CHEMISTRY LETTERS, pp. 1341-1344, 1978. Published by the Chemical Society of Japan

SYNTHESES AND PROPERTIES OF DIALKYLCYCLOPROPENYLIDENE PALLADIUM COMPLEXES

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As the transition metal complexes of dialkylcyclopropenylidene, the palladium complexes of 2,3-di-isopropyl- and 2,3-di-t-butyl cyclopropenylidene, trans-X_2-μ-$X_2Pd_2^{II}(C_3R_2)_2$, (1; X=Cl, 1'; X=Br), cis-(n-$Bu_3P)Cl_2Pd^{II}C_3R_2$ (2), and [trans-(n-$Bu_3P)_2ClPd^{II}C_3R_2]^+ClO_4^-$ (3), have been synthesized. The ^{13}C nmr and ir spectra of these complexes have been discussed for the structural elucidation.

Although cyclopropenylidene is expected to furnish us fascinating problems concerning nucleophilicity, aromaticity, and peculiar σ structure due to high strain, it has not been isolated yet because of its instability. However, by the coordi nation to the transition metals, cyclopropenylidenes could be isolated as their metal complexes. So far only two kinds of cyclopropenylidene transition metal complexes, namely 2,3-diphenylcyclopropenylidene[1)] and 2,3-bis(di-isopropylamino)-cyclopropenylidene[2)] transition metal complexes, have been isolated. In this communication we wish to report the syntheses and some spectroscopic properties of novel palladium complexes of 2,3-dialkylcyclopropenylidene (neutral and cationic palladium complexes of 2,3-di-isopropyl- and 2,3-di-t-butylcyclopropenylidene), where π conjugative interaction between the substituents and the C_3 ring is considered to be small. Therefore, they should be suitable compounds for the investigation of the electronic natures of cyclopropenylidene moiety in such complexes.

Di-μ-chloro complex 1 was obtained according to a modified procedure for di-μ-chloro-dichloro-bis(diphenyl)cyclopropenylidene-dipalladium.[1)] A mixture of 3,3-dichloro-1,2-di-isopropylcyclopropene and slightly excess amounts of palladium black in freshly distilled benzene was kept at 90° in an argon-replaced shield tube. After 20 hr, the reaction mixture was filtered off. Addition of ether to the filtrate gave orange crystals, 1a, which gave a satisfactory elemental analysis. As is seen in Table 3, it shows a characteristic ir band at 1787 cm^{-1}

