Simultaneous Generation of Anionic and Neutral Palladium(II) Complexes from η^3-Allylpalladium Chloride Dimer and Fluorinated β-enaminones

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Reactions between η^3-allylpalladium chloride dimer, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1-amino-2-fluoro-1-perfluoroethyl-3-phenylprop-1-en-3-one or 1,12-diamino-2,11-difluoro-1,12-bis(perfluorobutyl)dodeca-1,11-diene-3,10-dione simultaneously provided two types of Pd^{II} complexes. One is an anionic η^3-allylpalladium complex with protonated DBU as counterion while the other is a neutral η^3-allyl(β-ketoiminato)palladium complex. A mechanism involving the amidine function of DBU in the formation of the two complexes is proposed.

Chi et al. have recently reported η^3-allyl(β-ketoiminato)-palladium(II) complexes which can serve as precursors for chemical vapor deposition of thin palladium films; these films are attractive for the manufacture of various electronic devices.[1] In our studies on the synthesis and applications of polyfluorinated compounds,[2] we developed an effective synthesis of β-enaminones **1** (Figure 1). Our long-standing interest in Pd-mediated chemistry[3] coupled with the observations of Chi et al.[1] then prompted us to consider the synthesis of complexes **2a**, **2b** and **3** by treatment of **1a** and **1b** with $[(\eta^3\text{-allyl})PdCl]_2$ (**4**) (Figure 1).

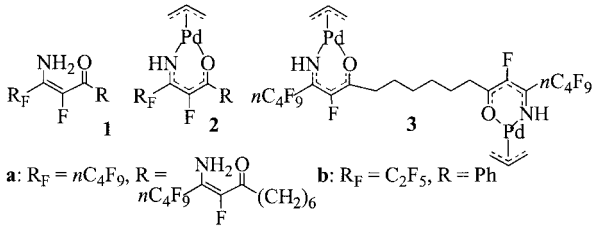
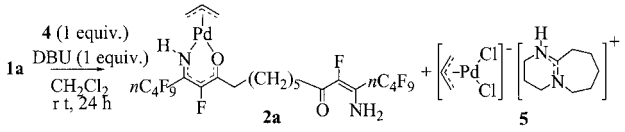


Figure 1. Compounds **1**−**3**

Unfortunately, the reaction of **1a** with **4** in the presence of aqueous NaOH,[1] MeONa[1] or NEt_3 in CH_2Cl_2 produced a deposit of palladium and degradation compounds. This failure urged us to look for other conditions. No reaction was observed with Na_2CO_3 or K_2CO_3 as base in CH_2Cl_2. In contrast, the use of a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the same solvent led to the complete consumption of a 1:1 mixture of **1a** and **4** in 24 h at room temperature. Evaporation of the solvent followed by addition of petroleum ether led to the formation of a precipitate. The removal of the mother liquors using a double-tipped needle allowed us to isolate the precipitate which was identified as the unexpected complex **5**. Subsequent evaporation of the mother liquors provided **2a** as an air-sensitive yellow oil (Scheme 1).



Scheme 1

The structure of **2a** was determined from its mass spectrum and analysis of its ^1H, ^{13}C and ^{19}F NMR spectra. The ^1H NMR spectrum indicated the presence of an allyl group, with the central hydrogen appearing at $\delta = 5.50$ ppm. The other four hydrogen atoms were nonequivalent, the peaks due to H_{syn} appearing at $\delta = 4.05$ and 3.57 ppm and those due to H_{anti} at $\delta = 3.14$ and about 2.60 ppm. The spectra also showed that a coordinated β-ketoimino group and a

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Table 1. Characteristic resonances in the ^{13}C and ^{19}F NMR spectra (δ/ppm) for substrates and complexes

	1a	2a	3	1b	2b
C−N	130.6	129.3[a], 143.8[b]	145.4	133.5	148.0
C−F	139.7	138.5[a], 140.6[b]	140.1	140.7	140.2
C=O	197.4	197.2[a], 181.1[b]	181.0	186.4	172.3
F−C	−166.8	−166.7[a], −177.6 [b]	−177.7	−163.1	−175.6

[a] Uncoordinated β-enaminone. [b] Coordinated β-enaminone.

free β-enaminone group were present (Table 1), and that the ratio of allyl and β-ketoiminato units was 1:1.

