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Crystal and Molecular Structure of Chloro(3-diethylaminopropionyl)[(diethylamino)(methylamino)carbene]palladium(II)

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The crystal and molecular structure of chloro(3-diethylaminopropionyl)[(diethylamino)(methylamino)carbene]palladium(II) (**2**) has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The crystals are monoclinic, space group $P2_1/c$ (No. 14), with eight formula units in a unit cell of dimensions $a = 8.481$ (3) Å, $b = 28.223$ (8) Å, $c = 14.626$ (4) Å, and $\beta = 91.295$ (5)°. The structure was refined by full-matrix least-squares methods to an R value of 0.037 ($R_w = 0.042$) for 4093 independent reflections with $F^2 > 3\sigma(F^2)$. The asymmetric unit contains two independent monomeric molecules (**2a** and **2b**), each of which exhibits approximately square-planar coordination geometry about the palladium(II) ion. In each case, the chloride ion is bonded in a trans configuration with respect to the σ-bonded acyl carbon atom. The competition between the two very powerful σ donors (Pd–C(acyl) = 1.988 (6) and 2.005 (7) Å in molecules **2a** and **2b**, respectively; Pd–C(carbene) = 2.010 (5) and 2.020 (5) Å), together with the strong trans influences of the σ-bonded carbon atoms, results in the formation of unusually long bonds from palladium to nitrogen (Pd–N = 2.175 (4), 2.181 (5) Å) and chlorine (Pd–Cl^- = 2.464 (2), 2.457 (2) Å) ligand atoms in this compound.

Introduction

Recent synthetic studies in these laboratories have yielded a variety of β-aminoacylpalladium(II) complexes.[1] These novel compounds, which are synthesized by successive amination and carbonylation reactions from palladium–olefin complexes, have been shown to possess a wide range of reactivity, with facile oxidative cleavage giving β-amino acid derivatives and ligand exchange giving a variety of palladium(II) complexes.[2] In addition, certain members of this group of compounds have shown some anticancer activity in preliminary screenings (see below).

Our previous structural study[2] of one of these parent β-aminoacyl compounds, chloro(3-diethylaminopropionyl)(diethylamino)palladium(II) (species **1**), demonstrated that the Pd–C(acyl) bond in these compounds was of unusual strength compared to other Pd–C(sp^2) bonds. The strength of this bond is reflected in the chemistry of these β-aminoacyl complexes, as the very stable palladium–acyl moiety survives a wide variety of reaction conditions which allow replacement or exchange of the other ligands bound to the metal. One such reaction of **1**, with 1 equiv of methyl isocyanide in THF, produces the carbenoid complex which is the subject of the present structural study, chloro(3-diethylaminopropionyl)[(diethylamino)(methylamino)carbene]palladium(II) (species **2**), by a well-established route[3] involving displacement of diethylamine by CH_3NC and subsequent nucleophilic attack by Et_2NH on the coordinated isocyanide. The presence of the carbene ligand as a second powerful σ donor in the coordination sphere of the palladium(II) ion in **2** is expected to perturb the bonding from the metal to the remaining ligands significantly. To ascertain the nature and magnitude of these expected changes in bonding pattern, a single-crystal x-ray structural investigation of **2** was undertaken.

Experimental Section

The synthesis, spectroscopic characterization, and microanalytical results for the title compound have been previously described.[2]

Crystal Data. For Pd($C_{13}H_{28}N_3O$)Cl: mol wt 384.2; monoclinic, $a = 8.481$ (3) Å, $b = 28.223$ (8) Å, $c = 14.626$ (4) Å, $\beta = 91.295$ (5)°, $V = 3500$ Å^3; $\rho_{\text{calcd}} = 1.46$ g cm^{-3}; $Z = 8$; $F(000) = 1584$; space group $P2_1/c$; Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 11.8 cm^{-1}.

