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SYNTHESIS, REACTION AND STRUCTURAL DETERMINATION OF NOVEL ORGANO-TRANSITION METAL COMPLEXES

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CONTENTS

1. Introduction

Even though the first recognized organometallic complex, Zeise's salt' $K[PtCl_3(\text{ethylene})]$, was prepared in 1827, significant interest in such compounds did not develop until after the structure of ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, was determined in 1952. Since then, organotransition metal chemistry, bridging organic and inorganic chemistry, exploded into activity. The isolation and stabilization of cyclopentadiene, cyclobutadiene and benzene derivatives of transition metal organometallics were achieved because of academic interest.

However, industrial processes, such as the Wacker oxidation of ethylene to acetaldehyde, the hydroformylation of olefins (oxo reaction) and the Ziegler-Natta olefin polymerization have provided practical applications for the achievements of organotransition metal chemistry. The parallel development of an understanding of organometallic chemistry and of a variety of homogeneous catalysts (mainly organotransition metal complexes) has produced a vast literature in the past twenty five years.

In our Laboratory, synthesis and application for organic syntheses of low valent palladium complexes were studied in these ten years. In 1969, Mr. Ts. Ito, then a graduate student, attempted to investigate the reaction of palladium chloride with dibenzylideneacetone (DBA), and obtained a novel zerovalent complex, $Pd(DBA)_2$. The short communication published in Chemical Communications of the Chemical Society England in 1970 had received much attention by a number of chemists major in organometallic chemistry. Professor Maitlis of McMaster University followed our work, and found analogous platinum complexes, $Pt(DBA)_2$ and $Pt(DBA)_3$ in 1971. Both groups (Maitlis and Ishii) published papers on the reactions of $Pd(DBA)_2$ with acetylenic and olefinic compounds in 1972. After the careful X-ray structural determination done by Professor Ibers of Northwestern University, the complex $Pd(DBA)_2$ was found to have the composition and structure of $Pd_2(DBA)_3$(solvent).

In this article, details of our works following the above-mentioned observations are presented, namely, 1) Chemistry of $Pd_2(DBA)_3$ complexes, 2) Reactions of Tetrakis(methoxycabonyl)palladiacyclopentadiene complex and 3) Novel Rhodium and Palladium complexes with activated isocyanates or isothiocyanates as ligand.

The relation of the contents of this article with the corresponding publications is shown below.

Chapter and Section of this article	Publications : Authors, Journal, Volume, page, year
2. 1. (except 2. 1. 5.) 2. 2. 6 and 2. 2. 7.	T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnett, J. A. Ibers, J. Organometal. Chem., **65**, 253 (1974)
2. 1. 5.	H. Kawazura, H. Tanaka, K. Yamada, T. Takahashi Y. Ishii, J. Organometal. Chem., to be published
2. 2. (except 2. 2. 6 and 2.2.7.)	Ts. Ito, S. Hasegawa, Y. Takahashi, Y. Ishii, J. Organometal. Chem., **73**, 401 (1974)
3. 2. 2.	H. Suzuki, K. Itoh, I. Matsuda, Y. Ishii, Chem. Letts., 1975, 197
3. 2. 3.	H. Suzuki, K. Itoh, I. Matsuda, Y. Ishii, to be published
3. 3.	H. Suzuki, K. Itoh, Y. Ishii, K. Simon, J. A. Ibers, J. Amer. Chem. Soc., **98**, in press (1976)
3. 4.	H. Suzuki, M. Ohashi, K. Hirai, K. Itoh, Y. Ishii, to be published

4. 2.	S. Hasegawa, K. Itoh, Y. Ishii, Inorg. Chem., **13**, 2675 (1974)
4. 3.	K. Itoh, M. Matsuda, F. Ueda, Y. Ishii, M. Cowie, J. A. Ibers, Submitted to J. Amer. Chem. Soc.
4. 3. 3.	M. Cowie, J. A. Ibers, Y. Ishii, K. Itoh, I. Matsuda, F. Ueda, J. Amer. Chem. Soc., **97**, 4748 (1975)
4. 3. 6.	Y. Ishii, K. Itoh, I. Matsuda, F. Ueda, J. A. Ibers, J. Amer. Chem. Soc., **98**, 2014 (1976)

Preliminary Communications:

Y. Takahashi, Ts. Ito, S. Sakai, Y. Ishii, Chem. Commun., 1970, 1055
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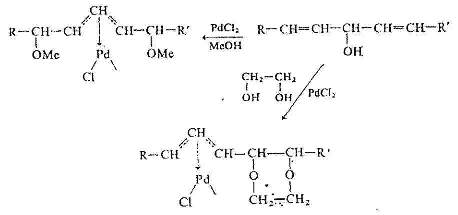
2. Chemistry of Dibenylideneacetone-Palladium(0) Complexes

2. 1. Tris(dibenzylideneacetone)dipalladium(0) Complexes: Preparation, Properties and Structural Determination

2. 1. 1. Introduction

In a former paper,[1] the reactions of $PdCl_2$ with various 1, 4-dienol(3)-type compounds were found to give either 1, 5-dialkoxy-2, 3, 4-π-allyl palladium complexes or 4, 5-dialkoxy-1, 2, 3-π-allyl palladium complexes, depending upon R, R′ and the solvent alcohol used, as shown in Equation (1).



(1)

As an extension of this work, we attempted to investigate the reaction of $PdCl_2$ with dibenzylideneacetone (DBA), a 1, 4-dienone(3)-type compound, and obtained a novel zerovalent palladium complex: $Pd(DBA)_2$.[2] Among the nickel triad, $Ni(COD)_2$, and $Pt(COD)_2$ are well-known zerovalent complexes containing an organic ligand. Since $Pd(COD)_2$ is unknown, $Pd(DBA)_2$ is an useful and interesting zerovalent complex. Hitherto, ligands used for the preparation of palladium(0) complexes have been limited to phosphines,[3~5] phosphites,[3] arsines,[3] isocyanides,[4] and carbon monoxide.[6] Moseley and Maitlis found analogous platinum complexes, $Pt(DBA)_2$ and $Pt(DBA)_3$.[7] Both groups (Maitlis and Ishii) published papers on the reactions with acetylenic[8,9] and olefinic compounds.[10] Recently three papers concerning Pd and Pt-DBA complexes were published.[11~13]

In this chapter, the preparation and properties of novel binuclear $Pd_2(DBA)_3$ (solvent) complexes and their structural elucidation (IR, UV, mass and NMR spectra) are reported, together with X-ray structural determination) done by Professor Ibers of Evanston. Various types of reaction of these new zero-valent complexes are described in the following chapter.

2. 1. 2. Preparations of the Binuclear Complexes: $Pd_2(DBA)_3(solvent)$

An attempt to elucidate the structure of $Pd(DBA)_2$[2] led us to a discovery of novel binuclear palladium complexes. Recrystallization of $Pd(DBA)_2$ in chloroform gives purplish needle-like crystals whose composition shows good agreement with the formula $Pd_2(DBA)_3(CHCl_3)$ (Ia). Use of benzene or toluene as a recrystallization solvent also gives purple crystals satisfying the composition $Pd_2(DBA)_3(C_6H_6)$ (Ib) and $Pd_2(DBA)_3(C_6H_5CH_3)$ (Ic), respectively. In addition a complex with decadeuteriodibenzylideneacetone$(C_6D_5CH{=}CH)_2CO$ (II), and a complex with p,p'-dimethoxydibenzylideneacetone, $(p\text{-}CH_3OC_6H_4CH{=}CH)_2CO$ (III), were prepared. Both of these are binuclear. While (III) has no chloroform, (II) does.

Dibenzylideneacetone (DBA) was prepared by a condensation of acetone and benzaldehyde.[14] The analogous decadeuterio-DBA and p,p'-dimethoxy-DBA were also prepared by the same method by using the corresponding aldehyde. DBA-d_{10}: M. p. 102–104°, 91% yield. Commercial guaranteed grade $PdCl_2$ was used without any purification.

Tris(dibenzylideneacetone)dipalladium(chloroform) (Ia). Palladium chloride, 1.05 g (5.92 mmole), was added to hot (ca. 50°) methanol, 150 ml, containing DBA 4.60 g (19.6 mmole) and sodium acetate 3.90 g (47.5 mmole). The mixture was stirred for 4 h at 40° to give a reddish-purple precipitate and allowed to cool to complete the precipitation. The precipitate was removed by filtration, washed successively with water and acetone and dried in vacuo. The precipitate, 3.39 g, was dissolved in hot chloroform, 120 ml, and filtered to give a deep violet solution. To the solution, diethyl ether, 170 ml, was added slowly. Deep purple needles precipitated. These were removed by filtration, washed with diethyl ether, and dried in vacuo. The complex (Ia), M.p. 122–124° dec., satisfying the composition $Pd_2(DBA)_3(CHCl_3)$ was obtained in 80% yield.

Tris(dibenzylideneacetone)dipalladium(benzene) (Ib). As the recrystallization solvent in the above procedure benzene was used instead of chloroform to give a similar deep-violet needle-like crystalline complex (Ib), M. p. 142–144° dec., satisfying the composition $Pd_2(DBA)_3(C_6H_6)$. The compound was obtained in 62.5% yield.

Tris(dibenzylideneacetone)dipalladium(toluene) (Ic). Toluene as a recrystallization solvent gave a similar deep violet needle-like crystalline complex (Ic), M. p. 140–141° dec., satisfying the composition $Pd_2(DBA)_3(C_6H_5CH_3)$. It was obtained in 36.0% yield.

Tris(decadeuteriodibenzylideneacetone)dipalladium(chloroform) (II). By a method similar to that used to prepare (Ia), deep violet needle-like crystalline complex (II), M. p. 132–133° dec., satisfying the composition $Pd_2(DBA\text{-}d_{10})_3(CHCl_3)$ was obtained in 80% yield.

Tris(p, p'-dimethoxy-DBA)dipalladium(III). Also by the similar method, deep violet needle-like crystalline complex (III), M. p. 141–143° dec., satisfying the composition $Pd_2(p,\ p'\text{-dimethoxy-DBA})_3$ was obtained in 72.3% yield.

2. 1. 3. Physical Characteristics of the Complexes (Ia)-(Ic), (II) and (III)

M. p. and elemental analysis of these new complexes are summarized in Table 1. These five complexes appear as deep purple needles, fairly stable in air in the solid state. They decompose gradually in organic solvents to precipitate metallic palladium. The complexes are slightly soluble in CH_2Cl_2, $CHCl_3$, C_6H_6 and THF to give deep violet solutions.

Interconversions between (Ia), (Ib) and (Ic) may be effected through recrystallization from the appropriate solvent. The yield was found to be highest in $CHCl_3$ and lowest in $C_6H_5CH_3$.

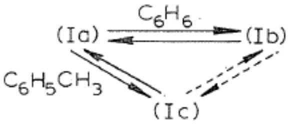


Table 1. Yield, M.p. and analysis of the complexes (Ia)—(Ic), (II) and (III).

