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THE MOLECULAR AND CRYSTAL STRUCTURE OF AN ALLYLPALLADIUM-(II) TRIAZENIDO COMPLEX: $[(1\text{-}3\text{-}\eta\text{-}C_3H_5)Pd(II)(p\text{-}CH_3C_6H_4NNNC_6H_4CH_3\text{-}p)]_2$

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Summary

For the class of compounds mentioned in the title it is difficult to establish the structure unambiguously on the basis of spectroscopic data. We studied the molecular and crystal structure of $[(1\text{-}3\text{-}\eta\text{-}C_3H_5)Pd(II)(p\text{-}CH_3C_6H_4NNNC_6H_4\text{-}CH_3\text{-}p)]_2$ by single crystal X-ray analysis. The crystal data are: $M = 743$ a.m.u. Space group $P2_1/c$. $a = 8.510(2)$, $b = 40.652(9)$, $c = 9.762(2)$ Å, $\beta = 103.61(2)°$. $D_c = 1.50$ g/cm^3. $R = 0.041$, $R_w = 0.060$, based on 3978 independent reflections. The two π-allylpalladium residues are bridged by two 1,3-di-*p*-tolyltriazenido groups, gaining an approximate square planar coordination around each heavy atom. The two allyl units are stereochemically equivalent, with the central carbon atoms pointing outwards. The rigid triazenido groups force the two palladium atoms into close contact (2.86 Å). The aromatic rings are somewhat rotated with respect to the bonded N—N—N planes, but some π-conjugation over the whole ligand is still retained.

Introduction

The chemical and coordination behaviour of the triazenido ligand ArNNNAr (Ar = aryl or alkyl) in transition metal complexes has aroused much interest in view of the variety of cases to which it gives rise [1—4]. As with the isoelectronic acetate ligand [5—9], it has been found to act in monodentate (A) [10,11], chelating (B) [12,13], and bridging (C) [14—18] modes.

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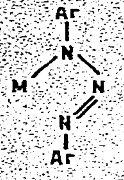
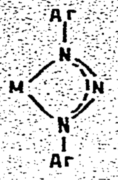


(A)



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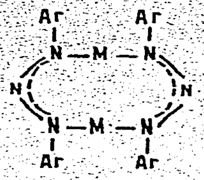
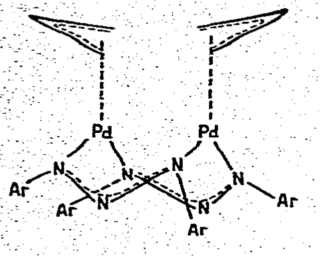


(C)

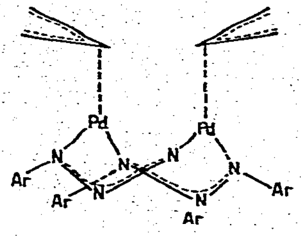
A presents a σ-bonded ligand; B has a σ,σ'-attached π-delocalized group while C presents a σ,σ'-bridging linkage with a delocalized π-electron system. Variable temperature NMR experiments show fluxional behaviour for type A complexes [3,11,19,20]. Another bridging arrangement has been found in [Pd(π-methallyl)(1,3-dimethyltriazenido)]$_2$, where the bridging triazenido ligand presents a π-electron system not completely delocalized [21].

π-Allyl complexes of the transition metals, and particularly of palladium(II), have shown great potential as catalysts [22]. Many X-ray diffraction studies on allylpalladium(II) complexes have established the delocalization of the C=C double bond of the allylic moiety π-coordinated to the metal [23—26].

Recently, we have synthesized a series of new dimeric allylpalladium(II) complexes containing bridging 1,3-diaryltriazenido ligands [27]. ^{1}H NMR studies have shown the presence of two isomers with symmetric (D or E) and asymmetric (F) π-allyl groups [27].



(D)



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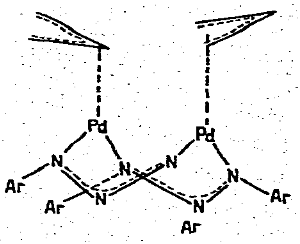

(F)

In order to establish the nature of one of these isomers and the geometry of the triazenido linkage we have studied the structure of one of the synthesized compounds, di-μ-(1,3-di-p-tolyltriazenido)di-(1-3-η-allyl)dipalladium(II), by X-ray diffraction analysis.

Experimental

The preparation of the compound has been reported in a previous paper [27]. Good prismatic yellow crystals were obtained on recrystallization from a benzene/ethanol mixture.

The crystal data are: [(1-3-η-C_3H_5)Pd(II)(p-$CH_3C_6H_4NNNC_6H_4CH_3$-p)]$_2$ M = 743 amu. Space group $P2_1/c$. a = 8.510(2) Å, b = 40.652(9) Å, c = 9.762(2) Å, β = 103.61(2)°. D_c = 1.50 g/cm^3. μ = 94 cm^{-1}. Data were collected on a crystal (0.18 mm × 0.24 mm) with a computer controlled Philips PW 1100 four-circle diffractometer with graphite monochromator using Cu-K_α radiation because of the long b axis. The cell parameters and their standard deviations (in brackets) were found by least-squares fitting on the best peak positions evaluated for 25 reflections with $4° \leq \theta \leq 20°$. Reflections were collected up to $\theta = 60°$ using a $\theta/2\theta$ scan, with scanning velocity of 0.05°/sec and scanning width of 1°. Each background was measured for 5 sec. The 3978 reflections for which the intensity was greater than 2.5 σ were used in the calculations. The data were reduced and Lp corrected with a program written by A. Immirzi (program not published).