The ^1H and ^{13}C NMR spectra of **5** indicated the presence of an allyl ligand and a protonated DBU molecule, in agreement with the mass spectrum. The exact molecular structure was determined by X-ray crystallography of suitable crystals obtained from recrystallization of the complex in chloroform. This confirmed that **5** is an ion pair consisting of an anionic dichloro(π-allyl)palladium(II) complex and a diazabicyclo[5.4.0]undec-7-enium cation (Figure 2). The Pd atom is coordinated in a square planar configuration. The distances to the mean square plane defined by the atoms Cl(1), Cl(2), C(20) and C(22) are as follows: Cl(1) +0.017, Cl(2) −0.017, C(20) −0.025, C(22) +0.025, Pd −0.089 and C(21) −0.655 Å. This shows that only the central carbon atom of the allyl group lies out of the mean square plane.

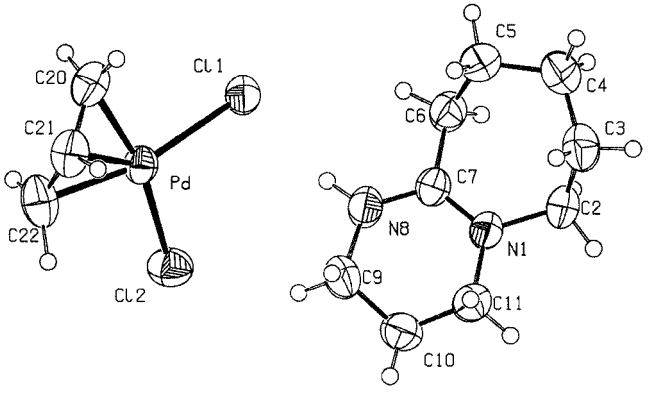
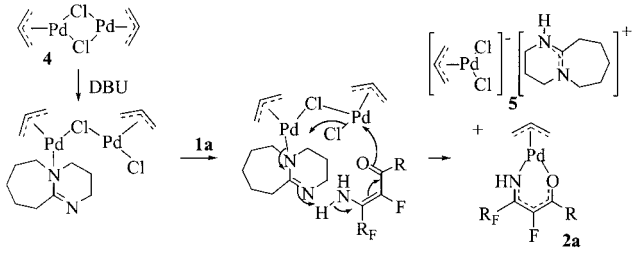


Figure 2. ORTEP diagram[7] of **5**

The Pd−C bond lengths in the complex cation are equal; their mean value (2.123 Å) is within the range found for other palladium complexes containing π-allyl ligands.[4] As already observed for similar structures, the C−C bond lengths in the allylic group are not significantly different; we observed values of 1.410(5) and 1.389(5) Å (i.e. with $\Delta C - C/\sigma = 4.2$). The *trans* influence of the π-allyl ligand explains the two long Pd−Cl bond lengths [2.402(1) and 2.370(1) Å]. The observed difference between these two bond lengths is probably due to the asymmetry of the associated cation. The bicyclic skeleton of the cation adopted the following conformation. The six-membered ring is an envelope (E) with ring puckering parameters of Q = 0.451, θ = 51.9° and φ = 242.3°;[5] the plane of symmetry runs through the atoms C7 and C10. The seven-membered ring also has only one mirror plane as a symmetry element; this passes through C4 and the midpoint of the N1−C7 bond. The four puckering parameters are Q(2) = 0.454, Q(3) = 0.648, φ(2) = 234.85 and φ(3) = 257.57°.[6] A hydrogen bond involving the ammonium hydrogen and one chlorine atom is observed. The geometry is as follows: N(8)−H(8)···Cl(1), N−H = 0.94(2) Å, H···Cl = 2.33(3) Å, N···Cl = 3.253(3)Å and N−H···Cl = 168(1)° [Cl(1): 0.5 + *x*, 1.5 − *y*, 1 − *z*].