Data Collection and Reduction. Examination of the pale yellow crystals of the title compound by Weissenberg and precession photography revealed only Laue symmetry $2/m$ and the following conditions for observation of reflections: $h0l$, $l = 2n$; $0k0$, $k = 2n$. These observed conditions are consistent only with the space group $P2_1/c$ (No. 14).[4]

The crystal chosen for data collection was mounted on the Enraf–Nonius CAD-3 diffractometer, with the a axis approximately coincident with the diffractometer ϕ axis. After accurate centering, the orientation matrix for data collection and the unit-cell parameters reported above were obtained from least-squares calculations on the automatically determined[5] 2θ, χ, and ϕ settings of 43 reflections (at ambient temperature, 20 ±1 °C) with 2θ values in the range 20–24°. No measured density is reported, due to the propensity of the crystals toward dissolution and/or decomposition in the aqueous or halocarbon solvents which were employed in the attempted density determinations.

The intensities of all reflections for which $4.5° < \theta < 25°$ and h, $k \geq 0$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. At lower θ values, it was possible for reflections to be cut off on the low-θ side by the beam stop. The scan range employed was 0.4° (in θ) to either side of the calculated Kα position, at a constant scan rate of 10° min^{-1}. The number of times a given reflection was scanned varied according to the intensity, with weak reflections being scanned a maximum of four times. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and zirconium-foil attenuators were inserted automatically (to avoid coincidence losses) if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of three reference reflections ($15\bar{7}$, 402, 460) was measured every 25 reflections. These control reflections showed no significant or systematic changes in intensity during the course of data collection.

Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter, g, in the formula used for the standard deviation in the intensity[6,7] was taken to be 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were judged to be observed, and the 4093 reflections (of 6131 independent reflections measured) which met this criterion were employed in the solution and refinement of the structure. Due to the data crystal's small size (roughly 0.18 × 0.20 × 0.35 mm) and low absorption coefficient for MoKα radiation, no absorption correction was applied to the data.

With eight molecules in the unit cell, each asymmetric unit was required to contain two crystallographically independent palladium(II) atoms in general positions. The positions of these metal ions were assigned from a sharpened, origin-removed Patterson map, and initial positions for all nonhydrogen atoms of both molecules were then obtained from a Fourier synthesis phased by the metal ions. Scattering factors for palladium(II), oxygen, nitrogen, carbon, and the chloride ion were taken from ref 8. Scattering factors for spherically bonded hydrogen atoms[9] were also taken from ref 8, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to palladium and chlorine.

The first pair of cycles of isotropic refinement on all nonhydrogen atoms provided satisfactory refinement for all atoms, with the exception of the aliphatic carbon atom (C2) adjacent to the acyl carbon atom of molecule **2a** and the terminal carbon atom (C8) of one of the ethyl groups of the 3-diethylaminopropionyl moiety of molecule **2b**. Examination of a difference Fourier synthesis at this point clearly indicated the presence of disorder for these atoms, with two fractionally occupied sites being suggested for each atom. Pairs of atoms with population parameters equal to 0.5 were placed at the suggested sites, and isotropic refinement was carried to convergence, with the population parameters of the disordered atoms being allowed to vary along with the positional and isotropic thermal parameters. At this

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Table I. Atomic Coordinates (Fractional)[a]

