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A convenient reagent for generation and stabilization of cationic methallylpalladium complexes containing nitrogen ligands

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Abstract—A convenient synthesis of the easily handled, air stable methallyloxyphosphonium salt $[CH_2=C(Me)CH_2^{-}O-P(NMe_2)_3]^+$ $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ **5** is described. The utility of this reagent in the generation and stabilization of cationic η^3 -methallyl palladium complexes through oxidative addition reactions is illustrated by the preparation of the stable salts of $[(\eta^3-C_4H_7)Pd(NN)]^+[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ from Pd₂(dba)₃. The molecular structure of one of them has been determined by a single-crystal X-ray diffraction.

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Palladium allyl complexes attracted much attention as a result of their importance as intermediates in palladiumcatalyzed allylic substitution reactions. Attack of the nucleophile on a cationic palladium π -allyl complex is at present conventionally accepted as the crucial step in the catalytic cycle.^{1–3} To our knowledge, very few palladium complexes possessing a potentially bidentate nitrogen ligand and an allyl moiety have been described so far.^{4–7} We have described a simple and effective synthesis of cationic η^3 -allyl complexes of palladium with α -diimine ligands **1** and **2**.⁸

The lack of reactivity and non-nucleophilic character of $[PF_6]^-$ have led to his widespread use as non coordinating counterion supporting cationic organometallic complexes.^{9,10} With the generation of sufficiently electrophilic complexes, however, the limitation of $[PF_6]^-$ as a non-reactive entity is encountered. Jordan has reported the deactivation of the highly reactive d⁰ $[Cp_2Zr(CH_3)]^+$ ethylene polymerization catalyst by F⁻ abstraction from the PF₆⁻ counterion.¹¹ In addition to recognized requirements for weakly coordinating anions, an effective counteranion must necessarily be chemically robust and exceptionally resistant to electrophilic attack. In this regard, (fluoroaryl) borates are worthy of attention. Marks has reported the synthesis of

the highly active olefin polymerization catalyst $[Cp_2^*ThCH_3]^+[B(C_6F_5)_4]^-$ by reaction of $[HN^nBu_3]^+$ $[B(C_6F_5)_4]^-$ with $Cp_2^*Th(CH_3)_2$.¹² However, in view of the fact that the preparation of such anion is costly and involves significant synthetic effort, we have investigated the possibility of generating new bulky and weakly coordinating anions in a more straightforward manner.

In this note we report a convenient synthesis of the methallyloxyphosphonium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate $[CH_2=C(Me)CH_2^{-}O-P(NMe_2)_3]^+$ $[BAr'_4]^- (Ar'=3,5-C_6H_3(CF_3)_2)$ 5 and illustrate its utility in the generation and stabilization of the cationic η^3 -allyl palladium(II) complexes with α -diimine ligands.

According to published procedure, the tetrakis[3,5bis(trifluoromethyl)phenyl] borate TFPB was isolated in the form of hydrated sodium salt.¹³ The addition of a solution of methallyloxyphosphonium chloride¹⁴ $[CH_2=C(Me)CH_2-O-P(NMe_2)_3]^+Cl^- 3$ to a saturated hot aqueous solution of sodium TFPB results in the immediate precipitation of 5 (Scheme 1).



Keywords: palladium; cationic allyl complexes; α -diimine; methylallyloxyphosphonium salt.

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Scheme 1.

Compound 5 was isolated as an air stable, analytically pure, white crystalline solid. The presence of the strongly electron-withdrawing CF₃ groups rendered TFPB virtually inert toward strongly acids and resistant to a variety of oxidants. The chemical stability of TFPB have led to his wide use as the counterion for stabilizing cationic electrophilic metal alkyl complexes whose catalytic properties have recently been investigating. A common route for generating such species involves protonolysis of a dialkyl complex using the trialkylammonium salt $[HN^nBu_3]^+[B(C_6F_5)_4]^-$ or the oxonium acid $[(3,5-(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$. The first has limitation in that he is not sufficiently acidic to effect the protonolysis reaction, particularly in the late metal species. The oxonium acid is very hygroscopic and must be stored and used under strict conditions. Our salt presents the advantage to react at ambient temperature to give nearly quantitative yields of well-defined cationic Pd(II)- η^3 -allyl complexes containing nitrogen ligands. In fact, the oxidative addition of the methallyloxyphosphonium salt 5 to $Pd_2(dba)_3$ in the presence of

the nitrogen donor function of ligands (**a**,**b**) gives rise to the cationic η^3 -methallyl complexes of palladium with α -diimine ligands $[(\eta^3-C_4H_7)Pd(NN)]^+$ which are isolated as stable $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ salts (Scheme 2).

