π-2-Methylallylpalladium(II) complexes containing a nine-membered chelate ring with an azine diphosphine ligand: crystal structure of [(η³-2-MeC₃H₄)Pd{E,Z–PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}]Cl

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Abstract

Treatment of the azine diphosphine Z,Z–PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂ (1) with 0.5 equiv. of [{(η³-2–MeC₃H₄)PdCl}₂] gave the cationic palladium(II) complex [(η³-2–MeC₃H₄)Pd{PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}]Cl (2a), containing a nine-membered chelate ring with the azine in the E,Z-configuration. The crystal structure of 2a shows that the E,Z-azine backbone C–C=N–N=C–C is essentially planar and the methylallyl ligand is non-planar. The corresponding PF₆ salt 2b was prepared using NH₄PF₆ in EtOH. The proton NMR spectra of 2b were temperature dependent, and at 243 K the slow exchange limiting spectrum was obtained in which all four CH₂P protons were inequivalent, as were the four allylic protons with $^4J(H_{syn}H_{syn}) = 2.2$ Hz. Proton, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data are given. Crystals of 2a are monoclinic, space group $P2_1/n$ with $a = 10.3449(8)$, $b = 18.457(2)$, $c = 21.705(2)$ Å, $\beta = 101.140(7)°$ and $Z = 4$, $R_1 = 0.0495$ for 5769 observed reflections with $I > 2.0\ \sigma(I)$.

Keywords: Crystal structures; Palladium complexes; Allyl ligand complexes; Chelate ring complexes

1. Introduction

In a previous paper [1] we described the synthesis of a novel azine diphosphine PPh₂CH₂C(Buᵗ)=N–N=C-(Buᵗ)CH₂PPh₂ (1), which was shown to have the Z,Z-configuration by X-ray crystallography. The carbon-¹³NMR spectrum of 1 suggested that the two phosphorus atoms were coupled to each other with the seven bond coupling $^7J(PP)$ estimated to be 4.8 Hz [2]. When the azine diphosphine 1 was treated with [M(CO)₄(norbornadiene)] (M = Cr, Mo or W) it underwent isomerisation around one of the C=N bonds to give [M(CO)₄{PPh₂CH₂C(Buᵗ)=N–N=C-(Buᵗ)CH₂PPh₂}] in which the azine diphosphine was bonded in the E,Z-configuration through both phosphorus atoms giving a nine-membered chelate ring [1,3]. These tetracarbonyl complexes were thermally unstable and when heated in benzene at ~75 °C, the corresponding tricarbonyl complexes *fac*-[M(CO)₃{PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}] were formed with the E,Z-azine disphosphine acting as a terdentate ligand with P,P- and N-donor atoms [1]. We have also investigated the coordination chemistry of 1 with Pd and Pt [4,5] and showed that Z,Z–PPh₂CH₂C(Buᵗ)=N–

N=C(Buᵗ)CH₂PPh₂ could also bridge two metal atoms to give binuclear species e.g. [Pd₂Cl₄{μ-PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}₂] [4] with 18-atom rings and *trans* PPh₂ groups. This complex was thermally unstable and readily gave the mononuclear cationic complex [PdCl-{PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}]Cl in which the E,Z-azine diphosphine was a terdentate P,P-, N-ligand. The isomeric neutral complex [PdCl₂{PPh₂CH₂C(Buᵗ)=N–N=C(Buᵗ)CH₂PPh₂}] containing a nine-membered chelate ring was not detected probably due to the rapid displacement of the labile chloride ligand by the azine nitrogen. Diphosphine complexes containing nine-membered chelate rings are rare; for example, attempts to prepare chelates of Ph₂P(CH₂)₆PPh₂ with palladium gave only binuclear or polynuclear complexes with the diphosphine bridging two metal atoms [6]. In the present paper we describe the synthesis of a cationic 2-methylallylpalladium(II) complex in which the E,Z-isomer of the diphosphine 1 forms a nine-membered chelate ring.

