Some Aspects on the Mechanism of Palladium-complex-catalyzed Decomposition of and Cyclopropanation with Ethyl Diazoacetate

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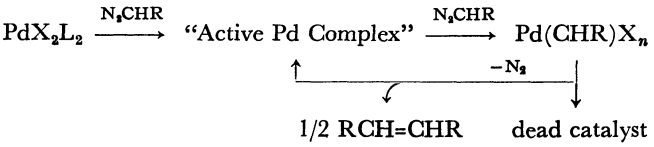
Carbenoid decomposition of ethyl diazoacetate in the presence of various palladium complexes as catalysts was found to kinetically depend on the identity of halide ligands. The use of several chiral ligands did not induce appreciable enantioselective catalytic cyclopropanation between ethyl diazoacetate and styrene. The active catalyst species is not under the influence of the chiral ligands but under control of halides which are bound more strongly to the metal.

Transition metal-catalyzed cyclopropanation reactions are one of the important organic synthesis.[1] Although (a) various Ag and Cu salts, (b) ligand-modified Cu, Pd, and Rh catalysts and (c) Lewis-acidic metal halides have been known[1–10] to induce homo- or heterogeneously-catalyzed decomposition of diazoalkanes, the mechanism or the nature of active species, however, has remained to be elucidated. Since a variety of ligand-modified palladium complexes act as efficient catalysts, we have examined the Pd-catalyzed reaction in some detail and the results are reported here.

Results and Discussion

Palladium(II) complexes of type, PdX_2L_2 (X= halide, L=neutral ligand), are active for decomposition of ethyl diazoacetate at room temperature in homogeneous solutions. The ligand effect was studied to obtain information on the active species. The catalytic activity can be assesed by rates of nitrogen evolution from the diazo compound (Table 1). An induction period is generally observed. After attaining the maximum rate, the decomposition by $PdCl_2(PPh_3)_2$ and $PdBr_2(PPh_3)_2$ slowed down according to apparent first- to third-order kinetics with respect to concentration of the free diazoacetate. The order also depends on concentration of the catalyst (Table 1). The rate for the corresponding iodide, however, seemed to obey zero- to first-order kinetics depending on the initial concentration of the catalyst. The length of the induction period was proportional to the initial catalyst concentration. The maximum rate attained after the induction period was also roughly proportional to the catalyst concentration but independent of the diazo concentration (*cf.* Table 1). The rate especially at low catalyst concentrations fell rapidly as the reaction proceeds. Apparently this is due to deterioration of the active catalyst. The following reaction scheme is consistent with the kinetics.



The reaction of the active Pd species with diazo acetate becomes the rate-determining step after the induction period. In the case of the decomposition by $PdI_2(PPh_3)_2$, the subsequent unimolecular decomposition of $Pd(CHR)I_n$ becomes rate-determining. The rate-determining step thus varies depending on the halide ligands.

The palladium-complex-catalyzed carbenoid reaction in neat cyclohexene gave a mixture of carbene dimers and cyclopropanation products (*endo*- and *exo*-norcarane-7-carboxylates) listed in Table 2. The isomeric product ratios obtained by the several palladium complexes catalysts are not critically influenced by the identity of the neutral ligands. By contranst, the length of induction period depends on L when a comparison was made among five $PdCl(\eta^3\text{-}C_3H_5)L$ catalysts; L=Py, 2 min, PPh_3 10 min, P-*n*-Bu_3, 15 min, $P(OPh)_3$ 15 min; P(O-*n*-Bu)$_3$, 2 min. The results contrasts with the catalysis by cobalt(II) dioximato chelates[11,12] which show a dramatic effect by added donor molecules, *e.g.* pyridine. Asymmetric synthesis of ethyl 2-phenylcyclopropanecarboxylate was attempted by reaction of ethyl diazoacetate with styrene in the presence of the following chiral palladium complexes; dichlorobis((*S*)-α-methylbenzylamine) palladium, di-μ-chlorobis(7,1,2-η^3(−)-pinenyl) dipalladium, bis[(−)-hydroxymethylenecamphorato] palladium, di-μ-chlorobis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2-*C*, *N*]dipalladium,[21] di-μ-chlorobis[(*S*)-*N*,*N*-dimethyl-2-naphthylamine-3-*C*,*N*]palladium,[22] and bis(β-camphorquinone dioximato)palladium.[16] However, the optical yields of the cyclopropane isomers were only 0—2% although

Table 1. Dependence of apparent order of the carbenoid reaction of ethyl diazoacetate and induction periods on concentration of palladium(II) catalysts

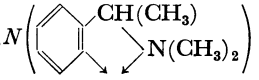
Catalyst	Catalyst concentration (mmol/l)	Apparent[a] order with $[N_2CHCO_2Et]$ concn	Induction periods (min)	Max. rates (N_2 evolved/min) (ml)
$PdCl_2(PPh_3)_2$	4	2.0	33	3.3
	2	2.2	25	2.0
	1	4.0	15	0.9
$PdBr_2(PPh_3)_2$	4	1.5	15	3.2
	2	2.1	14	1.7
	1	2.8	8	0.9
$PdI_2(PPh_3)_2$	4	0	35	0.5
	2	1.0	30	0.7
	1	1.6	30	0.4

a) The order was determined graphically by plotting the rate (ml/min) *vs.* time after the maximum rate is attained.