The $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ anion was found to impart good solubilities to the new cationic complexes, a property which renders characterization straightforward. The new complexes exhibit spectroscopic data in accord with the proposed structures. The formation of the allyl complexes 6a and 6b is clear from the resonance of the allyl group in ¹H NMR spectroscopy. The two allylic signals are characteristic of a symmetrical η^3 -allyl ligand. Thus, the two resonances are at 2.80 ppm (H_{anti}) ; 3.05 ppm (H_{svn}) for **6a** and at 2.97 ppm (H_{anti}); (3.23; 3.27) ppm (H_{syn}) for **6b**. In ¹³C NMR spectroscopy, the two terminal allylic carbons C1 and C3 appears at 64.5 ppm for **6a** and at (64.4; 64.6) ppm for **6b**. The C=N functions are shifted to high-frequency when compared to free ligands and appear at 168.3 ppm for 6a and at (184.4; 185.2) for **6b**. The 19 F NMR spectrum of **6a**



Ar' = $3,5-C_6H_3(CF_3)_2$ HMPT = hexamethylphosphotriamide dba = dibenzylideneacetone

presents one signal at 101.5 ppm and shows no substantial chemical shift from that of salt 5 at room temperature, suggesting that coordination of anion to Pd centre is weak and labile. The C=N stretching vibration in the IR spectroscopy is observed at 1620–1660 cm⁻¹.

A single-crystal X-ray diffraction study confirms the identity of complex 6a. The molecular structure of 6a with the adopted numbering scheme is shown in Figure 1. The structure of complex 6a consists of loosely associated $[(\eta^3-C_4H_7)Pd(NN)]^+$ cations and tetrahedral $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ counteranions (Fig. 1). The fluorine atoms (F19, F20, F21) are in the closest proximity to the metal cation (Pd-F19=5.38(4) Å,Pd-F20 = 5.07(6) Å, Pd-F21 = 4.19(7) Å). These $Pd\cdots F$ distances are extremely longer than the sums of Pd²⁺ and F^- ionic radii (2.19 Å). These data, in addition to the fact that the anion structure is not perturbed by the presence of the metal cation, show clearly that the cation-anion interaction is rather weak. The anion $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ adapts a structure in which the four fluoroaryl groups are tetrahedrally bonded to the central boron atom.

The $[(\eta^3-C_4H_7)Pd(NN)]^+$ cation of **6a** adapts the usual slightly distorted square planar arrangement (Fig. 2). The allyl ligand is bonded almost symmetrically to the palladium centre (2.116(1) and 2.147(1) Å for Pd–C1 and Pd–C3, respectively). We note that the Pd–C(allyl) distances are reasonable for an allyl *trans* to a ligand of moderate *trans* influence.^{15,16}

The α -diimine ligand **a** is also coordinated in a symmetric fashion: the Pd–N separations, 2.081(9) and 2.122(9) Å are consistent with known literature values for related complexes.^{8,15} The two bond angles N1–Pd–N2 and C1–Pd–C3 of 77.5(5) and 68.1(3)°, respectively, are



Figure 1. Perspective ORTEP drawing of complex **6a**. Thermal ellipsoids are at 30% probability. Selected bond lengths (Å) and angles (°): B-C23=1.63(1), B-C31=1.65(2), B-C39=1.65(1), B-C47=1.67(1); C23-B-C31=111.0(8), C23-B-C39=112.4(8), C23-B-C47=105.2(8), C31-B-C39=104.3(8), C31-B-C47=112.2(8), C39-B-C47=111.9(8).

normal.^{8,15} The allyl and Pd–N,N planes make an angle of 107.7°, which is comparable with those found for other allylpalladium complexes containing α -diimine ligand.^{5,8,15} The α -diimine plane N=C–C=N is roughly planar (torsion angle N1–C5–C6–N2=5.3°) and makes a dihedral angles of 85.2 and 77.6° with the aromatic substituents on the nitrogen atoms. Comparison with similar complexes in the literature indicates that as the steric bulk of the aryl *ortho* substituents increases, the *N*-aryl rings tend to lie more perpendicular to the square plane of the complex, and the *ortho* substituents more effectively block the axial sites.¹⁷ All other distances and angles are as expected.

