X-Ray Diffraction Studies on Catalysis: The Crystal Structure of Di-μ-chloro-bis[(2′—3′-η-*exo*-3-allylnorborn-2-yl)palladium] and Comparison with Related Complexes Relevant to the Polymerization of Norbornene

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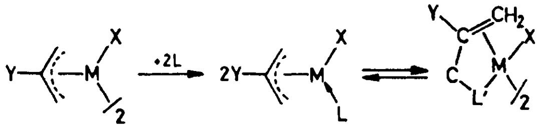
The crystal structure of the title complex [a = 11.057(2), b = 7.346(1), c = 6.537(1) Å, α = 80° 32′(2′), β = 104° 31′(2′), γ = 94° 39′(2′), space group $P\bar{1}$] has been determined from *X*-ray diffractometer data and refined by least squares to R = 0.040. Evidence is given for the existence of two factors relevant to catalytic activity: (*i*) a strong *trans* influence on the bridging chloride ions favouring dissociation into mononuclear active species; and (*ii*) a relatively small π component in the metal–olefin bond. These and other structural features are compared with those of similar binuclear complexes.

It is well known [1,2] that π-allylic nickel and palladium complexes with halide and carboxylate groups can react with a cyclic (strained) olefin, such as norbornene, to give complexes in which the olefin is initially co-ordinated to the metal and then inserted into the allyl–metal bond. According to the scheme below,[2] the insertion is accompanied by the formation of binuclear molecules. Under suitable experimental conditions the reaction proceeds through the formation of mononuclear species which, by further addition and insertion of other monomeric units, initiate the propagation step with final formation of polymers and/or oligomers.[2-4]



M = Ni or Pd; X = halide or carboxylate; Y = H or Me; L = monomer (cyclic olefin) = HL′; L′ = σ-bonded alkyl moiety

Since in some cases it is possible to crystallize the products of the insertion reaction, we have carried out a systematic *X*-ray diffraction study of these crystals with the aim of obtaining some insight into the following mechanistic features: (*i*) the steric aspects of the insertion reaction; (*ii*) the possible structural factors favouring the dissociation of the binuclear insertion products into mononuclear species; and (*iii*) the stability of the bond between the olefinic end of the hydrocarbon ligand and the metal, as a function of M, X, and Y, in view of its possible relevance in the propagation step of the reaction. Thus, in the last few years we have investigated the crystal structures of four binuclear complexes with L = norbornene and with M, X, and Y, as follows:

	(1) [5,7]	(2) [6,7]	(3) [8]	(4) [9]
M	Ni	Ni	Ni	Pd
X	O_2CMe	O_2CMe	O_2CCF_3	O_2CMe
Y	Me	Me	Me	Me

Complexes (1) and (2) are configurational isomers which probably coexist in solution,[7,8] and (3) is isostructural with (2), as is (4) with (1).

Comparison of the structures of these products of the norbornene insertion reaction allowed us to make the following main conclusions.[8] (*a*) The insertion reaction of norbornene is always of the *exo* type, confirming the indications given by many reactions that access to the *exo* face of the olefinic function of this molecule, based on the bicycloheptane skeleton, is considerably easier than is access to the *endo* face. (*b*) In the polymerization of norbornene the molecular configuration of the insertion product seems to be a key factor in determining the fate of the reaction. In fact the prevalence in the reacting solution of molecules of type (2) with respect to those of type (1) clearly helps the formation of the mononuclear active species. (*c*) The main factors controlling the stability of the bond between the $>C{=}CH_2$ moiety and the metal are the asymmetry induced in the π* orbital of the olefinic group when Y = Me and the effective charge on the metal atom.