No absorption correction was applied at the beginning. A Fourier difference synthesis calculated at the end of the refinement with isotropic thermal parameters did not show any feature which could be attributed to relevant absorption and therefore no absorption correction was applied throughout.

Solution and refinement of the structure

The structure was solved by the standard Patterson method and was refined by block-diagonal least-squares. The quantity minimized was $\Sigma w(|F_0| - |F_c|)^2$ where $w = (110.0 + |F_0| + 0.001|F_0|^2)^{-1}$. The final discrepancy indexes $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$ were 0.041 and 0.060, respectively.

The parameters varied were the coordinates of the 42 non-hydrogen atoms and their isotropic temperature factors replaced by anisotropic thermal parameters in the course of the calculation.

The hydrogen atoms were generated at the expected positions (C—H 1.08 Å) and were included, but not refined, in the last three cycles by assuming $B = 5.5$ Å^2, which is an average of the thermal parameter values of the attached atoms.

In the last three-squares cycle the average ratio of parameter shift to standard deviation was 0.04. The final difference Fourier synthesis showed 15 peaks of height between 0.4 and 0.5 electrons/Å^3, 8 of which surrounded the palladium atoms and the others were randomly placed.

The atomic scattering factors used were those of Cromer and Mann [28] for the non-hydrogen atoms and those of Hanson et al. [29] for hydrogen while the correction for the real part of the anomalous dispersion for the palladium atoms was taken from the table given by Cromer [30].

(continued on p. 414)

TABLE 1

FINAL ATOMIC COORDINATES WITH e.s.d.'s

Atoms	x/a	y/b	z/c
Pd(1)	0.24282(5)	0.07294(1)	0.44268(5)
Pd(2)	0.07190(5)	0.13377(1)	0.38597(5)
C(1)	0.0913(10)	0.0384(2)	0.3107(9)
C(2)	0.1323(11)	0.0262(2)	0.4469(9)
C(3)	0.1003(11)	0.0454(2)	0.5564(9)
C(4)	—0.0766(11)	0.1304(3)	0.1782(8)
C(5)	—0.1678(11)	0.1404(3)	0.2690(10)
C(6)	—0.1759(9)	0.1219(2)	0.3869(10)
N(1)	0.3729(6)	0.1036(1)	0.6037(5)
N(2)	0.3153(6)	0.1273(1)	0.6668(5)
N(3)	0.1735(6)	0.1386(1)	0.6043(5)
C(11)	0.5380(7)	0.0979(2)	0.6660(6)
C(12)	0.6046(9)	0.0669(2)	0.6603(7)

(continued)

TABLE 1 (continued)

Atoms	*x/a*	*y/b*	*z/c*
C(13)	0.7666(8)	0.0608(2)	0.7250(7)
C(14)	0.8654(8)	0.0855(2)	0.7977(7)
C(15)	0.7989(7)	0.1164(2)	0.7984(7)
C(16)	0.6392(8)	0.1232(2)	0.7342(7)
C(17)	1.0384(9)	0.0792(2)	0.8746(8)
C(31)	0.1132(7)	0.1611(2)	0.6940(6)
C(32)	0.1749(8)	0.1616(2)	0.8381(7)
C(33)	0.1089(9)	0.1841(2)	0.9193(8)
C(34)	−0.0162(9)	0.2050(2)	0.8599(9)
C(35)	−0.0759(9)	0.2040(2)	0.7154(8)
C(36)	−0.0131(8)	0.1821(2)	0.6322(7)
C(37)	−0.0796(12)	0.2292(3)	0.9547(11)
N(4)	0.3609(6)	0.0926(1)	0.2962(5)
N(5)	0.3811(6)	0.1236(1)	0.2750(6)
N(6)	0.2910(6)	0.1441(1)	0.3248(6)
C(41)	0.4559(8)	0.0725(2)	0.2287(7)
C(42)	0.5035(9)	0.0821(2)	0.1086(8)
C(43)	0.5974(9)	0.0617(2)	0.0476(8)
C(44)	0.6479(8)	0.0312(2)	0.1036(7)
C(45)	0.5970(10)	0.0213(2)	0.2218(8)
C(46)	0.5016(9)	0.0417(2)	0.2832(7)
C(47)	0.7507(9)	0.0084(2)	0.0356(8)
C(61)	0.3370(9)	0.1774(2)	0.3053(7)
C(62)	0.2581(12)	0.2030(2)	0.3532(11)
C(63)	0.2992(13)	0.2350(2)	0.3332(14)
C(64)	0.4171(10)	0.2434(2)	0.2670(11)
C(65)	0.4903(11)	0.2186(2)	0.2135(13)
C(66)	0.4535(11)	0.1858(2)	0.2326(13)
C(67)	0.4562(10)	0.2793(2)	0.2462(11)
H′(C1)	0.115	0.024	0.222
H″(C1)	0.037	0.063	0.290
H(C2)	0.190	0.002	0.469
H′(C3)	0.048	0.069	0.538
H″(C3)	0.134	0.036	0.667
H′(C4)	−0.011	0.108	0.199
H″(C4)	−0.073	0.145	0.088
H(C5)	−0.236	0.163	0.249
H′(C6)	−0.109	0.099	0.407
H″(C6)	−0.248	0.130	0.458
H′(C17)	1.069	0.053	0.862
H″(C17)	1.056	0.084	0.986
H‴(C17)	1.120	0.094	0.832
H(C12)	0.531	0.047	0.606
H(C13)	0.816	0.036	0.719
H(C15)	0.876	0.136	0.853
H(C16)	0.593	0.148	0.738
H′(C37)	−0.015	0.226	1.063
H″(C37)	−0.065	0.254	0.923
H‴(C37)	−0.208	0.225	0.947
H(C32)	0.272	0.145	0.888
H(C33)	0.161	0.185	1.032
H(C35)	−0.178	0.220	0.666
H(C36)	−0.061	0.182	0.518
H′(C47)	0.779	0.020	−0.055
H″(C47)	0.863	0.002	0.112
H‴(C47)	0.685	−0.015	0.003
H(C42)	0.467	0.106	0.063
H(C43)	0.632	0.070	−0.048
H(C45)	0.634	−0.003	0.270
H(C46)	0.459	0.033	0.374

