CHEMISTRY LETTERS, pp. 241-244, 1978. Published by the Chemical Society of Japan

SYNTHESIS AND PROPERTIES OF DIAMINOCYCLOPROPENYLIDENE TRANSITION METAL COMPLEXES

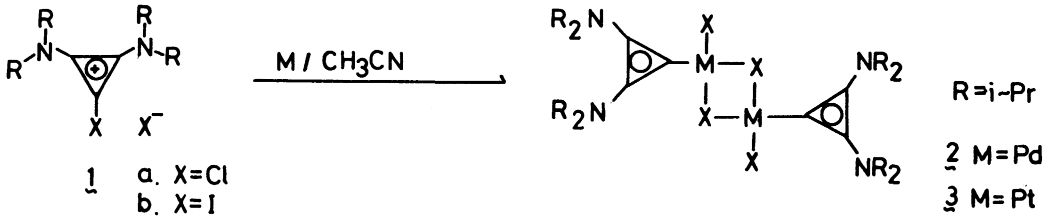
Hisatoshi KONISHI,[1] Shiro MATSUMOTO, Yasuhiro KAMITORI,
Hisanobu OGOSHI, and Zen-ichi YOSHIDA*
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606

Neutral and cationic diaminocyclopropenylidene complexes of palladium (II) and platinum (II), trans-X_2-μ-$X_2M_2^{II}(C_3(NR_2)_2)_2$, (2; M=Pd, 3; M=Pt), cis-$R'_3PX_2M^{II}C_3(NR_2)_2$ (4; M=Pd), and [trans-$(R'_3P)_2$-$XM^{II}C_3(NR_2)_2]^+ClO_4^-$ (5; M=Pd, 6; M=Pt) were synthesized. Stereochemistry of the peripheral dialkylamino groups was briefly discussed on the basis of infrared and ^{13}C-nmr spectra. Low C-N stretching frequency and small rotational barrier about the C-N bond indicate that diaminocyclopropenylidene coordinates to the transition metal as a carbene.

A variety of neutral and cationic transition metal complexes of nucleophilic carbenes have been synthesized.[2] The heteroatom (O, N, S) directly bonded to the carbene carbon stabilizes the complex by electron donation to the electron deficient carbene carbon atom. It is expected that substitution of amino group on cyclopropenylidene increases the nucleophilic character in the ground state. Thus, diaminocyclopropenylidene is considered to be a promising ligand to prepare the novel carbene complex. We wish to report the synthesis of palladium and platinum complexes of diaminocyclopropenylidene, and discuss their structures briefly.

A mixture of 1,2-bisdiisopropylamino-3-chlorocyclopropenium chloride (1a) and slightly excess of palladium black in freshly distilled acetonitrile was refluxed under nitrogen atmosphere for 24 hr.[3] Crude product was chromatographed on a silicagel column with chloroform-ether to give reddish brown crystals (2a) in 44% yield.[4] The chlorine anion was not exchanged with perchlorate anion by treatment of a solution of 2a in CH_2Cl_2 with dil. $HClO_4$. A dimeric structure was proposed for 2a as has been reported for palladium complex of diphenylcyclopropenylidene.[5] Iodine bridged complex (2b) and platinum complex (3a) were prepared in a similar manner.

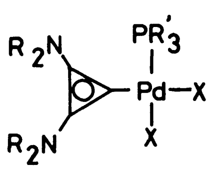
The nucleophilic cleavage of halogen-bridged complex afforded mononuclear

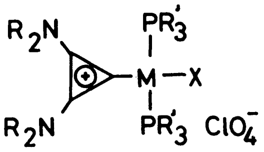


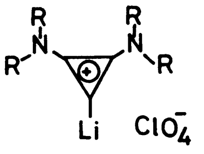
complexes. To a cooled solution (-60°) of 2a in CH_2Cl_2 was added twice molar amounts of tri-n-butylphosphine with stirring under nitrogen. The solution was allowed to warm up to room temperature, and further stirred for 2 hr. After removal of the solvent, recrystallization of the crude product from CH_2Cl_2-ether afforded neutral palladium complex (4a) in 78% yield, as orange crystals. The ^{31}P-^{13}C coupling constant (J=4.9 Hz) shows that the complex 4a is the *cis* isomer.$^{6)}$ It is supposed that bridge-splitting reaction gives the *trans* mononuclear complex. Consequently the trans complex isomerizes to the cis complex, which seems to be thermodynamically more stable than the former.

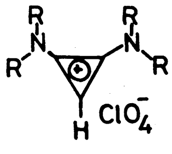
Cationic palladium complexes (5a-c) and the cationic platinum complexes (6a-c) were prepared by the reaction of lithium compound (7)$^{7)}$ with Pd(II) and Pt(II) complexes, respectively. To an ethereal solution of lithium carbenoid 7 was added an ethereal solution of *trans*-$(n\text{-}Bu_3P)_2PdCl_2$ with stirring at room temperature. After 2 hr, the reaction mixture was poured into dil. $HClO_4$, and precipitates were separated by filtration. Recrystallization of the crude product from ethanol-ether afforded the cationic palladium complex (5a) as colorless crystals in 67% yield. In the cmr spectrum of 5a, the carbene carbon appears as a triplet due to equal coupling of the three-membered ring carbon with two phosphorus nuclei. Thus the *trans* configuration is reasonably proposed for geometry of two phosphines in square planar complex 5a.