Complex	Yield (%)	M.p. (℃ dec.)	Analysis found (calcd.) (%)	
			C	H
(Ia)	80	122—124	60.15(60.34)	4.23(4.19)[a]
(Ib)	62.5	142—144	68.88(68.89)	4.92(4.87)
(Ic)	36	140—141	68.86(69.12)	5.07(5.00)
(II)	80	132—133		
(III)	72	141—143	62.59(62.47)	5.06(4.97)

[a] (Ia) Cl 10.04(10.27); O 4.81(4.64); Pd 20.76(20.56).

Spctroscopic analyses of the complexes (Ia) and (II)

Assignable infrared active vibrational frequencies of (Ia) and (II) are summarized in Table 2 along with those of the corresponding free ligand molecules. Notable differences in the spectra of (Ia) and (II) in comparison with those of dibenzylideneacetone and dibenzylideneacetone-d_{10} may be depicted as follows: a characteristic δ[CH(*trans*)] vibration observed at 983 cm^{-1} in the free ligands disappears almost completely in (Ia) and (II) though a weak broad band appears at a slightly lower frequency (975 cm^{-1} w, br) in both. The CO stretching bands of (Ia) and (II) are shifted about 40 cm^{-1} to lower frequencies compared with those of the free ligands. Although the behavior of the ν(C=C) bands in (Ia) and (II) is uncertain because of accidental masking by the strong CO bands, the spectra, as described, are completely consistent with coordination of DBA to the metal through the C=C moiety.

Table 2. Infrared vibrational frequencies (cm^{-1}) of (Ia) and (II) [KBr].

(Ia)	DBA	(II)	DBA-d_{10}[a]	Assignment
1620 vs(sh)	1657 m(sh)	1620 m(sh)	1658 m(sh)	ν(C=O)
1614 vs	1651 vs	1615 vs	1651 vs	
	1627 m		1627 m	ν(C=C)
1600 m(sh)	1591 vs(br)	1591 m(sh)	1594 m	ν[C=C(arom.)]
1574 m	1574 s	1550 m		
[975 w(br)]	983 vs	[977 w(br)]	983 vs	δ[CH(trans)]

[a] Decadeuteriodibenzylideneacetone.

The incorporation of chloroform in complex (II) was substantiated by the presence of absorption bands of medium intensity at 747 and 766 cm^{-1} [assignable to ν(C−Cl)]. The bands are hidden in the spectrum of (Ia) by strong δ[CH(arom)] absorptions.

Electronic spectra

Electronic absorption maxima of (Ia) and DBA in THF are shown in Table 3 along with a tentative assignment. Both the $n-\pi^*$ and $\pi-\pi^*$ transitions of (Ia) remain unchanged from those of the free ligand. These observations strongly suggest the coordination of the ligand to palladium by its olefinic double bond and not by its carbonyl moiety as suggested by Moseley and Maitlis for Pd(DBA)$_2$^{7}.

Table 3. Electronic absorption maxima (nm) of (Ia) and DBA (in THF).

(Ia)	DBA	Assignment
236 m	234 m	$\pi-\pi^*$
300 (sh)		
321 s	321 s	$n-\pi^*$
374 w		C,T.
520 vw		$d-d$

In coordinated DBA the olefinic proton resonances are shifted considerably to high field as are the phenyl ring proton resonances. This observation not only implies an influential role of the olefinic double bond but also a contribution of the phenyl ring to the coordination of dibenzylideneacetone to palladium.

Mass spectra

Mass spectra of the complexes (Ia) and (II) clearly indicate the presence of $CHCl_3$, DBA, and DBA-d_{10} in the complexes as evidenced by the appearance of the fragments $CHCl_2^+$(m/e 83, 85, 87), $CHCl_3^+$ (m/e 118, 121), $(C_6H_5CH{=}CH)_2CO^+$(m/e 234), and $(C_6D_5CH{=}CH)_2CO^+$ (m/e 244).

Mass spectroscopic analyses of the complexes (Ib) and (Ic) were also conducted and gave fragments $C_6H_6^+$ (m/e 78) and tropylium cation $C_7H_7^+$ (m/e 91), respectively, which are indicative of the presence of C_6H_6 in (Ib) and of $C_6H_5CH_3$ in (Ic).

Thermogravimetric analysis

The results of a thermogravimetric analysis of (Ia) in air indicate that the complex loses weight in steps. The first decrease of about 12% of the total weight corresponds to liberation of $CHCl_3$; the second decrement amounts to 46%, exactly corresponding to loss of two DBA molecules in the complex; and the third step, though rather gentle, may be interpreted as liberation of the final DBA ligand. A final plateau at about 24.3% is attributed to formation of palladium oxide.

2. 1. 4. *X-ray Structural Analysis of the Complex (Ia)*

$Pd_2(DBA)_3(CHCl_3)$ (Ia) crystallizes in space group $C_{2h}^5-P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions: a 13.536(3), b 13.474 (2), c 25.415(4) Å, β 109.5(1)°. Intensity data were collected on a FACS-1 automatic x-ray diffractometer out to 2θ(Cu-K_α) 106°. A total of 3819 unique reflections having $F_0{}^2 > 3\sigma(F_0{}^2)$ were obtained and were corrected for the effects of absorption. The structure was solved by standard methods and refined by full-matrix least-squares techniques to a final conventional R index of 6.7%.

The molecular structure of (Ia) is shown in Fig. 1. The binuclear complex consists of two Pd atoms (Pd—Pd 3.245 Å) bridged by the three DBA molecules. Coordination of the Pd atoms to these DBA molecules is through the C=C olefin portions of the ligands. The coordination about Pd is trigonal if one considers only the centers of the double bonds. Average distances in the molecule are Pd—C 2.25(1); C=C 1.20(3); C—C 1.54(2) and C=O 1.19(4) Å. The Pd—C distances are approximately 0.15 Å longer than in typical Pt—olefin π-complexes. The extreme shortness of the C=C distance is most surprising, and may be partially the result of the foreshortening of these bonds through excessive thermal motion.

Independently, Mazza and Pierpont[11] have carried out a structural study of $Pd_2(DBA)_3 \cdot CH_2Cl_2$. The structure of the $Pd_2(DBA)_3$ molecule is essentially that reported here, the major difference being that Mazza and Pierpont find two DBA molecules in the *s-cis, s-trans* conformation and one in the more symmetric *s-cis, s-cis* conformation, whereas we find all three to be in the *s-cis, s-trans* conformation (Fig. 1). Mazza and Pierpont find a more reasonable vaule of 1.36(2) Å for the C=C distance upon application of approximate corrections for vibrational disorder in some instances. Their Pd—Pd distance of 3.240(2) Å is in excellent agreement with the value of 3.245(2) Å found here. Thus while a change of solvent from $CHCl_3$ to CH_2Cl_2 results in a change in conformation of one of the DBA ligands, it has little effect on the bond distances within the molecule.

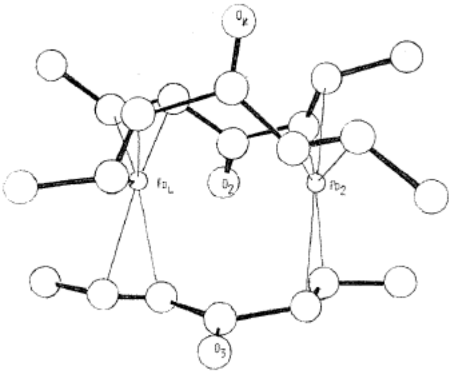


Fig. 1. A drawing of the $Pd_2(DBA)_3$ molecule, showing the *s-cis, s-trans* conformation of each of the DBA ligands. Only the α-C atoms of the phenyl rings shown. The H atoms are omitted for the sake of clarity.

Discussion of the structure of $Pd_2(DBA)_3 \cdot$*solvent*

The spectral and X-ray evidence presented here leaves no doubt that $Pd_2(DBA)_3 \cdot$solvent is formed under the conditions noted and that the bonding of the DBA ligands to the Pd is through the olefinic double bonds. Moseley and Maitlis[7] have suggested that coordination of DBA is through the carbonyl group in $Pd(DBA)_2$. This interpretation may not be valid as the composition of the Pd complex appears to be markedly solvent dependent. Thus there is the possibility of dissociation of the complex in $CHCl_3$. Moreover, the low-frequency shift of about 40 cm^{-1} in $\nu(C=O)$ seems rather small for CO coordination when compared with a shift of about 150 cm^{-1} for metal—CO coordination in $Mo(CO)_2(Acrolein)_2$.[15]

We have re-examined the IR and electronic spectra and find almost the same spectral patterns from $Pd(DBA)_2$[2] as those from complex (Ia), except for a superposition of free DBA bands on the spectra. Since various solvents appear to crystallize easily with $Pd_2(DBA)_3$ we suggest that a DBA solvent of crystallization is a distinct possibility, leading to the characterization of $Pd(DBA)_2$[2] as $Pd_2(DBA)_3 \cdot DBA$.

2. 1. 5. *Nuclear Magnetic Resonance Study on $Pd_2(DBA)_3$ Complex*

^1H NMR spectra of (Ia) were measured in $CDCl_3$ or in CD_2Cl_2 and the interpretation of the spectra was assisted by the availability of ^1H NMR spectra of (II) and (III) in these solvents. Owing to the low solubility of these complexes, repeated scans were necessary in order to obtain comparatively good signal to noise ratios (Fig. 2). During the long time necessary for such repeated scans part of the coordinated DBA was liberated, as is evident from the intensity changes. The resonances resulting from the free ligand are shown as striped lines in Fig. 2.

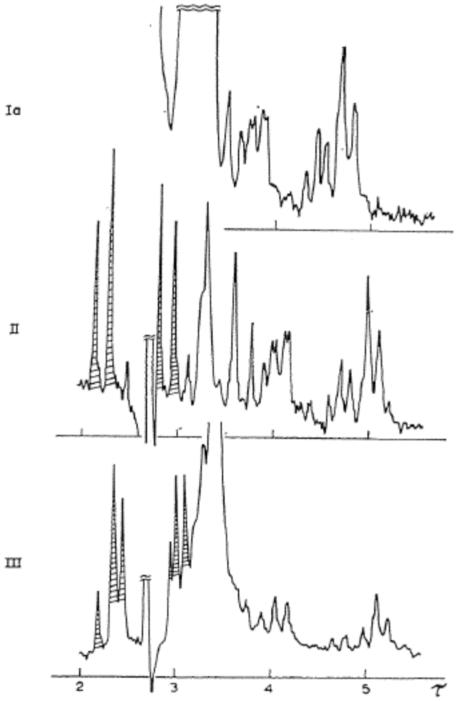


Fig. 2. The ^1H NMR spectra of complxes (Ia), (II) and (III) taken in $CDCl_3$ or CD_2Cl_2. Resonances resulting from the presence of free DBA are cross-hatched.

In the spectrum of (Ia) a multiplet centered at 3.5τ is the ten ring-proton resonance of the coordinated DBA as confirmed by its disappearance in the spectrum of (II). The eight ring-proton resonance of the coordinated *p*-methoxy-DBA in (III) appears as a multiplet in the same region. Olefinic proton resonances of the coordinated DBA spread over 2.5 to 5.5τ while, as expected, for the DBA-d_{10} complex (II) the spread is smaller (3.5 to 5.5τ).