(continued)

TABLE 1 (continued)

Atoms	*x/a*	*y/b*	*z/c*
H'(C67)	0.385	0.295	0.293
H''(C67)	0.584	0.284	0.290
H'''(C67)	0.431	0.285	0.132
H(C62)	0.161	0.198	0.404
H(C63)	0.230	0.254	0.371
H(C65)	0.583	0.224	0.158
H(C66)	0.515	0.166	0.190

TABLE 2

THERMAL PARAMETERS (Å^2) [a] WITH e.s.d.'s

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	136.4(7)	4.6(0)	83.9(5)	—8.5(2)	82.9(10)	—7.7(2)
Pd(2)	120.8(7)	6.3(0)	79.8(5)	1.6(2)	51.8(10)	—3.7(2)
C(1)	238(16)	8(1)	168(12)	—43(5)	100(22)	—28(4)
C(2)	264(17)	7(1)	190(13)	—49(5)	193(24)	—15(4)
C(3)	259(16)	6(1)	179(12)	—23(5)	232(24)	—6(4)
C(4)	226(16)	15(1)	77(9)	6(6)	—2(19)	3(4)
C(5)	176(15)	16(1)	165(13)	19(6)	—29(23)	—2(6)
C(6)	138(12)	13(1)	172(12)	—7(5)	93(20)	—6(5)
N(1)	134(8)	5(0)	85(6)	2(3)	50(11)	—5(2)
N(2)	142(8)	4(0)	82(6)	1(3)	54(11)	—4(2)
N(3)	151(9)	6(0)	82(6)	1(3)	49(12)	—4(2)
C(11)	127(10)	5(0)	87(7)	—3(3)	76(13)	—0(3)
C(12)	198(12)	4(0)	102(8)	6(4)	114(16)	—5(3)
C(13)	176(12)	6(0)	104(8)	7(4)	83(16)	—0(3)
C(14)	148(11)	6(1)	91(8)	7(4)	76(15)	4(3)
C(15)	123(10)	6(0)	115(8)	2(3)	47(15)	—1(3)
C(16)	144(11)	5(0)	121(9)	5(3)	66(16)	—1(3)
C(17)	161(12)	9(1)	145(11)	21(4)	46(18)	5(4)
C(31)	126(9)	6(0)	97(8)	—3(3)	95(14)	—3(3)
C(32)	135(10)	6(1)	119(9)	—2(4)	82(15)	—9(3)
C(33)	199(13)	7(1)	113(9)	—13(4)	103(18)	—15(3)
C(34)	201(14)	6(1)	164(11)	—5(4)	169(20)	—19(4)
C(35)	174(12)	7(1)	146(10)	11(4)	103(18)	—5(4)
C(36)	149(11)	6(1)	107(8)	8(4)	90(15)	5(3)
C(37)	280(20)	12(1)	206(15)	21(7)	179(29)	—42(6)
N(4)	148(9)	6(0)	98(6)	—1(3)	94(12)	—4(2)
N(5)	140(9)	5(0)	109(7)	—3(3)	81(12)	—5(3)
N(6)	125(8)	6(0)	105(7)	4(3)	80(12)	—3(2)
C(41)	147(10)	6(0)	90(8)	—5(3)	89(14)	—7(3)
C(42)	205(13)	6(1)	125(9)	—2(4)	153(19)	—3(3)
C(43)	176(12)	8(1)	126(9)	—2(4)	153(18)	—3(4)
C(44)	156(12)	7(1)	120(9)	1(4)	100(17)	—15(3)
C(45)	234(15)	7(1)	120(9)	12(4)	117(19)	1(3)
C(46)	211(13)	7(1)	108(9)	10(4)	121(18)	—1(3)
C(47)	207(15)	8(1)	143(11)	15(5)	109(20)	—11(4)
C(61)	180(12)	5(0)	124(9)	5(4)	94(17)	5(4)
C(62)	258(17)	7(1)	270(17)	0(5)	295(29)	—8(5)
C(63)	319(22)	5(1)	379(24)	10(5)	372(39)	—5(6)
C(64)	187(14)	6(1)	280(17)	12(4)	151(25)	14(5)
C(65)	205(16)	7(1)	332(21)	4(5)	289(31)	9(6)
C(66)	176(13)	6(1)	294(18)	10(4)	239(26)	3(5)
C(67)	265(19)	5(1)	410(26)	3(5)	262(37)	15(6)

