

Dichlorotetrakis(isocyanide)dipalladium(I) Containing a Metal–Metal Bond¹⁾

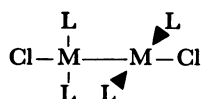
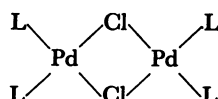
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Synopsis. The structure of $[\{\text{PdCl}(t\text{-BuNC})_2\}_2]$ has been determined by X-ray diffraction. A metal–metal bond joins two Pd atoms, each of which possesses an essentially square-planar coordinate site. The photochemical reaction of $[\{\text{PdCl}(\text{RNC})_2\}_2]$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

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 $\text{cis-}[\text{PtCl}_2(\text{RNC})_2]$ gave $[\{\text{PtCl}(\text{RNC})_2\}_2]$ **1** containing a metal–metal bond.³⁾ This finding prompted us to reexamine the structure of $[\{\text{PdCl}(t\text{-BuNC})_2\}_2]$, assigned to chloride bridged structure.⁴⁾

**1:** M = Pt**2****2X:** M = Pd

When we were preparing the paper on the X-ray crystallographic analysis of $[\{\text{PdCl}(t\text{-BuNC})_2\}_2]$ **2a**, we knew of the study on crystal structure of $[\{\text{PdI}(\text{MeNC})_2\}_2]$ **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⁾ $\text{PdCl}_2(\text{RNC})_2$,⁷⁾ and $[\{\text{PdCl}(\text{RNC})_2\}_2]$ ⁷⁾ were prepared according to the literature.

$\text{PdCl}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2$: IR (Nujol): 2205, 2172 cm^{-1} ($\text{N}\equiv\text{C}$). Found: C, 49.15; H, 4.18; N, 6.37%. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{-Cl}_2\text{Pd}$: C, 49.17; H, 4.13; N, 6.37%.

$\text{PdCl}_2(2,6\text{-Me}_2\text{-4-BrC}_6\text{H}_2\text{NC})_2$. IR (Nujol): 2224, 2205 cm^{-1} ($\text{N}\equiv\text{C}$). Found: C, 36.17; H, 2.73; N, 4.59%. Calcd for $\text{C}_{18}\text{H}_{16}\text{-N}_2\text{Cl}_2\text{Br}_2\text{Pd}$: C, 36.19; H, 2.70; N, 4.69%.

$[\{\text{PdCl}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_2\}_2]$ **2b**. IR (Nujol): 2155 cm^{-1} ($\text{N}\equiv\text{C}$). $^1\text{H NMR}(\text{CDCl}_3)$: $\delta=2.53$ (s, CH_3), 7.2 (aromatic protons). Found: C, 53.50; H, 4.46; N, 6.84%. Calcd for $\text{C}_{36}\text{H}_{36}\text{-N}_4\text{Cl}_2\text{Pd}_2$: C, 53.49; H, 4.49; N, 6.93%.

$[\{\text{PdCl}(2,6\text{-Me}_2\text{-4-BrC}_6\text{H}_2\text{NC})_2\}_2]$ **2c**. IR (Nujol): 2154 cm^{-1} ($\text{N}\equiv\text{C}$). $^1\text{H NMR}(\text{CDCl}_3)$: $\delta=2.50$ (s, CH_3), 7.31 (aromatic protons). Found: C, 38.19; H, 2.95; N, 4.92%. Calcd for $\text{C}_{36}\text{H}_{32}\text{-N}_4\text{Br}_4\text{Cl}_2\text{Pd}_2$: C, 38.47; H, 2.87; N, 4.98%.

$[\text{Pd}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6](\text{PF}_6)_2(2\text{C}_6\text{H}_6)$ **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 $\text{C}_{66}\text{H}_{66}\text{N}_6\text{P}_2\text{F}_{12}\text{Pd}_2$: C, 54.82; H, 4.60; N, 5.81%.

$[\text{Pd}_2(2,6\text{-Me}_2\text{-4-BrC}_6\text{H}_2\text{NC})_6](\text{PF}_6)_2$ **4c**. IR (Nujol): 2170 cm^{-1} ($\text{N}\equiv\text{C}$). UV (CH_2Cl_2): λ 275 (58640), ca. 335 sh nm. Found: C, 36.75; H, 2.75; N, 4.82%. Calcd for $\text{C}_{54}\text{H}_{48}\text{-N}_6\text{Br}_6\text{P}_2\text{F}_{12}\text{Pd}_2$: C, 36.79; H, 2.74; N, 4.77%.