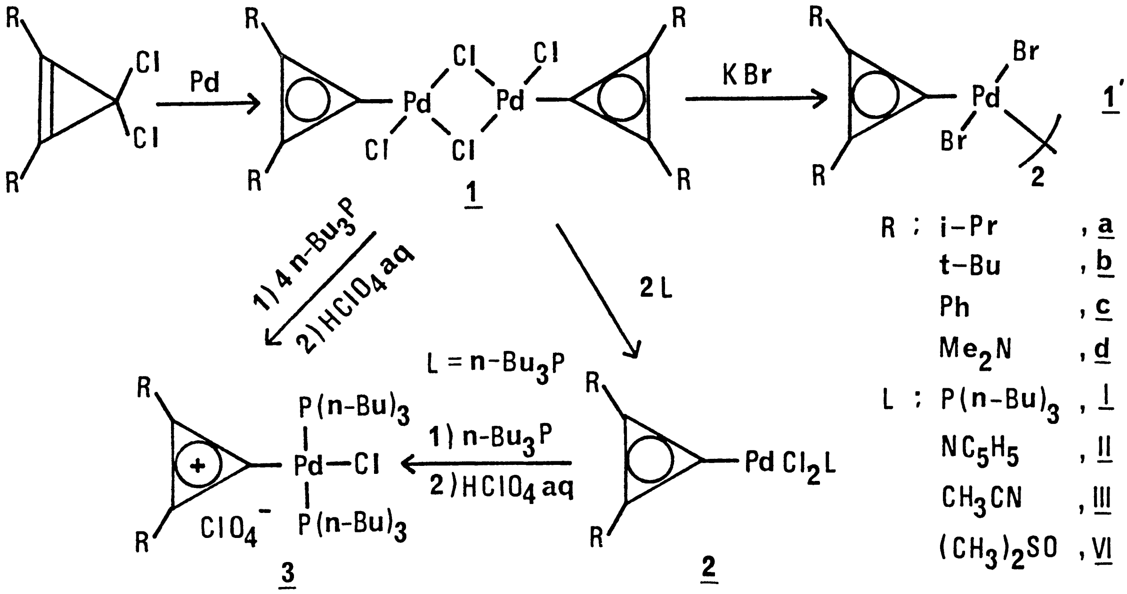

Table 1. Yields and properties of dialkylcyclopropenylidene palladium complexes (1 ∿ 3)

Compound		Color	Yield (%)	Mp (°C)	Pmr (δ; from TMS, CDCl3)	
R= i-Pr	1a	orange	45	164	1.44(d, $C\underline{H}_3$)	3.41(sep, $C\underline{H}$)
	1'a	orange	95	172	1.44(d, $C\underline{H}_3$)	3.41(sep, $C\underline{H}$)
	2a-I	colorless	69	153	1.50(d, $C\underline{H}_3$)	3.36(sep, $C\underline{H}$)
	3a	colorless	92	151	1.60(d, $C\underline{H}_3$)	4.08(sep, $C\underline{H}$)
R= t-Bu	1b	orange	60	223(dec.)	1.48(s, $C\underline{H}_3$)	
	2b-I	colorless	75	153	1.52(s, $C\underline{H}_3$)	
	2b-II	yellow	82	150	1.56(s, $C\underline{H}_3$)	
	2b-III	orange	75	183(dec.)	1.48(s, $C\underline{H}_3$)	
	2b-IV	yellow	67	202(dec.)	1.48(s, $C\underline{H}_3$)	
	3b	colorless	68	164	1.55(s, $C\underline{H}_3$)	

attributed to the deformation of the C_3 ring. Furthermore, it exhibits three bands at 347, 294, and 272 cm^{-1} assignable to Pd-Cl stretching, indicating that 1a is di-μ-chloro type complex.3) To a cooled solution (ca. -60°) of 1a in dichloromethane was added two molar amounts of tri-n-butylphosphine with stirring. After 30 min the solution was warmed to room temperature and stirred for additional 2 hr. Removal of the solvent and subsequent recrystallization from benzene-hexane afforded a neutral complex, 2,3-di-isopropylcyclopropenylidene palladium complex, 2a-I, as colorless crystals.4) In the ir spectrum, 2a-I reveals a characteristic band at 1797 cm^{-1} assigned to the ring deformation of the C_3 ring. A solution of 1a and 4 equiv. of tri-n-butylphosphine in dichloromethane was stirred at -60° for

Table 2. ^{13}C-NMR spectra of cyclopropenylidene palladium complexes (ppm from TMS, $CDCl_3$ solution)