2. 2. *Reactions of Tris(dibenzylideneacetone)dipalladium(0) Complex*

2. 2. 1. *Introduction*

New binuclear palladium (0) complexes $Pd_2(DBA)_3$(solvent), (Ia), (Ib), (Ic) and (III) have the same reactivity patterns reported earlier for $Pd(DBA)_2$[2].

In this chapter, ligand exchange, oxidative addition reactions, preparation of olefin-palladium complexes, reactions pf $Pd_2(DBA)_3$ with acetylenedicarboxylate, palladium-p-quinone complexes, those of o-quinone complexes and finally reactions with oxygen are introduced.

2. 2. 2. *Ligand Exchange Reactions*

The dark red coloured suspension of (Ia) (48.5 mmole) and PPh_3 (779 mmol) in benzene gave yellowish crystals. After purification by washing with benzene and then ether, the complex $(Ph_3P)_4Pd^0$ was obtained in 82% yield.

The reaction of (Ia) with carbon monoxide (DBA was recovered quantitatively) and the reaction with excess of PPh_3 in benzene at room temperature under nitrogen to give $(Ph_3P)_4Pd^0$ in high yield are consistent with the π-bonding of the DBA ligand to the Pd atom.

The reaction of (Ia) (1.05 mmole) with bipy (10 mmole) at RT under N_2 in ether took place with the precipitation of yellow-orange coloured crystals of the complex (DBA)Pd(bipy) (IV), M. p. > 135° dec. in 87% yield. (Found: C, 65.11; 4.55; N, 5.68. Calcd.: C, 65.27; H, 4.46; N, 5.64%.) When acetone was used as a solvent, a complex (DBA)Pd(bipy)(acetone), M. p. 110°, was obtained in 71% yield.

In the reaction between (Ia) and a large excess of bipy in acetone yellow-orange coloured crystals of the complex (DBA)Pd(bipy) (IV), M. p. 135° dec. in 87% yield, were obtained. The complex (IV) is unstable in air and decomposes in a few days.

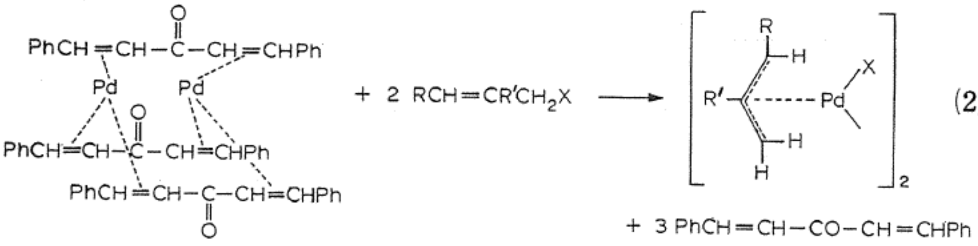
Analogous complexes were prepared: (DBA)Pd(*o*-phen)(H_2O), (DBA)Pd(bipy)-(acetone), (DBA-d_{10})Pd(bipy)(acetone), and (DBA-d_{10})Pd(*o*-phen)(H_2O).

2. 2. 3. *Oxidative Addition Reactions of the $Pd_2(DBA)_3$ Complex*

Due to the zero-valent state of $Pd_2(DBA)_3$, oxidative addition reactions with allylic halides occurred, giving free DBA and π-allylic palladium halide complexes (eqn. (2)).

The rate of the reactions of Eqn. (2) varied according to R, R′ and X. The relative rate found was: allyl bromide > allyl chloride > methallyl chloride > crotyl chloride > cinnamyl chloride. The reaction was completed after 5 min in the case of allyl bromide, but 30 min necessary in the reaction of cinnamyl chloride.

As an example, the oxidative addition reactions of methallyl chloride are given here. An excess of methallyl chloride (20.4 mmol) was added to a benzene solution of (Ia) (3.1 mmol) with stirring at room temperature under nitrogen. The deep purple color of the solution changed to yellow-greenish after 20 min. Upon vacuum

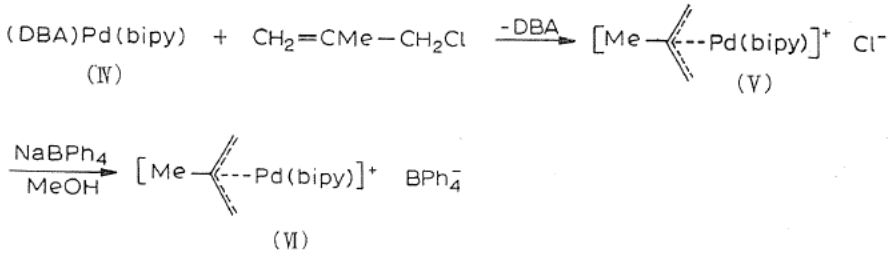


(2)

(I) $[Pd_2(DBA)_3]$

distillation of solvent and excess methallyl chloride, the residue was washed with hexane to remove DBA and then recrystallized from methanol, giving yellow colored μ, μ'-dichlorodi-π-methallyldipalladium, M. p. 165-168° (dec.), obtained in 75% yield [(NMR: τ(Me) 7.88 (3H), τ(H, *anti*) 7.13 (2H), τ(H, *syn*) 6.15 (2H)].

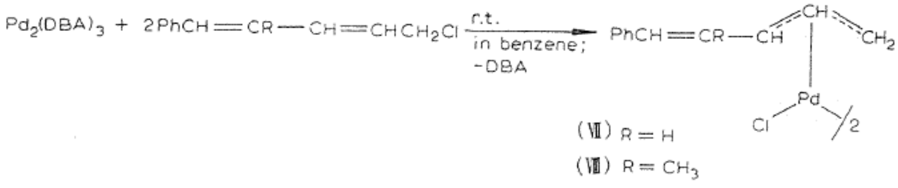
When an excess of methallyl chloride was added to (DBA)Pd(bipy) (IV) (bipy=2, 2′-bipyridyl) in methanol solution, the cationic complex (V) was obtained in 83% yield. Allyl bromide and methallyl chloride gave the corresponding cationic complexes



(3)

in yields of 87 and 83%, respectiyely. As shown in Eqn. 3, (V) was converted to (VI), M. p. 164-166° (dec.), in 68% yield, recrystallized from mixed solvent of MeOH and CH_2Cl_2. NMR spectrum (CH_2Cl_2): τ7.93 (3H), 6.95 (2H) and 6.37 (2H) (Analysis: found C, 71.5; H, 5.58; N, 4.39. $C_{38}H_{35}N_2BPd$ calcd.: C, 71.66; H, 5.54; N, 4.40%).

Into a benzene suspension of (Ia), excess 1-chloro-5-phenyl-2.4-pentadiene was added, and the reaction at room temperature under nitrogen gives free DBA and a yellowish π-allylic complex (VII), dec. 195-197° in 85% yield.



(4)

By reaction with Tl(acac), (VII) was converted into the acac derivative of (VII), M. p. 128-130° dec. in 77% yield. This complex is soluble in $CHCl_3$ and C_6H_6 and was identified by its NMR spectrum.

With 1-chloro-4-methyl-5-phenyl-2, 4-pentadiene the corresponding π-allylic chloro complex (VIII) (yellow, M.p. 174-174°, 76% yield) and acac derivative (yellow-orange, M. p. 96-97° dec., 61% yield) were obtained.

2. 2.4. *Formation of Olefin-Palladium Complexes via the $Pd_2(DBA)_3$ Complex*

In the absence of ligand, (Ia) reacted with olefinic compounds in acetone solution, but stable olefin-palladium complexes could not be isolated, since they decomposed at room temperature to give metallic palladium and free DBA. However, when an excess of bipy was added to a suspension of (Ia) in acetone under nitrogen, further addition of olefin [e. g. dimethyl fumarate (dmf)] caused a color change from orange to yellow. Yellow crystals then precipitated. These were fairly stable in air and in benzene solution but rather unstable in chloroform. They were identified by their IR (Table 4) and NMR spectra (Table 5) and elemental analyses (Table 6).

Yields were quite high and free DBA was recovered quantitatively. Among the olefins which were examined, stable complexes were isolated only from maleic anhydride (ma), dimethyl maleate (dmm), dimethyl fumarate (dmf), divinylsulfone (dvs) and acrylonitrile (an), all of which have an *e*-value[17] above 1.2. Olefins with *e*-values below 1.2 (n-butyl acrylate 1.06, methacrylonitrile 0.81, acrylic acid 0.77, methyl vinyl ketone 0.68, ethyl acrylate 0.22) did not afford stable olefin complexes, and complexes such as (DBA)Pd(bipy) were obtained as major products in most of these cases.

As shown in Table 7, ligands examined were bipyridyl, *o*-phenanthroline, triphenyl phosphite and trimethyl phosphite. With the two phosphites, only maleic anhydride formed stable olefin-palladium complexes and with phosphine as ligand, no olefin-palladium complex was isolated. Therefore, good σ-donor and poor π-acceptor ligands such as bipy and *o*-phen are more favorable than poor σ-donor ligands (i. e. phosphites).

The complexes thus obtained were very stable in the crystalline state and almost insoluble in common organic solvents except methanol or chloroform, in which they slowly decomposed. Only acetone was of use as solvent for *N*-donor ligands or benzene for *P*-donor ligands.

Table 4. Yield and properties of (olefin)PdL_2 complexes.

Complex	Yield (%)	Mp. (dec.)	ν(C=O)
(ma)Pd(bipy)[a]	97	229—231	1785, 1720
(ma)Pd(*o*-phen)	95	200	1795, 1757, 1710
(ma)Pd$[P(OPh)_3]_2$	96	132—133[b]	1808, 1759, 1742
(ma)Pd$[P(OMe)_3]_2$	94	92—93[b]	1798, 1769, 1732
(dmm)Pd(bipy)	74	153—155	1720
(dmm)Pd(*o*-phen)	73	171—172	1709, 1680
(dmf)Pd(bipy)	74	195—198	1696, 1680
(dmf)Pd(*o*-phen)	69	210—212	1685, 1669
(dvs)Pd(bipy)	60	143—145	
(dvs)Pd(*o*-phen)	81	168—171	
(an)Pd(bipy)	91	64—67	
(an)Pd(*o*-phen)	77	55—58	

[a] ma = maleic anhydride, dmm = dimethyl maleate, dmf = dimethyl fumarate, dvs = divinyl sulfone and an = acrylonitrile. [b] M.p. without dec.

Table 5. Nmr data of (olefin)PdL$_2$ complexes (in CDCl$_3$).