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[a] The term of the anisotropic thermal ellipsoids is: $\exp [-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

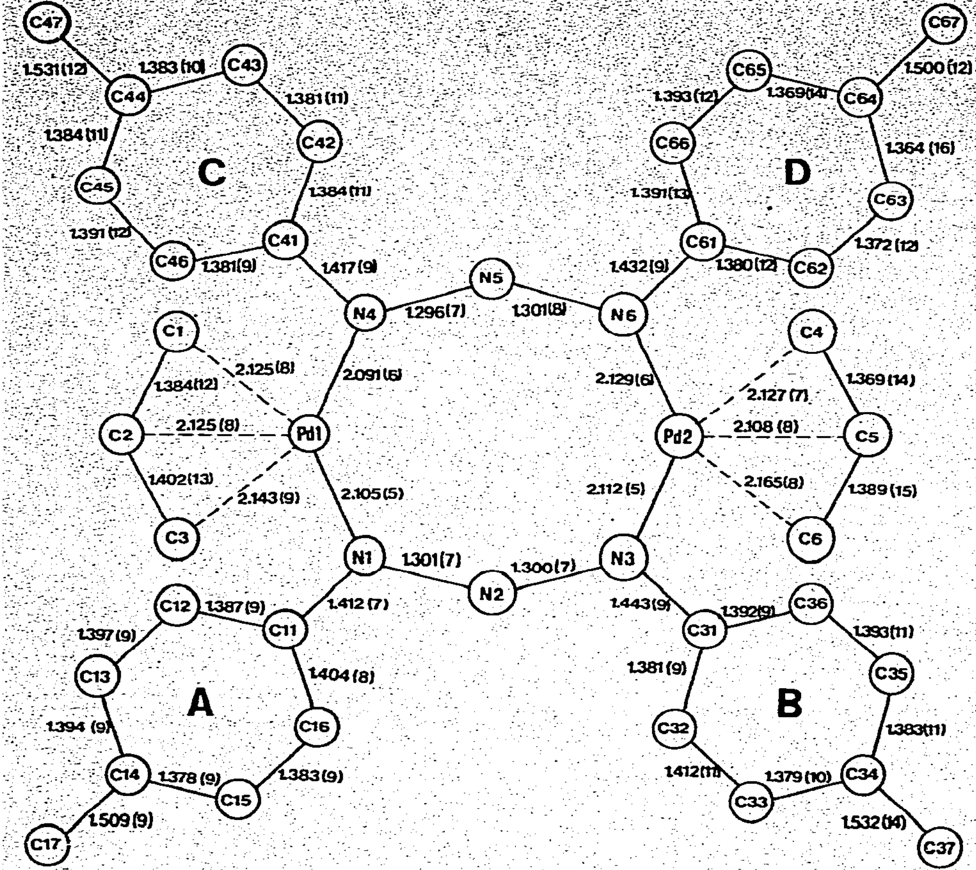

Fig. 1. Schematic drawing of the allylpalladium triazenido complex showing bond distances with e.s.d.'s.

All the reported calculations, except those for the data reduction, were done with a set of programs written for the UNIVAC 1108 computer by Domenicano, Spagna and Vaciago [31] together with a versatile structure factor least-squares program written by R. Carruthers.

The final positional parameters are collected in Table 1 and the anisotropic thermal parameters for the non-hydrogen atoms are shown in Table 2.

TABLE 3

SOME INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s

Distances		Angles	
Pd(1)—Pd(2)	2.856(1)	Pd(1)—C(2)—C(1)	71.0(5)
N(1)—N(3)	2.215(8)	Pd(1)—C(2)—C(3)	71.5(5)
N(4)—N(6)	2.211(8)	C(1)—Pd(1)—C(2)	38.0(3)
N(1)—N(4)	3.013(7)	C(2)—Pd(1)—C(3)	38.3(3)
N(3)—N(6)	3.127(8)	Pd(2)—C(5)—C(6)	73.3(5)
N(2)—N(5)	3.997(8)	Pd(2)—C(5)—C(4)	71.9(5)
		C(5)—Pd(2)—C(6)	37.9(4)
		C(4)—Pd(2)—C(5)	37.7(4)