2. Experimental

The apparatus used and general techniques were the same as in other recent publications from this laboratory [7]. The

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azine diphosphine 1 [1] and [{(η^3-2–MeC$_3$H$_4$)PdCl}$_2$] [8] were prepared according to published procedures.

2.1. [(η^3-2–MeC$_3$H$_4$)Pd{PPh$_2$CH$_2$C(Bu^t)=N–N=C(Bu^t)-CH$_2$PPh$_2$}]Cl (2a)

A solution of the azine diphosphine 1 (1.57 g, 2.8 mmol) in ethanol (70 cm^3) was added to a warm solution of [{(η^3-2–MeC$_3$H$_4$)PdCl}$_2$] (0.55 g, 1.4 mmol) in ethanol. After 30 min ethanol was removed under reduced pressure and the residue was then dissolved in benzene and iso-octane added. The required product 2a precipitated as a white powder. Yield: 1.58 g, 74%. An analytical sample was obtained by crystallisation from MeOH/Et$_2$O. Anal. Found: C, 62.2; H, 6.7; Cl, 4.5, N, 3.25. Calc. for C$_{40}$H$_{49}$ClN$_2$P$_2$Pd · 1.0 MeOH: C, 62.05; H, 6.7; Cl, 4.45, N, 3.55%. m/z (FAB): 761 (M+1) and 725 (M–Cl). ^{31}P{^{1}H} NMR (36.2 MHz, CDCl$_3$, 20 °C, relative to 85% H$_3$PO$_4$) (ppm): δ_P 11.8 (d), 15.3 (d), ^2J(PP) = 40 Hz. ^{1}H NMR (100 MHz, CDCl$_3$, 20 °C, relative to TMS): δ_H 0.75 (9H, s, Bu^t), 1.45 (9H, s, Bu^t), 1.84 (3H, s, MeC$_3$H$_4$), 2.90 (2H, d, ^2J(PH) = 13.7 Hz, CH$_2$P), 3.63 (4H, br, MeC$_3$H$_4$), 4.63 (2H, d, ^2J(PH) = 9.3 Hz, CH$_2$P). ^{13}C{^{1}H} NMR (62.9 MHz, CD$_2$Cl$_2$, 20 °C, relative to TMS) (ppm): δ_C 23.5 (1C, s, MeC$_3$H$_4$), 27.4 (1C, d, ^1J(PC) = 17.5 Hz, CH$_2$P), 27.9 (3C, s, CMe$_3$), 28.5 (3C, s, CMe$_3$), 36.0 (1C, d, ^1J(PC) = 36.2 Hz, CH$_2$P), 39.1 (1C, s, ^3J(PC) = 2.2 Hz, CMe$_3$), 39.2 (1C, s, ^3J(PC) = 2.7 Hz, CMe$_3$), 75.4 (2C, br, =CH$_2$), 136.7 (1C, t, ^2J(PC) = 5.3 Hz, PdCMe), 173.7 (1C, d, ^2J(PC) = 8.2 Hz, C=N), 174.2 (1C, d, ^2J(PC) = 4.0 Hz, C=N).

2.2. [(η^3-2–MeC$_3$H$_4$)Pd{PPh$_2$CH$_2$C(Bu^t)=N–N=C(Bu^t)-CH$_2$PPh$_2$}]PF$_6$ (2b)