Atom	*x*	*y*	*z*
		Molecule **2a**	
Pd(II)	0.47121 (5)	0.01024 (1)	−0.22982 (3)
Cl⁻	0.67116 (16)	−0.00780 (5)	−0.34419 (9)
C1	0.3238 (8)	0.0224 (2)	−0.1288 (4)
C2	0.4083 (18)	0.0567 (5)	−0.0588 (8)
C2′	0.3577 (37)	0.0716 (11)	−0.0988 (18)
C3	0.5157 (9)	0.0903 (3)	−0.1008 (6)
C4	0.3284 (6)	−0.0404 (2)	−0.2811 (3)
C5	0.7535 (8)	0.0448 (2)	−0.1275 (4)
C6	0.8718 (9)	0.0768 (3)	−0.0782 (5)
C7	0.6625 (9)	0.1028 (2)	−0.2389 (5)
C8	0.5346 (11)	0.1197 (2)	−0.3029 (6)
C9	0.4200 (7)	−0.0982 (2)	−0.1652 (4)
C10	0.2293 (7)	0.0155 (2)	−0.3962 (4)
C11	0.1044 (8)	0.0471 (2)	−0.3576 (5)
C12	0.1283 (6)	−0.0670 (2)	−0.3978 (4)
C13	0.2097 (8)	−0.0939 (2)	−0.4713 (4)
N1	0.6103 (5)	0.0679 (2)	−0.1713 (3)
N2	0.3283 (5)	−0.0844 (1)	−0.2467 (3)
N3	0.2325 (5)	−0.0316 (1)	−0.3531 (3)
O1	0.2134 (6)	0.0020 (2)	−0.1066 (3)
H1C2	0.3333	0.0736	−0.0271
H2C2	0.4709	0.0378	−0.0175
H1C2′	0.2887	0.0916	−0.1325
H2C2′	0.3245	0.0727	−0.0347
H1C3	0.4546	0.1151	−0.1277
H2C3	0.5839	0.1031	−0.0548
H1C5	0.8078	0.0287	−0.1742
H2C5	0.7171	0.0224	−0.0842
H1C6	0.9417	0.0579	−0.0419
H2C6	0.9298	0.0939	−0.1221
H3C6	0.8171	0.0982	−0.0402
H1C7	0.7429	0.0887	−0.2740
H2C7	0.7047	0.1294	−0.2069
H1C8	0.4712	0.1422	−0.2724
H2C8	0.5805	0.1340	−0.3547
H3C8	0.4714	0.0935	−0.3218
H1C9	0.4227	−0.1318	−0.1610
H2C9	0.5243	−0.0863	−0.1696
H3C9	0.3720	−0.0854	−0.1126
H1C10	0.2092	0.0117	−0.4599
H2C10	0.3293	0.0301	−0.3868
H1C11	0.1323	0.0549	−0.2961
H2C11	0.0967	0.0752	−0.3931
H3C11	0.0061	0.0309	−0.3593
H1C12	0.0396	−0.0511	−0.4241
H2C12	0.0939	−0.0887	−0.3529
H1C13	0.2743	−0.1178	−0.4441
H2C13	0.1329	−0.1081	−0.5108
H3C13	0.2731	−0.0728	−0.5052
H1N2	0.2655	−0.1078	−0.2768
		Molecule **2b**	
Pd(II)	0.03147 (5)	0.18804 (1)	0.16430 (3)
Cl⁻	−0.15978 (16)	0.19097 (5)	0.28769 (10)
C1	0.1744 (8)	0.1809 (2)	0.0580 (4)
C2	0.0875 (11)	0.1991 (3)	−0.0272 (5)
C3	−0.0070 (10)	0.2437 (3)	−0.0035 (6)
C4	0.1741 (6)	0.1464 (2)	0.2421 (3)
C5	−0.2567 (9)	0.2121 (3)	0.0525 (5)
C6	−0.3665 (38)	0.2303 (7)	−0.0224 (22)
C6′	−0.3818 (43)	0.2517 (10)	0.0033 (28)
C7	−0.1437 (11)	0.2817 (3)	0.1210 (7)
C8	−0.0172 (12)	0.3057 (3)	0.1687 (7)
C9	0.0669 (6)	0.0749 (2)	0.1681 (4)
C10	0.2847 (7)	0.2169 (2)	0.3133 (4)
C11	0.4087 (9)	0.2389 (2)	0.2546 (5)
C12	0.3785 (6)	0.1379 (2)	0.3652 (4)
C13	0.3013 (8)	0.1283 (3)	0.4553 (4)
N1	−0.1057 (6)	0.2346 (2)	0.0740 (3)
N2	0.1664 (5)	0.0997 (1)	0.2353 (3)
N3	0.2745 (5)	0.1653 (1)	0.3031 (3)
O1	0.2983 (6)	0.1636 (2)	0.0548 (3)
H1C2	0.1617	0.2067	−0.0727
H2C2	0.0177	0.1754	−0.0500
H1C3	0.0638	0.2688	0.0109
H2C3	−0.0715	0.2525	−0.0547
H1C5	−0.3147	0.2126	0.1072
H2C5	−0.2333	0.1802	0.0368
H1C7	−0.2237	0.2756	0.1640
H2C7	−0.1840	0.3027	0.0753
H1C8	0.0108	0.2884	0.2224
H2C8	0.0710	0.3078	0.1301
H3C8	−0.0508	0.3367	0.1849
H1C9	−0.0180	0.0950	0.1496
H2C9	0.1279	0.0670	0.1166
H3C9	0.0267	0.0469	0.1948
H1C10	0.3091	0.2241	0.3755
H2C10	0.1853	0.2304	0.2969
H1C11	0.5091	0.2265	0.2719
H2C11	0.3860	0.2317	0.1923
H3C11	0.4084	0.2723	0.2630
H1C12	0.4731	0.1552	0.3761
H2C12	0.4030	0.1085	0.3371
H1C13	0.2770	0.1576	0.4837
H2C13	0.2071	0.1107	0.4447
H3C13	0.3715	0.1107	0.4936
H1N2	0.2292	0.0812	0.2764