Complex	τ (CH=)	τ (L)	τ (MeO)
(ma)Pd[P(OPh)$_3$]$_2$	6.78 (2H)	2.9 (30H)	
(ma)Pd[P(OMe)$_3$]$_2$	5.67 (2H)	6.40 (18H)	
(dmm)Pd(bipy)	3.80 (2H)	1.0—2.7 (8H)	6.22 (6H)
(dmm)Pd(*o*-phen)	3.83 (2H)	1.5—2.7 (8H)	6.27 (6H)
(dmf)Pd(bipy)	6.14 (2H)	1.4—2.9 (8H)	6.44 (6H)
(dmf)Pd(*o*-phen)[a]	5.89 (2H)	1.0—2.3 (8H)	6.35 (6H)
(dmf)Pd(tmeda)[a]	6.32 (2H)	7.30 (12H)	6.63 (6H)
(dvs)Pd(*o*-phen)[a]	4—5 (6H)	0.6—2.1 (8H)	
(an)Pd(*o*-phen)	4.81 (2H)	0.8—2.3 (8H)	

[a] DMSO-d_6.

Table 6. Analyses of (olefin)PdL$_2$ complexes [found (calcd.) (%)].

Complex	C	H	N
(ma)Pd(bipy)	46.64 (46.63)	2.68 (2.79)	7.42 (7.77)
(ma)Pd[P(OPh)$_3$]$_2$	58.23 (58.65)	3.91 (4.15)	
(ma)Pp[P(OMe)$_3$]$_2$	26.66 (26.54)	4.33 (4.45)	
(dmm)Pd(*o*-phen)	50.20 (50.19)	3.75 (3.74)	6.47 (6.50)
(dmf)Pd(*o*-phen)	49.91 (50.19)	3.95 (3.74)	6.23 (6.50)
(dmf)Pd(bipy)	47.49 (47.25)	4.09 (3.97)	6.86 (6.89)

Table 7. Stability of the complexes (olefin)PdL$_2$.

Olefinic compound	*e*-value	bipy	*o*-phen	P(OPh)$_3$	P(OMe)$_3$
maleic anhydride	2.25	++[a]	++	++	++
dimethyl fumarate	1.49	++	++	+	+
divinyl sulfone	1.33	++	++	+	+
dimethyl maleate	1.27	++	++	—	—
acrylonitrile	1.20	++	++	—	—

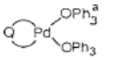
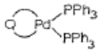
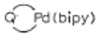
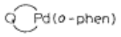
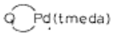
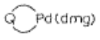
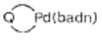
[a] ++ stable enough to be isolated, + complex formation possible but difficult to be isolated, and — only decomposed into metallic palladium and free DBA.

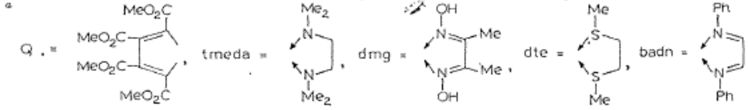
2. 2. 5. *Reactions of Pd$_2$(DBA)$_3$ with Dimethyl Acetylenedicarboxylate (DMAD) in the Presence of Ligand*

Treatment of Pd$_2$(DBA)$_3$ (I) with dimethyl acetylenedicarboxylate (DMAD) in acetone under nitrogen gave the palladiacyclopentadiene complex (IX), which reacted with excess of ligand [L=bipy or P(OPh)$_3$] to give the monomeric palladiacyclopentadiene complex (X). More conveniently, palladiacyclopentadiene complex (X) could be prepared by the simultaneous addition of ligand and DMAD to a suspension of (I) in acetone.

Into an acetone solution (30 ml) of (I) (0.3 mmol) and an excess of a ligand (0.63 mmol), dimethyl acetylenedicarboxylate (DMAD) (0.3 mmol) was added, and one hr later, crystals of palladiacyclopentadiene-L_2 complex (X) were precipitated. Ligands used in this reaction were as follows: triphenyl phosphite (a), PPh_3 (b), bipy (c), *o*-phen (d), tmeda (e), dimethylglyoxime (f), 1, 2-bis(methylthio)ethane (g) and biacetyldianil (h). The properties and analyses of (Xa-Xh) are tabulated in Table 8.

Table 8. Properties and analyses of palladiacyclopentadine-L_2 complexes.

Complex	Structure	Color	Yield (%)	m.p.(°C, dec.)	τ(Me)($CHCl_3$)	ν(C=O) (KBr)	Analysis: Found (Calcd.) (%)		
							C	H	N
Xa		yellow	88	165-166	6.23^b, 6.34^b	1690 1720	57.21 (57.01)	4.41 (4.19)	
Xb		yellow	70	160-164	6.35, 7.30	1650 1720	52.90 (52.68)	4.50 (4.42)	
Xc		yellow	78	218-220	5.98^b, 6.12^b	1690 1720	47.59 (48.32)	3.60 (3.69)	5.03^c (5.12)
Xd		yellow.	53	205-210	5.95^b, 6.12^b	1690 1715	50.68 (50.50)	3.76 (3.53)	4.64 (4.91)
Xe		yellow-brown	87	205-210	6.30, 6.38	1690 1715	43.46 (42.66)	5.52 (5.65)	5.35 (5.53)
Xf		golden-yellow	50	193-196	6.25, 6.30	1685 1705	38.43 (37.92)	3.96 (3.98)	5.25 (5.53)
Xg		yellow-brown	28	164-165	6.26, 6.33	1690 1715	37.60 (37.47)	4.33 (4.32)	
Xh		golden-yellow	88	217-218	6.03, 6.35	1690 1705	53.65 (53.64)	4.61 (4.50)	4.30 (4.47)



[b] In nitrobenzene. [c] Pd 19.3(19.4).

Palladiacyclopentadiene complexes (X) also could be formed via a zerovalent π-acetylenepalladium intermediate. The addition of DMAD (10.3 mmol) to an excess of $P(OPh)_3$ (0.3 ml) and (I) (0.3 mmol) in benzene solution gave $(DMAD)Pd[P(OPh)_3]_2$ (XIa), yellow needle-like crystals of M. p. 136-138° (dec.) in 50% yield. IR $\nu(C{\equiv}C)$ 1845cm^{-1} and NMR $\tau(CDCl_3)$ 6.57 (s, OMe) and 2.9 (Ph) (Analysis: found C, 58.15; H, 4.13. $C_{42}H_{36}O_{12}PdP_2$ calcd.: C, 58.04; H, 4.18%). The complex (XIa) is surprisingly stable in air and in benzene or chloroform solution. Further addition of DMAD to (XIa) did not afford the expected palladiacyclopentadiene complex [Xa; L=$P(OPh)_3$], which was prepared independently via (IX).

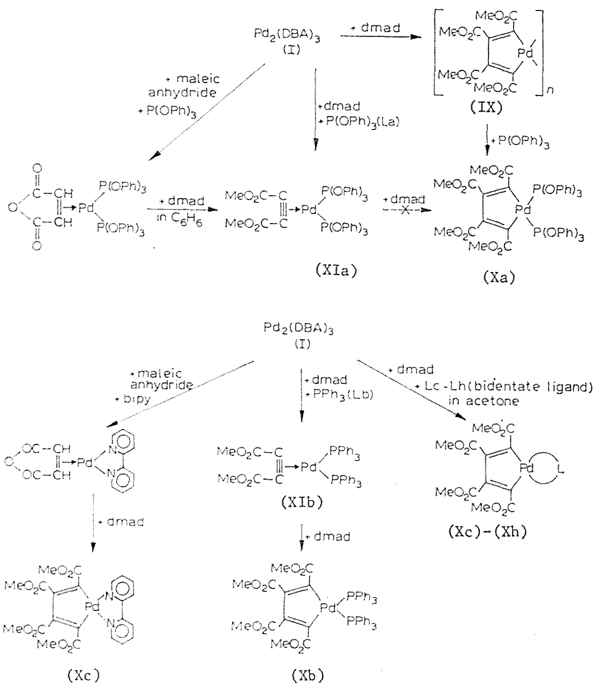
However, with PPh_3 as ligand, the stepwise reactions (I) → (XIb) and (XIb) → (Xb) were successful. In the case of PPh_3 as a ligand, the complex $(DMAD)Pd(PPh_3)_2$ (XIb), M. p. 195-196° (dec.), was obtained in 52% yield. IR $\nu(C{\equiv}C)$ 1845 cm^{-1} and NMR $\tau(CDCl_3)$ 6.8 (s, OMe). The addition of a second molecule of DMAD to (XIb) in benzene at room temperature gave the palladiacyclopentadiene complex (Xb), M. p. 160-164° (dec.), in 70% yield.

A similar complex (XIb, L=PPh_3) gave (Xb) by the addition of a second molecule of DMAD in benzene solution at room temperature, strongly suggesting that the π-complex (XIb) is an intermediate in the formation of (Xb). The complex $(ma)Pd[P(OPh)_3]_2$ (Table 4) gave (XIa) quantitatively in the reaction with DMAD in benzene at room temperature, but (ma)Pd(bipy), which has a more basic ligand, gave directly the corresponding palladiacyclopentadiene complex (Xc, L=bipy) with DMAD.

In conclusion, intermediate π-complexes (XI) are more stabilized as the π-acceptor character of L increases, in the order: bipy $\approx$ o-phen $\ll$ PPh_3 $<$ $P(OPh)_3$, indicating the following results: (1) intermediate (XI) would be stabilized by a π-acceptor ligand such as $P(OPh)_3$ and thus not give (X); (2) the less stable intermediate (XIb, $L=PPh_3$) could afford (Xb), and (3) ligands such as bipy (c), o-phen (d), tetramethylethylenediamine (tmeda) (e), dimethylglyoxime (dmg) (f), 1, 2-bis(methylthio)ethane (dte) (g) and biacetyldianil (badn) (h) gave directly the corresponding palladiacyclopentadiene complexes (Xc-h), respectively.

These results are illustrated in Scheme 1.

SCHEME 1



2. 2. 6. *Preparation of Palladium—p-Quinone—Ligand Complexes*

Schrauzer prepared a number of Ni^0—duroquinone complexes.[18] Takahashi and Hagiwara prepared $(Ph_3P)_2Pd(p\text{-}Q)$ complexes in the reactions of $Pd(PPh_3)_4$ with p-benzoquinone and 1, 4-naphthoquinone in benzene.[19]

$Pd_2(DBA)_3$ has been found to be an excellent starting material for the preparation of Pd—p-quinone π-coordinated complexes. When an acetone suspension of (Ia) is treated with p-quinone (Q)(p-benzoquinone, duroquinone, 1, 4-naphthoquinone and 2-methyl-1, 4-naphthoquinone) at room temperature under nitrogen, the complexes $(Q)PdL_2$(XII) crystallize in good yield.

$$Pd_2(DBA)_3 + 4L + 2Q \xrightarrow[RT]{N_2} \underset{\text{(XII)}}{2(Q)PdL_2} + 3DBA \qquad (5)$$

As an example, the preparation of (BQ)Pd(*o*-phen), M.p. 240° dec., is described. To an acetone suspension of (Ia), *o*-phenanthroline was added at RT under N$_2$, and when the color of the solution became yellow addition of *p*-benzoquinone in acetone caused the crystallization of ruby-red needle-like crystals. After recrystallization from chloroform/acetone, 90% yield of the complex was obtained. (Found: C, 58.78; H, 3.29; N, 6.38. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) IR; ν(CO) 1610, 1597 cm^{-1} and NMR (CDCl$_3$) 4.20 (s, 4) (coordinated quinone ligand) [free Q 3.35 (s)], 2.23 (q, 2), 2.11 (s, 2), 1.56 (dd, 2) and 1.15 (dd, 2)τ (coordinated *o*-phen).