To a solution containing the azine diphosphine 1 (114 mg, 0.2 mmol) and [{η^3-2–MeC$_3$H$_4$)PdCl}$_2$] (40 mg, 0.1 mmol) in hot ethanol (1.5 cm^3) was added an excess of NH$_4$PF$_6$ (50 mg) in ethanol (1 cm^3). The required product 2b precipitated as a white solid. Yield: 149 mg, 85%. Anal. Found: C, 54.65; H, 5.7; N, 3.05. Calc. for C$_{40}$H$_{49}$F$_6$N$_2$P$_3$Pd · 0.5EtOH: C, 55.0; H, 5.85; N, 3.15%. m/z (FAB): 725 (M–PF$_6$). ^{31}P{^{1}H} NMR (36.2 MHz, CD$_2$Cl$_2$, 20 °C, relative to 85% H$_3$PO$_4$) (ppm): δ_P 11.3 (d), 14.8 (d), ^2J(PP) = 40 Hz. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, –30°C): δ_H 0.70 (9H, s, Bu^t), 1.48 (9H, s, Bu^t), 1.96 (3H, s, MeC$_3$H$_4$), 2.51 (1H, m, ^2J(HH) = 13.0, ^2J(PH) = 13.7 Hz, CH$_2$P), 2.58 (1H, m, ^2J(HH) = 13.0, ^2J(PH) = 13.7 Hz, CH$_2$P), 2.94 (1H, d, ^3J(PH) = 9.9 Hz, H$_{anti}$), 2.95 (1H, d, ^3J(PH) = 10.3 Hz, H$_{anti}$), 3.52 (1H, br, ^4J(HH) = 2.2 Hz, H$_{syn}$), 3.67 (1H, br, ^4J(HH) = 2.2 Hz, H$_{syn}$), 3.73 (1H, m, ^2J(HH) = 18.5, ^2J(PH) = 9.0 Hz, CH$_2$P), 3.79 (1H, m, ^2J(HH) = 18.5, ^2J(PH) = 9.0 Hz, CH$_2$P). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 20 °C, relative to TMS) (ppm): δ_C 23.6 (1C, s, MeC$_3$H$_4$), 26.8 (1C, d, ^1J(PC) = 18.5 Hz, CH$_2$P), 27.9 (3C, s, CMe$_3$), 28.5 (3C, s, CMe$_3$), 35.6 (1C, d, ^1J(PC) = 37.2 Hz, CH$_2$P), 39.4 (1C, d, ^3J(PC) = 2.1 Hz,

CMe$_3$), 39.8 (1C, d, ^3J(PC) = 2.7 Hz, CMe$_3$), 74.8 (2C, br, =CH$_2$), 137.1 (1C, t, ^2J(PC) = 5.3 Hz, PdCMe), 174.3 (1C, d, ^2J(PC) = 3.8 Hz, C=N), 174.5 (1C, d, ^2J(PC) = 7.6 Hz, C=N).

2.3. Single crystal X-ray diffraction analysis of 2a

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite monochromated molybdenum K_α X-radiation (λ = 71.069 pm). The data-set was corrected for absorption using azimuthal ψ-scans (maximum and minimum transmission factors 0.8863 and 0.9998 respectively).

The structure was determined by heavy atom methods using SHELXS-86 [9] and was refined by full-matrix least-squares (based on F^2) using SHELXL-93 [10]. All data was used in the refinement. One of the t-butyl groups on the azine diphosphine backbone was found to be disordered over two positions. All non-hydrogen atoms were refined with aniso-tropic thermal parameters including those of the methanol solvate molecule. Restraints were applied to the phosphine phenyl groups so each group remained flat with overall C_{2v} symmetry. The methylene hydrogen atoms of the π-allyl group were located on a Fourier difference synthesis and freely refined with isotropic displacement parameters; all other hydrogen atoms were constrained to calculated positions (C–H = 0.95, 0.98 and 0.99 Å for phenyl, methyl and methylene hydrogen atoms, respectively, and O–H = 0.84 Å) with fixed isotropic thermal parameters of $n(U_{eq})$ of the parent non-hydrogen atom where n was 1.5 for methyl and hydroxyl hydrogens and 1.2 for all others. The weighting scheme $w = [\sigma^2(F_o^2) + (0.0508P)^2 + 5.0379P]^{-1}$ (where $P = (F_o^2 + 2F_c^2)/3$) was used. Apart from a small ripple close to the palladium atom, the final Fourier difference synthesis was flat and showed no features of chemical significance (maximum and minimum residual densities 1.030 and -0.862 e Å^{-3}). Final non-hydrogen atomic coordinates are given in Table 1. An ORTEP [11] diagram of 2a is given in Fig. 1.

