June, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 1843—1844 (1985)* 1843

Dichlorotetrakis(isocyanide)dipalladium(I) Containing a Metal-Metal Bond[1)]

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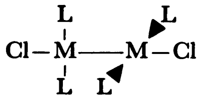
(Received November 21, 1984)

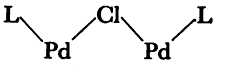
Synopsis. The structure of $[\{PdCl(t\text{-}BuNC)_2\}_2]$ has been determined by X-ray diffraction. A metal-metal bond joins two Pd atoms, each of which possesses an essentially square-planar coordinate site. The photochemical reaction of $[\{PdCl(RNC)_2\}_2]$ in CH_2Cl_2 led to a cleavage of the metal-metal bond to give *trans*-$[PdCl_2(t\text{-}BuNC)_2]$.

Metal clusters attract considerable attention as plausible models of surfaces in heterogeneous catalysts.[2)] Binuclear complexes are the simplest units which can provide information on the metal-metal interactions. Previously we reported that the electrochemical reductions of *cis*-$[PtCl_2(RNC)_2]$ gave $[\{PtCl(RNC)_2\}_2]$ **1** containing a metal-metal bond.[3)] This finding prompted us to reexamine the structure of $[\{PdCl(t\text{-}BuNC)_2\}_2]$, assigned to chloride bridged structure.[4)]



1: M = Pt

2X: M = Pd



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When we were preparing the paper on the X-ray crystallographic analysis of $[\{PdCl(t\text{-}BuNC)_2\}_2]$ **2a**, we knew of the study on crystal structure of $[\{PdI(MeNC)_2\}_2]$ **3** described by Balch and his co-workers.[5)] We report here the X-ray analysis of **2a** and the characterization of related complexes having aromatic isocyanides as ligands.

Experimental

The isocyanides,[6)] $PdCl_2(RNC)_2$,[7)] and $[\{PdCl(RNC)_2\}_2]$[7)] were prepared according to the literature.

$PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2$: IR (Nujol): 2205, 2172 cm^{-1} (N≡C). Found: C, 49.15; H, 4.18; N, 6.37%. Calcd for $C_{18}H_{18}N_2Cl_2Pd$: C, 49.17; H, 4.13, N, 6.37%.

$PdCl_2(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_2$. IR (Nujol): 2224, 2205 cm^{-1} (N≡C). Found: C, 36.17; H, 2.73; N, 4.59%. Calcd for $C_{18}H_{16}N_2Cl_2Br_2Pd$: C, 36.19; H, 2.70; N, 4.69%.

$[\{PdCl(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$ **2b**. IR (Nujol): 2155 cm^{-1}. (N≡C). ^{1}H NMR($CDCl_3$): δ=2.53 (s, CH_3), 7.2 (aromatic protons). Found: C, 53.50; H, 4.46; N, 6.84%. Calcd for $C_{36}H_{36}N_4Cl_2Pd_2$: C, 53.49; H, 4.49; N, 6.93%.

$[\{PdCl(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_2\}_2]$ **2c**. IR (Nujol): 2154 cm^{-1} (N≡C). ^{1}H NMR ($CDCl_3$): δ=2.50 (s, CH_3), 7.31 (aromatic protons). Found: C, 38.19; H, 2.95; N, 4.92%. Calcd for $C_{36}H_{32}N_4Br_4Cl_2Pd_2$: C, 38.47; H, 2.87; N, 4.98%.

$[Pd_2(2,6\text{-}Me_2C_6H_3NC)_6](PF_6)_2(2C_6H_6)$ **4b**. IR (Nujol): 2194, 2173 cm^{-1}. UV (CH_2Cl_2): λ 264 (49230), 325 sh nm. Found: C, 54.78; H, 4.40; N, 5.74%. Calcd for $C_{66}H_{66}N_6P_2F_{12}Pd_2$: C, 54.82; H, 4.60; N, 5.81%.

$[Pd_2(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_6](PF_6)_2$ **4c**. IR (Nujol): 2170 cm^{-1} (N≡C). UV(CH_2Cl_2): λ 275(58640), *ca.* 335 sh nm. Found: C, 36.75; H, 2.75; N, 4.82%. Calcd for $C_{54}H_{48}N_6Br_6P_2F_{12}Pd_2$: C, 36.79; H, 2.74; N, 4.77%.