Analyses of other (XII) complexes. *(BQ)Pd(bipy)*: (Found: C, 51.68; H, 3.31; N, 7.52. Calcd.: C, 51.84; H, 3.26; N, 7.56%.) *(DQ)Pd(o-phen)(H$_2$O)*. (Found: C, 56.88; H, 4.77; N, 5.98. Calcd.: C, 56.36; H, 4.73; N, 5.98%.) *(DQ)-Pd(bipy)*. (Found: C, 55.91; H, 4.74; N, 6.57. Calcd.: C, 56.29; H, 4.72; N, 6.56%.) *(NQ)Pd(o-phen)*. (Found: C, 59.07; H, 3.30; N, 6.23. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) *(NQ)Pd(bipy)*. (Found: C, 56.82; H, 3.45; N; 6.68. Calcd.: C, 57.09; H, 3.35; N, 6.66%.) *(NQ)Pd*(tmeda). (Found: C, 50.17; H, 5.79; N, 7.21. Calcd.: C, 50.47; H, 5.83; N, 7.36%.) *(K$_3$)Pd(bipy)*. (Found: C, 57.51; H, 3.76; N, 6.47. Calcd.: C, 58.01; H, 3.71; N, 6.44%.) *(K$_3$)Pd(o-phen)(H$_2$O)*. (Found: C, 57.56; H, 3.53; N, 5.75. Calcd.: C, 57.64; H, 3.80; N, 5.87%.) *(K$_3$)Pd(PPh$_3$)$_2$*. (Found: C, 70.05; H, 4.81. Calcd: C, 70.29; H, 4.77%.)

The complexes (XII) with *o*-phen or bipy ligand are obtained as yellow-red crystals. The complexes are stable in the solid state. With the exception of duroquinone complexes with tmeda they are also stable in solution.

Table 9. Yield and physical properties of the quinone complexes (XII).

complex[a]	Yield (%)	M.p. (dec.)	Color	$\Delta\nu$ (CO) (cm^{-1})
BQ				(1662, 1647)
(BQ)Pd(*o*-phen)	90	240	Ruby-red	51
(BQ)Pd(bipy)	94	190	Red-orange	56
(BQ)Pd(tmeda)	76	133—135	Red	(65)
(BQ)Pd(PPh$_3$)$_2$	92	155—157	Dark red	35
DQ				(1637)
(DQ)Pd(*o*-phen)(H$_2$O)	85	205	Deep red	112
(DQ)Pd(bipy)	85	210	Deep red	75
(DQ)Pd(tmeda)	59	130	Brown-red	95
NQ				(1662)
(NQ)Pd(*o*-phen)	95	285	Orange	60
(NQ)Pd(bipy)	84	215	Yellow-orange	61
(NQ)Pd(tmeda)	89	130—132	Ruby-red	62
(NQ)Pd(PPh$_3$)$_2$	86	161—163	Red-orange	21
K$_3$				(1668)
(K$_3$)Pd(*o*-phen)(H$_2$O)	85	235	Orange	81
(K$_3$)Pd(bipy)	85	225	Yellow-orange	72
(K$_3$)Pd(tmeda)	58	138—140	Yellow-orange	74
(K$_3$)Pd(PPh$_3$)$_2$	77	128—130		37

[a] BQ *p*-benzoquinone; DQ duroquinone; NQ 1,4-naphthoquinone and K$_3$ 2-methyl-1,4-naphthoquinone.

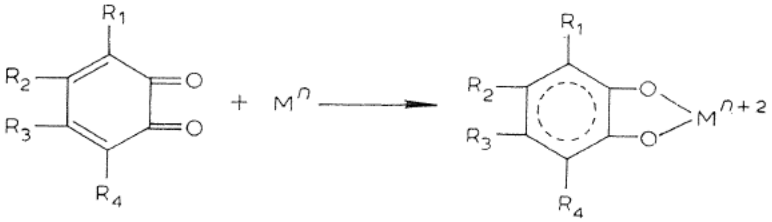
Quinone—Pd—PPh$_3$ complexes (p-benzoquinone and 1, 4-napthoquinone) have already been reported.[19] However they are prepared more readily and with higher purity and yield by the method outlined here.

Yield, m. p., color and $\Delta\nu$(CO) of the complexes (XII) are tabulated in Table 9. Also in Table 9 values of $\Delta\nu$(CO), the carbonyl stretching frequency of the coordinated quinone ligand compared with that of the free quinone, are tabulated. Generally a 30-100 cm^{-1} shift of ν(CO) to lower frequencies is observed. These values may be compared with $\Delta\nu$(CO) (36, 31 cm^{-1}) of π-olefinic—Pd complexes $(Ph_3P)_2Pd$(Olefin) (Olefin: dimethyl fumarate, dimethyl maleate) and $\Delta\nu$(CO) (76 cm^{-1}) of (Duroquinone)Ni(COD)[20] and are very different from $\Delta\nu$(CO) (150 cm^{-1}) observed for oxygen coordination to the metal atom in $Mo(CO)_2(Acrolein)_2$.[15] Therefore, it seems likely that the coordination of p-quinones to the Pd atom involves the olefinic double bonds and not the carbonyl moiety.

The order of $\Delta\nu$(CO) (tmeda $>$ bipy $\geqslant$ o-phen $>$ Ph$_3$P) reflects the polarity of the carbonyl group of the quinone ligand in the complexes (XII). The higher $\Delta\nu$(CO) value indicates greater polarity.

2. 2. 7. Preparation of Pd—o-Quinone Complexes

There is an extensive literature on oxidative addition reactions of low valent metal complexes.[21~24] Among these, oxidative addition reactions of tetrachloro-1, 2-benzoquinone with $M^0(PPh_3)_4$ (M=Pt,Pd), $M^1(CO)Cl(PPh_3)_2$ (M=Rh, Ir)[25] and *trans*-$Ru(CO)_3(PPh_3)_2$ as well as that of 9, 10-phenanthrenequinone with $Ir(CO)Cl(PPh_3)_2$[26] are well established. In general, the reaction scheme is:



(6)

We find reactions between (Ia) and o-quinones in the presence of ligand afford new o-quinone—Pd complexes, such as (o-Q)PdL$_2$. When an N-donor ligand (o-phen, bipy, tmeda, and py) was added to an acetone suspension of (Ia), the color of the solution changed to yellow. Then the addition of o-quinone caused a sudden color change of the solution, and the crystallization of the o-quinone—Pd complex. Yield and physical properties of (o-Q)PdL$_2$ (XIII) are shown in Table 10.

As shown in Table 10, twelve complexes (XIII) were obtained in good yield. Analyses of them are given here. (9, 10-phenanthrenequinone)Pd(o-phen), (Found: C, 62.14; H, 3.49; N, 5.74. Calcd.: C, 63.11; H, 3.26; N, 5.66 %.) *(9,10-PQ)Pd(bipy)*. (Found: C, 59.52; H, 3.66; N, 5.76. Calcd.: C, 61.33; H, 3.43; N, 5.95%.) *(9, 10-PQ)Pd(py)*$_2$. (Found: C, 60.95; H, 3.85; N, 4.87. Calcd.: C, 60.97; H, 3.84; N, 5.92%.) (9, *10-PQ)Pd*(tmeda). (Found: C, 54.25; H, 5.39; N, 6.40. Calcd.: C, 55.76; H, 5.62; N, 6.50%.) *(1, 2-NQ)Pd(o-phen)*. (Found: C, 58.61; H, 3.46; N, 6.22%.) *(1, 2-NQ)Pd(bipy)*. (Found: C, 56.57; H, 3.41; N, 6.64. Calcd.: C, 57.10; H, 3.35; N, 6.66%.) *(4,5-MeO-1,2-BQ)Pd(o-phen)*. (Found: C, 50.47; H, 3.52; N, 5.89. Calcd.: C, 52.82; H, 3.55; N, 6.16%.) *(4,5-MeO-1,2-BQ)Pd(bipy)*. (Found: C, 49.68; H, 3.74; N, 6.18. Calcd.: C, 50.19; H, 3.77; N, 6.50%.) *(4, 5-*

MeO-1, 2-BQ)Pd(py)$_2$. (Found: C, 49.98; H, 4.28; N, 6.48. Calcd.: C, 49.96; H, 4.19; N, 6.47%.) *(4-t-Bu-1, 2-BQ)Pd(o-phen)*. (Found: C, 59.20; H, 3.20; N, 6.42. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) *(4-t-Bu-1,2-BQ)Pd(bipy)*. (Found: C, 56.12; H, 4.75; N, 6.63. Calcd.: C, 56.29; H, 4.72; N, 6.56%.) *(4-t-Bu-1, 2-BQ)Pd(py)*$_2$. (Found: C, 54.90; H, 5.19; N, 6.44. Calcd.: C, 56.02; H, 5.17; N, 6.53%.)

Table 10. Yield and physical properties of the complexes (XIII)[a].

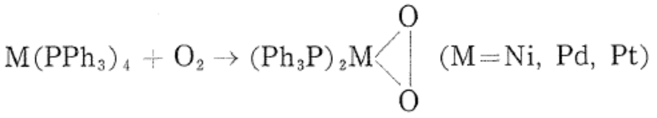
Complex	Color	Yield (%)	M.p. (℃) (dec.)
(9,10-PQ)Pd(*o*-phen)	Blue	95	300 <
(9,10-PQ)Pd(bipy)	Green	97	300 <
(9,10-PQ)Pd(py)$_2$	Yellow	88	210—218
(9,10-PQ)Pd(tmeda)	Yellow	89	145—150
(1,2-NQ)Pd(*o*-phen)	Blue	91	300 <
(1,2-NQ)Pd(bipy)	Blue	81	300 <
(4,5-MeO-1,2-BQ)Pd(*o*-phen)	Blue	95	~ 284
(4,5-MeO-1,2-BQ)Pd(bipy)	Blue	98	~ 250
(4,5-MeO-1,2-BQ)Pd(py)$_2$	Yellow-brown	80	~ 155
(4-t-Bu-1,2-BQ)Pd(*o*-phen)	Blue-violet	83	300 <
(4-t-Bu-1,2-BQ)Pd(bipy)	Violet	91	300 <
(4-t-Bu-1,2-BQ)Pd(py)$_2$	Purple	52	~ 165

[a] 9, 10-PQ 9, 10-phenanthrenequinone; 1, 2-NQ 1, 2-naphthoquinone; 4, 5-MeO-1, 2-BQ 4, 5-dimethoxy-1, 2-benzoquinone; 4-t-Bu-1, 2-BQ 4-tert-butyl-1, 2-benzoquinone.

These complexes are stable in the solid state, but decompose in solution in air. The strong ν(CO) (1650-1700 cm^{-1}) band of the original *o*-quinones disappears in all (XIII), and characteristic *o*-diolato absorption band emerges. Therefore, it seems that contrary to the π-olefin—Pd complexes of *p*-quinone, the two carbonyl oxygen atoms of *o*-quinone (pseudobutadiene structure) coordinate to the Pd atom.