2.4. Crystal data

C$_{40}$H$_{50}$ClN$_2$P$_2$Pd · CH$_3$OH, 0.76 × 0.46 × 0.34 mm, M = 793.64 (includes solvate molecule), monoclinic, space group $P2_1/n$, a = 10.3449(8), b = 18.457(2), c = 21.705(2) Å, β = 101.140(7)°, V = 4066.2(6) Å^3, Z = 4, D_x = 1.296 g cm^{-3}, μ = 0.633 mm^{-1}, $F(000)$ = 1656.

2.5. Data collection

4.0 < 2θ < 50.0°; scan widths = 1.05° + α-doublet splitting, scan speeds 1.0–8.0° min^{-1} (subject to a fast pre-scan). Number of data collected = 8110; number of unique data, n = 7144; number with F_o > 4.0$\sigma(F_o)$ = 5769; R_{int}(= $\Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$) = 0.0303; R_{sig}(= $\Sigma [\sigma F_o^2] / \Sigma [F_o^2]$) = 0.0259; T = 200 K.
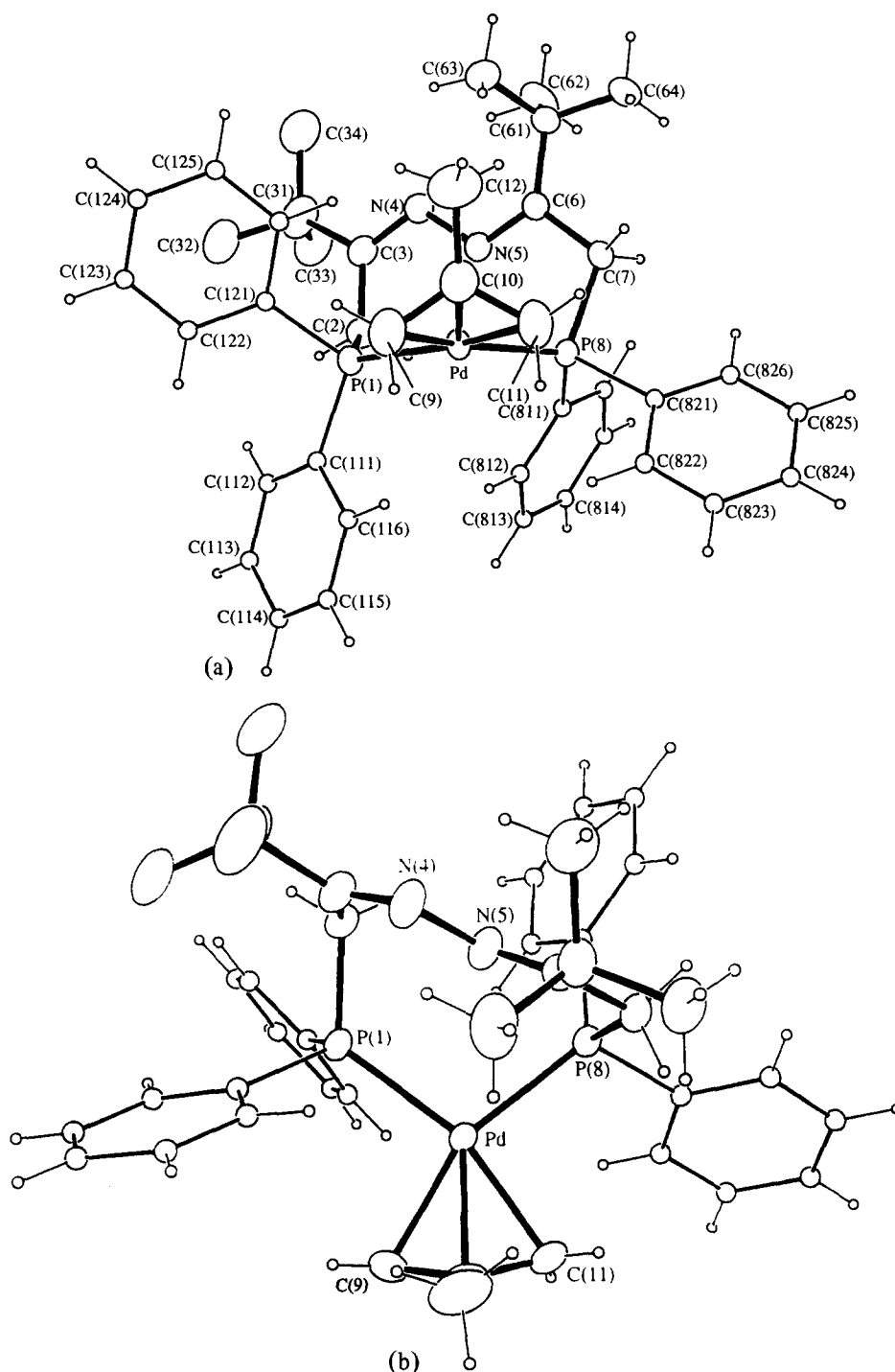
Fig. 1. ORTEP representation of the cation of **2a** viewed (a) perpendicular to the π-2-methylallyl group, and (b) perpendicular to the coordination plane of the palladium atom. Ellipses are shown at the 50% probability level. In the interests of clarity both phenyl carbon atoms and hydrogen atoms are drawn as circles each with an arbitrary small radius.

