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A CYCLOBUTADIENE—PALLADIUM COMPLEX WITH A NON-PLANAR CYCLOBUTADIENE RING OBTAINED FROM THE PALLADIUM CATALYZED DIMERIZATION OF AN YNAMINE *

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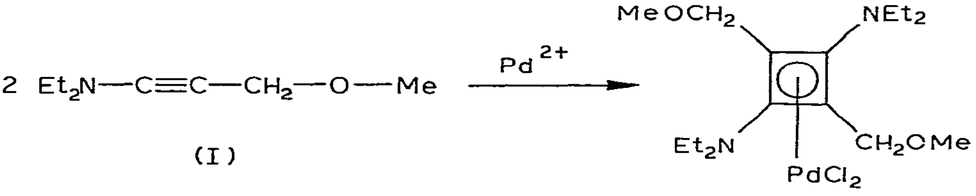
Summary

A cyclobutadiene—palladium complex, obtained by dimerization of an ynamine is described. The crystal structure of this compound shows, as salient feature, that the cyclobutadiene ring is not planar, but highly puckered. Antibonding interactions have been suggested as an explanation for this puckering.

We describe here the synthesis of the cyclobutadiene complex II, obtained by cyclodimerization of the ynamine I [1] in the presence of bis(benzonitrile)-palladium chloride (symbolized by Pd^{2+} in reaction 1).



(I)

(II)

(1)

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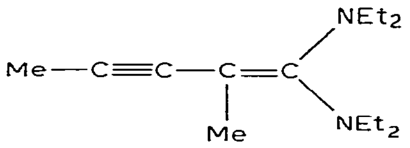
The formation of a cyclobutadiene via transition metal catalyzed oligomerization of ynamines is peculiar to the ynamine I using bis(benzonitrile)palladium chloride as catalyst [2] We have indeed observed previously that the dimerization which occurs with *N*,*N*-diethylaminopropyne and cuprous salts [3a] or palladium chloride (stoichiometric amounts) [3b] is a linear one which affords the keteneaminal III, whereas a trimerization leading to IV occurs with the same ynamine and nickel salts [3a].



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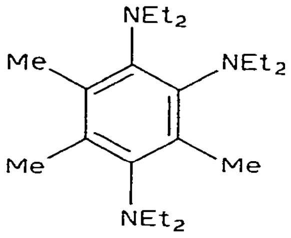

(IV)

The most salient feature of the result described here is the structure of the cyclobutadiene complex II This structure, established by X-ray diffraction analysis, shows that the cyclobutadiene ring is not planar but highly puckered To our knowledge, it is the first example of a puckered cyclobutadiene, the four-membered rings of transition metal cyclobutadiene complexes have always been found to be planar [4—6] *.

A perspective view of the title compound with atom numbering is shown in Figs. 1 and 2. The complex II (Fig 1) forms a well defined entity Nevertheless, in contrast with the previously described related structures [4], in which the chlorine atoms are involved in a dimer, a water molecule of crystallization bridges two molecules of complex II through hydrogen bonds involving the Cl atoms (oxygen—chlorine distances 3 28 and 3 41 Å).

The four-membered ring of I has, within experimental error, sides of equal length with an average value of 1.470 Å, which is in agreement with C—C ring distances (1.46—1.47 Å) previously reported for cyclobutadiene—metal complexes [4,5].

The cyclobutadiene ring can be described as being formed by two planes including, respectively, C(1), C(2), C(4) and C(2), C(3), C(4) with a dihedral angle of 155° (see Fig. 2). It is worthy to note that the $PdCl_2$ unit is located in the convex side of this angle. The C—N bond distances indicate a strong participation of the lone pair to this bond. These values (1 291 and 1 295 Å) are indeed, in agreement with the C—N double bond lengths found in salicylidene aniline derivatives (1 28 Å [7], in oximes (average 1 286 Å) [8] and in immonium cations (average 1.285 Å) [9]. The participation of the lone pair is corroborated by the planarity of the three bonds around the nitrogen atoms

The carbon atoms C(10) and C(18) are not located in the planes C(1), C(2), C(3) and C(1), C(4), C(3) respectively. They are pushed out of these planes, away from the Pd atom with an angle of 18° for C(10) and 17° for C(18).

