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Crystal Structures of Dichlorobis(azocyclohexane)palladium(II) and Dichlorobis(azoisopropane)palladium(II)

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The structures of dichlorobis(azocyclohexane)Pd(II) and dichlorobis(azoisopropane)Pd(II) have been determined. The crystallographic data are: dichlorobis(azocyclohexane)Pd(II), Im3, $a=16.538(2)$ Å, $Z=6$, $R=8.9\%$ for 667 reflections; dichlorobis(azoisopropane)Pd(II), Pbca, $a=7.461(1)$, $b=17.096(1)$, $c=14.784(1)$ Å, $Z=4$, $R=6.8\%$ for 1451 reflections. In dichlorobis(azocyclohexane)Pd(II), a disorder occurs at the azo group, and the coordination mode of the ligand is not clear. The structure of dichlorobis(azoisopropane)Pd(II) agrees with that of dichlorobis(azobenzene)Pd(II).

The transition-metal which generates a nitrene R–N has attracted much attention from both organic and inorganic chemists in the last decade. A possible precursor is *N*,*N*-dichloroamine, which may generate nitrenes or nitrenoids by a reductive elimination of two chlorine atoms with some low-valent transition-metal complexes. Little is known about this process. Previously, some of the present authors reported that *N*,*N*-dichloroamine or -amide generated nitrenoids by a reaction with $Fe_2(CO)_9$,[1] and that tetrakis(methoxycarbonyl)palladiacyclopentadiene, $[PdC_4(COOCH_3)_4]_n$,[2,3] induced a ring-opening of the palladole skeleton with *N*,*N*-dichloroacylamides.[4]

This paper will describe some X-ray structure analyses of dichlorobis(azocyclohexane)palladium(II), $PdCl_2(c\text{-}C_6H_{11}\text{–}N{=}N\text{–}C_6H_{11}\text{-}c)_2$ I, which was obtained by the reaction of $[PdC_4(COOCH_3)_4]_n$ and $c\text{-}C_6H_{11}\text{–}NCl_2$, and of the related dichlorobis(azoisopropane)palladium(II), $PdCl_2(i\text{-}C_3H_7\text{–}N{=}N\text{–}C_3H_7\text{-}i)_2$ II, which was prepared by a ligand-exchange reaction between an excess of azoisopropane and dichlorobis(benzonitrile)palladium(II). The X-ray structure indicated unequivocally that the cyclohexylnitrene generated by the palladium complex was dimerized to azocyclohexane, which was then coordinated to the palladium(II). The azocyclohexane complex, I, exhibits a substantial disorder around the azo nitrogen atoms. However, the structure of the azoisopropane complex, II, has the lone-pair coordination of the azo group, in a fashion similar to the dichlorobis(azobenzene)palladium(II).[5]

Experimental

Preparation of Dichlorobis(azocyclohexane)palladium(II) I. A benzene (2 ml) solution of *N*,*N*-dichlorocyclohexylamine (0.678 g, 4.04 mmol) was stirred into a benzene (10 ml) suspension of $[PdC_4(COOCH_3)_4]_n$ (0.359 g, 0.921 mmol) under an argon atmosphere at room temperature. The mixture turned to an orange solution, which was then stirred overnight. Ethyl ether (5 ml) was added to the mixture, resulting in the formation of a reddish brown solid of $c\text{-}C_6H_{11}NH_2\cdot HCl$, which was then filtered off. The brown filtrate was concentrated to *ca.* 2 ml under reduced pressure. A mixed solvent composed of ethyl ether and methanol (1:1 vol ratio) was added to the oily residue, and the mixture was kept in a refrigerator for a few days to give $PdCl_2(c\text{-}C_6H_{11}\text{–}N{=}N\text{–}C_6H_{11}\text{-}c)_2$ as yellow prisms in a 16.7% yield. Mp 159.5—160.0 °C. IR(KBr); 2930, 2850(C–H), 1596, 1433, and 338(Pd–Cl)cm^{-1}. NMR($CDCl_3$); δ 5.45(br, 2H, CH–N), 5.35(br, 2H, CH–N), 0.79—2.55(m, 40H, other cyclohexyl protons). CMR($CDCl_3$); δ 32.59(C(1)), 29.40, 29.29(C(2)), 25.41, 25.12, 24.03, and 23.84(C(3), C(4)).

Found: C, 51.05; H, 7.89; N, 9.74%. Calcd for $C_{24}H_{44}N_4Cl_2Pd$: C, 50.94; H, 7.84; N, 9.90%.