2. 2. 8. *Preparation of (bipy)Pd(OH)*$_2$ *via Pd*$_2$*(TBA)*$_3$

The peroxo complexes were formed in the oxygen oxidation of low valent Group VIII metal complexes[2,7~29] Peroxo-isonitrile nickel and palladium complexes (RNC)$_2$MO$_2$ were prepared by Otsuka et al.[20]

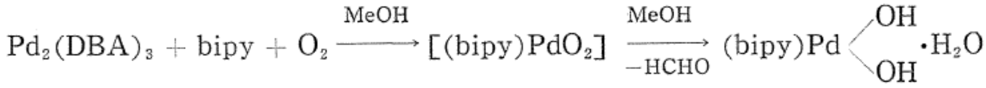


$$M(PPh_3)_4 + O_2 \rightarrow (Ph_3P)_2M\begin{matrix}O\\|\\O\end{matrix} \quad (M{=}Ni,\ Pd,\ Pt) \qquad (7)$$

We attempted to obtain an oxidation product starting from (I) in the presence of a ligand. In the oxygen oxidation of (I) in the presence of 2, 2′-bipyridine and methanol, another type of product, (bipy)Pd(OH)$_2$, was obtained, which has been unknown so far. This complex, M.p. 105—110° (dec.), of the composition (bipy)Pd(OH)$_2 \cdot$H$_2$O (XIV), could be obtained via reduction of a peroxo intermediate (not isolated) by methanol.

The complex (XIV) was obtained in a yield of 60% (Analysis: found C, 38.77;

H, 3.85; N, 8.60. $C_{10}H_{12}N_2O_3Pd$ calcd.: C, 38.18; H, 3.56; N, 8.90%). IR data $\nu(OH)$ 3400 and $\nu(C-N)$ 1450 cm^{-1}.



$$Pd_2(DBA)_3 + bipy + O_2 \xrightarrow{MeOH} [(bipy)PdO_2] \xrightarrow[-HCHO]{MeOH} (bipy)Pd(OH)_2 \cdot H_2O \quad (8)$$

(I) (XIV)

The complex (XIV) could be prepared by the reaction of 7% H_2O_2 with (DBA)Pd(bipy) (IV) in methanol under nitrogen. Therefore, the formation of the complex (XIV) might be caused by the presence of the bipy ligand instead of PPh_3. The structure of (XIV) was confirmed by (1) addition of HCl to aqueous (XIV) gave $(bipy)PdCl_2$, (2) (XIV) and acetic acid afforded $Pd(OAc)_2 \cdot 2H_2O$ and (3) the addition of bipyridine and $HClO_4$ to aq. (XIV) gave $[(bipy)_2Pd](ClO_4)_2$, M.p. >270 ℃. IR data $\nu(C-N)$ 1450 and $\nu(ClO_4)$ 1100 cm^{-1} (Analysis: found C, 38.67; H, 2.68; N, 9.10. $C_{20}H_{16}O_8N_4Cl_2Pd$ calcd.: C, 38.89; H, 2.61; N, 9.07%).

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3. Reactions of Tetrakis(methoxycarbonyl)palladiacyclopentadiene Complex

3. 1. *Introduction*

Tetrakis(methoxycarbonyl)palladiacyclopentadiene complex was found by two groups: Maitlis (Sheffied) and our group (Nagoya). The complex is prepared readily in the reaction between $Pd_2(DBA)_3$ complex and dimethyl acetylenedicarboxylate as shown in the former chapter.

We discover the utility of this complex during our study on the reactions with N, N-dichloroamine and amide, and on a selective cyclocotrimerization of two acetylenic and one olefinic components in the presence of the complex. Full details of the results so far obtained are shown in this chapter.

3. 2. *Ring-Opening Reactions of Palladiacyclopentadiene Complex with N, N-Dichloro-amine and -amide.*

3. 2. 1. *Introduction*

Recently the chemical behavior of the N-haloamines has been investigated extensively.[1] N, N-Dichloroamine or -amide is expected to generate nitrene in the reaction with low valent noble metal complexes which would readily tend to form metal dichloride, L_nMCl_2, oxidatively. Maitlis[2] reported that the palladiacyclopentadiene complex afforded the acetylenic trimer. A reaction of this complex with nitrene, generated by a metal-assisted reactions of N, N-dichloroamine or -amides, is expected to give pyrrole in a similar fashion. In order to examine the possibility of a metal-assisted nitrene generation, this chapter describes the reaction between palladiacyclopentadiene bipyridine complex (I) with four N, N-dichloroamine and -amides.

3. 2. 2. *Reactions of Bipyridinepalladiacyclopentadiene complex with N, N-Dichloro-t-butylamine, -p-toluamide, -benzenesulfonamide and -p-chlorobenzamide*

An equimolar mixture of palladiacyclopentadiene complex (I) and N, N-dichlorobutylamine or N, N-dichloro-*p*-toluamide in benzene was kept at room temperature. After 10 hr stirring, σ-4-chloro-1, 2, 3, 4-tetrakis(methoxycarbonyl)buta-1, 3-dienylpalladium complex (II) precipitated, which was recrystallized from CH_2Cl_2 as pale yellow crystals.

Reaction of Bipyridinepalladiacyclopentadiene with N, N-*Dichloro-t-butylamine.* To bipyridinepalladiacyclopentadiene (0.698 g, 1.28 mmol) suspended in 5 ml of benzene N, N-dichloro-*t*-butylamine (0.182 g, 1.23 mmol) was added dropwise at 0 ℃ under an atomsphere of nitrogen. After stirring for 10 hr, pale yellow powder was precipitated. Filtration followed by recrystallization from the mixed solvent of acetone and ethyl ether (6/5) gave yellow crystals in a 64% yield, which was identified σ-4-chloro-1, 2, 3, 4-tetrakis(methoxycarbonyl)buta-1, 3-dienylpalladium (II) from the elemental analysis and the spectroscopic data cited below. Mp 168.0–170.0 ℃. Found: C, 43.29; H, 3.23; N, 4.55; Cl, 11.37%. Calcd for $C_{22}H_{20}N_2O_8Cl_2Pd$: C, 42.73; H, 3.27; N, 4.53; Cl, 11.48%. IR (in KBr) 1722, and 323 (νPd-Cl) cm^{-1}. ^1H NMR (in CD_3COCD_3) τ6.57 (3H, s), 6.36 (6H, s), and 6.30 (3H, s).

Reaction of Bipyridinepalladiacyclopentadiene with N, N-*Dichloro-p-tolu-*

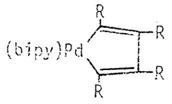
amide. N, N-Dichloro-*p*-toluamide (0.119g, 0.583 mmol, in 5ml of dry benzene) was added dropwise to bipyridinepalladiacyclopentadiene (0.213 g, 0.390 mmol) suspended in 20 ml of dry benzene at 0 ℃ under nitrogen. Immediately, reaction mixture turned yellowish orange solution, and pale yellow powder was precipitated in several minutes. Recrystallization from the mixed solvent of dichloromethane and *n*-hexane (1/1) gave σ-4-chloro-1, 2, 3, 4-tetrakis(methoxycarbonyl)buta-1, 3-dienylpalladium (II) as yellow crystals in 73% yield.

The reaction of (I) with N, N-dichlorobenzenesulfonamide or N, N-dichloro-*p*-chlorobenzamide under similar reaction conditions gave (III) or (IV), respectively. In both cases, any nitrene adduct with the ligand $C_4(COOCH_3)_4$ was not isolated.

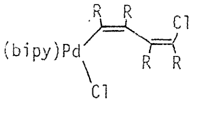
Reaction of Bipyridinepalladiacyclopentadiene with N, N-*Dichlorobenzenesulfonamide.* Equimolar amounts of N, N-dichlorobenzenesulfonamide was added to a stirred suspension of bipyridinepalladiacyclopentadiene in benzene at room temperature. From the solution a pale yellow solid slowly precipitated. This was filtered off and crystallized from dichloromethane- ethyl ether to give yellow prisms of III in 84% yield. Mp 185.0–186.0℃. Found: C, 40.61; H, 3.17; N, 4.96%. Calcd for $C_{28}H_{25}N_3O_{10}Cl_2Pd \cdot CH_2Cl_2$ (solvent of crystallization): C, 40.61; H, 3.17; N, 4.90%. IR (in KBr) 1722 cm^{-1}. ^1H NMR (in $CDCl_3$) $\tau 6.92$ (3H, s), 6.29 (3H, s), 6.20 (3H, s), and 6.16 (3H, s).

Reaction of Bipyridinepalladiacyclopentadiene with N, N-*Dichloro-p-chlorobenzamide.* N, N-Dichloro-*p*-chlorobenzamide (0.073 g, 0.326 mmol) was added to a stirred suspension of bipyridinepalladiacyclopentadiene (0.166 g, 0.304 mmol) in 20 ml of dry benzene at room temperature under an atomsphere of argon. Reaction proceeded immediately and a pale yellow solid was precipitated after 3 min. This was filtered off and crystallized from dichloromethane-*n*-hexane to give yellow plates of IV in 57% yield. Mp 115.5-117.5℃. Found: C, 37.43; H, 2.49; N, 4.26; Cl, 29.66%. Calcd for $C_{33}H_{24}N_3O_{11}Cl_9Pd$: C, 37.22; H, 2.27; N, 3.95; Cl, 29.96%. IR (in KBr) 1737, 1720, and 1689cm^{-1}. ^1H NMR (in $CDCl_3$ at 90℃) $\tau 6.39$ (3H, s), 6.34 (3H, s), 6.30 (3H, s), 6.18 (3H, s), and 1.90-2.70 (12H, m). Mass (I.P. 70eV) m/e 223 (5) $[Cl\text{-}C_6H_4CONCl_2]^{\cdot +}$, 155 (33) $[^{37}Cl\text{-}C_6H_4\text{-}CON\colon$ or $^{37}Cl\text{-}C_6H_4\text{-}NCO]^{\cdot +}$, 153 (100) $[^{35}Cl\text{-}C_6H_4\text{-}CON$ or $^{35}Cl\text{-}C_6H_4\text{-}NCO]^{\cdot +}$, 127 (15) $[^{37}Cl\text{-}C_6H_4\text{-}N\colon]^{\cdot +}$, and 125 (45) $[^{35}Cl\text{-}C_6H_4\text{-}N\colon]^{\cdot +}$.

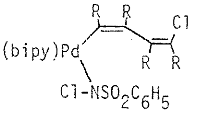
Three resonance peaks at $\tau 6.57$(3H), 6.36(6H), and 6.30(3H) due to the methoxycarbonyl group appeared in the ^1H nmr spectrum of (II) in CD_3COCD_3, whereas the original palladiacyclopentadiene complex (I) showed only one resonance peak at $\tau 6.25$ in $CDCl_3$ or two peaks at $\tau 6.34$ and 6.32 in CD_2Cl_2. Similarly (III) and (IV) showed four resonance peaks in the methoxycarbonyl region. This nmr result strongly suggests that (II), (III), and (IV) have the linear (σ-1, 3-butadienyl) structures by the cleavage of one Pd-C bond of the five-membered metallocycles.