Following this reasoning and the suggestions given by these results we decided to extend our investigation by determining the crystal and molecular structure of the title complex, (5), for which M = Pd, X = Cl, and Y = H. Another complex, (6), was considered, for which M = Pd, X = Cl, and Y = Me, but unfortunately it was not possible in this case to grow a single crystal suitable for *X*-ray diffraction analysis. However, the indexing of the *X*-ray powder patterns of both complexes clearly showed that (5) and (6) are isostructural.[10]

Our initial interest in the structures of (5) and (6) derived from the observation [4] that these chloride-bridged complexes have some catalytic activity in the oligomerization of norbornene, and from the fact that the structure of (5) is probably not very different from that of the intermediate products of the reaction between norbornene and η-allylnickel chloride, which eventually leads to the polymerization of this cyclic olefin.[2]

EXPERIMENTAL

Complex (5) was obtained by treating η-allylpalladium chloride with norbornene in benzene–heptane (1 : 1 v/v) solution at 50 °C. Crystals suitable for *X*-ray analysis were prepared by recrystallizing the reaction product from toluene.[4]

Crystal Data.—$(C_{10}H_{15}ClPd)_2$, M = 554.17, Triclinic, a = 11.057(2), b = 7.346(1), c = 6.533(1) Å, α = 80°32′(2′), β = 104°31′(2′), γ = 94°39′(2′), U = 506.27 Å^3, space group $P\bar{1}$, Z = 1 (dimer), D_c = 1.817 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 20.0 cm^{-1}, $F(000)$ = 276.

The intensities of 3 562 non-zero independent reflections were measured on a Philips PW 1100 diffractometer (graphite monochromatized Mo-K_α radiation), up to $(\sin\theta)/\lambda = 0.787$, by the ω-scan technique. Data were corrected for Lorentz and polarization factors, as well as for absorption. A ψ scan of several reflections showed that multiple diffraction and extinction effects were not important in this crystal.

Structure Determination.—The position of the Pd atom was easily determined from a Patterson map, and a subsequent Fourier map showed all the non-hydrogen atoms of the structure. After a preliminary least-squares refinement, based on unit weighting factors and anisotropic thermal parameters in the block-diagonal approximation, a Fourier-difference synthesis allowed us to localize all the hydrogen atoms. All the computing routines used here are part of a system of crystallographic programs written by A. Immirzi (version for the Univac 1108 computer). Further full-matrix least-squares refinement, including the positional parameters of the hydrogen atoms, resulted in a final R factor of 0.040.

Atomic scattering factors were calculated from the values given by Cromer and Waber [11] for Pd and Cl, and by Hanson *et al.*[12] for C and H. The refined atomic positional parameters and their least-squares standard deviations are given in Table 1. Anisotropic thermal parameters for all the non-hydrogen atoms and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22471 (27 pp.).*

TABLE 1

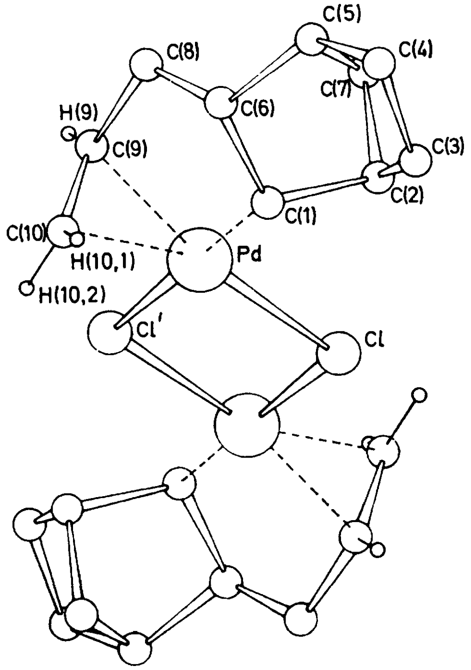
Atomic positional parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd	0.106 93(2)	0.457 12(3)	0.349 41(4)
Cl	−0.008 3(1)	0.712 7(1)	0.362 1(2)
C(1)	0.182 3(3)	0.584 8(5)	0.106 1(6)
C(2)	0.221 1(5)	0.792 1(6)	0.110 1(9)
C(3)	0.235 8(7)	0.872 7(10)	−0.117 0(13)
C(4)	0.355 5(8)	0.785 0(11)	−0.127 3(12)
C(5)	0.395 8(5)	0.668 4(9)	0.093 3(10)
C(6)	0.305 7(4)	0.498 4(6)	0.105 7(8)
C(7)	0.355 7(7)	0.786 4(11)	0.235 1(12)
C(8)	0.350 9(5)	0.358 5(9)	0.307 7(12)
C(9)	0.242 9(6)	0.254 8(8)	0.381 1(11)
C(10)	0.133 7(6)	0.202 6(6)	0.246 2(11)
H(1)	0.122(7)	0.591(10)	−0.043(12)
H(2)	0.154(7)	0.854(11)	0.138(12)
H(3,1)	0.157(9)	0.813(13)	−0.233(14)
H(3,2)	0.232(8)	1.006(13)	−0.150(15)
H(4,1)	0.313(8)	0.681(13)	−0.237(14)
H(4,2)	0.409(8)	0.885(12)	−0.174(13)
H(5)	0.482(9)	0.635(13)	0.135(15)
H(6)	0.285(7)	0.412(11)	−0.018(13)
H(7,1)	0.376(8)	0.917(14)	0.187(14)
H(7,2)	0.342(8)	0.721(13)	0.381(15)
H(8,1)	0.391(7)	0.251(11)	0.240(12)
H(8,2)	0.393(8)	0.433(13)	0.431(15)
H(9)	0.259(8)	0.214(12)	0.540(14)
H(10,1)	0.123(7)	0.228(11)	0.080(12)
H(10,2)	0.067(7)	0.130(11)	0.293(13)