The same complex was prepared in a 55.2% yield by the reaction of dichlorobis(benzonitrile)palladium(II) (209.8 mg) with an excess of azocyclohexane (0.6 ml) in benzene (10 ml). The X-ray analysis indicated that this is the same as the above complex. Found: C, 50.96; H, 8.07; N, 9.72%.

Preparation of Dichlorobis(azoisopropane)palladium(II) II. An excess of azoisopropane (0.5 ml) was stirred, drop by drop, into a benzene (10 ml) solution of dichlorobis(benzonitrile)palladium(II) (198 mg, 0.517 mmol) at room temperature. The reaction took place instantaneously to give a pale yellow solution. The benzene and the excess azoisopropane were removed under reduced pressure after 1 h. The crude II was obtained quantitatively and was recrystallized from 8 ml of dry methanol to yield yellow prisms. Mp 136—137 °C. IR(KBr); 2960, 2920 (C–H), 1594, and 335(Pd–Cl)cm^{-1}. NMR($CDCl_3$); δ 5.60(brm, 2H, CH–N), 4.87(m, 2H, $J=7$ Hz, CH–N), and 1.51(d, 24H, $J=7$ Hz, CH_3).

Found: C, 35.49; H, 7.29; N, 13.92%. Calcd for $C_{12}H_{28}N_4Cl_2Pd$: C, 35.53; H, 6.96; N, 13.81%.

Crystallographic Procedure. The crystal data are as follows. Complex I; *F.W.*$=566.0$, Im3, $a=16.538(2)$ Å, $Z=6$, $D_m=1.27$, $D_x=1.247$ g cm^{-3}, and μ(Mo $K\alpha$)$=8.17$ cm^{-1}. Complex II; *F.W.*$=405.7$, Pbca, $a=7.461(1)$, $b=17.096(1)$, $c=14.784(1)$ Å, $Z=4$, $D_m=1.38$, $D_x=1.434$ g cm^{-3}, and μ(Mo $K\alpha$)$=12.1$ cm^{-1}.

For I, the intensity data were collected on a Hilger & Watts automatic diffractometer (at the Faculty of Science, Nagoya University) using Zr-filtered Mo $K\alpha$ radiation. 741 reflections with $2\theta \leq 50°$ were measured by the θ-2θ step-scan technique. For II, 2148 reflections with $2\theta \leq 55°$ were obtained by the use of a Rigaku automatic diffractometer (at the Institute for Protein Research, Osaka University), using Mo $K\alpha$ radiation and a Graphite-crystal monochro-

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Table 1. Dichlorobis(azocyclohexane)Pd(II): the atomic parameters and their estimated standard deviations($\times 10^4$)
The thermal parameters are in the form: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	Wyckoff position[a]	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	b	5000	0	0	34(1)	38(1)	42(1)	0	0	0
Cl	e	5000	0	1392(3)	61(2)	76(3)	45(2)	0	0	0
N(1)	g	3811(13)	257(12)	0	32(8)	41(11)	44(8)	−1(12)	0	0
N(2)	g	3237(16)	−176(14)	0	40(9)	36(21)	70(12)	9(15)	0	0
C(1)	g	3506(11)	1079(11)	0	54(7)	53(7)	80(10)	49(13)	0	0
C(2)	h	3059(12)	1382(7)	748(6)	115(10)	44(4)	40(4)	29(11)	−10(11)	−8(7)
C(3)	h	3017(14)	2318(9)	754(10)	110(11)	51(5)	66(7)	37(13)	20(15)	−18(10)
C(4)	g	2600(18)	2597(17)	0	91(15)	84(13)	59(11)	75(22)	0	0

a) See Ref. 9.

Table 2. Dichlorobis(azocyclohexane)Pd(II): the positional parameters of the hydrogen atoms($\times 10^3$)
The standard deviations are given in parentheses.

	x	y	z
H(1)	401(13)	103(13)	0
H(21)	341(8)	109(8)	120(8)
H(22)	247(8)	99(10)	73(9)
H(31)	376(10)	250(7)	79(8)
H(32)	261(9)	249(8)	108(12)
H(41)	242(10)	331(13)	0
H(42)	198(16)	246(10)	0

mator (monochromator $2\theta=12.16°$). The θ-2θ scan was adopted . The crystals used for the data collection had the dimensions of $0.20\times0.25\times0.16$ mm for I and of $0.33\times0.30\times0.14$ mm for II. The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was made.