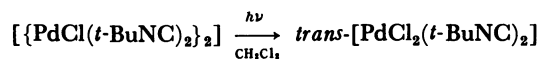
X-Ray Data and Structure Determination. Crystal data:

space group C_c . $a=12.665(2)$, $b=14.449(2)$, $c=18.402(3)$ Å, $\beta=102.94(1)^\circ$, $V=3282(9)$ Å³. $Z=4$. $R=0.060$ for 2588 reflections. The choice of the space group C_c was justified on the basis of the successful refinement of the structure. 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 non-hydrogen 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 $0.4\text{ e}\text{\AA}^{-3}$.

Results and Discussion

The dimeric complexes $[\{\text{PdCl}(\text{RNC})_2\}_2]$ (**2a**: $\text{R}=t\text{-Bu}$; **2b**: $\text{R}=2,6\text{-Me}_2\text{C}_6\text{H}_3$; **2c**: $\text{R}=2,6\text{-Me}_2\text{-4-BrC}_6\text{H}_2$) were prepared by the reaction of $\text{Pd}_2(\text{dba})_3(\text{CHCl}_3)$, 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 $[\text{Pd}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_6](\text{PF}_6)_2$ **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 $\text{trans-}[\text{PdCl}_2(t\text{-BuNC})_2]$, indicating a cleavage of a metal–metal bond. The band at 307 nm was assigned as a $\sigma\text{-}\sigma^*$ transition.



Similar $\sigma\text{-}\sigma^*$ transitions connected with metal–metal bonds have also been observed in the same range with $[\{\text{PtCl}(2,4\text{-}t\text{-Bu}_2\text{-6-MeC}_6\text{H}_2\text{NC})_2\}_2]$ **1d**³⁾ [324 nm (CH_2Cl_2)] and $[\text{Pd}_2(\text{MeNC})_6](\text{PF}_6)_2$ **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 PdClCl_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

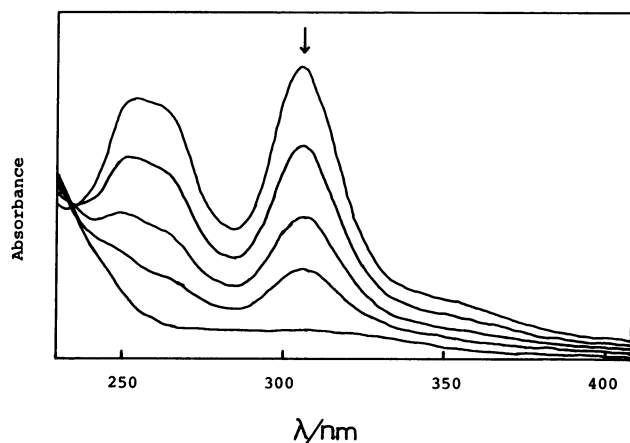


Fig. 1. Electronic spectrum of $[\text{PdCl}(t\text{-BuNC})_2]_2$ in CH_2Cl_2 as a function of photolysis time.

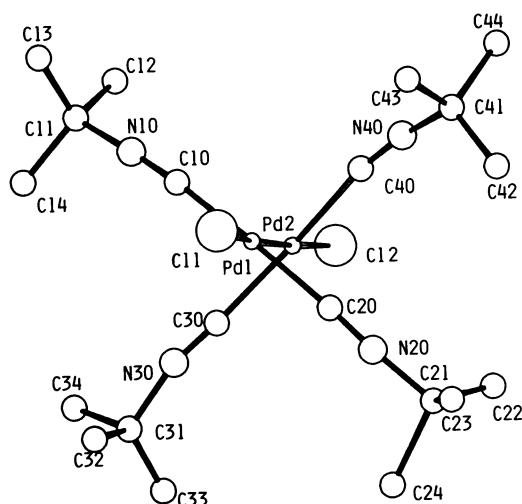


Fig. 2. A perspective drawing of $[\text{PdCl}(t\text{-BuNC})_2]_2$ with the numbering scheme.

(2) and $177.4(2)^\circ$. The Pd-Cl bond lengths of 2.403(9) and $2.416(9)\text{\AA}$, are longer than those [$2.300(2)$ and $2.302(2)\text{\AA}$] of $\text{cis-}[\text{PdCl}_2(\text{c-C}_6\text{H}_{11}\text{NC})_2]$.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 equatorial 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 equatorial 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 $[\{\text{PdCl}(\text{RNC})_2\}_2]$ 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.

References

- 1) Studies on interactions of isocyanides with transi-

TABLE 2. POSITIONAL PARAMETERS FOR $[\{\text{PdCl}(t\text{-BuNC})_2\}_2]^a$

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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