Cationic π -allylpalladium complexes are reported to be efficient catalysts in the presence of phosphines for the dimerization of methyl acrylate¹⁸ and co-dimerization of 1,3-dienes with acrylic esters.¹⁹ We wish to report that isolated pure cationic allylpalladium complex **6b** catalyze the polymerization of methyl acrylate with good conversion (40%). When its $[PF_6]^-$ analogue is used under the same conditions in the catalytic polymerization of methyl acrylate, the conversion decreases dramatically (<1%). Those results suggest that the weak coordinating ability of $[(3,5-(CF_3)_2-C_6H_3)_4B]^-$ leads to an important increase in the catalytic activity of cationic allylpalldium complexes containing α -diimine ligands.

In conclusion, we have described a convenient synthetic procedure for the preparation of the new methallyloxyphosphonium salt **5**. The generation and characterization of cationic methallylpalladium complexes containing Nitrogen ligands supported by the (fluoroaryl)borate anion were also described. The application of these complexes in catalytic reactions such as oligomerization and polymerization of alkenes (ethylene, propylene) and functional alkenes (methyl acrylate) is in progress.



ORTEP Figure 2. Perspective drawing $[(\eta^{3}$ of C_4H_7)Pd(NN)]⁺ cation. Thermal ellipsoids are at 30% probability. Selected bond lengths (Å) and angles (°): Pd-N1 = 2.081(9),Pd-N2 = 2.122(9),Pd-C1 = 2.116(1), Pd-C2 = 2.141(1),Pd-C3 = 2.147(1),N1-C5 = 1.278(1), N2-C6 = 1.266(1),N1-C7 = 1.435(1), N2-C15 = 1.449(1), C2-C3 = 1.418(2); N1-Pd-N2 = 77.5(4), C1-C2 = 1.444(2),N1-Pd-C1 = 105.3(5), N2-Pd-C3 = 108.6(5), Pd-N1-C5 =114.6(7), Pd-N2-C6 = 113.6(8), C1-Pd-C2 = 68.1(3).

Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk tube techniques. Dichloromethane and diethylether were distilled under argon from P_2O_5 and sodium benzophenone ketyl, respectively, and stored under argon. The $Pd_2(dba)_3$ complex was synthesized following established procedure.²⁰ NMR spectra were recorded on a Bruker AMX 300 spectrometer and infrared spectra on a BioRad FTS-6000 spectrophotometer.

Preparation of 5: To an aqueous solution of methallyloxytris(dimethylamino) phosphonium chloride prepared in situ¹⁴ was added a saturated hot aqueous solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.13 Precipitation was immediately observed. The white suspension was stirred for 1 h at room temperature and then filtered through a frit. The white solid was then dissolved in diethyl ether and the solution was stirred over Na₂SO₄, filtered, and pentane (100 ml) was layered on top of the solution. After 3 days, the recrystallized product was collected by filtration and dried under vacuum to give the white crystalline salt 5. Mp: 98°C. Anal. found (calcd) for $C_{42}H_{37}N_3F_{24}BOP$: C, 45.78 (45.96); H, 3.17 (3.39). IR [ν cm⁻¹] (KBr): 1100–1200; 1280; 1360. ¹H NMR (300 MHz, CDCl₃): δ 1.72 (s, 3H, CH₃); 2.63 (d, $J_{PH} = 10$ Hz, 18H, NCH₃); 4.37 (d, $J_{PH} = 7.6$ Hz, 2H, H₃); 4.98 (s, 1H, H₁); 5.05 (s, 1H, H'₁); 7.53 (s, 4H, H_p); 7.68 (s, 8H, H_o). ¹³C NMR (75 MHz, CDCl₃): δ 18.4 (C₄); 36.5, 36.6 (NMeMe'); 72.5 (C₃); 115.5 (C₁); 117.4 (C_p); 125.0 (q, ${}^{1}J_{CF}$ =272 Hz, CF₃); 129.0 (q, ${}^{2}J_{CF}$ =34.5 Hz, C_m); 134.7 (C_o); 137.4 (C₂); 161.6 (q, ${}^{1}J_{CB}$ =49 Hz, C_{*ipso*}). ¹⁹F NMR (282 MHz, CDCl₃): δ (referenced to external C₆F₆) 99.5 (s, CF₃).