2.6. Structure refinement

Number of parameters, $p = 483$; $R_1(=\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0495$; $wR_2(=(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}) = 0.0969$; goodness of fit s ($=\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}) = 1.059$; max. $\Delta/\sigma = 0.43$, mean $\Delta/\sigma = 0.01$.

3. Results and discussion

Treatment of the azine diphosphine **1** [1] with 0.5 equiv. of [{(η^3-2-MeC$_3$H$_4$)PdCl}$_2$] in ethanol gave the cationic allylpalladium(II) chloride salt **2a** as a white solid in 74% yield. The corresponding PF$_6$ salt **2b** was prepared in 85%

Table 1

Fractional non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$) for 2a with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} [a]
Pd(1)	3961.0(2)	1385.47(12)	959.92(11)	21.11(8)
Cl⁻	7866.5(11)	333.8(5)	1623.4(5)	49.4(2)
P(1)	4390.2(8)	2578.1(4)	1295.2(4)	23.0(2)
C(111)	5816(3)	2664(2)	1930.9(14)	25.6(6)
C(112)	6116(3)	3299(2)	2279(2)	33.9(8)
C(113)	7167(4)	3317(2)	2785(2)	41.1(9)
C(114)	7932(4)	2703(2)	2943(2)	46.5(10)
C(115)	7665(4)	2076(2)	2594(2)	45.8(10)
C(116)	6603(3)	2057(2)	2089(2)	34.2(8)
C(121)	4711(3)	3146(2)	650.2(15)	30.0(7)
C(122)	5752(4)	3628(2)	702(2)	45.6(9)
C(123)	5897(5)	4051(2)	188(2)	61.6(13)
C(124)	5019(5)	3995(2)	−372(2)	59.6(13)
C(125)	4002(5)	3509(2)	−433(2)	54.2(11)
C(126)	3844(4)	3080(2)	74(2)	41.8(9)
P(8)	2450.7(7)	931.6(4)	1522.0(4)	21.3(2)
C(811)	2365(3)	1268(2)	2302.2(14)	23.7(6)
C(812)	3542(3)	1466(2)	2695(2)	31.3(7)
C(813)	3561(4)	1639(2)	3319(2)	37.8(8)
C(814)	2421(4)	1621(2)	3554(2)	37.9(8)
C(815)	1242(4)	1432(2)	3164(2)	38.7(8)
C(816)	1213(3)	1255(2)	2541(2)	33.3(7)
C(821)	2671(3)	−40(2)	1695.8(14)	27.7(7)