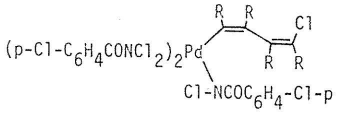
[I]



[II]



[III]



[IV]

($R=COOCH_3$)

In IR spectra, (II) had an absorption band of the Pd-Cl stretching vibration at

323 cm^{-1} while no absorptions appeared around this region in those of (III) and (IV). In addition, (IV) showed three absorptions at 1737, 1720, and 1689 cm^{-1} due to carbonyl stretching vibrations. The absorption at 1737 cm^{-1} could be assigned to the carbonyl stretching frequency of p-Cl-$C_6H_4CONCl_2$ ligand. The data of mass spectrum of (IV) were also well consistent with the proposed structure.

It is indicated that the delocalization of lone pair electrons by electronwithdrawing carbonyl groups increased the stability of the Pd-N σ-bond in (III) and (IV). The formation of (IV) is explained in terms of the Pd-C bond cleavage of (I) by the attack of the N-Cl bond and the subsequent ligand exchange of bipyridine by N, N-dichloro-p-chlorobenzamide. The Mp, ir, and nmr data of (II), (III), and (IV) are summarized in following Table. Satisfactory analyses for all new complexes were obtained.

Table 1. The Mp, ir, and nmr data of (II), (III), and (IV).

Complex	Yield (%)	Mp (℃)	$\nu_{C=O}$, ν_{Pd-Cl} (cm^{-1})		τ_{COOCH_3}
II	64[a)] 73[b)]	168.0-170.0	1722,	323	6.57 (3H), 6.36 (6H) 6.30 (3H)
III	84	185.0-186.0	1722	—	6.92 (3H), 6.29 (3H) 6.20 (3H), 6.16 (3H)
IV	57	115.5-117.5	1737 1720 1689	—	6.36 (3H), 6.34 (3H) 6.30 (3H), 6.18 (3H)

a), b) ; N, N-Dichloro-t-butylamine and N, N-dichloro-p-toluamide were used as reagents, respectively.

3. 2. 3. Reaction of Coordinatively Unsaturated Palladiacyclopentadiene with N, N-Dichloro-t-butylamine

No nitrene adducts were obtained in the reaction of N, N-dichloramine or -amides with (bipy)Pd[$C_4(COOCH_3)_4$]. N, N-Dichloramine or -amide skeletons must split up into three fragments, that is, nitrene and two chlorine atoms to generate nitrene. Coordinatively unsaturated and low valent complexes are, therefore, required to obtain nitrene complexes from N, N-dichloramine.

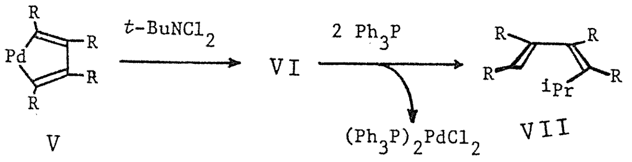
2, 3, 4, 5-Tetrakis(methoxycarbonyl)palladiacyclopentadiene (V), formed by the oxidative addition of two equivalents dimethyl acetylenedicarboxylate to tris(dibenzylideneacetone)dipalladium,[2], is regarded as a coordinatively unsaturated complex. There are two Pd-C σ-bonds and two weak intermolecular coordinate bonds in V. The latter are easily displaced by entering ligands.

Reaction of palladiacyclopentadiene with N, N-*Dichloro-t-butylamine.* To a suspension of palladiacyclopentadiene (0.155 g, 0.398 mmol) in 5 ml of dry benzene was added N, N-dichloro-t-butylamine (0.120 g, 0.847 mmol, in 1ml of dry benzene) with stirring at room temperature. After stirring at room temperature for 1 hr the solid was dissolved to give a clear orange solution, from which a brown solid was slowly precipitated. This was removed by a filtration, and the filtrate was evaporated *in vacuo*. To the remaining yellowish orange oily liquid was added acetone and ethyl ether (3/2). From this solution brown solid was precipitated after standing for 2 days, which was again removed by filtration. From the clear yellow filtrate, solvent was evaporated under reduced pressure, and then acetone and *n*-hexane was added to the remaining yellow oil. After standing for 1 day at 0℃, yellow solid was precipitated. Recrystallization from benzene and ethyl ether gave dichloro [1, 2, 3, 4-tetrakis(methoxycarbonyl)-5-methyl-1, 3-hexadiene] palladium (VI) as yellow prisms in 57% yield. Decomp. 142.0-143.0℃. Found: C, 36.88; H, 4.29; Cl, 14.57%. Calcd for $C_{15}H_{20}O_8Cl_2Pd$: C, 35.63; H, 3.99; Cl, 14.02%. IR (in KBr) 1753, 1737, and 1729 cm^{-1}. ^1H NMR (in $CDCl_3$) τ8.81(3H, d, J=6 Hz), 8.31 (3H, d, J=6 Hz), 7.58 (1 H, sept, J=6 Hz), 6.30 (6H), 6.22 (6H), and 3.61 (1 H, olefinic).

Reaction of VI with Triphenylphosphine. Triphenylphospine (0.044 g, 0.168 mmol) was added to a stirred solution of VI (0.041 g, 0.081 mmol) in 5 ml of dichloromethane at room temperature under nitrogen. From the solution a pale yellow solid was immediately precipitated. After stirring at room temperature for 3 hr, this was filtered off and crystallized from the mixed solvent of benzene and ethyl ether to give yellow needles of dichlorobis(triphenylphosphine)palladium in 84% yield, which were identified by the comparison with the authentic sample. From the filtrate the solvent removed by evaporation to give, after chromatography on silica gel in benzene, 1, 2, 3, 4-tetrakis(methoxycarbonyl)-5-methyl-1, 3-hexadiene (VII) as a viscous yellow oil (0.014 g) in 53% yield. ^1H NMR (in CCl_4) τ9.03 (6H, d, J=6 Hz), 7.90 (1H, sept, J=6 Hz), 6.36 (3H, s), 6.31 (3H, s), 6.25 (3H, s), 6.19 (3H, s), and 3.33 (1H, olefinic).

The results of the ligand exchange reaction with triphenylphosphine indicates that 1, 3-hexadiene (VII) is coordinated to palladium as a bidentate ligand in the π-manner. Whereas the resonance absorption of methyl protons of isopropyl group of VII appeared in doublet (τ9.03, J=6 Hz), those of VI in doublet of doublets (τ8.81 and 8.31, J=6 Hz). This non-equivalency of two methyl groups in ^1H NMR would be induced by the hindered rotation of isopropyl group. Therefore, it would be concluded that isopropyl group is directed to inside (*cis* to C(2)-C(3) bond) as shown in Fig. 1.

And the reaction sequence is shown in Eq. (1).



(1)

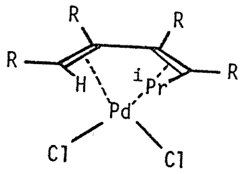
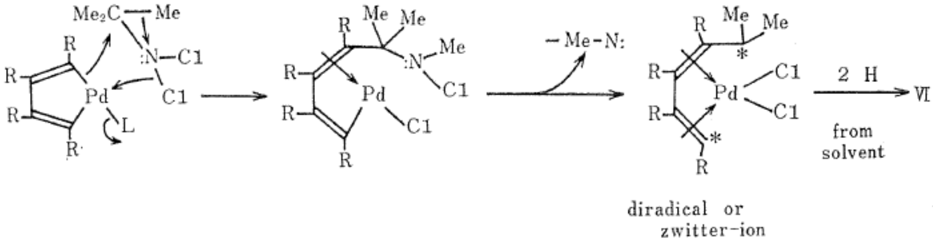


Fig. 1. Structure of VI.

The exclusive formation of VI (*cis*-isopropyl group to C(2)-C(3) bond) would suggest that the ring cleavage of V with N,N-dichloro-*t*-butylamine proceeds *via* a four-centered transition state with simultaneous methyl migration from carbon to nitrogen atom (Eq. 2).



(2)

3. 3. The Preparation, the Structure, and the Role in a Selective Palladium-catalyzed Cyclocotrimerization of Tetrakis(methoxycarbonyl) palladiacyclopentadiene Cyclic Diolefin Complexes

3. 3. 1. Intorduction

The Catalytic cyclotrimerization of acetylenes has been intensively investigated.[3~5] The cyclotrimerization of two acetylene with one olefin components, to form cyclohexa-1, 3-diene derivatives[6~9] has been studied, but no highly selective, catalytically efficient reactions have been found. The most fatal side reaction is the formation of benzene derivatives from the competitive acetylene trimerization. These two reactions have been postulated to proceed *via* a metallocyclopentadiene complex as the key intermediate as shown in Scheme. In order to attain the high selectivity in the objective cyclotrimerization, an olefin component should coordinate to the transition metal of the intermediate metallocyclopentadiene complex in the complete preference to the acetylene component which is generally present greater amount than olefin component. Chalk[6] reported the selective cyclotrimerization between phenylacetylene or hexa-2,4-diyne and N-maleinmide which is a strongly electron-withdrawing olefin. Yamazaki[7, 8] noted an equimolar reaction between η^5-cyclopentadiene-cobaltacyclopentadiene with olefins in order to avoid undesirable cyclotrimerization of three acetylene components. The most successful case so far studied employed olefins having electron-withdrawing substituents.

This chapter describes first the preparation of a model of what we believe to be the key intermediate in the palladium mediated cyclocotrimerization between two molecules of dimethyl acetylendicarboxylate (DMAD) and one molecule of the electron-donating olefins. Secondly, the three dimensional X-ray analysis of the model complex; $Pd[C_4(CO_2CH_3)_4]$(Norbornadiene) is discussed. Finally, the catalytic and selective cyclocotrimerization between two DMAD molecules and norbornadiene or norbornene in the presence of the $Pd[C_4(CO_2CH_3)_4]$ catalyst is explained. This catalytic process is inverse in the electron demand (with two electron-withdrawing acetylene components and an electron-donating olefin) to the previously reported reactions to which electron-withdrawing olefins were required.