Preparation of 6a: To 30 ml of CH₂Cl₂ solution of $Pd_2(dba)_3$ (140 mg, 0.15 mmol) was added 0.3 g of salt 5 (0.28 mmol) and DAB a (80 mg, 0.30 mmol) at room temperature. After 24 h of stirring the mixture was filtered through Celite filter and the residue was washed with CH_2Cl_2 (2×10 ml). The combined filtrates were evaporated to 5 ml. The product was precipitated by the addition of hexane (20 ml), washed with diethylether/hexane 1:5 (3×10 ml) and dried in vacuo, yielding 0.36 g of **6a** as an orange solid (93%). Decomposition: 197°C. IR [v cm⁻¹] (KBr): 1621 (C=N). ¹H NMR (300 MHz, CD₂Cl₂): δ 1.97 (s, 3H, H₄); 2.11 (s, 6H, o-CH₃); 2.15 (s, 6H, o'-CH₃); 2.80 (s, 2H, H_{anti}); 3.05 (s, 2H, H_{syn}); 7.11 (s, 6H, H_{arom}); 8.26 (s, 2H, N=CH-HC=N); [3,5-C₆H₃(CF₃)₂]₄B⁻: 7.50 (s, 4H, p-H); 7.71 (s, 8H, o-H). ¹³C NMR (75 MHz, CD_2Cl_2): δ 19.2, 19.3 (o-CH₃); 24.7 (C₄); 64.5 (C_{1,3}); 127.2, 127.3 (C_{0,0'}); 128.9 (C_p); 130.2, 130.3 (C_{m,m'}); 138.9 (C₂); 148.1 (C_{ipso}); 168.3 ($\hat{C}=N$); [(CF_3)₂- C_6H_3]₄B⁻: 119.7(C_p); 126.8 (q, ${}^{1}J_{CF} = 272.3$ Hz, CF₃); 130.9 (q, ${}^{2}J_{CF} = 31.5$ Hz, C_m); 137.0 (C_o); 164.0 (q, ${}^{1}J_{CB} = 49.8$ Hz, C_{ipso}). ${}^{19}F$ NMR (282 MHz, CD₂Cl₂): δ (referenced to external C₆F₆) 101.5 (s, CF₃).

Preparation of 6b: The complex **6b** was obtained in 89% yield by the same procedure as a green–yellow solid.

Decomposition: 213°C. IR [ν cm⁻¹] (KBr): 1623; 1658 (C=N). ¹H NMR (300 MHz, CD₂Cl₂): δ 0.58 s (3H), 0.87 s (3H), 0.99 s (3H), H_{12,13,14}; 1.97 (s, 3H, H₄); 1.73 m (1H), 1.92 m (2H), 2.2 m (1H), H_{8,9}; 2.78 (d, J_{HH} = 4.8 Hz, 1H, H₁₀); 2.97 (s, 2H, H_{anti}); 3.23 s (1H), 3.27 s (1H), H_{syn}; 7.04 d (J_{HH} = 7.2 Hz, 2H), 6.96–7.10 m (2H), 7.2–7.4 m (6H), H_{ar}; [(CF₃)₂-C₆H₃]₄B⁻: 7.46 (s, 4H, p-H); 7.67 (s, 8H, o-H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 11.7, 17.6, 22.0, C_{12,13,14}; 23.9 (C₄); 24.9, 33.5 (C_{8,9}); 51.0 (C₇); 51.6 (C₁₀); 58.2 (C₁₁); 64.4, 64.6 (C_{1,3}); 122.4 (C_m); 128.7, 129.6 (C_p); 130.1, 130.5 (C_o); 137.2 (C₂); 147.3, 147.7 (C_{ipso}); 184.4, 185.2 (C_{5,6}); [(CF₃)₂-C₆H₃]₄B⁻: 118.2(C_p); 125.3 (q, ¹J_{CF}=272.3 Hz, CF₃); 129.9 (q, ²J_{CF}=31.7 Hz, C_m); 135.5 (C_o); 162.50 (q, ¹J_{CB}=49.8 Hz, C_{ipso}).

Crystallographic data for 6a: $C_{54}H_{39}N_2BF_{24}Pd$; fw = 1289.09; monoclinic; $P2_1/c$ (No. 14); Z=4; a= 16.752(9) Å; b=18.291(8) Å; c=19.964(3) Å; $\beta = 114.32(3)^{\circ}$; V = 5574(4) Å³; $D_{calcd} = 1.536$ g cm⁻³; R = 0.059; $R_w = 0.086$; $-21 \le h \le 21$; $0 \le k \le 25$; $0 \le l \le 22$; Mo ($\lambda = 0.7107$ Å); T = 296 K.

Atomic coordinates and anisotropic temperature factors have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ (CCDC 179134).

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