Structure Determination

The structures were solved by the heavy-atom method. The refinement was carried out by the full-matrix least-squares method for I and by the block-diagonal least-squares method for II.[6] In the refinement, non-zero reflections were included and the weight $w=1/(\sigma^2(F)+a|F_o|+b|F_o|^2)$ was assigned, where $\sigma(F)$ is the standard deviation based on the counting statistics. The isotropic temperature factors for the H atoms were kept constant at 5.0 Å^2.

The space group of I is either Im3, I23, or I$2_1$3, judging from the systematic absences of the reflections. However, I$2_1$3 is excluded because the space group can not contain 6 molecules in a unit cell. If the space group is Im3, there exists an mmm symmetry in the complex, while in I23 a complex has a 222 symmetry. The refinement was carried out independently with Im3 and I23. The final R's for 667 reflections were: 8.9%(a=0.1181 and b=0.0062) for Im3 and 8.3% for I23. The R value with Im3 is inferior to that with I23. However, the structure of the cyclohexane group in I23 is greatly distorted from normal, while the structure in Im3 is reasonable. Thus the space group Im3 seems the more plausible. There is a disorder associated with the azo group. The correlation matrix, λ, shows that the correlation between the x parameters of N(1) and N(2) is significant ($\lambda_{jj'}=0.32$). The other correlations are insignificantly small. The final R of II is 6.8% (a=0.0221 and b=0.0011) for 1451 reflections.

The atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. IV.[7] The calculations were carried out on the FACOM 230-60/75 computers at Nagoya University. The final atomic parameters are listed in Tables 1, 2, 3, and 4.[8]

Table 3. Dichlorobis(azoisopropane)Pd(II): the atomic parameters and their estimated standard deviations($\times 10^4$)
The thermal parameters are in the form: $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0	0	0	173(1)	29(1)	35(1)	−2(1)	5(1)	−1(1)
Cl	2439(3)	694(1)	516(1)	201(3)	47(1)	54(1)	−38(3)	−11(3)	−15(1)
N(1)	1590(9)	−826(3)	−538(4)	228(13)	38(2)	36(2)	1(9)	30(10)	−3(4)
N(2)	2375(10)	−1380(4)	−168(4)	265(13)	35(2)	45(3)	26(11)	20(11)	5(4)
C(1)	1777(11)	−816(5)	−1558(4)	264(17)	51(3)	35(3)	26(13)	51(13)	13(5)
C(2)	2696(16)	−63(5)	−1800(4)	553(34)	57(4)	7(2)	−37(17)	109(15)	3(4)
C(3)	2516(14)	−1524(5)	−1950(5)	418(26)	49(3)	37(3)	3(17)	14(18)	−9(5)
C(4)	2132(11)	−1429(4)	820(5)	295(20)	37(3)	39(3)	33(12)	−12(13)	10(5)
C(5)	733(16)	−2032(6)	1013(6)	372(27)	72(5)	61(5)	−42(20)	55(21)	27(9)
C(6)	3952(16)	−1678(6)	1188(7)	410(31)	79(6)	66(6)	−38(23)	−67(23)	30(9)

Table 4. Dichlorobis(azoisopropane)Pd(II): the positional parameters of the hydrogen atoms($\times 10^3$)
The standard deviations are given in parentheses.

	x	y	z
H(1)	34(11)	−87(5)	−175(6)
H(21)	268(11)	−4(4)	−242(6)
H(22)	205(11)	40(5)	−137(6)
H(23)	380(13)	−9(4)	−138(7)
H(31)	239(10)	−151(5)	−259(5)
H(32)	177(12)	−197(5)	−173(6)
H(33)	389(12)	−155(5)	−171(6)
H(4)	175(12)	−90(5)	106(6)
H(51)	117(11)	−248(5)	72(6)
H(52)	−44(12)	−193(5)	73(7)
H(53)	58(12)	−215(5)	162(6)
H(61)	373(12)	−169(5)	180(6)
H(62)	463(11)	−124(5)	110(6)
H(63)	408(12)	−223(5)	99(6)

Table 5. Dichlorobis(azoisopropane)Pd(II): the best planes

(a) Equations of the best planes.

$X=ax,\ Y=by,\ Z=cz$

Plane I: Pd, Cl, N(1)
$-0.0293X-0.5090Y+0.8603Z=0$

Plane II: Pd, N(1), N(2)
$0.7978X+0.5830Y+0.1540Z=0$

Plane III: N(1), N(2), C(1), C(4)
$-0.8280X-0.5517Y-0.1006Z+0.1135=0$

Plane IV: C(1), C(2), C(3)
$0.6049X-0.1025Y+0.7897Z+0.8745=0$

Plane V: C(4), C(5), C(6)
$-0.2065X+0.4506Y+0.8685Z+0.3755=0$

(b) Dihedral angles(°) between the planes.