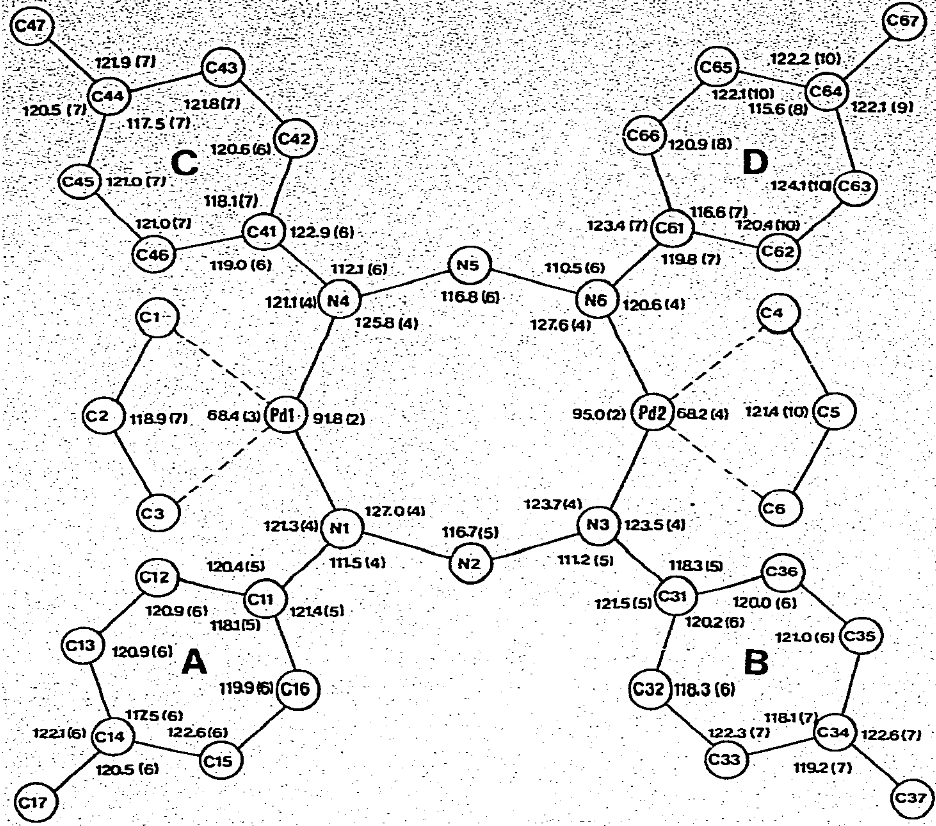

Fig. 2. Schematic drawing of the allylpalladium triazenido complex showing bond angles with e.s.d.'s.

A list of the observed and calculated structure factors is available *. Two reflections, 020 and 040 with $\sin\theta/\lambda < 0.05$ Å^{-1}, appeared to be strongly affected by extinction and were kept out of the refinement after a few cycles.

Discussion of the molecular and crystal structure

The bond lengths and angles are reported in Fig. 1 and 2, where some relevant intramolecular distances and angles are given too, as in Table 3.

Torsional angles calculated according to the sign convention of Klyne and Prelog [32] are listed in Table 4.

The overall stereochemistry of the $[(1\text{-}3\text{-}\eta\text{-}C_3H_5)Pd(dtt)]_2$ molecule (dtt denotes for p-$CH_3C_6H_4NNNC_6H_4CH_3$-p), viewed along the crystallographic axis a, is shown in Fig. 3 and the inner coordination sphere around the palladium atoms is depicted in Fig. 4.

The π-allylpalladium residues are bridged by the two dtt groups, gaining an approximate square planar coordination around each heavy atom. The average

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* Supplementary material available on request from the authors.

TABLE 4

TORSIONAL ANGLES (°)

N(3)—N(2)—N(1)—C(11)	168.5
N(1)—N(2)—N(3)—C(31)	171.4
N(4)—N(5)—N(6)—C(61)	174.5
N(6)—N(5)—N(4)—C(41)	175.5
N(3)—N(2)—N(1)—Pd(1)	—17.5
N(1)—N(2)—N(3)—Pd(2)	—22.6
N(6)—N(5)—N(4)—Pd(1)	—16.3
N(4)—N(5)—N(6)—Pd(2)	—18.6
N(4)—Pd(1)—N(1)—N(2)	113.4
N(1)—Pd(1)—N(4)—N(5)	—48.1
N(5)—N(6)—Pd(2)—N(3)	108.1
N(6)—Pd(2)—N(3)—N(2)	—41.0
N(1)—Pd(1)—Pd(2)—N(3)	—25.6
N(4)—Pd(1)—Pd(2)—N(6)	—21.9

C—C distance in the two allyl groups is 1.39 Å and ranges between 1.37 and 1.40 Å.

