Journal of Organometallic Chemistry, 295 (1985) 233–238
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MOLECULAR STRUCTURE OF η^5-[Pd(CH$_2$$\cdots$CH$\cdots$CMeCH$_2CH_2$CH=CMe$_2$)(MeCN)](BF$_4$), A CATIONIC π-ALLYLPALLADIUM COMPLEX WITH AN ALMOST IN-PLANE INTRAMOLECULAR OLEFIN COORDINATION

ROSARIA CIAJOLO, MOHAMUD A. JAMA *, ANGELA TUZI, and ALDO VITAGLIANO*
Dipartimento di Chimica, Università di Napoli, via Mezzocannone 4, 80134 Napoli (Italy)

(Received March 12th, 1985)

Summary

The complex η^5-[Pd(CH$_2$$\cdots$CH$\cdots$CMeCH$_2CH_2$CH=CMe$_2$)(MeCN)](BF$_4$), a model for a key intermediate in diene polymerization, crystallizes in the monoclinic space group $P2_1/c$, a 11.362(2), b 13.655(4), c 10.046(2) Å, β 134.80(1)°. The structure was solved by conventional Patterson and Fourier syntheses and refined by full matrix least squares techniques to a final discrepancy index $R = 0.058$ for 1710 independent reflections. The palladium and nitrogen atoms, the center of gravity of the allyl triangle, and the middle point of the coordinated double bond are coplanar. The side chain of the organic moiety is located in the *syn* position with respect to the η^3-allyl group. The orientation of the coordinated double bond, which forms an angle of 26° with the coordination plane, is novel for palladium(II) complexes.

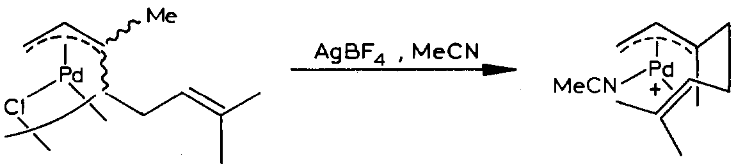
During a recent study of the *syn–anti* isomerization and reactions of η^3-geranyl- and neryl-palladium(II) complexes [1,2], the title complex (**2**) was synthesized from the chloride bridged dimers **1**. Pentahapto complexes analogous to **2** had been previously detected in solution [3] and isolated as solids [4], but none had been structurally characterized in spite of interest in them as possible intermediates in the catalytic polymerization of dienes [3,5,6].

Experimental

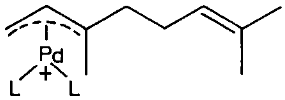
The chloride bridged isomeric complexes **1** were prepared as a mixture as previously described [1]. The cationic complex **2** was prepared [2] by adding the stoichiometric amount of anhydrous AgBF$_4$ and a few drops of acetonitrile to a solution of 500 mg (1.8 mmol Pd) of **1** in 5 ml of dichloromethane at 0°C. The silver

---

* On leave from the National Somali University, Mogadisho (Somalia).



(1) (2)



(3)

chloride was filtered off and the filtrate was evaporated to leave an oil, which gave crude crystals when kept at $-30°C$ under high vacuum for 24 h. Single crystals (pale yellow regular prisms) suitable for the X-ray diffraction studies were obtained by crystallization from dichloromethane/diethyl ether in the presence of a small amount of acetonitrile. (A trace of the crude solid was required to initiate the crystallization).

The crystals are monoclinic, space group $P2_1/c$, a 11.362(2), b 13.655(4), c 10.046(2) Å, β 134.80(1)°, $Z = 4$, D_c 1.600 g cm^{-3}, D_{obs} 1.59 g cm^{-3}. Cell parameters were obtained by least-squares refinement of 25 accurately centered reflections. Intensities were measured using a CAD-4 Enraf–Nonius diffractometer, equipped with PDP8/E and PDP11/34 digital computers (Mo-K_α), Zr filtered radiation). Reflections were scanned in the 2θ–ω mode up to 2θ 60°; 2714 independent reflections were collected and corrected for polarization and Lorentz effects but 1004 reflections having $I < 3\sigma(I)$ were discarded for the refinement. The structure was solved by the Patterson method and the metal atom positions thus derived yielded phase values good enough for location of all the light atoms by means of Fourier synthesis. Refinement was achieved by full-matrix least-squares procedures for all non-hydrogen atoms. H atoms were placed in calculated positions and were assigned by isotropic thermal factors equal to those of the carrier atom. The conversion of all non-hydrogen atoms to anisotropic thermal parameters and further refinement yielded a final R value of 0.058. Tables of thermal parameters and lists of structure factors are available from the authors.