[a] Estimated standard deviations in parentheses. If no standard deviation is given, the parameter was not refined.

point, the population parameters of the disordered pairs of atoms were frozen for the remainder of the refinement, with the resultant population parameters being for C2 0.63, for C2′ 0.37, for C6 0.57, and for C6′ 0.43. Because of computer limitations, the full-matrix least-squares refinement[10] (on *F*) was carried out in two large blocks. On cycle A, the scale factors, all atoms of molecule **2a**, and the palladium and chlorine atoms of molecule **2b** were refined, with anisotropic thermal parameters for all atoms. Each cycle B was exactly the reverse of cycle A with respect to molecules **2a** and **2b**. Hydrogen atoms were included in the model when they could be clearly discerned in a difference Fourier map based on the converged isotropic model. The hydrogen atoms located were placed in fixed, idealized positions 0.95 Å from carbon, with isotropic thermal parameters 1 Å^2 larger than that of the atom to which they were attached. Four repetitions of the A–B sequence of cycles resulted in convergence of the model, with the final value of R ($=\sum||F_o| - |F_c||/\sum|F_o|$) being 0.037 and R_w ($=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) being 0.042. The error in an observation of unit weight was 1.19. On the final pair of cycles, only the disordered pairs of atoms exhibited shifts in positional and thermal parameters significantly greater than 10% of the estimated standard deviations (ranging in a few cases up to approximately 100% of the esd's for these disordered atoms). The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection ($=4F_o^2/\sigma^2(F_o^2)$). Correction for secondary extinction was not deemed necessary. In the final difference Fourier electron density map peaks of 1.2 e Å^{-3} were found in the vicinity of the two Pd(II) ions with all other peaks well below this value. The deepest trough in this map was −0.6 e Å^{-3}.

Final atomic positional parameters are listed in Table I, while Table II lists the anisotropic thermal parameters obtained for the nonhydrogen atoms.

Results and Discussion

Table III contains bond lengths and angles for each of the two independent molecules (**2a** and **2b**) of the title compound **2**, while a perspective view of molecule **2a**, together with the numbering scheme applied to these species, is displayed in Figure 1.

Conversion of the parent species **1** to **2**, the chloro(β-aminoacyl)carbenepalladium(II) derivative, has clearly not

Table II. Anisotropic Thermal Parameters[a]