Cationic palladium complex 5a was also obtainable from the halogen-bridged complex 2a by action of 4 mol. equiv. of phosphine. A mixture of 2a and tri-n-butylphosphine in CH_2Cl_2 was stirred for 30 min at room temperature. Treatment with dil. $HClO_4$ followed by recrystallization from CH_2Cl_2-ether gave 5a in quantitative yield, which was identical with an authentic sample on the basis of ir, pmr and cmr spectra. Yields and some physical properties of palladium and platinum complexes are summarized in Table 1. Mononuclear complexes are quite stable to air and moisture for a long time, but binuclear complexes are rather unstable.


4


5 6


7


8

R = i-Pr
R' = n-Bu

Table 1. Palladium and Platinum Complexes of Diaminocyclopropenylidene

	metal	halogen	color	yield(%)	mp	ir(KBr, cm^{-1})	
2a	Pd	Cl	reddish brown	44	240(dec.)	1856	1500
2b	Pd	I	reddish brown	55	264(dec.)	1853	1496
3	Pt	I	reddish brown	18	226(dec.)	1846	1484
4a	Pd	Cl	orange	78	208	1858	1487
4b	Pd	I	orange	60	145	1848	1486
5a	Pd	Cl	colorless	67	120	1855	1492
5b	Pd	Br	colorless	53	220(dec.)	1855	1495
5c	Pd	I	colorless	49	210(dec.)	1850	1492
6a	Pt	Cl	colorless	55	225	1862	1494
6b	Pt	Br	colorless	48	247	1856	1490
6c	Pt	I	colorless	46	255	1855	1490

The infrared spectra of these complexes exhibit two strong bands in the region 1862-1846 and 1500-1484 cm^{-1}. The higher frequency bands are assigned to the framework deformation of three-membered ring, and the lower frequency bands are assigned to the C(ring)-N stretching mode. It is noteworthy that the frequencies of the characteristic infrared absorptions of neutral complexes are not different from those of cationic complexes. The structure of diaminocyclopropenylidene moiety in the neutral complexes are similar that of cationic complexes. Diaminocyclopropenium ions 1a and 8 exhibit the C-N stretching frequencies at 1585 and 1572 cm^{-1} respectively. The newly prepared transition metal complexes show the corresponding absorption below 1500 cm^{-1}. The position of the C-N stretching vibration is thought to be good indication of the double bond character of the C-N bond. The lower frequency implies the less contribution of the canonical structure represented by B.

Table 2 lists the carbon-13 nmr parameters for a series of chlorine-containing complexes. There is no significant difference in the chemical shifts of the ring carbons bearing amino group (C-2, -3) of these complexes. The contribution of the immonium structure B to the resonance hybrid seems to be not greatly different in these complexes. The rotational barrier about the C-N bond in 5a and 6a are estimated to be less than 9.7 and 9.9 Kcal/mol, respectively, from cmr measurement.[8)]

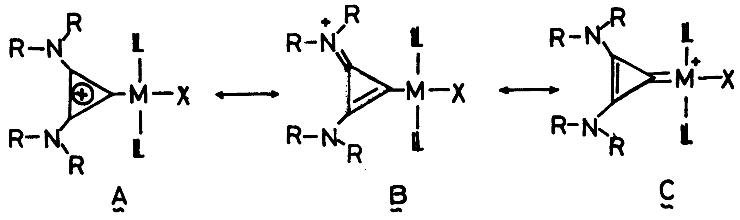


Table 2. Carbon-13 NMR parameters of Diaminocyclopropenylidene Complexes

	C_1	C_2,C_3
2a	106.5	148.3
4a	128.4 (4.9)*	147.4
5a	125.6 (11.3)*	147.8
6a	_____**	144.1

* J(C-M-P), Hz. **Not observed.

These values are considerably small compared with those of 8 (17.8Kcal/mol) and cationic mercury complex of diaminocyclopropenylidene (17.1 Kcal/mol).[9] This trend coincides with relative low frequencies of the C-N stretching modes. The present results lead us to conclude that the formal positive charge localizes on metal atom in cationic complexes, and diaminocyclopropenylidene has character of carbene as is represented by canonical structure C.

Further study to clarify the stereochemistry and the ground state properties of diaminocyclopropenylidene complexes are now in progress.

REFERENCES AND NOTES

1) Present address, Department of Environmental Chemistry and Technology, Faculty of Enigineering, Tottori University, Tottori 680.
2) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, Chem. Rev., 72, 545 (1972).
3) The method employed was modified that of Öfele: ref. 5.
4) Satisfactory elementary analyses (C, H, N, and halogen) were obtained for all new compounds.
5) K. Öfele, J. Organometallic Chem., 22, C9 (1970).
6) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. W. Randall and E. Rosenberg, J. Chem. Soc., Dalton, 1982 (1973).
7) To be published. Cf. Magnesium complex, Z. Yoshida, H. Konishi, Y. Miura, and H. Ogoshi, Tetrahedron Lett., in press.
8) Measured in acetone-d_6.
9) Z. Yoshida, H. Konishi, Y. Kamitori, and H. Ogoshi, Chem. Lett., 1341 (1977).

(Received December 21, 1977)