Results and discussion

The positional and thermal parameters for the complex are listed in Table 1. A substantial disorder affected the position of the fluoroborate ion, so that the B and F atoms exhibit rather high thermal parameters. Bond distances and angles are given in Table 2. An ORTEP view of the complex is shown in Fig. 1.

The Pd and N atoms, the center of gravity of the allyl triangle (M) and the middle point of the C=C double bond (DB), lie almost in a plane (maximum deviation 0.04 Å), which can be assumed to be the coordination plane. Two alternative descriptions are possible for the coordination geometry, and both have been used in similar cases. The complex can be regarded as distorted square planar [7], with C(1), C(3), N, and

TABLE 1

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS WITH e.s.d.'s, IN UNITS OF THE LEAST SIGNIFICANT FIGURE, IN PARENTHESES

Atom	x/a	y/b	z/c	B_{eq} [a]
Pd	0.19991(7)	0.60334(6)	0.34397(6)	4.67(2)
N	0.3231(8)	0.7260(6)	0.4676(6)	5.5(2)
C(1)	0.2757(10)	0.6218(9)	0.2412(7)	7.2(3)
C(2)	0.1393(10)	0.5626(9)	0.1687(7)	6.3(3)
C(3)	0.1457(9)	0.4768(8)	0.2276(7)	5.5(3)
C(4)	0.2964(10)	0.4129(9)	0.3205(8)	6.9(3)
C(5)	−0.0129(11)	0.4270(8)	0.1690(8)	6.8(3)
C(6)	−0.0154(11)	0.4228(9)	0.2758(9)	7.0(4)
C(7)	−0.0002(10)	0.5271(9)	0.3238(8)	6.4(3)
C(8)	0.1067(9)	0.5618(8)	0.4464(7)	5.5(3)
C(9)	0.2449(12)	0.5038(10)	0.5673(9)	7.9(4)
C(10)	0.0694(11)	0.6546(9)	0.4763(9)	8.5(4)
C(11)	0.4038(9)	0.7876(8)	0.5357(7)	5.3(3)
C(12)	0.5098(11)	0.8707(9)	0.6230(9)	7.4(4)
B	0.362(2)	0.173(1)	0.572(1)	15.7(5)
F(1)	0.340(2)	0.0927(8)	0.5730(14)	26 (1)
F(2)	0.285(1)	0.2017(12)	0.4576(7)	19.6(5)
F(3)	0.247(1)	0.1951(16)	0.5723(10)	26.1(8)
F(4)	0.455(1)	0.2213(12)	0.6616(14)	28.9(8)

[a] $B_{eq} = (B_{11}B_{22}B_{33})^{1/3}$ where $B_{11} = 4\beta_{11}/a^{\star 2}$, $B_{22} = 4\beta_{22}/b^{\star 2}$, $B_{33} = 4\beta_{33}/c^{\star 2}$.

DB defining the edges of the square, or as trigonal planar [8], with M, N, and DB defining the edges of the triangle.

As in other allylpalladium complexes [9,10], the allyl plane forms a dihedral angle of 112° with the coordination plane, and C(4) and C(5) are not coplanar with the allyl triangle, being displaced by 0.76 and 0.42 Å, respectively, away from the metal and towards the metal [10]. All the bond distances and bond angles involving the Pd, C(1), C(2) and C(3) atoms fall in the expected range [9], while a rotation of about 13° around the Pd–M axis, which brings the C(1) atom 0.08 Å above and the C(3) atom 0.47 Å below the coordination plane, can be regarded as a deviation from a "normal" geometry.