	I	II	III	IV
II	100.8			
III	102.6	176.1		
IV	135.5	123.0	121.6	
V	121.6	103.4	99.5	121.0

(c) Displacements($\times 10^3$ Å) of atoms from the planes.

The atoms with asterisks are not included in the best plane calculations.

II		III	
Pd	0	N(1)	−9
N(1)	0	N(2)	−27
N(2)	0	C(1)	17
C(1)*	−111	C(4)	21
C(4)*	32	Pd*	114

Description of Structures

Complex I. A disorder is observed at the azo group. A quarter part of the composite Fourier map is drawn in Fig. 1, where Cl is not drawn, since the Cl atom is in front of Pd. The two N atoms of the azo group are equivalent, and should be located at the d position of the space group Im3.[9] However, the Fourier and D-Fourier maps prepared with and without N(1) and N(2) made clear that the azo nitrogen atoms do not satisfy this situation. Therefore N(1) and N(2), with occupancies of 0.5 each, were located at the other special positions, g. This disordered model satisfies the symmetry, though no reasonable skeleton with proper covalent bonds can be proposed for this

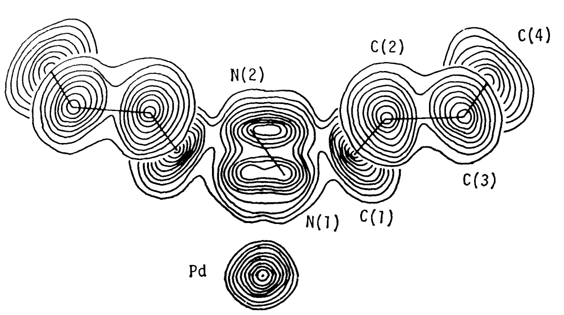


Fig. 1. Dichlorobis(azocyclohexane)Pd(II): The composite Fourier map. Cl is in front of Pd, and is not shown. For Pd, first contour 5 eÅ^{-3}, interval 10 eÅ^{-3}. For N and C, first contour 0.5 eÅ^{-3}, interval 0.5 eÅ^{-3}.

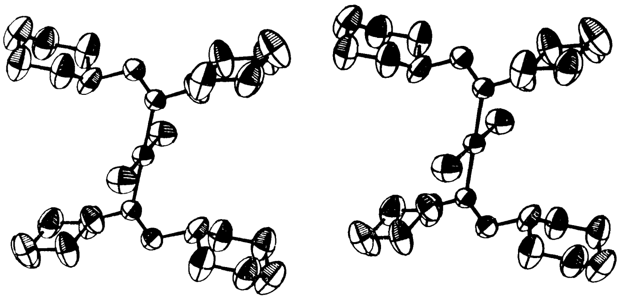


Fig. 2. Dichlorobis(azocyclohexane)Pd(II): The stereoscopic view of the model structure.

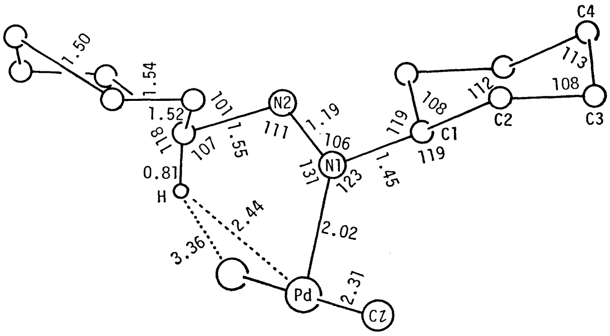
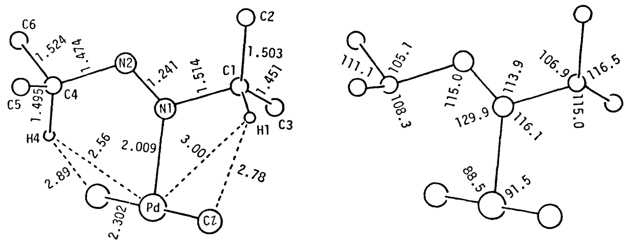


Fig. 3. Dichlorobis(azocyclohexane)Pd(II): Bond lengths(Å) and angles(°).



(a) (b)

Fig. 4. Dichlorobis(azoisopropane)Pd(II): (a) Bond lengths(Å). (b) Bond angles(°).