C(822)	3946(4)	−312(2)	1829(2)	40.8(9)
C(823)	4155(5)	−1046(2)	1968(2)	57.7(12)
C(824)	3110(5)	−1504(2)	1967(2)	54.7(11)
C(825)	1843(4)	−1237(2)	1840(2)	45.1(10)
C(826)	1613(4)	−504(2)	1708(2)	34.5(8)
C(2)	3123(3)	3096(2)	1605.2(14)	25.9(7)
C(3)	1937(3)	3351(2)	1134(2)	30.8(7)
C(31)	1706(5)	4167(2)	1005(2)	57.5(8)
C(32)	2978(7)	4586(4)	942(4)	56.4(11)
C(33)	1185(8)	4472(4)	1582(4)	58.1(11)
C(34)	735(9)	4269(4)	367(4)	65.9(12)
C(32')	2942(11)	4624(5)	1310(6)	60.4(12)
C(33')	475(11)	4387(5)	1226(6)	57.6(12)
C(34')	1522(14)	4288(6)	271(5)	61.5(12)
N(4)	1027(3)	2922.3(14)	864.5(14)	33.5(6)
N(5)	1272(3)	2195.1(14)	1057.6(13)	28.8(6)
C(6)	479(3)	1717(2)	770.0(14)	24.4(6)
C(61)	−691(3)	1829(2)	230(2)	30.5(7)
C(62)	−1698(4)	2328(2)	447(2)	51.0(11)
C(63)	−199(4)	2169(2)	−332(2)	48.3(10)
C(64)	−1367(3)	1106(2)	11(2)	38.7(8)
C(7)	801(3)	963(2)	1031.1(14)	25.1(6)
C(9)	5310(4)	1383(2)	306(2)	38.8(9)
C(10)	4249(4)	936(2)	60(2)	34.8(8)
C(11)	3996(4)	375(2)	461(2)	38.9(9)
C(12)	3286(5)	1118(3)	−526(2)	59.1(12)
C(1s)	7707(5)	5121(3)	1780(2)	68.5(13)
O(1s)	6465(3)	5238(2)	1913(2)	66.2(9)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} matrix.

yield, by adding an excess of NH_4PF_6 to a mixture of 1 and $[\{\eta^3\text{-}2\text{-}MeC_3H_4)PdCl\}_2]$ in ethanol, (Scheme 1). These complexes were characterised by microanalyses and by proton, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectroscopy, and the molecular structure of 2a was determined by an X-ray crystal structure determination (Fig. 1, see below). The $^{31}P\{^1H\}$ NMR spectra
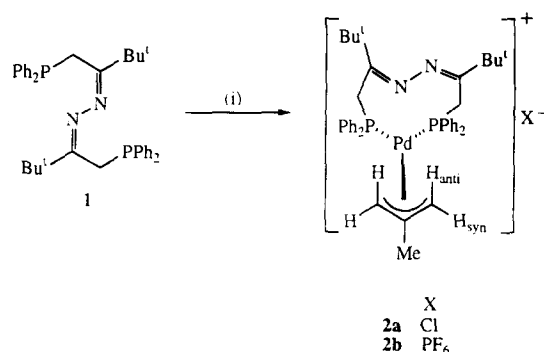
Scheme 1. (i) For 2a, 0.5 equiv. $[\{(2\text{-}MeC_3H_4)PdCl\}_2]$; for 2b, 0.5 equiv. $[\{(2\text{-}MeC_3H_4)PdCl\}_2]/NH_4PF_6$.