There is a remarkable mode of coordination of the C=C double bond, which forms an angle of 26° with the coordination plane, thus being much closer to the "in plane" geometry than to the "upright" one. A coordinated C=C double bond in a square planar d^8 complex is usually perpendicular, or nearly so, to the coordination plane [11,12], and the preference for the upright coordination has been ascribed mainly to steric factors [12,13]. Only three examples of "in plane" coordination have been described to date: (a) (5-methylenecycloheptene)platinum dichloride [14], in which the two double bonds are sterically constrained to be mutually perpendicular, (b) the η^3-methallyl(triphenylphosphine)(styrene)platinum(II) cation [15], and (c) its *Z*-(2-butene) analogue [16]. In the two last cases the "in plane" geometry of the olefin was suggested to be favoured by the presence of the allyl ligand, both for steric and electronic reasons [15]. The present case represents the first example of an orientation close to "in plane" for a coordinated olefin in a palladium(II) complex.

The unusual orientation of the coordinated double bond in **2** and the tilting of the

TABLE 2

RELEVANT MOLECULAR PARAMETERS, WITH e.s.d.'s, IN PARENTHESES [a]

Bond lenghts (Å)					
Pd–C(1)	2.154(3)	C(1)–C(2)	1.367(14)	C(7)–C(8)	1.311(10)
Pd–C(2)	2.111(4)	C(2)–C(3)	1.407(14)	C(8)–C(9)	1.490(13)
Pd–C(3)	2.149(9)	C(3)–C(4)	1.499(13)	C(8)–C(10)	1.487(15)
Pd–C(7)	2.329(8)	C(3)–C(5)	1.516(12)	N–C(11)	1.108(12)
Pd–C(8)	2.379(4)	C(5)–C(6)	1.523(15)	C(11)–C(12)	1.470(14)
Pd–N	2.086(7)	C(6)–C(7)	1.532(16)		

Bond angles (°)			
C(1)–Pd–C(3)	67.7(5)	C(1)–C(2)–C(3)	120(1)
C(1)–Pd–N	96.5(5)	C(2)–C(3)–C(4)	123(1)
C(3)–Pd–DB	92.3(4)	C(2)–C(3)–C(5)	120(1)
N–Pd–DB	104.8(3)	C(3)–C(5)–C(6)	109(1)
N–Pd–M	130.7(3)	C(5)–C(6)–C(7)	109(1)
M–Pd–DB	124.3(1)	C(6)–C(7)–C(8)	129(1)
Pd–N–C(11)	171.7(11)	C(7)–C(8)–C(9)	124(1)
N–C(11)–C(12)	179(1)	C(7)–C(8)–C(10)	120(1)

Internal rotational angles			
C(1)–C(2)–C(3)–C(4)	−38(1)	C(6)–C(7)–C(8)–C(9)	3(1)
C(1)–C(2)–C(3)–C(5)	161(2)	C(6)–C(7)–C(8)–C(10)	−161(2)
C(2)–C(3)–C(5)–C(6)	−121(1)	Pd–C(8)–C(7)–C(6)	99(2)
C(3)–C(5)–C(6)–C(7)	57(1)	Pd–C(7)–C(8)–C(10)	100(2)
C(5)–C(6)–C(7)–C(8)	−126(2)		

[a] DB = middle point of the C(7)–C(8) double bond; M = center of gravity of the C(1)–C(2)–C(3) allyl triangle.

allyl triangle, are probably the result of the steric and geometric requirements of the chelating chain. A preliminary conformational analysis [17] seems to indicate that both the upright and the completely coplanar conformations would involve severe steric constraints. Nevertheless, it is noteworthy that the complex adopts a mono-

