and pyridine groups, as compared with the bond lengths Pd–N1 = 2.020(7) Å and Pd–N2 = 2.044(6) Å observed in the related palladium complex [78]. The Pd–C bond length ranged within 2.100(5)–2.139(4) Å compared to that of the Pd–C bond length observed in other related palladium complexes [79-83].

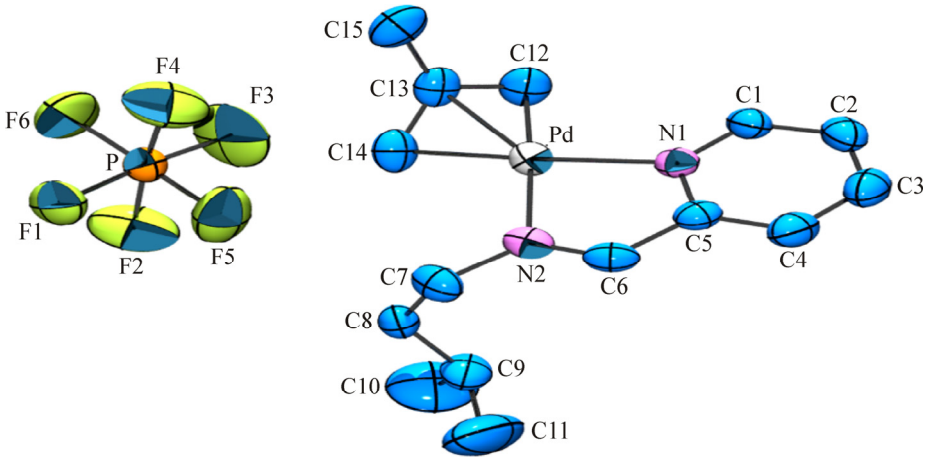


Fig. 1. ORTEP representation of the molecular structure of C1 with the atom labelling scheme and anisotropic displacement ellipsoids depicted at a 30% probability. Hydrogen atoms are omitted for clarity.

TABLE 2. Experimental and Theoretical Bond Distances (Å) of $[(\eta^3\text{-}C_4H_7)Pd(L1)]^+PF_6^-$

Bond length	Experimental	Theoretical
Pd–N1	2.100(3)	2.170
Pd–N2	2.091(3)	2.165
Pd–C12	2.100(5)	2.165
Pd–C13	2.139(4)	2.216
Pd–C14	2.120(5)	2.163
N1–C1	1.332(5)	1.338
N1–C5	1.339(5)	1.358
N2–C6	1.248(6)	1.282
N2–C7	1.489(7)	1.468

TABLE 3. Experimental and Theoretical Bond Angles (deg.) of $[(\eta^3\text{-}C_4H_7)Pd(L1)]^+PF_6^-$

Bond length	Experimental	Theoretical
N1–Pd–N2	78.39(13)	77.75
N1–Pd–C12	105.60(19)	107.18
N2–Pd–C14	108.26(19)	108.17
N1–Pd–C13	137.86(16)	138.16
N2–Pd–C13	139.83(17)	139.06
C12–Pd–C14	67.4(2)	66.77
N1–Pd–C14	172.01(17)	173.45
N2–Pd–C12	173.70(19)	174.38
C12–Pd–C13	38.6(2)	37.72
C13–Pd–C14	37.9(2)	37.77

The N(1)–Pd(1)–N(2) bond angle of 78.39(13)° in C1 is relatively small, as a result of chelating ligand steric constraints. The metal-chelate ring (Pd(1)–N1–C5–C6–N2) in complex C1 is almost flat as indicated by the torsion angles of 2.3(5)°, –2.5(4)°, –0.7(4)° for N1–C5–C6–N2, Pd(1)–N(1)–C5–C6, and Pd(1)–N(2)–C6–C5, respectively. The C15–C13–C12–C14 torsion angle of 167.44(8)° indicated that the methyl on the allyl group is slightly inclined out of the allyl plane by

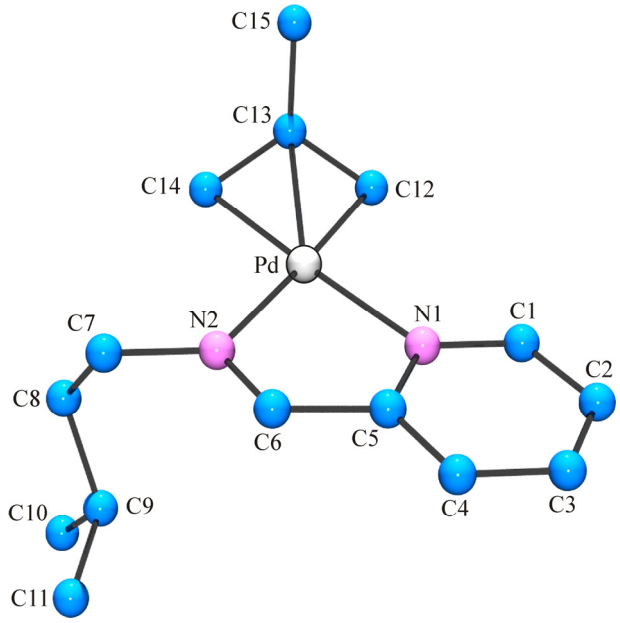


Fig. 2. DFT-optimized structure of the $[(\eta^3\text{-}C_4H_7)Pd(L1)]^+$ cation with the same atom labelling scheme as in the ORTEP representation. Hydrogen atoms are omitted for clarity.

approximately 12°. The allyl plane form an angle of 112.1(4)° with the palladium coordinative plane, that is normal for η^3-2-methylallyl complexes of palladium [79-83].

DFT calculations. The geometry around the Pd atom of the $[(\eta^3\text{-}C_4H_7)Pd(L1)]^+$ cation reveals a distorted square planar arrangement (Fig. 2). The formal charge of palladium is 2+ in complex C1. The calculated charge on the Pd atom slated from the natural population analysis is 0.190. This result may be obtained from a charge donation from the ligand to the metal center and also showed a strong σ-donor character of the ligand.

The experimental data are well replicated in the calculations, as one can see from the data given in Tables 2 and 3. In general, the predicted bond lengths and angles are in good agreement with the values of the X-ray crystal structure data. It can be seen from the data collected in Tables 2 and 3 that the bond angles changed maximum by 2° while the bond lengths are maxim elongated by 0.07 Å in the calculated gas phase structure. Experimental and theoretical geometric parameters are summarized in Tables 2 and 3.

CONCLUSIONS

The oxidative addition of methallyloxytris(dimethylamino)phosphonium hexafluorophosphate to zerovalent $Pd(dba)_2$ in the presence of pyridylimine aliphatic compounds produced new monometallic cationic methallyl palladium(II) complexes in which the ligands coordinated via the pyridine and imine nitrogen atoms. The coordination geometry around the Pd(II) centre in cationic pyridylimine Pd(II) complex C1 was distorted square planar. The DFT calculation using the wB97XD functional indicated that the general trends observed in the experimental data were well replicated in the calculations, as one could see from the data given in Tables 2 and 3. Catalytic properties of complexes C1–C3 are being investigated.

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ADDITIONAL INFORMATION

Supplementary material. CCDC 1557908 contains the crystallographic data for the structural analysis of C1. Copies of this information can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; United Kingdom; Fax: +44 (0)1223 336033.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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