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* Recent ab initio molecular orbital calculations indicate that puckering may stabilize cyclobutadiene dications [6].

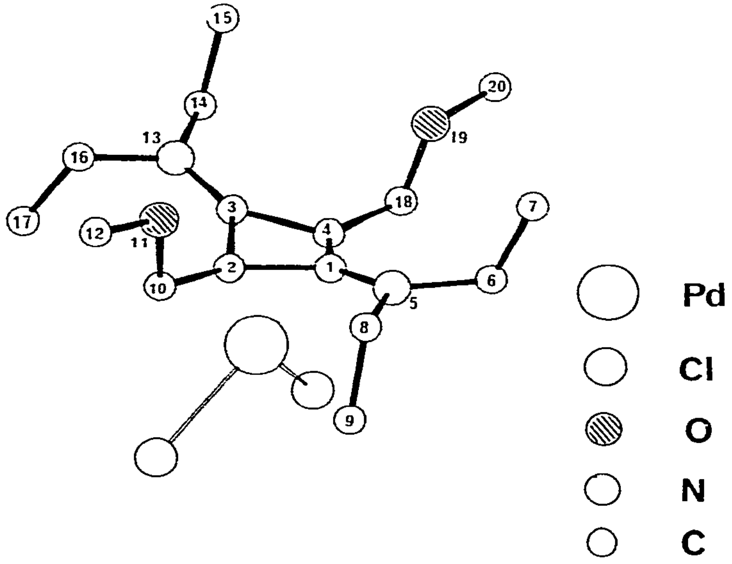

Fig 1 A perspective view of complex II

The Pd—C (cyclobutadiene) bond lengths are not equivalent The C(2)—Pd and C(4)—Pd distances of 2 101 and 2 111 Å are in agreement with the C—Pd (cyclobutadiene) distances observed [4] in the cation $(C_{28}H_{48}Cl_3Pd_2)^+$ (average value 2 13 Å) and with the C—Pd distances observed in allylic complexes 2 12 Å [10] and 2 115 Å [11]

On the other hand, the C(1)—Pd and C(3)—Pd bond lengths (average 2 30 Å) are unusual. Noteworthy is the peculiar conformation of $PdCl_2$ in the complex The two chlorine atoms exactly eclipse the C(2) and C(4) atoms of the ring (Fig 2) This particular point of geometry is especially important for a theoretical approach to the structure of II The actual shape of complex II is indeed an

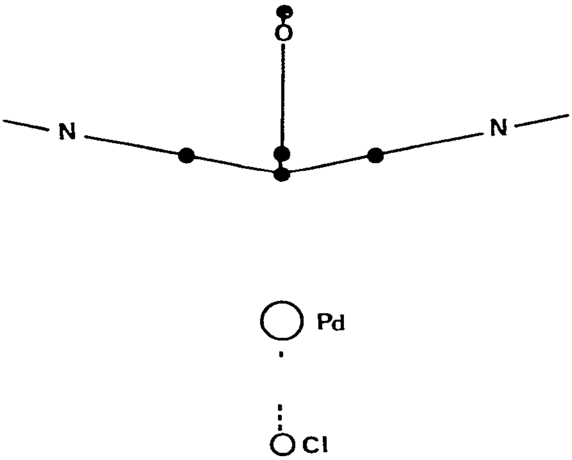

Fig 2 View down C(2)—C(4) showing the puckering of the cyclobutadiene ring of complex II