Coordination of both the β-enaminone functions of **1a** was achieved by increasing the quantities of both DBU and **4**. The use of a **1a**/DBU/**4** ratio of 1:2:2 provided **3** (as an air-sensitive yellow oil) and **5**. As expected from the above results, the reaction of **1b** with stoichiometric amounts of DBU and **4** afforded an almost 1:1 mixture of complexes **2b** and **5**. The structures of **2b** and **3** were established by NMR spectroscopy (Table 1) and mass spectrometry.

Regarding the mechanism of the formation of these complexes, we had at first thought that **2** might be formed from **1** by deprotonation with DBU followed by coordination of the resulting anion to palladium in a manner similar to that assumed by Chi et al.,[1] which would give also DBU·HCl. The reaction of the latter with **4** would afford **5** — similar anionic complexes have been obtained from η^3-allylpalladium halide complexes and either KCl[8] or nBu$_4$NCl.[4b] However, such a pathway was ruled out because the treatment of **4** with DBU·HCl did not provide **5**. In contrast, **5** was obtained by the addition of DBU (2 equiv.) to **4** followed by HCl (2 equiv.). Monitoring this reaction by ^1H NMR spectroscopy showed that the coordination of DBU to palladium preceded the formation of **5**. Since the use of NEt_3 in place of DBU did not permit the synthesis of **2a** or **3** from **1a** and **4**, we suspect that the amidine functionality of DBU plays a key role, as depicted in Scheme 2 for the case of **2a**.



Scheme 2

In conclusion, the simultaneous appearance of two η^3-allylpalladium complexes (one neutral and the other anionic) in the same pot has been observed for the first time. It is of interest to note that anionic η^3-allylpalladium complexes similar to **5** have been used as highly active catalysts for Suzuki and Heck reactions by the CIBA Company.[9]

Experimental Section

General: Melting points are uncorrected. FT-IR spectra were recorded on a MIDAC Corporation Spectrafile IR™ apparatus. ^1H,

^{13}C and ^{19}F spectra were recorded on a Bruker AC-250 spectrometer using $CDCl_3$ as the solvent. Tetramethylsilane, $CHCl_3$ and $CFCl_3$ were used as internal references for the ^1H, ^{13}C and ^{19}F NMR spectra respectively. MS data were obtained on a AUTOSPEC (VG Instruments) apparatus at 70 eV in the electron impact mode. Elemental analyses were performed with a Perkin−Elmer CHN 2400 apparatus. All reactions were carried out under argon atmosphere. Solvents were freshly distilled before use (Et_2O over sodium/benzophenone, CH_2Cl_2 and petroleum ether over CaH_2). Complex **4** was prepared following a published procedure.[10]