DISCUSSION

The two halves of the dimeric molecule are related by a crystallographic inversion centre and each Pd ion is co-ordinated to two chlorine atoms, one carbon atom of the norbornyl moiety, and the enyl end of the allyl group, and has an approximately square-planar geometry (see Figure). Selected bond lengths and angles are given in Table 2.

The main feature of this co-ordination geometry is the Pd–Cl′ distance (2.517 Å) *trans* to the σ-bonded carbon atom C(1) which is very significantly longer than the Pd–Cl distance (2.376 Å) *trans* to the co-ordinated olefinic bond. In analogous carboxylato-complexes [5-9] we noted that a similar *trans* effect was the major destabilizing factor responsible for the dissociation of the dimers and the formation of the mononuclear species active in the catalytic process. If we define an index E_T for this *trans* effect as the ratio (× 100) of the difference between the two M–X distances to the M–X distance *trans* to the co-ordinated olefinic bond, in the case of (5) one has $E_T = 5.9\%$, while in the case of the previously studied carboxylato-complexes the E_T values are 4.4% for (1) and (4), 3.9 and 5.1% for the two non-equivalent Ni ions in (2), and 4.5 and 6.7% for the corresponding geometries in (3). The importance of the *trans* effect in (3) had already been pointed out.[8] A comparison of the E_T values indicates that in (5) this



Molecular structure of (5) showing the atom-numbering system

TABLE 2

Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses

Pd–Cl	2.376(1)	Pd–C(9)	2.148(6)
Pd–Cl′	2.517(1)	Pd–C(10)	2.155(4)
Pd–C(1)	2.037(4)	C(9)–C(10)	1.372(10)
Pd–C(9)–C(10)	71.7(3)	C(10)–C(9)–H(9)	121(5)
Pd–C(10)–C(9)	71.2(3)	C(9)–C(10)–H(10,1)	121(5)
C(9)–Pd–C(10)	37.2(4)	C(9)–C(10)–H(10,2)	124(5)
C(8)–C(9)–C(10)	124.3(4)	C(8)–C(9)–H(9)	115(5)
		H(10,1)–C(10)–H(10,2)	115(5)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

effect is equally important, thus justifying the relative activity[4] of this complex in the oligomerization of norbornene. Recently[13] an even more important *trans* effect (E_T 6.8%) was found in the similar dimeric palladium complex [{Pd(C_8H_{11})Cl}$_2$], where the hydrocarbon ligand is a cyclo-octa-1,5-dienyl group. In view of the close similarity between this complex and (5), a careful consideration of the finer structural differences between the two co-ordination geometries may be worthwhile.