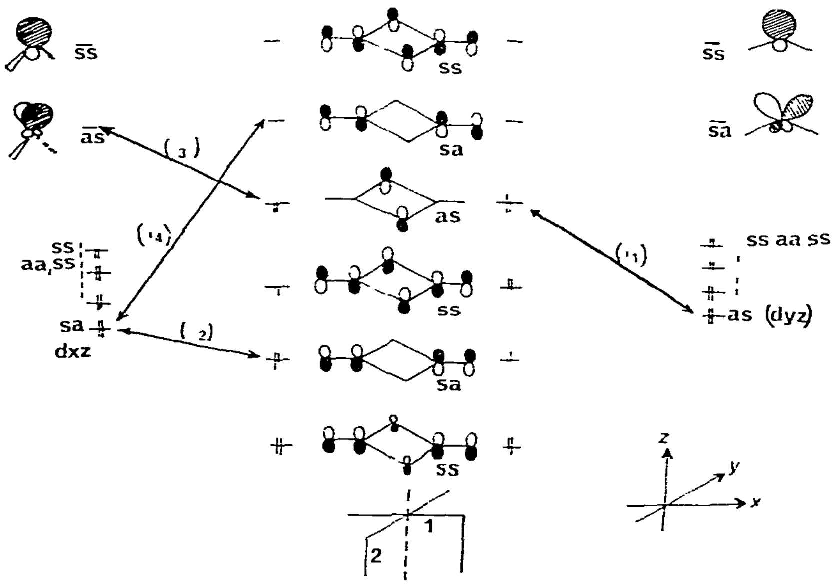

Fig 3 Molecular Orbitals of complex II

interesting problem which can be solved by simple molecular orbital (MO) considerations, using perturbation theory arguments

Let us examine separately the two fragments of this molecule, a modified cyclobutadiene unit and the $PdCl_2$ moiety, resulting from an extended Huckel calculation [12] Assuming first that the ring is planar, the two degenerate cyclobutadiene MO's are split by interactions with the attached nitrogen atoms The resulting MO's (Fig 3) are obtained *. The $PdCl_2$ moiety has formally a d^8 structure since two electrons of the d^{10} palladium atom are shared with the chlorine atoms to form the two Pd—Cl bonds The LUMO of this fragment thus has the d symmetry, located in the $PdCl_2$ plane

If we now look at two extreme arrangements of $PdCl_2$ in the complex (left and right sides of Fig. 3), two distinct situations arise In a first geometry (right part), in which the nitrogen atoms are located in the $PdCl_2$ plane, strong repulsive interactions(i_1) are developed between the HOMO of the ring and the filled d_{yz} MO of $PdCl_2$ In a second one (left part), in which the C(2) and C(4) atoms of the cyclobutadiene unit are located in the $PdCl_2$ plane, the attractive interaction (i_3) between the HOMO of the ring and the LUMO of the $PdCl_2$ fragment is optimal (small energy gap)

In the latter case, some repulsion also occurs within the SA symmetry class. The d_{xz} MO is repelled by the filled SA level according to (i_2) and an attractive interaction is developed according to (i_4) If we add the two contributions, with their respective phase character, we obtain the resulting filled MO (Fig 4) in which strong out of phase interactions take place It is therefore clear that a motion of the nitrogen atoms will occur in order to avoid this unfavorable over-

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* An ab initio calculation on the same structure affords the same orbital arrangement (Minimal basis set option STO-3G, of the Gaussian 70 series of program) [13]

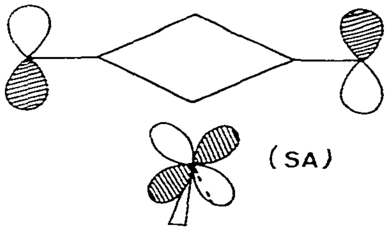

Fig. 4 SA Molecular Orbital of complex II

lap, hence the observed ring puckering (In both cases, interactions between SS MO's remain identical, while d_{xx} of AA symmetry is unchanged)

To conclude, the qualitative MO perturbation scheme explains very simply the dominant structural features of complex II, first, a rigid arrangement of the $PdCl_2$ unit in a plane containing the C(2) and C(4) atoms of the cyclobutadiene and, second, a ring puckering resulting from repulsive interactions between the filled *d* orbitals of palladium and the *p* lobes located on both nitrogen atoms.