Its geometry agrees with that found in known structures [23—26] of π-allyl complexes of palladium and so do the values of the palladium—carbon distances (average 2.13 Å) and those of the angles subtended by the terminal carbons at the respective palladium atoms (average value 68.3°). The dihedral angles that the planes of the allyl groups make with that defined by the respective N—Pd—N group (120 and 118°) (see Table 5) compare reasonably well with the value of 125° predicted theoretically [33] and with the values found in other π-allyl complexes known [21, 23—26]. The spectroscopic studies of allylpalladium(II) triazenido complexes, accomplished [27,34] to clarify the allyl groups stereo-

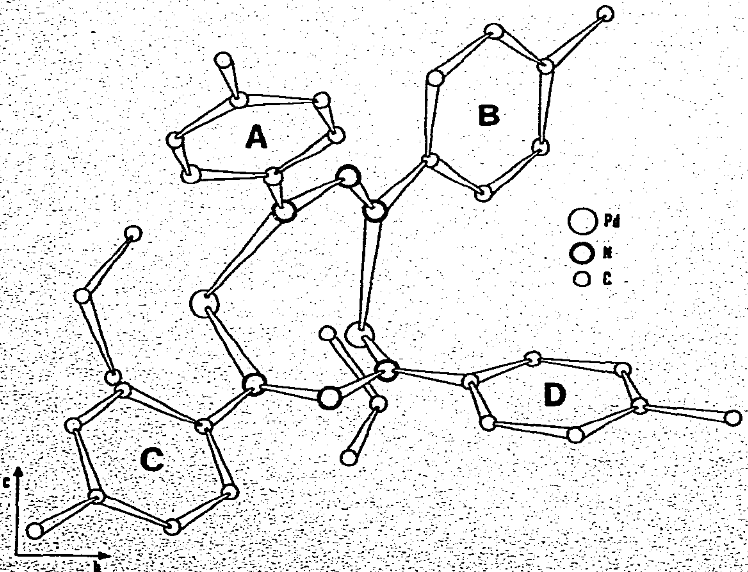

Fig. 3. Stereochemistry of the allylpalladium triazenido complex viewed along the *a* axis.

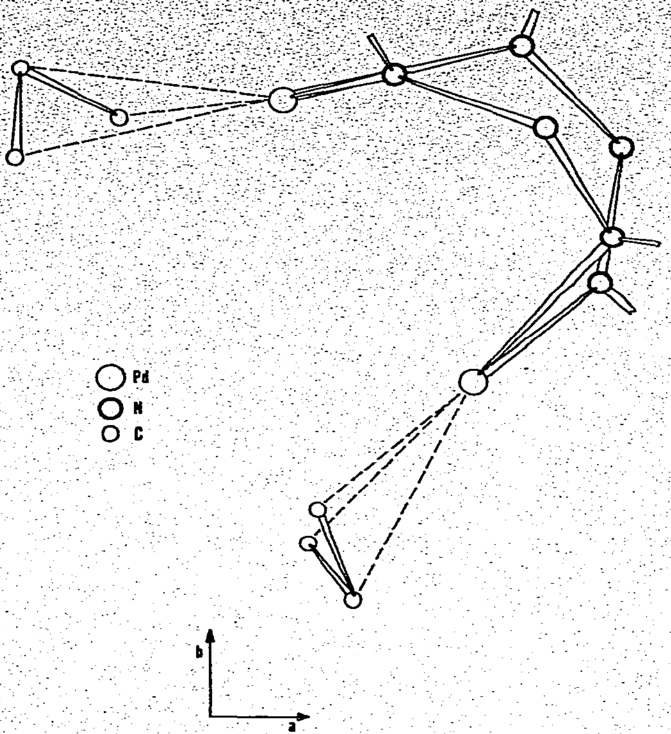

Fig. 4. The coordination around the palladium centers in the allylpalladium triazenido complex, viewed along the *c* axis.

chemistry in solution, indicate two possible conformers: with the allylic units stereochemically non-equivalent (F), or equivalent (D or E). In the solid state, the first conformer was found for the related $[Pd(1\text{-}3\text{-}\eta\text{-}C_3H_5)(AcO)]_2$ [8].

In our complex, the allyl groups are stereochemically equivalent, with the central carbon atoms pointing outwards (see Fig. 4 and [27] for discussion).

The Pd—Pd distance is 2.86 Å, which has to be compared with 2.97 Å in $[Pd(\pi\text{-methallyl})(dmt)]_2$ [21] (dmt = 1,3-dimethyltriazenido), 2.75 Å in metallic palladium [5], 2.56 Å in $[Pd(dpt)_2]_2$ [17] (dpt = 1,3-diphenyltriazenido), and 2.94 Å in $[Pd(OAc)(1\text{-}3\text{-}\eta\text{-}C_3H_5)]_2$ [8]. Very short metal—metal distances were also found in other bridged complexes such as $[Cu(dpt)_2]_2$, $[Ni(dpt)_2]_2$ [17], $[Cu(OAc)]_2$ [14]. In $[Ni(dpt)_2]_2$, in spite of a Ni—Ni distance of 2.39 Å, spectral studies and the diamagnetic behaviour oppose a metal—metal bond [16]. Only in $Cu_2(OAc)_4 \cdot 2H_2O$ [6] a metal—metal bond is evidenced by spectroscopic and magnetic criteria (see, for example, ref. [35]). For example, in the case of $[M(dpt)_2]_2$, where M = Cu, Ni, Pd, if the metal—metal bond is absent, the short intermetallic distances may be a result of the rather rigid triazenido ligands which form a cage, together with the metal atoms, and compel the metal atoms to approach closely. The rigidity of the triazenido ligand is proved by its geometry which appears to be the same in all the known structures (see Fig. 1 and 2, and [14—18, 21]), independently of the number of ligands bridging the metal atoms and of the degree of crowding and strain in the complex molecules. However, it must be pointed out that al-