1a: $C_6F_{13}I$ (11.24 g, 25.2 mmol) and MeLi (16.8 mL, solution 1.5 M in diethyl ether, 25.2 mmol) were added successively to a solution of 1,8-bis(trimethylsilyl)-1,8-octanedione[11] (3.00 g, 10.5 mmol) in diethyl ether (85 mL) at −78 °C. The mixture was stirred at −78 °C for 30 min and then was allowed to warm to room temperature (1.5 h). After cooling to 0 °C, NH_3 was bubbled into the solution over 3 h. The mixture was diluted with diethyl ether (30 mL) and washed with water (20 mL). The aqueous phase was extracted with diethyl ether (5 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude mixture (estimated 80 % crude yield from the ^{19}F NMR spectrum using $PhCF_3$ as an internal standard) was distilled using a kugelrohr apparatus (90−100 °C/0.05 mbar) and then recrystallized from petroleum ether to give **1a** as a white solid (2.41 g, 33 %). M.p. 77−78 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3497, 3314, 2943, 1670, 1618, 1359. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.2 (br. s, 4 H), 2.61 (td, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,F}$ = 3.1 Hz, 4 H), 1.7−1.5 (m, 4 H), 1.5−1.3 (m, 4 H) ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 197.4 (d, $^2J_{C,F}$ = 28.2 Hz, CO), 139.7 (d, $^1J_{C,F}$ = 239.4 Hz, CF), 130.6 (td, $^2J_{C,F}$ = 23.5 Hz, 18.9, CN), 117.3 (qt, $^1J_{C,F}$ = 288.8 Hz, $^2J_{C,F}$ = 32.9 Hz, CF_3), 113.1 (tt, $^1J_{C,F}$ = 262.9 Hz, $^2J_{C,F}$ = 32.9 Hz, CF_2), 120−110 (m, 2 CF_2), 37.8 (s, CH_2), 28.9 (s, CH_2), 23.3 (s, CH_2) ppm. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ = −166.8 (m, 2F, CF), −126.6 (m, 4F, CF_2), −123.9 (m, 4F, CF_2), −117.3 (m, 4F, CF_2), −81.3 (t, $^3J_{FF}$ = 7.6 Hz, 6F, CF_3) ppm. MS(EI): *m/z* (%) = 696 (84) [M^+], 676, 619, 372, 321 (100), 306, 279. $C_{20}H_{16}F_{20}N_2O_2$ (696.33): calcd. C 34.50, H 2.32, N 4.02; found C 34.08, H 2.04, N 3.69.

1b: NH_3 was bubbled through a solution of the fluorinated enone (300 mg, 1.05 mmol), (obtained from benzoylsilane and perfluorobutylmagnesium bromide as described previously[12]) in anhydrous diethyl ether (20 mL) at 0 °C for 1 h. The mixture was diluted with diethyl ether (30 mL) and washed with a saturated solution of ammonium chloride. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude mixture was purified by flash chromatography (eluant: petroleum ether/EtOAc, 90:10) to give **1b** as a yellow solid (285 mg, 96 %). M.p: 36−37 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3405, 3285, 3081, 1643, 1595, 1520, 1448, 1217, 735, 694. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.89 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H) 7.60−7.44 (m, 3 H), 6.65 (br. s, 2 H) ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 188.0 (d, $^2J_{C,F}$ = 24.7 Hz, CO), 140.2 (d, $^1J_{C,F}$ = 242.7 Hz, CF), 136.3 (d, $^2J_{C,F}$ = 5.6 Hz, C_q arom.), 133.5 (q, $^2J_{C,F}$ = 24.1 Hz, CN), 128.9−128.3 (CH arom.) ppm. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ = −163.1 (tq, $^4J_{FF}$ = 22.9 Hz, $^5J_{FF}$ = 15.3 Hz, 1F, CF), −120.1 (d, $^4J_{FF}$ = 22.9 Hz, 2F, CF_2), −84.0 (d, $^5J_{FF}$ = 15.3 Hz, 3F, CF_3) ppm. MS (EI): *m/z* (%) = 283 (35) [M^+], 206, 178, 137, 105 (100). $C_{11}H_7F_6NO$ (283.16): calcd. C 46.66, H 2.49, N 4.95; found C 46.51, H 2.43, N 4.81.

Synthesis of the Palladium Complexes. Standard Procedure: DBU (9.6 mg, 0.063 mmol) was added to a stirred solution of **1a** (44 mg, 0.063 mmol) in CH_2Cl_2 (10 mL). After 30 min, this solution was added dropwise to a solution of **4** (23 mg, 0.063 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred for 24 h at room temperature. Evaporation of the solvent under reduced pressure afforded an oil. Addition of petroleum ether (20 mL) induced the precipitation of **5** (21 mg, 0.056 mmol, 90 %) as a brown-yellow powder which was isolated by filtration. Evaporation of the resulting solution afforded **2a** (38 mg, 0.045 mmol, 72 %) as a yellow oil.