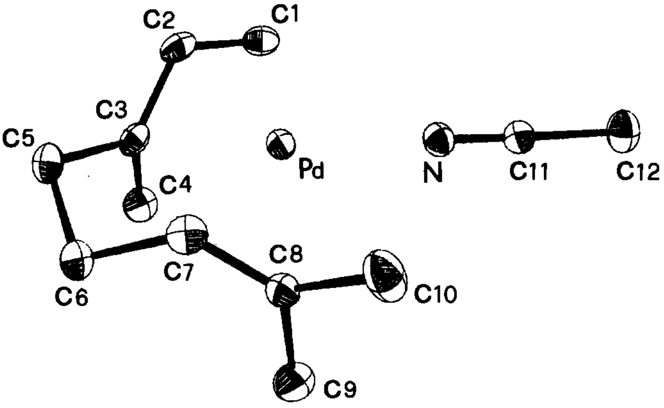
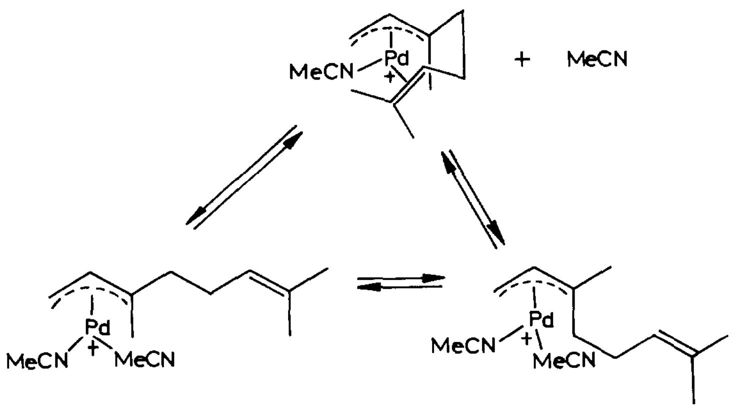


Fig. 1. ORTEP view of the $[\mathrm{Pd}(\mathrm{CH_2}\cdots\mathrm{CH}\cdots\mathrm{CMeCH_2CH_2CH{=}CMe_2})(\mathrm{MeCN})]^+$ cation. For clarity the hydrogen atoms are omitted.



SCHEME 1

meric chelate structure, both in the solid state and in solution [2], rather than a more flexible dimeric structure which would easily allow the upright coordination of the double bond. This is a good evidence that in the case of the olefin palladium complexes also electronic factors do not play a dominant role in stabilizing the upright geometry.

The Pd–C(7) and Pd–C(8) bond lengths of 2.329(8) and 2.379(4) Å, respectively, are quite large compared with the usual range observed for olefin palladium complexes [18], indicating a rather weak bond with the metal. The C(7)–C(8) bond distance of 1.31(1) Å is not longer than for a normal, uncoordinated olefin, but the bending back of the carbons of the double bond, evidenced by the torsion angles [11] C(6)–C(7)–C(8)–C(10) −161(2)°, Pd–C(8)–C(7)–C(6) 99(2)°, and Pd–C(7)–C(8)–C(10) 100(2)°, suggests that π-back donation still contributes significantly to the metal–olefin bond [12,19]. Since the π-acceptor ability of a ligand is an activating factor in the π–σ–π interconversion of allylic complexes [20], this finding is consistent with the observed ability of the coordinated double bond to promote *syn–anti* isomerizations in complexes related to **2** [3,21]. Recent results on the *syn–anti* isomerization of complexes derived from **2** [2] indicated that in **2** the coordination of the double bond is again able to promote *syn–anti* isomerization around the C(2)–C(3) bond. For example, when strongly coordinating ligands, like PPh_3, bipyridine or amines, are bound to palladium(II) in complexes such as **3**, the coordination of the double bond is forbidden and, accordingly, no *syn–anti* isomerization is observed [2]. By contrast, in the reaction of **2** with a weak ligand such as MeCN the reversible reaction in Scheme 1 takes place, leading to a mixture of *syn–anti* isomers [2]. In spite of the ability of the coordinated double bond to promote *syn–anti* isomerization around the C(2)–C(3) bond, the present structure and the solution NMR data [2] show that in **2** there is only one allyl stereochemistry with the side chain in *syn* position, as proposed for analogous compounds [4]. These findings suggest, in agreement with the results of a conformational analysis [17], that for the 7,8 unsaturated, 1,2,3-η-allyl complexes which are believed to be intermediates in the transition metal catalyzed polymerization of dienes [6], the backcoordination of the 7,8 double bond can only take place in a stable square planar (or trigonal) geometry if the chain is located in the *syn* position of the allyl group. In fact the intramolecular coordination of the double bond from an *anti* side chain would require the *anti* substituent to be pulled towards the metal [17], thus reversing the usual geometry of π-allyl complexes, in which the *anti* substituent is always found to be displaced (as in the present case) away from the metal [9,10].