TABLE 5

EQUATION OF THE ATOMIC PLANES AND ATOMIC DEVIATIONS. X, Y AND Z ARE IN Å AND RELATED TO THE ORTHOGONAL AXES a, b, c

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Equations for the planes:

Plane TRIAZ1 for N(1), N(2) and N(3) atoms

$0.4290X + 0.6708Y - 0.6050Z - 1.0348 = 0$

Plane TRIAZ2 for N(4), N(5) and N(6) atoms

$0.6954X + 0.0486Y + 0.7169Z - 3.8138 = 0$

Plane N1P1N4 for N(1), Pd(1) and N(4) atoms

$-0.7108X + 0.6987Y - 0.0810Z - 0.3336 = 0$

Plane N3P2N6 for N(3), Pd(2) and N(6) atoms

$-0.2260X + 0.9741Y + 0.0001Z - 5.1632 = 0$

Plane ALLYL1 for C(1), C(2) and C(3) atoms

$0.9036X + 0.4214Y - 0.0786Z - 1.1158 = 0$

Plane ALLYL2 for C(4), C(5) and C(6) atoms

$0.7859X + 0.4986Y + 0.3657Z - 2.8379 = 0$

Plane PN1N3P for Pd(1), N(1), N(3) and Pd(2) atoms

$-0.6360X - 0.4932Y + 0.5935Z + 0.6881 = 0$

Plane PN4N6P for Pd(1), N(4), N(6) and Pd(2) atoms

$0.6105X + 0.2585Y + 0.7486Z - 4.6717 = 0$

Plane TOL1 for C(11)—C(17) atoms

$-0.2766X - 0.2339Y + 0.9321Z - 2.8604 = 0$

Plane TOL2 for C(31)—C(37) atoms

$-0.6673X - 0.6876Y + 0.2863Z + 3.2428 = 0$

Plane TOL3 for C(41)—C(47) atoms

$0.8260X + 0.4035Y + 0.3936Z - 4.8120 = 0$

Plane TOL4 for C(61)—C(67) atoms

$0.6922X - 0.0264Y + 0.7212Z - 3.3835 = 0$

Dihedral angles (°) formed by the planes given above:

TRIAZ1/TRIAZ2	84.1	PN1N3P/PN4N6P	85.9
N1P1N4/N3P2N6	32.7	TOL1/TRIAZ1	32.9
ALLYL1/ALLYL2	26.9	TOL2/TRIAZ1	23.0
N1P1N4/ALLYL1	120.0	TOL3/TRIAZ2	28.8
N3P2N6/ALLYL2	117.9	TOL4/TRIAZ2	4.3

Atomic deviations (Å) from the planes:

PN1N3P		PN4N6P	
Pd(1)	−0.225	Pd(1)	−0.192
N(1)	0.296	N(4)	0.252
N(3)	−0.293	N(6)	−0.250
Pd(2)	0.221	Pd(2)	0.190

Atomic distances (Å) from the planes:

N1P1N4		N3P2N6	
C(1)	0.011	C(4)	−0.146
C(2)	0.699	C(5)	−0.711
C(3)	0.057	C(6)	0.006

TRIAZ1		TRIAZ2	
Pd(1)	0.504	Pd(1)	−0.477
Pd(2)	−0.676	Pd(2)	0.538

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though the triazenido ligand in [Pd(π-methallyl)(dmt)]$_2$ shows the same geometry, the corresponding N(1)—N(2) and N(5)—N(6) bond distances differ from the N(2)—N(3) and N(4)—N(5) distances, suggesting that the π-electron system is not completely delocalized [21]. It has been suggested that the asymmetry for the C—C bonds in the allyl units and for Pd—C bonds may be due to the different *trans* effect of the non-equivalent coordinating N atoms [21]. The compound described here does not show such an asymmetry. Moreover, the equivalence of the N—N bonds is strengthened by the fact that the two N—N—N angles are 116.7 and 116.8°, while in [Pd(π-methallyl)(dmt)]$_2$ they are enlarged (average 118.3°) [21] indicating that the π-electron delocalization is more pronounced in our case, with a more localized N—N double bond in the other, as suggested by the Gillespie and Nyholm theory [36] *.

Thus, it seems likely that a Pd—Pd bond is not necessary in order to form the dimers and when there is no cage, the repulsive forces between the filled *d* orbitals cause the palladium atoms to move apart.

In the present structure the N(1)—Pd(1)—Pd(2)—N(3) and N(4)—Pd(1)—Pd(2)—N(6) torsional angles are −25.6° and −21.9° respectively and the N(1)—Pd(1)—N(4) and N(3)—Pd(2)—N(6) planes make a dihedral angle of 32.7°.