Thus, in Table 3 the bond lengths in (5) are compared with the corresponding distances in [{Pd(C_8H_{11})Cl}$_2$]. It may be noted that in (5) the Pd–C σ bond is longer and *trans* to the shorter Pd–Cl bond, and that an analogous correspondence exists between the two Pd–(C=C) distances and the Pd–Cl bonds *trans* to them, with complex (5) featuring the shorter metal–olefin bond. We had already reported[8] that in (3) the shorter Ni–C σ bond is *trans* to the longer Ni–O distance, and therefore this effect seems to be general. While the inverse correlation between metal–olefin bond lengths and *trans* metal–ligand distances seems theoretically justified by recent SCF-Xα-SW calculations on Zeise's anion,[14] to the best of our knowledge no theoretical considerations have yet been published in the case of a metal–carbon σ bond.

TABLE 3

Correlation between Pd–C and *trans*-Pd–Cl bond lengths (Å) in complex (5) and in [{Pd(C_8H_{11})Cl}$_2$][13] (see text). Estimated standard deviations are in parentheses

Complex	σ-Pd–C	*trans* Pd–Cl	Pd–(C=C)	*trans* Pd–Cl
(5)	2.037(4)	2.517(1)	2.152(5) *	2.376(1)
[{Pd(C_8H_{11})Cl}$_2$]	2.005(6)	2.527(1)	2.169(6) *	2.366(1)

* Average of the two Pd–C(olefin) bond lengths.

In (5) the C(9)–C(10) olefinic ligand has a co-ordination geometry similar to the one of ethylene in Zeise's anion,[15] with a small shift of the bond axis from a symmetrical position perpendicular to the co-ordination plane, *i.e.* from the position which is considered ' normal ' in a square-planar co-ordination. This shift can be defined in terms of the angle δ [lying in the M–(C=C) plane] formed by the C=C bond axis with the normal to the average co-ordination plane and by the distance *d* of the centre of that bond from this plane. While in (5) the shift [δ 6.9(4)°, *d* 0.17(1) Å] is identical, within experimental error, to that in Zeise's anion [δ 5.8(12)°, *d* 0.20(3) Å], in (1)—(3)[8] and (4)[9] δ and *d* assume higher values as a consequence of the asymmetry in the π^* orbital of the olefinic group induced by the CH_3 substituent, which thus contributes to the destabilization of the olefin–metal bond.[8] Indeed in all the cases investigated so far (see the cited references), the larger shifts correspond to the longer M–(C=C) distances and therefore to the weaker bonds. A possible influence on this shift by the crystal packing cannot be very important in view of the rotational freedom about the two C–C single bonds in the allylic chain of the hydrocarbon ligand.[9] The importance of the above considerations in the general context of our *X*-ray diffraction studies on catalysis is indicated by the fact that in (2) and (3) the relative weakness of one of the two metal–olefin bonds in the dimers is partly responsible for the destabilization of these molecules, in addition to the effect (expressed by the different E_T values, see above) observed for the two non-equivalent Ni ions. In the case of (5), since this asymmetric effect does not exist, an alternative reason for the dissociation of the molecule can be found in the smallness of the electron charge on the metal, due to the strong electronegativity of the chloride anion,[16] leading to some instability of the olefin–metal bond.

Indeed the π component of the M–(C=C) bond is not very different from that (25% of the total bonding) calculated[14] for Zeise's anion, as indicated by the small, but significant, lengthening of the C=C bond [1.372(10) Å] with respect to the standard value (1.334 Å),[17] and by the small deviation of the olefinic ligand from planarity. The latter deviation is manifested in the bending back of the hydrogen atoms away from the metal and therefore can be measured by the angles β between the C=C bond axis and the normals to the H–C–H planes.[18] The average value of these angles in (5) is 85°, thus confirming that the deviation from planarity is very small in this case. It is of interest that in the recently reported[19] structure of a rhodium–ethylene complex, in which there is an important π component in the metal–olefin bond, the values of the two β angles are 61 and 71°.

In view of the above results and of the fact that Ni^{II} has a basicity even lower than Pd^{II}, it is not surprising to find that the corresponding complex obtained by treating norbornene with η-allylnickel chloride, which is a good catalyst in the polymerization of this cyclic olefin,[3] is not sufficiently stable for its crystallization.

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