The above conclusions, together with the observed close to "in-plane" coordination of the double bond, may be useful in explaining the steric outcome of diene polymerizations catalyzed by d^8 complexes [6].

Acknowledgements

The authors wish to thank Prof. Paolo Corradini for valuable suggestions and discussions, and the Italian CNR for financial support.

References

1 B. Åkermark, S. Hansson, B. Krakenberger, A. Vitagliano, and K. Zetterberg, Organometallics, 3 (1984) 683.

2 B. Åkermark and A. Vitagliano, Organometallics, in press.

3 R.P. Hughes, and J. Powell, J. Am. Chem. Soc., 94 (1972) 7723; R.P. Hughes, T. Jack, and J. Powell, J. Organomet. Chem., 46 (1973) 451.

4 Y. Takahashi, S. Shizuyoshi, and Y. Ishii, Inorg. Chem., 11 (1972) 1516.

5 J. Furukawa, Pure Appl. Chem., 42 (1975) 495.

6 Ph. Teyssié, A. Devaux, P. Hadjiandreou, M. Julémont, J.M. Thomassin, E. Walckiers, and R. Warin, in 'Preparation and properties of stereoregular polymers', R.W. Lenz and F. Ciardelli eds., D. Reidel Publ. Co. 1979, p. 131–150.

7 E. Benedetti, G. Maglio, R. Palumbo, and C. Pedone, J. Organomet. Chem., 60 (1973) 189.

8 K. Miki, M. Yama, Y. Kai, and N. Kasai, J. Organomet. Chem., 239 (1982) 417.

9 S.J. Lippard, and S. Morehouse, J. Am. Chem. Soc., 91 (1969) 2504, and references therein; S.J. Lippard, and S.M. Morehouse, ibid., 94 (1972) 6956.

10 R. Mason, and A.G. Wheeler, Nature, 217 (1968) 1253; L.Y. Ukhin, V.L. Il'In, Z.I. Orlova, N.G. Bokii, Y.T. Struchov, J. Organomet. Chem., 113 (1976) 167.

11 S.D. Ittel, and J.A. Ibers, Adv. Organomet. Chem., 14 (1976) 33.

12 T.A. Albright, R. Hoffman, J.C. Thibeault, and D.L. Thorn, J. Am. Chem. Soc., 101 (1979) 3801.

13 C.E. Halloway, G. Hulley, B.F.G. Johnson, and J. Lewis, J. Chem. Soc. A, (1969) 53.

14 L.L. Wright, R.M. Wing, M.F. Rettig, and J.R. Wiger, J. Amer. Chem. Soc., 102 (1980) 5949.

15 K. Miki, Y. Kai, N. Kasai, and H. Kurosawa, J. Am. Chem., Soc., 105 (1983) 2482.

16 K. Miki, K. Yamatoya, N. Kasai, H. Kurosawa, M. Emoto, and A. Urabe, J. Chem. Soc., Chem. Commun., (1984) 1520.

17 P. Corradini, G. Guerra, M.A. Jama, G. Zhi, and A. Tuzi, Polymer Commun., in press.

18 Literature range: 2.15–2.30 A. See R.M. Wing, and M.F. Rettig, J. Am. Chem. Soc., 104 (1982) 610.; M.F. Rettig, R.M. Wing, and G.R. Wiger, ibid., 103 (1981) 2980; K. Miki, O. Shiotani, Y. Kai, N. Kasai, H. Kanatani, and H. Kurosawa, Organometallics, 2 (1983) 585.

19 M.J.S. Dewar, and C.P. Ford, J. Am. Chem. Soc., 101 (1979) 783.

20 K. Vrieze, in L.M. Jackman and F.A. Cotton (Eds.), Dynamic NMR spectroscopy, Academic Press, New York, San Francisco, London, 1975, p. 441–487.

21 D.J.S. Guthrie, R. Spratt, and S.M. Nelson, Chem. Commun., (1971) 935.