of 2a or 2b showed AB-patterns with $^2J(PP) = 40$ Hz suggesting that the PPh$_2$ groups were mutually cis. In the $^{13}C\{^1H\}$ NMR spectra, the resonances at $\delta \sim 24$ (s), ~ 75 (br) and ~ 137 (t, $^2J(PC) = 5.3$ Hz) are assigned to the 2-MeC_3H_4, $=CH_2$ and PdCMe carbons, respectively [12]. At room temperature (20 °C) the allylic proton resonances are broad probably due to the rapid rotation of the allyl group, and the methylene protons of each CH$_2$P group are equivalent because of the rapid ring inversion of the nine-membered chelate ring. We studied the ^1H and $^1H\{^{31}P\}$ NMR spectra of 2b at different temperatures (see Fig. 2) and found that the proton NMR spectra at 243 K correspond to the slow exchange limit. At this temperature all four CH$_2$P protons are non-equivalent (as found in the X-ray structure), in the $^1H\{^{31}P\}$ NMR spectrum each pair of the methylene protons (CH$_2$P) shows two AB-patterns with geminal proton–proton couplings of 13.0 and 18.5 Hz. The two doublets at δ 2.94 ($^3J(PH) = 9.9$ Hz) and 2.95 ($^3J(PH) = 10.3$ Hz) are assigned to the two anti-protons of the methylallyl group [13,14] whilst the two syn-protons appeared as broad peaks at δ 3.52 and 3.67 with $^4J(H_{syn}H_{syn}) = 2.2$ Hz [14] (the $^3J(PH)$ values were not resolved).

3.1. Crystal structure of $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)Pd\{PPh_2\text{-}CH_2C(Bu^t)=N\text{-}N=C(Bu^t)CH_2PPh_2\}]Cl$ (2a)

The 2-methylallylpalladium(II)-azine diphosphine complex 2a was crystallised from methanol/diethyl ether as monoclinic orange prisms in the space group $P2_1/n$. The molecular structure of 2a is shown in Fig. 1 with atom coordinates in Table 1, and selected bond lengths and angles in Table 2. The bond lengths are quite normal as found in the azine phosphine ligands [1–5] and allylpalladium(II) complexes [15–18] i.e. there is an extended conformation as in the chromium tricarbonyl complex [3]. The structure showed that the azine diphosphine is chelated to the palladium forming a nine-membered ring in which the CH–C=N–N=C–CH moiety is essentially planar. The allyl group is bonded to the palladium atom in an η^3-fashion occupying two coordination sites in a distorted square-planar coordination sphere. The central carbon C(10) is above the plane P–Pd–P and the other
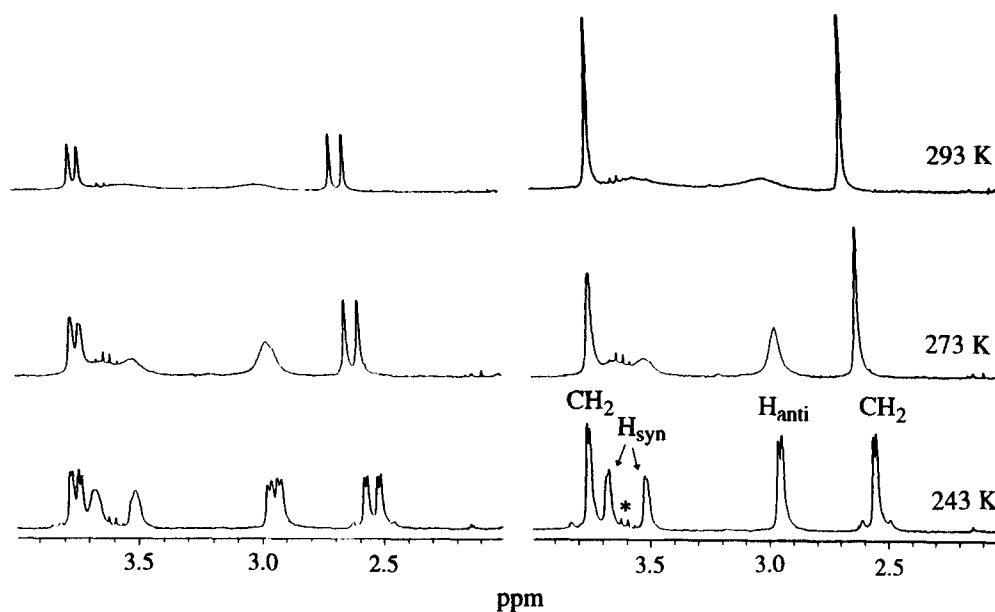
Fig. 2. ^{1}H (left) and ^{1}H{^{31}P} (right) NMR spectra for the two CH$_2$ groups, and H$_{anti}$ and H$_{syn}$ protons of the complex **2b** in CD$_2$Cl$_2$ at different temperatures (243 to 293 K). The peaks marked with an asterisk (*) arise from EtOH.