X-Ray Data and Structure Determination. Crystal data: space group C_c. a=12.665(2), b=14.449(2), c=18.402(3) Å, β=102.94(1)°, V=3282(9) Å^3. Z=4. R=0.060 for 2588 reflections. The choice of the space group C_c was justified on the basis of the successful refinement of the struture. Intensity data were collected with the crystals mounted in a nitrogen filled capillary. The positions of the palladium atoms were determined from Patterson maps. Subsequent difference Fourier maps and cycles of block-diagonal least-squares refinement revealed the positions of the remaining nonhydrogen atoms. The scattering factors were taken from "International Table for X-Ray Crystallography" (1974). The two *t*-butyl groups displayed disorder. The Pd and Cl, and C–N–C groups were refined anisotropically and other nonhydrogen atoms isotropically. The final difference synthesis showed no peaks higher than 0.4 e Å^{-3}.

Results and Discussion

The dimeric complexes $[\{PdCl(RNC)_2\}_2]$ (**2a**: R=*t*-Bu; **2b**: R=2,6-$Me_2C_6H_3$; **2c**: R=2,6-Me_2-4-BrC_6H_2) were prepared by the reaction of $Pd_2(dba)_3(CHCl_3)$, isocyanide and dichlorobis(isocyanide)palladium(II) in a 1:4:2 ratio. They are yellow and stable. The IR spectra showed a peak near 2155 cm^{-1} due to terminal isocyanide groups. The reaction of **2b** with 2,6-xylyl isocyanide in the presence of NH_4PF_6 took place readily to give $[Pd_2(2,6\text{-}Me_2C_6H_3NC)_6](PF_6)_2$ **4b** quantitatively.

The photochemical reaction of **2a** in CH_2Cl_2 was monitored by the electronic spectra. The band at 307 nm in **2a** decreased with the photolysis time and finally the spectrum was in good agreement with that of *trans*-$[PdCl_2(t\text{-}BuNC)_2]$, indicating a cleavage of a metal-metal bond. The band at 307 nm was assigned as a σ-σ^* transition.

$$[\{PdCl(t\text{-}BuNC)_2\}_2] \xrightarrow[CH_2Cl_2]{h\nu} trans\text{-}[PdCl_2(t\text{-}BuNC)_2]$$

Similar σ-σ^* transitions connected with metal-metal bonds have also been observed in the same range with $[\{PtCl(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_2\}_2]$ **1d**[3)] [324 nm(CH_2Cl_2)] and $[Pd_2(MeNC)_6](PF_6)_2$ **5** [302 nm(CH_2Cl_2)].[8)]

Crystal Structure of **2a**.[9)] The crystal structure is shown in Fig. 2. Typical bond lengths and angles are given in Table 1. A metal-metal bond joins the two Pd atoms, each of which possesses essentially a square-planar coordinate geometry with the Pd–Pd bond occupying one of the coordination sites. The overall geometry is nearly D_{2d} symmetry. The Pd(1)–Pd(2) bond length of 2.532(2) Å is similar to those [2.533(1) and 2.531(9) Å] found in **3** and **5**, and somewhat shorter than those [2.563(2) and 2.561(2) Å] found in **1d**. The dihedral angle between the two $PdClC_2$ coordination planes is 82.7°, compared with those (85.3 and 86.4°) in **3** and **5**. The Cl-Pd-Pd-Cl unit is nearly linear. The Pd-Pd-Cl angles are 176.7

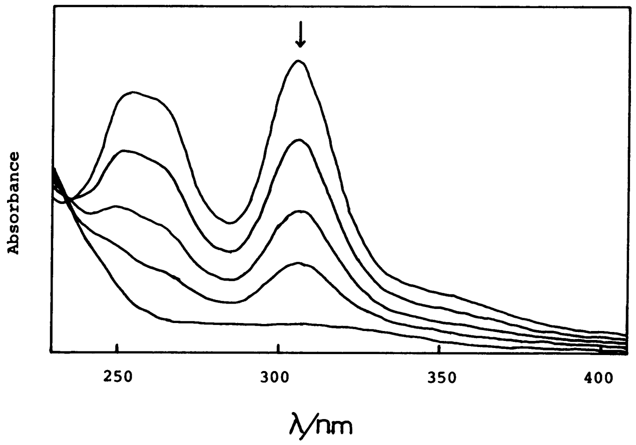

Fig. 1. Electronic spectrum of $[PdCl(t\text{-}BuNC)_2]_2$ in CH_2Cl_2 as a fnction of photolysis time.