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
			Molecule **2a**			
Pd(II)	42.0 (2)	39.8 (4)	36.8 (2)	−4.5 (2)	−1.8 (2)	−1.7 (2)
Cl^-	55.7 (8)	50.1 (8)	49.2 (8)	−0.2 (8)	7.8 (6)	1.0 (8)
C1	64 (4)	58 (4)	49 (3)	−8 (3)	−3 (4)	−15 (3)
C2	92 (9)	66 (8)	44 (8)	9 (8)	12 (6)	−22 (7)
C2′	148 (24)	119 (21)	52 (18)	61 (17)	26 (15)	−7 (14)
C3	73 (5)	94 (4)	109 (6)	−22 (4)	22 (5)	−46 (4)
C4	38 (3)	49 (4)	34 (3)	−4 (3)	1 (2)	−2 (2)
C5	66 (4)	75 (4)	75 (4)	−12 (4)	−11 (4)	−12 (4)
C6	86 (5)	122 (8)	102 (6)	−13 (5)	−31 (4)	−30 (4)
C7	99 (5)	56 (4)	79 (4)	−24 (4)	−3 (4)	−8 (4)
C8	151 (8)	55 (4)	127 (7)	−10 (5)	−34 (6)	22 (4)
C9	61 (4)	59 (4)	42 (3)	−6 (2)	−9 (2)	12 (2)
C10	55 (4)	57 (4)	53 (3)	−3 (3)	−12 (2)	13 (2)
C11	83 (5)	60 (4)	85 (4)	15 (4)	−15 (4)	10 (4)
C12	48 (3)	60 (4)	49 (3)	−7 (2)	−13 (3)	−1 (2)
C13	79 (4)	65 (4)	53 (3)	3 (3)	−17 (3)	−9 (2)
N1	55 (3)	47 (4)	50 (3)	−7 (2)	−2 (4)	−6 (2)
N2	47 (3)	42 (4)	41 (2)	−5 (3)	−6 (2)	1 (2)
N3	46 (3)	45 (4)	42 (2)	−4 (3)	−8 (2)	4 (2)
O1	85 (4)	117 (4)	90 (3)	−39 (4)	37 (3)	−39 (2)
			Molecule **2b**			
Pd(II)	42.1 (2)	40.7 (4)	47.6 (2)	4.4 (2)	−2.5 (1)	7.4 (2)
Cl^-	53.4 (8)	55.8 (8)	55.5 (8)	1.6 (7)	1.8 (6)	−2.2 (6)
C1	61 (4)	57 (4)	71 (4)	13 (2)	−1 (2)	15 (2)
C2	141 (7)	94 (4)	54 (4)	2 (4)	14 (5)	16 (4)
C3	95 (6)	153 (8)	111 (6)	19 (5)	9 (4)	77 (6)
C4	37 (3)	47 (4)	40 (3)	4 (2)	0 (2)	2 (2)
C5	75 (5)	112 (4)	99 (5)	−21 (4)	−21 (4)	48 (4)
C6	91 (12)	86 (16)	99 (16)	16 (10)	−46 (11)	28 (12)
C6′	53 (13)	115 (25)	104 (22)	1 (15)	−33 (13)	−42 (18)
C7	122 (7)	71 (4)	160 (8)	25 (4)	−28 (7)	26 (6)
C8	140 (8)	66 (4)	155 (8)	9 (4)	−2 (11)	−12 (6)
C9	54 (4)	53 (4)	63 (3)	3 (2)	−8 (3)	−8 (2)
C10	61 (4)	52 (4)	83 (4)	9 (3)	−21 (3)	−16 (4)
C11	88 (5)	67 (4)	105 (6)	−15 (3)	−11 (4)	6 (4)
C12	45 (3)	66 (4)	54 (3)	12 (2)	−16 (3)	3 (2)
C13	88 (5)	103 (4)	55 (4)	6 (4)	−6 (4)	6 (4)
N1	51 (3)	57 (4)	73 (3)	1 (2)	−7 (3)	30 (2)
N2	44 (3)	39 (4)	50 (2)	5 (2)	−6 (2)	7 (2)
N3	43 (3)	43 (4)	52 (3)	6 (2)	−4 (2)	−2 (2)
O1	82 (4)	146 (4)	85 (3)	34 (3)	21 (3)	20 (4)

[a] Estimated standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

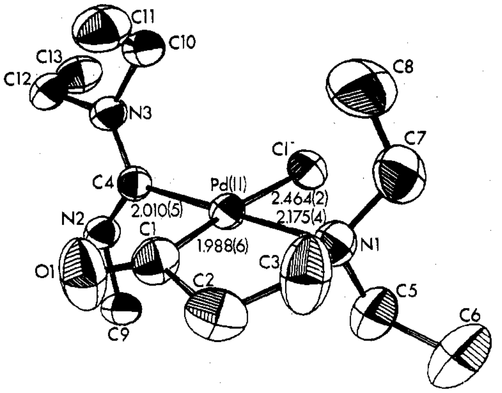

Figure 1. Perspective view of the carbenoid–palladium complex **2a**. Hydrogen atoms are not included, and 50% probability ellipsoids are depicted.

altered the relative positions of the ligands in the essentially square-planar (see Tables III, IV) coordination environment. The chloro ligand is found to be trans to the coordinated acyl group, as was the case in compound **1**, and the (methylamino)(diethylamino)carbene moiety occupies the position originally occupied by the diethylamine ligand in the parent complex **1**, trans to the amino nitrogen of the bidentate β-aminoacyl ligand. The detailed aspects of the bonding about the palladium(II) ions in the two crystallographically independent molecules (bond lengths, angles, least-squares planes (see Table IV), etc.) are found to be generally equivalent within experimental error. The only significant exceptions to this overall equivalency lie in those regions of the two molecules where disorder was found to play an important role in the structure. In the following discussion, when bond lengths or angles are quoted for this compound, two values will be given, with the first referring to molecule **2a** and the second to molecule **2b**.