This allows a separation of 2.86 Å between the two palladium atoms while the approximate sp^2 coordination around the terminal nitrogen atoms is retained. A much shorter distance is found in [Pd(dpt)$_2$]$_2$ where the double number of triazenido ligands forces the Pd atoms to approach one another.

The facing phenyl rings, except ring D, are rotated with respect to the plane of their bonded triazenido groups (see Table 5). In this way steric hindrance with the adjacent allyl groups and aromatic rings is avoided. However, the partial double bond character of the C—N bonds (average 1.43 Å) and the rotation angles around the C—N bonds (see Table 5) seem to indicate that the π-conjugation over the whole ligand is not completely destroyed.

The molecular conformation does not seem to be affected by the packing forces which are rather weak, all the intra- and inter-molecular contacts being no shorter than the usual values. The best Van der Waals interactions occur between carbon atoms belonging to the allyl groups and nitrogen atoms (~3.2 Å) and carbon atoms and methyl groups (~3.6—3.7 Å).

A view of the unit cell along the *a* axis is shown in Fig. 5. No evidence exists about π—π interactions.

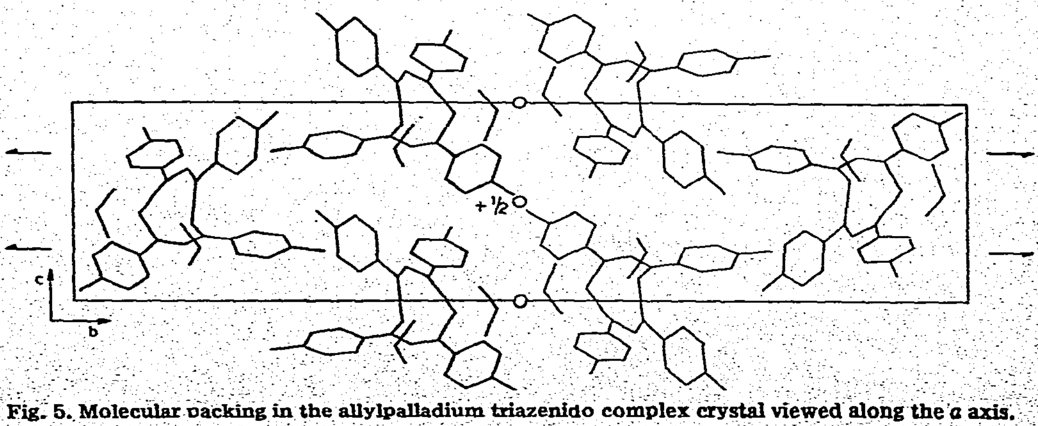

Fig. 5. Molecular packing in the allylpalladium triazenido complex crystal viewed along the *a* axis.

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* This comparison is possible because the *R* factors are about the same for both structures.

There is a point of interest regarding the mutual arrangement of the two allyl groups of the same molecule. The best interactions between them concern hydrogen—hydrogen contacts (~2.0 : 2.4 Å with the crude approximation inherent with the location of the hydrogen atoms) owing to the long carbon—carbon distances (~4.1 Å) found after the refinement of this crystal structure was completed. Therefore, isomers E and F, which can be formally obtained from D by 180° rotation of the allyl groups about an axis passing through the two carbon—carbon bonds are also possible, as found in solution for the analogous $[Pd(1\text{-}3\text{-}\eta\text{-}C_3H_5)(dmt)]_2$ by ^1H and ^{13}C NMR spectroscopy [21]. In our system, however, only isomers D and F have been identified by ^1H NMR spectroscopy [26,34]: the two equivalent allyl groups in D give rise to one *AA'BB'X* pattern; the non-equivalent ones in F to two *AA'BB'X* patterns. It might be possible that in solution E is also present but between —60 and 90°C (above this temperature some decomposition takes place) it is rapidly interconverting with D, thus giving rise to the observed single *AA'BB'X* pattern, through any process of the type proposed for the magnetic equivalence of the allyl groups of the D and E isomers of the closely-related allylpalladium(II) carboxylate systems [37,38]. However this possibility has to be dismissed since the F isomer of our system does not show any such dynamic processes *. Therefore, either isomer E does not form at all, or it may be present in non-detectable amounts.

Finally, it should be noted that the three carbon atoms of the allyl unit practically lie on the same side of the N—Pd—N plane (see Table 5), as found in $[Pd(\pi\text{-methallyl})(dmt)]_2$ [21], and in contrast with $[Pd(\pi\text{-methallyl})Cl]_2$ [26] where the two terminal carbon atoms lie below the Cl—Pd—Cl plane with the central carbon atom above the plane. It has been suggested that this contrast may be due either to an electron repulsion effect of the d_{z^2} electrons or to a Pd—Pd interaction [21]. It might be due also to the short hydrogen—hydrogen contacts (2.0—2.4 Å) mentioned above which compel the two allyl units to be far apart, with the three carbon atoms on the same side of the corresponding N—Pd—N plane.

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* The stereochemical rigidity of isomer F may be due to the above mentioned π-conjunction of the N—N—N linkage extended over the entire ligand, and/or to the strength of the Pd—N bond [27].

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