TABLE 2. RATIOS OF ISOMERIC CARBENOID REACTION PRODUCTS FORMED BY Pd-COMPLEX-CATALYZED REACTION BETWEEN ETHYL DIAZOACETATE AND CYCLOHEXENE[a)]

Catalyst precursor	Temp (°C)	Isomer ratios of products: Diethyl fumarate/diethyl maleate	Isomer ratios of products: *exo/endo* in ethyl norcaranecarboxylate
$PdCl_2(cod)$	60	2.5	4
$PdCl_2(PPh_3)_2$	20	2.5	10
$[PdCl(C,N\text{-phe})]_2$[b)]	60	2	5
$[PdCl(C,N\text{-phe})]_2$[b)]	20	1.3	8
$[PdCl(\eta\text{-}C_3H_5)]_2$	20	5	8
$PdCl(\eta\text{-}C_3H_5)(Py)$	20	6	10
$PdCl(\eta\text{-}C_3H_5)\cdot(PPh_3)$	20	4	10
$PdCl(\eta\text{-}C_3H_5)\cdot[P\text{-}(n\text{-}Bu_3)]$	20	4	10
$PdCl(\eta\text{-}C_3H_5)\cdot[P(OPh)_3]$	20	5	10
$PdCl(\eta\text{-}C_3H_5)\cdot[P(O\text{-}n\text{-}Bu)_3]$	20	4	10

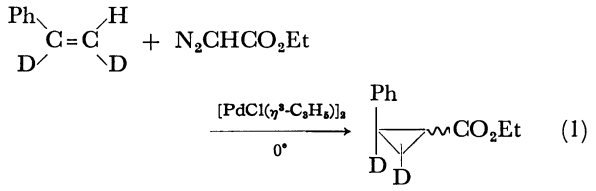
a) Reaction conditions: catalyst concentration; 0.01 mol/l, diazoacetate concentration 2 mol/l in neat cyclohexene. b) C,N-phe=*N,N*-Dimethyl-α-methylbenzylamine-2*C,N*



the chemical yields were good (*ca.* 70%). The absence of the appreciable chiral ligand effect implies that the neutral, η^3(C), C,N-, N,N-, or O,O-ligands are mostly eliminated during the formation step of the active species. The elimination of these ligands seems to take place by the reaction of transient reactive carbene-metal moiety generated from diazo compounds. The reaction of coordinated η^3-C_3H_5, phosphines, or isocyanides with diazoalkanes has been known to give CH_2=CH–CH_2=CHR,[15] alkylidenephosphorane (R_3P=CHR)[1] or ketenimine (RCH=C=NR).[1,14] The corresponding reaction with coordinated halides seems to be a very slow process.[13]

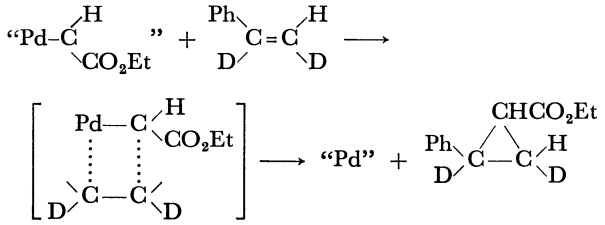
Some palladium complexes at the formal oxidation state of one and zero are also examined. A chloro-bridged Pd(I) complex, $[PdCl(t\text{-BuNC})_2]_2$, was found active without an induction period. The catalysis of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ also belongs to this category. Pd-$(PPh_3)_4$ and $Pd_2(t\text{-BuNC})_4$ were weakly active at room temperature, but the catalysis deteriorated readily. These observations indicate formal oxidation state of the metal to be unimportant. The catalysis critically depends on the identity of the metal in a similar ligand environment. Thus, $PtCl_2(PPh_3)_2$ showed only a weak activity even at 60 °C. By contrast $[RhCl(CO)_2]_2$, $[RhCl(C_8H_{12})]_2$, $[RhCl(C_2H_4)_2]_2$, and $RuCl_2(PPh_3)_3$ have very high activity at room temperature. No activity was found for $NiCl_2(PPh_3)_2$ or $CoCl_2(PPh_3)_2$.

The stereochemical paths of the $[PdCl(\eta^3\text{-}C_3H_5)]_2$-catalyzed cyclopropanation was investigated by using *cis*-dideuteriostyrene. As shown in Eq. 1, an almost complete retention of the original stereochemistry at the olefin was observed.