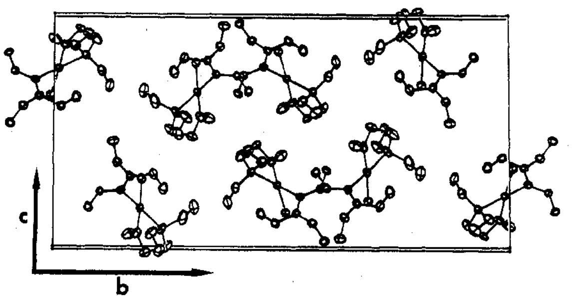

Figure 2. [100] projection showing carbenoid–palladium packing in the unit cell.

Table III. Bond Lengths (Å) and Angles (deg)[a]

(a) Bond Lengths

	Molecule **2a**	Molecule **2b**
Pd(II)-C1	1.988 (6)	2.005 (7)
Pd(II)-C4	2.010 (5)	2.020 (5)
Pd(II)-N1	2.175 (4)	2.181 (5)
Pd(II)-Cl$^-$	2.464 (2)	2.457 (2)
C1-C2	1.57 (1), 1.48 (3)[b]	1.53 (1)
C1-O1	1.153 (8)	1.161 (9)
C2-C3	1.46 (2), 1.44 (3)[b]	1.54 (1)
C3-N1	1.465 (9)	1.449 (11)
N1-C5	1.510 (8)	1.459 (9)
N1-C7	1.471 (8)	1.534 (10)
C5-C6	1.52 (1)	1.51 (3), 1.69 (3)[b]
C7-C8	1.50 (1)	1.44 (1)
C4-N2	1.339 (6)	1.325 (6)
C4-N3	1.340 (6)	1.331 (6)
N2-C9	1.462 (7)	1.459 (7)
N3-C10	1.470 (7)	1.468 (7)
N3-C12	1.477 (7)	1.472 (7)
C10-C11	1.505 (9)	1.507 (10)
C12-C13	1.499 (8)	1.510 (9)

(b) Bond Angles

	Molecule **2a**	Molecule **2b**
C1-Pd(II)-C4	90.9 (2)	90.8 (2)
C1-Pd(II)-N1	85.6 (2)	85.1 (2)
C1-Pd(II)-Cl$^-$	174.7 (2)	174.5 (2)
C4-Pd(II)-N1	175.8 (2)	175.3 (2)
C4-Pd(II)-Cl$^-$	91.0 (1)	90.1 (1)
N1-Pd(II)-Cl$^-$	92.7 (1)	94.2 (1)
Pd(II)-C1-O1	130.8 (5)	129.7 (5)
Pd(II)-C1-C2	107.8 (6), 105.1 (12)[b]	108.1 (5)
O1-C1-C2	119.0 (7), 122.5 (13)[b]	122.0 (6)
C1-C2-C3	113.9 (9), 120.7 (21)[b]	109.7 (6)
C2-C3-N1	112.0 (7), 112.4 (12)[b]	110.3 (7)
C3-N1-Pd(II)	107.4 (4)	105.7 (4)
C3-N1-C5	109.5 (5)	115.3 (6)
C3-N1-C7	111.4 (5)	109.2 (6)
C5-N1-Pd(II)	105.6 (3)	108.8 (4)
C5-N1-C7	108.8 (5)	106.4 (6)
C7-N1-Pd(II)	113.9 (4)	111.4 (5)
N1-C5-C6	117.5 (6)	122.1 (12), 110.0 (12)[b]
N1-C7-C8	114.2 (6)	117.6 (8)
Pd(II)-C4-N2	121.6 (3)	120.6 (3)
Pd(II)-C4-N3	120.7 (4)	120.8 (4)
N2-C4-N3	117.6 (4)	118.6 (4)
C4-N2-C9	123.3 (4)	123.6 (4)
C4-N3-C10	120.8 (4)	120.1 (4)
C4-N3-C12	124.6 (4)	124.7 (4)
C10-N3-C12	114.6 (4)	115.2 (4)
N3-C12-C13	112.4 (4)	111.6 (5)
N3-C10-C11	112.4 (5)	113.1 (5)

[a] Estimated standard deviations in parentheses. [b] The two values given refer to the disordered atoms of the model.