Experimental

Ynamine I was prepared (70% yield) by alkylation of the lithio derivative of diethylaminoacetylene with one equivalent of methylchloromethyl ether at —10°C, for one hour, in an ether-hexane solution [14] The resulting mixture was then treated with 4*N* aqueous ammonia at —40°C and the cold organic solution was rapidly dried on anhydrous potassium carbonate The crude ynamine, (IR 2210 cm^{-1}) which is thermally unstable, was used in ether-hexane solution without further purification

The ether-hexane solution of the ynamine (4 equivalents) was added to a solution of bis(benzonitrile)palladium chloride [2] in dry THF at —40°C. The mixture was then kept at 0°C for 24 h. The crystalline precipitate formed was washed with THF, water, and finally again with THF Two recrystallizations from acetonitrile finally gave green-yellow crystals of complex II (35% yield), m p 196—198°C, ^{1}H NMR (60 MHz, DMSO-d_6)· 1 3 (t) ($N—CH_2—CH_3$), 3 4 (s) ($O—CH_3$), 3 5 (m) ($N—CH_2—CH_3$), 4 0 (s) ($CH_2—O—CH_3$)

The crystal data are $C_{16}H_{30}N_2O_2Cl_2Pd$ H_2O, mol wt 477 8, monoclinic

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) WITH E S D s IN PARENTHESES

Atom	x	y	z	Atom	x	y	z
C(1)	9 146(3)	8674(2)	737(4)	N(13)	10 390(3)	8713(2)	3610(3)
C(2)	8 567(3)	8618(2)	1942(4)	C(14)	11 819(4)	8665(2)	3913(4)
C(3)	9 897(3)	8599(2)	2514(4)	C(15)	12 443(4)	9373(3)	4043(6)
C(4)	10 400(3)	8424(2)	1314(4)	C(16)	9 528(4)	8838(2)	4638(4)
N(5)	8 741(3)	8877(1)	—351(3)	C(17)	9 020(4)	8158(3)	5159(5)
C(6)	9 602(4)	8881(2)	—1402(4)	C(18)	11 748(3)	8344(2)	833(4)
C(7)	10 112(5)	9587(2)	—1693(5)	O(19)	12 288(2)	9025(1)	734(3)
C(8)	7 348(4)	9027(2)	—629(4)	C(20)	13 534(4)	8986(2)	199(5)
C(9)	6 600(4)	8364(3)	—971(5)	Pd	9 113(0)	7575(0)	1576(0)
C(10)	7 267(3)	8830(2)	2425(4)	Cl(1)	10 300(1)	6612(1)	812(1)
O(11)	7 246(2)	9573(1)	2512(3)	Cl(2)	7 237(1)	6959(1)	2184(1)
C(12)	6 053(4)	9821(3)	2976(5)	W	14 527(3)	7866(2)	2995(3)

TABLE 2

BOND DISTANCES OF COMPLEX II (Å)(MEAN E S D 0 005 Å)

C(1)—C(2)	1 465	C(4)—C(18)	1 503	C(8)—C(9)	1 511	C(18)—O(19)	1 414
C(1)—C(4)	1 482	N(5)—C(6)	1 473	C(10)—O(11)	1 417	O(19)—C(20)	1 426
C(1)—N(5)	1 295	N(5)—C(8)	1 471	O(11)—C(12)	1 421	Pd—C(4)	2 111
C(2)—C(3)	1 472	Pd—C(1)	2 279	N(13)—C(14)	1 487	Pd—Cl(1)	2 367
C(2)—C(10)	1 506	Pd—C(2)	2 101	N(13)—C(16)	1 473	Pd—Cl(2)	2 366
C(3)—C(4)	1 461	Pd—C(3)	2 323	C(14)—C(15)	1 494		
C(3)—N(13)	1 291	C(6)—C(7)	1 477	C(16)—C(17)	1 510		