	C_1	(J_{C-Pd-P}, Hz)	C_2	Others
1a	181.2		195.7	28.7($\underline{C}$H) 19.6($\underline{C}H_3$)
1b	183.1		198.0	34.7(t-C) 27.7($\underline{C}H_3$)
2a-I	205.7,	d (<1.2)	195.1	28.8($\underline{C}$H) 19.6($\underline{C}H_3$) 13.6-26.4(n-Bu)
2b-I	205.2,	d (<1.2)	196.5	34.5(t-C) 27.7($\underline{C}H_3$) 13.6-26.4(n-Bu)
2c-I	195.3,	d (2.9)	175.2	134.6, 133.4, 130.1, 121.7(Ar) 13.6-26.4(n-Bu)
2d-I	125.0,	d (6.0)	150.6	41.2($\underline{C}H_3$) 13.6-26.5(n-Bu)
3a	205.4,	t (9.8)	198.7	29.1($\underline{C}$H) 19.3($\underline{C}H_3$) 13.8-26.6(n-Bu)
3b	205.8,	t (9.8)	199.7	34.8(t-C) 27.6($\underline{C}H_3$) 13.6-26.5(n-Bu)
3c	195.2,	t (10.7)	176.1	137.8, 133.4, 130.9, 120.8(Ar) 13.6-26.6(n-Bu)
3d	122.0,	t (10.8)	151.5	42.5, 39.5($\underline{C}H_3$) 13.7-26.5(n-Bu)

Table 3. Characteristic IR spectra of cyclopropenylidene palladium complexes (cm^{-1}, KBr disk)

	C_3 core	Pd-Cl
1a	1787	347, 294, 272
2a-I	1797	304, 292
2b-I	1780	305, 282
3a	1788	——*
3b	1774	——*
3d	1900	295

* Not observed in the range of 250-300 cm^{-1}

1 hr. Treatment of the reaction mixture with dil. perchloric acid followed by recrystallization from benzene-hexane afforded a cationic complex, 3a, which is also obtainable by the treatment of 2a with equimolar of tri-n-butylphosphine. Also, the neutral and the cationic complexes of 2,3-di-t-butylcyclopropenylidene (1b, 2b and 3b) were obtained in similar manners. Di-μ-chloro complex, 1b, and excess amounts of pyridine, acetonitrile or dimethylsulfoxide gave corresponding neutral complexes 2b-II ∿ 2b-IV (Table 1). Di-μ-chloro complex, 1a, treated with KBr in acetone gave corresponding di-μ-bromo complex, 1'a, as orange crystals. These complexes are all stable in the air at room temperature.

In the ^{13}C NMR spectra, cyclopropenylidene ring carbons, C_1 and C_2, of 2,3-dialkylcyclopropenylidene palladium complexes exhibit two signals in the range of 180 ∿ 206 ppm from TMS (Table 2). It is noteworthy that the chemical shifts for

C_2 are very similar among 1a, 2a-I, and 3a (or 1b, 2b-I and 3b). The C_1 and C_2 of 2 and 3 are deshielded in the order of a (R= i-Pr) ≃ b (R= t-Bu)>c (R= Ph)> d (R= Me_2N), indicating that the electron densities of the ring carbons are decreased in this order. The ^{13}C signals for C_1 of 3a and 3b appear as triplets, due to the equal coupling of C_1 with two phosphorous nuclei, indicating the trans structure of these complexes. In the ^{13}C NMR spectra of the neutral complexes, 2a-I and 2b-I, the ring carbons directly bonded to palladium were observed as doublets. The small values of ^{31}P-Pd-^{13}C coupling constants indicate that the phosphine group ligates to the metal in cis position toward carbene carbon.5) This is also supported by the frequencies (ca. 305 and 285 cm^{-1}) of the two characteristic Pd-Cl stretching bands6) (Table 3). The band due to the Pd-Cl stretching in the ir spectra of 3a and 3b cannot be observed in the frequency region of 250∿300 cm^{-1}, while that of 3d can be observed at 290 cm^{-1}. This suggests the trans effect of dialkylcyclopropenylidene ligand to be large in comparison with that of bis(dimethylamino)cyclopropenylidene ligand.

Further study to clarify the ground state properties and the reaction behavior of dialkylcyclopropenylidene transition metal complexes are now in progress.

Acknowledgements We are grateful for the partial financial support from the Ministry of Education (Grant-in-Aid for Scientific Research B, No. 247078). We also would like to thank Dr. Teizo Kitagawa (Institute for Protein Research, Osaka University for the measurements of FIR spectra.

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(Received September 11, 1978)