Table IV. Least-Squares Planes[a]

(a) Deviations from the Planes

Plane 1 ($n = 5$): Pd1 (−0.051), Cl$^-$ (0.024), C1 (0.062), C4 (−0.105), N1 (−0.076), C2 (0.366), C2′ (−0.453), C3 (−0.220), O1 (0.220)
Plane 2 ($n = 4$): Pd1 (0.000), C4 (0.000), N2 (0.003), N3 (0.034)
Plane 3 ($n = 5$): Pd2 (0.067), Cl$^-$ (−0.035), C1 (−0.041), C4 (0.174), N1 (0.027), C2 (−0.462), C3 (0.239), O1 (0.092)
Plane 4 ($n = 4$): Pd2 (−0.018), C4 (0.006), N2 (−0.009), N3 (−0.001)

(b) Equations of the Planes[b]

Plane	A	B	C	D
1	3.759	−18.454	8.828	−0.396
2	6.128	−7.577	−9.570	5.009
3	4.278	21.985	5.286	5.070
4	6.096	0.853	−10.410	−1.340

(c) Dihedral Angles between Planes

1-2	84.00°	3-4	82.71°

[a] In section (a), numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first n atoms in each case determine the given plane. [b] In the form $Ax + By + Cz = D$.

Unlike the reported structure for compound **1**, in which perfect planarity of the coordination environment was a result of the crystallographic symmetry imposed upon the molecule,[2] the two crystallographically independent molecules of **2** are not subject to any such constraints. As a result, very small deviations of the atoms involved in palladium–ligand binding from the calculated least-squares planes through these atoms are found (see Table IV). Significant deviations from the idealized angles of the square plane are also found in the observed bond angles about palladium(II), in part because of the small chelate "bite" of the β-aminopropionyl ligand (C1–Pd–N1 = 85.6 (2), 85.1 (2)°), as was also found in the structure of the parent complex **1**.[2] Other angles also differ significantly from the ideal angles, however, since if C1 and C4 are said to be in the idealized square-planar positions (C1–Pd–C4 = 90.9 (2), 90.8 (2)°), the chloro ligand is seen to deviate slightly from the expected position relative to C1 (C1–Pd–Cl$^-$ = 174.7 (2), 174.5 (2)°). These small positional deviations from the idealized square-planar coordination positions are presumably due to intermolecular packing interactions in the crystalline lattice, although specific interactions of this type are difficult to discover in the model. Similar deviations have been reported for other nominally square-planar complexes of palladium(II).[11-15]

The carbenoid ligand is strongly bound to the palladium(II) ion (Pd–C4 = 2.010 (5), 2.020 (5) Å), as is readily apparent by comparison of these observed Pd–C(carbene) bond lengths with the expected Pd–C(sp^2) distance of 2.05 Å based on the sum of the σ covalent radii [1.31 Å (Pd(II)) + 0.74 Å (C(sp^2))].[14] The proximity of the observed Pd–C(carbene) distance to this calculated σ-only distance, together with the fact that the carbene ligand adopts a nearly perpendicular orientation relative to the coordination plane, would seem to indicate that π-bonding interaction between the metal and the carbene center is not present in this complex. The Pd–C(carbene) bond lengths observed here are significantly shorter than the Pd–C(carbene) bond length of 2.074 (9) Å seen in 4-[(diethylamino)(*tert*-butylamino)methylene]-4-(*tert*-butyl isocyanide)-2,2,5,5-tetrakis(trifluoromethyl)-1,3,4-dioxapalladolan[15] (although there the carbene is trans to sp^3 carbon, with a strong trans influence). Comparison of the observed Pd–C(carbene) bond length in **2** with known Pt–C(carbene) bond lengths is reasonable, since the Pt–C(sp^2) distance calculated from known bond lengths and σ-only covalent radii for sp^2 carbon is within 0.01 Å (at 2.041 Å) of the expected Pd–C(sp^2) σ-bonding distance mentioned above.[16] The Pd–C(carbene) bond length observed in **2** falls well within the range of 1.95 (2)–2.08 (1) Å observed in a variety of platinum(II) carbene complexes.[16-21] In the absence of appreciable π interaction with the metal, stabilization of the carbene center is expected to be accomplished by pπ–pπ interactions between the amino nitrogen atoms and the carbene carbon, and this is evidenced here by the short C(carbene)–N bond lengths observed (C4–N2 = 1.339 (6), 1.325 (6) Å; C4–N3 = 1.340 (5), 1.331 (6) Å). These values appear quite normal when compared with those for other aminocarbene systems,[15,16,22-24] as does the planarity observed about the carbene center.