TABLE 6. BOND LENGTHS AND ANGLES CONCERNING THE AZO GROUPS

	Dichlorobis(azo-isopropane)Pd(II)[a]	Dichlorobis (azobenzene)Pd(II)[b]	
(a) Bond lengths (Å)			
N(1)-N(2)	1.241	1.240	1.237
N(1)-C(1)	1.514	1.427	1.425
N(2)-C(4)	1.474	1.407	1.411
(b) Bond angles (°)			
Pd-N(1)-N(2)	129.0	129.0	129.3
Pd-N(1)-C(1)	116.1	117.8	117.7
N(2)-N(1)-C(1)	113.9	113.0	112.7
N(1)-N(2)-C(4)	115.0	118.7	118.1

a) This study. b) See Ref. 5.

complex. The refinement of the model structures gave the proper temperature factors for both N(1) and N(2), as compared with those of the other atoms. All the H atoms were found in the D-Fourier map. The H(1) peak is most prominent, with a height of 0.62 e$Å^{-3}$. The other peaks ranged from 0.30 to 0.54 e$Å^{-3}$. The stereoscopic view of one of the model structures drawn by ORTEP II[10] is shown in Fig. 2. The dimensions are given in Fig. 3. The e.s.d.'s are: 0.02—0.04 Å for bond lengths except for Pd-Cl (0.006 Å) and 1.7—2.2° for bond angles. The model shown in Figs. 2 and 3 is just a tentative one. Therefore, low-temperature work is desirable for this complex.

Complex II. The bond lengths and angles are given in Fig. 4. The e.s.d.'s are 0.007—0.014 Å for all the bond lengths except for Pd-Cl (0.002 Å), and 0.2—0.9° for the angles. The best planes and the related data are given in Table 5.

In II, there is no disorder, and a proper coordination mode is found which is similar to those of the other azo complexes. The symmetry of II is only a center of inversion. The two isopropyl groups are not equivalent to each other. The bond lengths and angles of the azo group of II are compared with those of dichlorobis(azobenzene)Pd(II), AZB,[5] in Table 6. The structures of the azo groups in both complexes are very similar to each other, though AZB has no symmetry in the molecule. The N(1)-C(1) length is larger than N(2)-C(4). The N-C bond lengths in AZB are much shorter than those in II. The bond angles concerning N(1), which coordinates to Pd, are in good agreement between II and AZB. However, the N(1)-N(2)-C(4) angles are significantly different in these complexes. The corresponding angle in II is smaller than that in AZB.

Short contacts involving the H atoms are found in these complexes. The H···Pd contacts are 2.56 Å in II, and 2.60 and 2.61 Å in AZB. Fairly short H···Cl contacts are observed: 2.78 Å in II, and 2.59 Å in AZB.

Discussion

When $[PdC_4(COOCH_3)_4]_n$[2,3] reacted with *N,N*-dichlorocyclohexylamine at room temperature, yellow-orange crystals with the composition of $PdCl_2(c\text{-}C_6H_{11}N)_4$, I, were obtained in a 16.7% yield. A complete elimination of the diene unit, $C_4(COOCH_3)_4$, from the palladiacyclopentadiene skeleton indicates the formation of a highly reactive Pd(0) state which abstracts two Cl atoms from *N,N*-dichlorocyclohexylamine to generate cyclohexylnitrene. The X-ray analysis of I made it clear that cyclohexylnitrene was dimerized to azocyclohexane, followed by the coordination of the dichloropalladium(II) moiety. The latter process was confirmed by the independent preparation of I from dichlorobis(benzonitrile)palladium(II) and azocyclohexane. This behavior is different from similar reactions between $[PdC_4(COOCH_3)_4]_n$ and several *N,N*-dichloroacyl amides,[4] which gave σ-4-chloro-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienylpalladium complexes by the ring-opening of only one Pd–C bond of the palladiacyclopentadiene skeleton.

The NMR spectrum of I indicates two broad signals due to H(1) at δ 5.45 and 5.35; these signals show substantial low-field shifts from free azocyclohexane (δ 3.26) on coordination. The separation and intensive broadening of the two signals indicate that the two H(1)'s are not equivalent to each other in solution. The difference between the two cyclohexyl rings in solution is also consistent with the CMR spectrum of I, in which three signals corresponding to the C(2), C(3), and C(4) atoms are observed.

On the contrary, the NMR spectrum of II shows a well-separated multiplet(J=7 Hz) at δ 4.87, indicative of H(4), as well as a broad multiplet at δ 5.60, which is ascribed to H(1). This fact clearly suggests that the coordination mode of II in solution is consistently identical with that in the solid state.

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