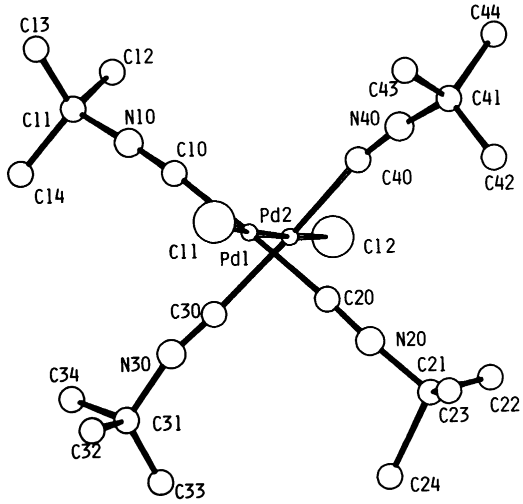

Fig. 2. A perspective drawing of $[PdCl(t\text{-}BuNC)_2]_2$ with the numbering scheme.

(2) and 177.4(2)°. The Pd–Cl bond lengths of 2.403 (9) and 2.416(9) Å, are longer than those [2.300(2) and 2.302(2) Å] of *cis*-$[PdCl_2(c\text{-}C_6H_{11}NC)_2]$.[10] This arises from the high trans effect of Pd–Pd bond. Similar behavior of terminal halide-metal bonds trans to metal-metal bonds has been noted in **3**.[5] The equatrial isocyanide ligands bend away from the axial Cl ligand giving rise to values of 97.2° for the mean C–Pd–Cl angle and 83.0° for the mean C–Pd–Pd angle. A similar distortion has been observed in **1d**, **3**, and **5**, where the averages of C–M–Cl (or equatrial C) angles are 93.8, 95.2, and 95.0°, the averages of C–M–M angles are 85.5, 84.7, and 85.0°, respectively. Thus, the type of the complexes $[\{PdCl(RNC)_2\}_2]$ was revised to the structure **2a** involving terminal halogens and a metal-metal bond.

A list of the final F_o—F_c table, bond lengths and angles (Table 1), and temperature factors are deposited as Document No. 8523 at the office of Bull. Chem. Soc. Jpn.

Table 2. Positional parameters for $[\{PdCl(t\text{-}BuNC)_2\}_2]$[a)]

ATOM	X	Y	Z
PD1	0(0)	1126(1)	2500(0)
PD2	1659(2)	1119(1)	3564(1)
CL1	−1538(6)	1052(6)	1464(3)
CL2	3281(6)	1063(6)	4548(4)
N10	−794(16)	−102(13)	3649(11)
C10	−515(16)	321(13)	3194(10)
C11	−1052(21)	−580(18)	4293(14)
N20	1117(14)	2586(12)	1695(9)
C20	730(16)	2029(13)	1986(11)
C21	1811(23)	3264(20)	1435(17)
N30	372(19)	2572(16)	4261(13)
C30	831(24)	2082(21)	4010(16)
C31	−30(21)	3385(18)	4622(15)
N40	2382(17)	−209(15)	2433(11)
C40	2104(25)	189(21)	2849(16)
C41	2484(24)	−514(20)	1697(15)
C12	0(3)	−107(3)	473(2)
C13	−177(2)	−133(2)	413(2)
C14	−151(2)	22(2)	472(2)
C22	300(6)	307(5)	167(4)
C23	128(7)	330(6)	57(5)
C24	158(6)	430(5)	192(4)
C22A	262(5)	274(4)	108(3)
C23A	99(5)	382(4)	83(3)
C24A	240(5)	384(4)	210(3)
C32	−112(8)	355(7)	405(5)
C33	61(7)	417(6)	475(5)
C34	−16(5)	307(4)	540(4)
C32A	43(5)	428(4)	442(3)
C33A	−130(5)	336(4)	435(3)
C34A	33(5)	329(4)	546(3)
C42	271(3)	28(2)	121(2)
C43	141(3)	−85(3)	130(2)
C44	349(5)	−134(4)	198(3)

a) Positional parameters from Pd1 to C41 atoms are multiplied by 10^4 and those from C12 to C44 atoms, by 10^3.

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