In species **2**, the coordinated acyl group and the diaminocarbene ligand constitute a pair of very strong σ donors, both of which are expected to exhibit a powerful trans influence, whereas the parent compound **1** only possessed one such ligand group (the acyl group). The trans influence of the diaminocarbene ligand is felt directly by the β-amino group of the bidentate β-aminoacyl ligand, with the observed Pd–N1 bond length (2.175 (4), 2.181 (5) Å) in **2** being considerably longer than the corresponding bond length (Pd–N = 2.11 (1) Å) in the previously reported parent compound **1**.[2] In fact, the above results for the Pd–N linkage of **2** are longer than any other known Pd–N bond length,[12] the largest value known previously being 2.148 (7) Å for a Pd–N bond trans to S-bonded thiocyanate.[25] The addition of the strongly σ-bonding diaminocarbene ligand has consequences, in fact, for all the groups bound to the metal ion, though the effect on the cis ligands is much less dramatic than for the trans ligand. The Pd–C(acyl) bond length (1.988 (6), 2.005 (7)Å) in the title compound **2** is considerably lengthened over the corresponding bond length (Pd–C1 = 1.95 (1) Å) in **1**. This means that this bond in **2** is much closer to the normal range of 2.02–2.07 Å observed for other Pd–C(sp^2) linkages.[11,13,26,27] This lengthening of the Pd–C(acyl) bond is due primarily to changes in the σ-bonding system, since the acyl(C═O) stretching frequency, which is strongly linked to the extent of Pd–C(acyl) π interaction, is not appreciably different in compounds **1** and **2**. The bond lengths and angles within the remainder of the β-aminoacyl ligand appear entirely normal, with a planar configuration about the acyl carbon atom, C–O distances (1.153 (8), 1.161 (9) Å) which compare favorably with results from a similar complex (C–O = 1.19 (2) Å in chloro(methoxalyl)bis(triphenylphosphine)palladium(II)),[28] and C–C (C1–C2 = 1.53 (1) Å, C2–C3 = 1.54 (1) Å) and C–N (C3–N1 = 1.45 (1) Å) single-bond lengths which agree well with expected values for these types of bonds. Note that in making these comparisons the strongly disordered C2–C3 portion of molecule **2a** has been ignored.

The Pd–Cl^- bond in **2** is also lengthened (relative to that in **1**) by the addition of the strongly σ-bonding diaminocarbene ligand and, with observed values of the Pd–Cl^- bond length of 2.464 (2) and 2.457 (2) Å, now supplants the Pd–Cl^- bond of **1** as the longest Pd–Cl^- bond known. The only other cases which come close to matching the extremely long Pd–Cl^- bond lengths observed in these β-aminoacyl complexes also involve a chloro ligand trans to σ-bonded carbon.[11,28,29] Thus, **2** is found to contain two very strong bonds together with two of the weakest palladium(II)–ligand bonds known.

Anticancer Activity. The carbene-containing complex **2** has been tested for activity by the mouse P388 lymphocytic leukemia survival time test[30] and against L1210 using standard NCI screening protocols.[31] Complex **2** exhibited modest activity in the P388 test, with a maximum T/C value of 127 observed at a dose of 15 mg/kg. While the parent compound **1** has not shown significant activity in these tests, a derivative of **1** in which the β-aminoacyl ligand is substituted at the β carbon by an n-butyl group has shown a T/C value of 130 against P388 at a dosage of 20 mg/kg. None of the compounds tested to date have shown significant activity in the less sensitive L1210 screening.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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