2a: IR (film, cm^{-1}): $\tilde{\nu}$ = 3236, 3122, 2935, 2860, 1647, 1589, 1445, 1323, 1240, 1208, 749. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.50 (br. s, 1 H, NH), 6.30 (br. s, 2 H, NH_2), 5.50 (tt, ^3J = 12.5 Hz and ^3J = 6.2 Hz, 1 H, H_{cent}), 4.05 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.57 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.14 (d, ^3J = 12.5 Hz, 1 H, H_{anti}), 2.70−2.48 [m, 5 H, H_{anti}, CH_2(a) and CH_2(a′)], 1.75−1.50 [m, H CH_2(b) and CH_2(b′)], 1.48−1.25 [m, 4 H, CH_2(c) and CH_2(c′)] ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 197.2 (d, $^2J_{C,F}$ = 27.9 Hz, CO), 181.1 (d, $^2J_{C,F}$ = 26.8 Hz, CO), 143.8 (m, CN), 140.6 (d, $^1J_{C,F}$ = 201.4 Hz, CF), 138.5 (d, $^1J_{C,F}$ = 221.6 Hz, CF), 129.3 (m, CN), 120−110 (m, CF_2, CF_3), 62.9 (s, CH_2 π-allyl), 50.6 (s, CH π-allyl), 37.9 (s, CH_2), 36.2 (s, CH_2), 29.2 (s, CH_2), 28.9 (s, CH_2), 26.1 (s, CH_2), 23.3 (s, CH_2) ppm. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ = −177.6 (m, 1F, CF), −166.7 (m, 1F, CF), −126.6 (m, 4F, CF_2), −123.9 (m, 2F, CF_2), −122.6 (m, 2F, CF_2), −117.3 (m, 2F, CF_2), −114.7 (m, 2F, CF_2), −81.3 (t, $^3J_{FF}$ = 9.4 Hz, 6F, CF_3) ppm. MS (EI): *m/z* (%) = 842 (13) [M^+], 494, 321 (100), 147.

5: Orange solid. M.p. 131 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3425, 3300, 2935, 3130, 2857, 1642, 1205. ^1H NMR ($CDCl_3$, 250 MHz): δ = 10.25 (br. s, 1 H, NH^+), 5.42 (tt, ^3J = 12.5 Hz and ^3J = 6.2 Hz, 1 H, H_{cent}), 4.10 (d, ^3J = 6.2 Hz, 2 H, H_{syn}), 3.70−3.50 [m, 6 H, CH_2(2), CH_2(9), CH_2(11)], 3.08 [m, 2 H, CH_2(6)], 3.00 (d, ^3J = 12.5 Hz, 2 H, H_{anti}), 2.10 [quint, ^3J = 6.3 Hz, 2 H, CH_2(10)], 1.98−1.55 [m, 6 H, CH_2(3), CH_2(4), CH_2(5)] ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 164.0, 118.2, 60.6, 61.0, 52.2, 49.5, 43.6, 35.2, 32.7, 31.7, 28.2, 23.9 ppm. MS (EI): *m/z* (%) = 372 (49) [M^+], 152 (100).

The standard procedure, using DBU (13 mg, 0.085 mmol), **1b** (24 mg, 0.085 mmol) in CH_2Cl_2 (10 mL) and **4** (31 mg, 0.085 mmol) in CH_2Cl_2 (5 mL) led to **5** (25 mg, 0.067 mmol, 79 %) and **2b** (31 mg, 0.072 mmol, 85 %) as a yellow oil.

2b: ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.90 (br. s, 1 H, NH), 7.75 (m, 2 H, Ph), 7.41 (m, 3 H, Ph), 5.51 (tt, ^3J = 12.5 Hz and ^3J = 6.2 Hz, 1 H, H_{cent}), 4.12 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.68 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.22 (d, ^3J = 12.5 Hz, 1 H, H_{anti}), 2.75 (d, ^3J = 12.5 Hz, 1 H, H_{anti}) ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 172.3 (d, $^2J_{C,F}$ = 26.0 Hz, CO), 148.0 (m, CN), 140.2 (d, $^1J_{C,F}$ = 201.2 Hz, CF), 130.2−127.9 (C arom.), 114.2−111.3 (m, CF_2, CF_3), 63.5 (s, CH_2 π-allyl), 50.8 (s, CH π-allyl) ppm. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ = −175.6 (m, 1F, CF), −117.3 (m, 2F, CF_2), −82.5 (m, 3F, CF_3) ppm. MS (EI): *m/z* (%) = 429 (46) [M^+], 282 (100), 147.