TABLE 3

VALENCE ANGLES OF COMPLEX II (°)(MEAN E S D 0 3°)

C(2)—C(1)—C(4)	88 6	C(1)—C(4)—C(3)	88 4	C(2)—C(10)—O(11)	107 8
C(2)—C(1)—N(5)	135 4	C(1)—C(4)—C(18)	132 5	C(10)—O(11)—C(12)	111 7
C(4)—C(1)—N(5)	135 9	C(3)—C(4)—C(18)	134 3	C(3)—N(13)—C(14)	122 4
C(1)—C(2)—C(3)	88 6	C(1)—N(5)—C(6)	122 1	C(3)—N(13)—C(16)	120 2
C(1)—C(2)—C(10)	133 6	Cl(1)—Pd—Cl(2)	98 8	C(14)—N(13)—C(16)	117 2
C(3)—C(2)—C(10)	132 4	C(1)—N(5)—C(8)	120 9	N(13)—C(14)—C(15)	112 2
C(2)—C(3)—C(4)	89 1	C(6)—N(5)—C(8)	116 5	N(13)—C(16)—C(17)	112 0
C(2)—C(3)—N(13)	134 6	N(5)—C(6)—C(7)	113 5	C(4)—C(18)—O(19)	107 5
C(4)—C(3)—N(13)	136 2	N(5)—C(8)—C(9)	111 4	C(18)—O(19)—C(20)	110 0

TABLE 4

DEVIATION (Å) FROM THE PRINCIPAL LEAST SQUARES PLANES OF COMPLEX II

	A[a]	B[b]	C[c]	D[d]	E[e]	F[f]
C(1)	0 112	—0 001			0 0	0 0
C(2)	—0 113	0 028	0 021	0 074	0 0	—0 435
C(3)	0 108		—0 004		0 0	0 0
C(4)	—0 113	—0 040	—0 026	—0 064	—0 436	0 0
N(5)	0 418	0 036				
C(6)		0 011				
C(8)		—0 072				
C(10)	0 026				0 455	0 429
N(13)	0 410		0 024			
C(14)			0 010			
C(16)			—0 044			
C(18)	0 002					
Pd	—1 95	—1 81	—1 78	—0 021	—2 01	—2 01
Cl(1)				0 025		
Cl(2)				—0 034		

[a] Plane A. C(1), C(2) C(3) C(4)

[b] Plane B C(1) C(4) C(2), N(5) C(6), C(8)

[c] Plane C: C(4) C(2), C(3), N(13) C(14) C(16).

[d] Plane D Pd Cl(1) Cl(2) C(2) C(4).

[e] Plane E: C(1), C(2), C(3).

[f] Plane F C(1) C(4), C(3).

space group $P2_1/n$, cell dimensions a 10 233(2), b 18 998(3), c 10 869(2) Å, β 92 5(1)°, four molecules in the unit cell ($Z = 4$), D_C 1 50, λ(Mo-K_α) 0 7107 Å Prismatic crystals grown in acetonitrile rapidly decayed to a powder due to loss of solvent of crystallization A crystal sealed in a thin walled capillary with a drop of mother liquor maintained its integrity during data collection 3190 reflexions of the 4329 collected were used for structure analysis They have $I > 3\ 0\ \sigma(I)$, $\sigma(I)$ is the standard deviation from counting statistics

Scattering factors were taken from the International Tables for X-ray crystallography (1974) [15] A three dimensional Patterson synthesis yielded the position of the two palladium atoms Successive Fourier syntheses gave the location of all non-hydrogen atoms Full matrix least-squares refinements were followed by a difference Fourier synthesis which clearly revealed the position of all hydrogen atoms The final least-squares refinements resulted in a R factor of 0 029 The function minimized was $\Sigma w\ (F_0 - F_c)^2$ and $w = 1/\sigma\ (F_0)^2$

The atomic coordinates and thermal parameters are listed in Table 1 Tables 2 and 3 give interatomic distances and valence angles Important planes are given in Table 4.

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