Table 2
Selected bond lengths (Å) and angles (°) for **2a** with e.s.d.s in parentheses

Pd(1)–C(11)	2.159(3)	Pd(1)–C(9)	2.175(3)
Pd(1)–C(10)	2.194(3)	Pd(1)–P(8)	2.3168(8)
Pd(1)–P(1)	2.3339(8)		
P(1)–C(2)	1.851(3)	P(8)–C(7)	1.830(3)
C(2)–C(3)	1.513(4)	C(3)–N(4)	1.281(4)
C(3)–C(31)	1.543(5)	N(4)–N(5)	1.414(4)
N(5)–C(6)	1.282(4)	C(6)–C(7)	1.516(4)
C(6)–C(61)	1.528(4)		
C(9)–C(10)	1.395(5)	C(10)–C(11)	1.408(5)
C(10)–C(12)	1.494(5)		
C(11)–Pd(1)–C(9)	66.2(2)	C(11)–Pd(1)–C(10)	37.73(14)
C(9)–Pd(1)–C(10)	37.23(14)	C(11)–Pd(1)–P(8)	91.73(11)
C(9)–Pd(1)–P(8)	157.85(11)	C(10)–Pd(1)–P(8)	123.57(10)
C(11)–Pd(1)–P(1)	161.78(11)	C(9)–Pd(1)–P(1)	95.63(11)
C(10)–Pd(1)–P(1)	125.73(10)	P(8)–Pd(1)–P(1)	106.49(3)
C(2)–P(1)–Pd(1)	119.69(10)	C(7)–P(8)–Pd(1)	109.27(10)
C(3)–C(2)–P(1)	117.0(2)	N(4)–C(3)–C(2)	123.0(3)
N(4)–C(3)–C(31)	116.5(3)	C(2)–C(3)–C(31)	120.2(3)
C(3)–N(4)–N(5)	112.1(3)	C(6)–N(5)–N(4)	116.6(3)
N(5)–C(6)–C(7)	112.1(3)	N(5)–C(6)–C(61)	128.2(3)
C(6)–C(7)–P(8)	111.1(2)		
C(10)–C(9)–Pd(1)	72.1(2)	C(9)–C(10)–C(11)	115.2(4)
C(9)–C(10)–C(12)	122.5(4)	C(11)–C(10)–C(12)	121.2(4)
C(9)–C(10)–Pd(1)	70.6(2)	C(11)–C(10)–Pd(1)	69.8(2)
C(12)–C(10)–Pd(1)	119.3(3)	C(10)–C(11)–Pd(1)	72.5(2)

two terminal carbons C(9) and C(11) are below the plane. The three carbon atoms bonded to palladium are approximately equidistant from the palladium (2.175(3), 2.194(3) and 2.159(3) Å) and the carbon–carbon bond lengths of the η^3-allyl group are nearly equal (1.395(5) and 1.408(5) Å) as found in other allylpalladium(II) complexes [15–18]. The angle at the central carbon, i.e. C(9)–C(10)–C(11) =

115.2(4)° is slightly larger than the value (112.4°) observed for [{(η^3-2-MeC$_3$H$_4$)Pd(PPh$_3$)Cl}$_2$] [15]. The methyl group on the central carbon C(10) is not in the same plane as the other three carbon atoms and is bent towards the palladium by 0.25°. The Pd–P distances of 2.3168(8) and 2.3339(8) Å are normal for phosphine–palladium complexes [16–18].

Acknowledgements

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