The standard procedure using DBU (21.9 mg, 0.144 mmol), **1a** (50 mg, 0.072 mmol) in CH_2Cl_2 (15 mL) and **4** (52.5 mg, 0.144 mmol) in CH_2Cl_2 (10 mL) led to **5** (38 mg, 0.102 mmol, 71 %) and **3** (45 mg, 0.045 mmol, 63 %).

3: IR (Film, cm^{-1}): $\tilde{\nu}$ = 3400, 2935, 2861, 1590, 1495, 1418, 1351, 1237, 1136, 743. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.53 (br. s, 1 H, NH), 5.57 (tt, ^3J = 12.5 Hz and ^3J = 6.2 Hz, 1 H, H_{cent}), 4.06 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.59 (d, ^3J = 6.2 Hz, 1 H, H_{syn}), 3.16 (d, ^3J = 12.5 Hz, 1 H, H_{anti}), 2.68 (d, ^3J = 12.5 Hz, 1 H, H_{anti}), 2.58−2.50 [m, 4 H, CH_2(a) et CH_2(a′)], 1.72−1.55 [m, 4 H, CH_2(b) et CH_2(b′)], 1.48−1.30 [m, 4 H, CH_2(c) et CH_2(c′)] ppm. ^{13}C NMR (69.2 MHz, $CDCl_3$): δ = 181.1 (d, $^2J_{C,F}$ = 26.9 Hz, CO), 140.1 (d, $^1J_{C,F}$ = 205.8 Hz, CF), 145.4 (td, $^2J_{C,F}$ = 23.1, 22.6 Hz, CN),

120−110 (m, CF_2, CF_3), 63.0 (s, CH_2 π-allyl), 50.6 (s, CH π-allyl), 36.2 (s, CH_2), 29.3 (s, CH_2), 26.0 (s, CH_2) ppm. ^{19}F NMR (235.36 MHz, $CDCl_3$): δ = −177.7 (m, 2F, CF), −126.6 (m, 4F, CF_2), −122.6 (m, 4F, CF_2), −114.8 (m, 4F, CF_2), −81.3 (t, $^3J_{FF}$ = 9.9 Hz, 6F, CF_3) ppm. MS (EI): *m*/*z* (%) = 990 (100) [M^+] 949, 842(100), 800, 494.

X-ray Analysis of 5: The recrystallization leading to suitable crystals for X-ray analysis took place in $CDCl_3$ solution in the NMR tube. After slow and partial evaporation of the solvent, the crystals were collected and washed with small amounts of diethyl ether and dried under a gentle flow of argon. The crystal was glued to a thin glass fiber and placed on the goniometer head of a MAR345 image plate detector equipped with Mo-K_α graphite monochromatized radiation. 60 Images at a crystal to detector distance of 130 mm and with ΔΦ = 3° were collected giving a total of 9782 reflections of which 3027 were independent (R_{int} = 0.060). The structure was solved by the Patterson heavy atom method and refined by full-matrix least-squares on F^2.[13] The hydrogen atoms of the cation and ammonium hydrogen were located from a difference Fourier synthesis. All the other hydrogen atoms were placed at a calculated geometry and allowed to ride on the parent atom during subsequent cycles of least-squares refinement. Non hydrogen atoms were refined using anisotropic parameters for thermal motion. All the hydrogen atoms were refined with a common isotropic temperature factor (V = 0.078 Å^2). The details of crystal data and parameters of the refinement are given in Table 1. CCDC-220981 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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