(1)

This contrasts to the bis(camphorquinone dioximato)-cobalt-catalysis where a considerable stereochemical inversion (up to 35%) is involved.[16] Thus, the Pd-catalysis is characterized with a stereochemical retention for the olefin component implying a multicentered transition state.



Since free carbenes with CO_2Et substituents are known to be triplet especially in the presence of compounds with heavy atoms, this result suggests the catalytically active species is not the free carbene.

We have a already studied thermal reactions of Pd(0) diazoalkane complexes, $PdL_2(dfl)$: L=PPh_3, *t*-BuNC; dfl=9-diazofluorene, where *N,N*-η^2-coordination of the diazoalkane was established.[14,17] The coordination retards the decomposition with nitrogen evolution and hinders the olefin attack leading to cyclopropanes. The observed low activity of Pd(0) complexes is thus understood. In contrast to the retardation of decomposition by virtue of these metal complexes with high metal electron densities, a Lewis acidic center, *e.g.* $ZnCl_2$, or $FeCl_3$, acts as an effective catalyst site.[1,10] The present palladium or rhodium catalysis does not involve such a strong Lewis acidic site. A different orbital interaction must be postulated for the present catalysis. Clearly, a further study including molecular orbital analysis is required.

Experimental

The following metal complexes were prepared by the methods in literature; $[PdCl(t\text{-BuNC})_2]_2$,[18] $PdCl_2(cod)$,[19] $[PdCl(\eta\text{-}C_3H_5)]_2$,[20] and known chiral Pd complexes[21,22] mentioned in the text. Some new chiral Pd complexes were prepared as follows.

a) Bis(hydroxymethylenecamphorato)palladium(II): An ethanol solution (4 ml) of (−)-hydroxymethylenecamphor (1.8 g) was mixed with an aq suspension of $PdCl_2$(0.6 g, 3.4 mmol) at 80 °C and then with aq KOH (1 M, 1.5 ml). The brown suspension turned into a yellow precipitate in 30 min. which was filtered and dried. Recrystallization from a mixture of hot benzene and hexane gave orange crystals (78% yield, mp 170 °C dec, $[\alpha]_D^{23}$ +153° (c=0.4)).

b) Dichlorobis(α-methylbenzylamine)palladium(II): A methanol solution (5 ml) of K_2PdCl_4 (0.22 g, 0.7 mmol) was mixed with (−)-α-methylbenzylamine (0.29 g, 2.4 mmol) with stirring to give a yellow precipitate which was filtered, dried, and recrystallized from a mixture of benzene and hexane (yield 87%, mp 131—134 °C, $[\alpha]_D^{23}$ −39.0° (c=4.95)).

Kinetics of Catalytic Decomposition of Ethyl Diazoacetate. A palladium complex in question (0.04—0.01 mmol) dissolved in benzene (20 ml) was mixed with a benzene solution (2 ml) of ethyl diazoacetate (0.23 g) under nitrogen in a 50 ml flask connected with gas burettes at 30.0°. The reaction mixture was stirred magnetically in a flask covered with aluminum foil to prevent any photodecomposition of the diazo compound during the catalysis. The amount of evolved gas was followed to measure the decomposition rate. The reaction mixture remained apparently homogeneous throughout the kinetic runs, but after the prolonged standing a small amount of metallic palladium deposited. The products from the catalyzed cyclopropanation in cyclohexene performed under the conditions described in Table 2 were analyzed by GLC (Apiezon Grease L).

Cyclopropanation of cis-*Dideuteriostyrene with Ethyl Diazoacetate by* $[PdCl(\eta\text{-}C_3H_5)]_2$. *cis*-Dideuteriostyrene was prepared by selective hydrogenation of phenylacetylene with deuterium gas in the presence of Lindlar catalyst and found to be stereochemically 86% pure. A solution of ethyl diazoacetate (2.09 g, 18.3 mmol) in the styrene-d_2 (1.3 ml) was added to a solution of $[PdCl(\eta\text{-}C_3H_5)]_2$ (0.21 g, 0.56 mmol) in the styrene-d_2 (2.5 ml) at 0° with stirring. After vigorous nitrogen evolution had ceased, the reaction mixture was distilled (85—87°C/2 Torr) to give ethyl 2,3-dideuterio-*cis*- and -*trans*-2-phenylcyclopropanecarboxylate (0.3 g, 8.6% yield, *trans*/*cis*=1.5). Each isomer of the cyclopropanes was separated by GLC and hydrolyzed to the corresponding acids. Since the ^{1}H-NMR spectra of each isomeric acids had been already assigned, the stereochemical distribution of deuterium was determined by the nmr to find *cis*-d_2/*trans*-d_2=6.1 for the *trans*-phenyl compound and *cis*-d_2/*trans*-d_2=2.6 for the *cis*-phenyl compounds. Corrections due to the stereochemical purity of 86% of the starting styrene were made to find the stereochemical process at the cyclopropanation leading to the *trans*-phenyl compounds to be completely retention.

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