3. 3. 2. The Preparation and Spectroscopy of $Pd[C_4(CO_2CH_3)_4]$ (cyclic diolefin) : (VIIIa) and (VIIIb)

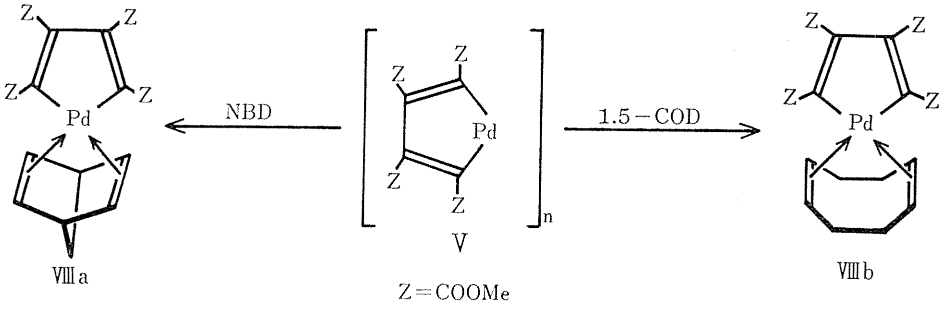
Tetrakis(methoxycarbonyl)palladiacyclopentadiene (V), $Pd[C_4(CO_2CH_3)_4]$ readily accessible from the reaction of $(DBA)_3Pd_2$ with excess DMAD, has been reported to involve an oligomeric structure which was known to be cleaved by various neutral ligands. The complex is also considered to be an intermediate in the palladium-catalyzed trimerization of DMAD to give hexamethyl mellitate at 70° 2) and therefore, V will be expected to be an efficient model to discover a new type of cyclotrimerization between two molecules of DMAD and the electron-rich olefin under mild condition.

Preparation of $Pd[C_4(COOCH_3)_4]$*(Norbornadiene) (VIIIa)*

To an acetone (7ml) suspension of V (96 mg; 2.5 mmol), NBD (0.04 ml) was added slowly with vigorous stirring at room temperature. The reaction mixture gradually turned to a greenish brown homogeneous solution. After stirring 30 min at room temperature, the solution was concentrated to 0.5 ml under reduced pressure. Ethyl ether (1 ml) and two drops of NBD were added. After 2 days at 0° VIIIa was precipitated as yellow brown prisms: Mp 130-132° dec. Anal. Calcd for $C_{19}H_{20}O_8Pd$: C, 47.27; H, 4.18. Found: C, 47.32; H, 4.42. IR(KBr): 1713, 1692 cm^{-1}(νC=O), 1231(νC=O). NMR($CDCl_3$): δ2.03 (t, 2, CH_2, J=0.8Hz), 3.65(s, 6, ester CH_3), 3.67 (s, 6, ester CH_3), 4.07 (m, 2, bridgehead), 6.49 (t, 4, vinyl, J=2.0Hz).

Preparation of $Pd[C_4(COOCH_3)_4]$*(1,5-cyclooctadiene) (VIIIb)*

To a methylenechloride (5 ml) suspension of V (66.8 mg; 0.17 mmol) COD-(0.025 ml) was added dropwise. The reaction proceeded instantaneously to give a homogeneous, yellowish brown solution. The solution was stirred for 1 hr and trace palladium metal was filtered off. The filtrate was condensed to 0.5 ml under reduced pressure, and ethyl ether was added to the resulting oil until darkening occurred. The solution was kept in a refrigerator overnight to yield orange crystals of VIIIb in 73% yield. Mp 151-152°. Anal. Calcd for $C_{20}H_{24}O_8Pd$: C, 48.16; H, 4.85. Found: C, 47.97; H, 4.85. IR(KBr): 1720, 1709, 1691(νC=O). NMR($CDCl_3$): δ2.82 (m, 8, CH_2), 3.62 (s, 6, CH_3O), 3.68(s, 6, CH_3O), 5.79 (broad s, 4, =CH).



VIIIa V VIIIb

Z=COOMe

(3)

The olefinic proton signals of the vinylic protons in the NMR of VIIIa occurred at δ6.49 as a triplet (4H, J=2.0Hz), which was only slightly higher than free NBD (δ6.67). Furthermore, the bridgehead protons of free NBD at δ3.49 shift substantially to low field (δ4.07; Δ=0.58 ppm) on coordination. Consequently, electrons in NBD, one of the typical electron-rich olefins, transferred to the palladiacyclopentadiene skelton. This is strongly supported by the chemical shifts of the two ester protons in VIIIa at δ3.65 and 3.67 which are at higher field than those of the parent complex V at δ3.58 and 3.62, indicative of the increase in the electron density of the palladiacyclopentadiene entity on the coordination of NBD.

1, 5-Cyclooctadiene (COD) also reacted readily with V to give Pd[C_4(CO_2-CH_3)$_4$] (COD) (VIIIb). The olefinic protons in the NMR of VIIIb occur at δ5.79 which suggested an unexpected low field shift on coordination (δ5.49 for free COD). This is consistent with the electron-accepting property of the tetrakis(methoxycarbonyl) palladiacyclopentadiene moiety to the electron-rich olefins.

3. 3. 3. The X-ray Structure of Pd[$C_4(CO_2CH_3)_4$](NBD); (VIIIa)

Preliminary optical and X-ray examination indicated that the dark yellow prismatic crystals of VIIIa belong to the triclinic system. This was confirmed by a cell reduction and by successful refinement of the structure in space group C_i^1-$P\bar{1}$ in a cell of dimensions a=10.560(2), b=10.583(2), c=9.710(2) Å, α=99.33(1), β=113.24(1), and γ=85.53(2)°. The structure has been refined by standard methods to a conventional R index of 0.027, based on 3646 reflections above background. A perspective view of Pd[$C_4(COOCH_3)_4$](NBD) is given in Fig. 2 along with selected distances.

Although there is no imposition of crystallographic symmetry, the Pd-NBD segment of the molecule is highly symmetric, as judged by the fact that planes 1, 2, and 3 are nearly perpendicular to one another. The metallocycle itself is essentially planar, the largest deviation from planarity being 0.03 Å. The carbomethoxy groups are approximately related by a noncrystallographic twofold axis through atoms Pd and C(19). The olefinic C=C bond lengths of 1.352(4) Å in the norbornadiene fragment together with spectroscopic results suggest a net transfer of electrons

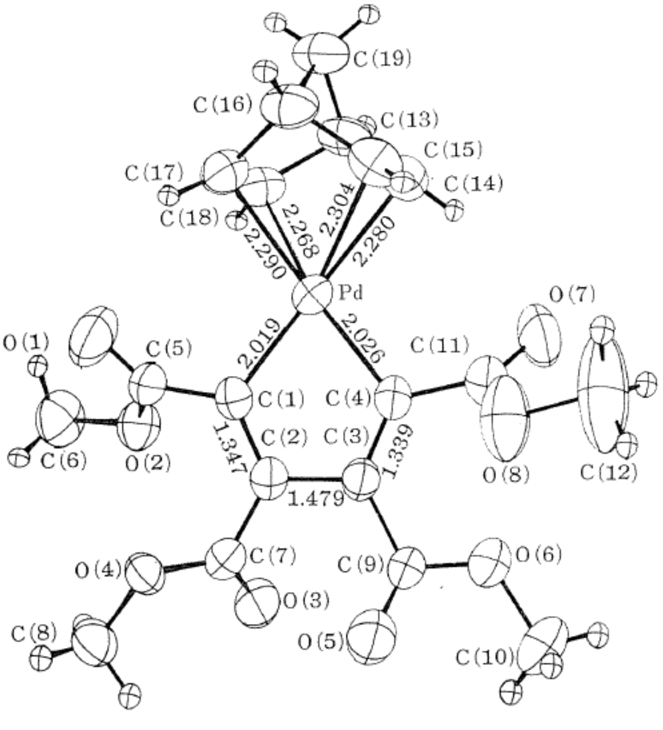


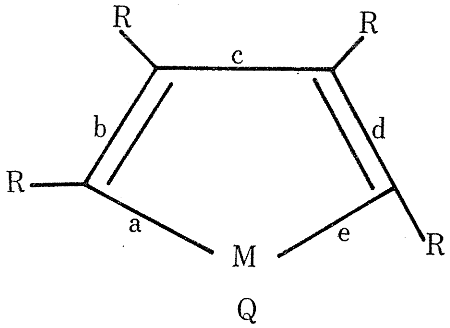
Fig. 2. A Perspective Drawing of the Complex VIIIa.

from the electron-rich norbornadiene to the metallocycle which has electron withdrawing substituents. The fact that the diolefin bonds more strongly to the metallocycle than does an activated acetylene is brought to bear on mechanisms of cyclotrimerization of acetylenes and cyclocotrimerization of two acetylene and one olefin molecules.

In Table 2 we compare the structural parameters of the present PdC_4 metallocycle with other five-membered metallocycles.[10~12] Although the estimated standard deviations in these other metallocycles are 3 to 5 times greater than in the present structure, the agreement among the ring systems, which contain different metals and different substituent groups, is remarkably good.

In Table 3 we summarize data on different π-bonded NBD structures.[13~17] Again the agreement is excellent. Electron transfer to an olefin lengthens the C=C bond.[18] In the present structure the C=C bond length is shorter than in the other

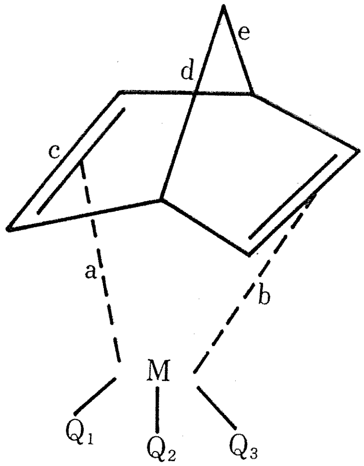
Table 2. Comparison of the Structual Data of Some Metallocycles. [a]



	$RhCl[Sb(C_6H_5)_3]_2$ $[C_4(CF_3)_4]\cdot CH_2Cl_2$	$RhCl(H_2O)[As(CH_3)_3]_2$ $[C_4(CF_3)_4]$	$Co(C_5H_5)[P(C_6H_5)_3][C_4(C_6F_5)_4]$	$Pd[C_4(COOCH_3)_4]$ (NBD)
M	Rh	Rh	Co	Pd
R	CF_3	CF_3	C_6F_5	$COOCH_3$
Q	Sb_2Cl	$(As(CH_3)_3)_2Cl$	$(\pi\text{-}C_5H_5)[C_6H_5)_3P]$	NBD
Reference	10	11	12	Present structure
a	2.000(10)	2.047(16)	1.995(11)	2.019(3)
b	1.330(16)	1.311(24)	1.326(15)	1.347(4)
c	1.388(14)	1.433(26)	1.467(16)	1.479(3)
d	1.367(15)	1.346(23)	1.335(15)	1.339(4)
e	1.964(11)	1.998(16)	1.993(11)	2.026(3)
a-e	77.2(4)	80.2(6)	82.4(4)	79.7(1)
a-b	116.4(7)	114.3(12)	112.1(8)	115.7(2)
b-c	116.1(9)	114.9(15)	116.8(9)	114.3(2)
c-d	111.4(10)	117.4(15)	114.8(9)	114.6(2)
d-e	118.8(7)	113.2(12)	113.1(7)	115.6(2)

[a] The estimated standard deviation in parentheses is the larger of an average individual standard deviation or of the standard deviation of a single observation as calculated from the mean.

Table 3. Comparison of the Structural Data of Some Norbornadiene π-Complexes.



	$PdCl_2$-(NBD)	$Co(SnCl_2)$-$(CO)_2(NBD)$	$Co_2(CO)_6$-(NBD)	$Ir(SnCl_3)$-$[P(CH_3)_2(C_6H_5)]_2(NBD)$	$Pd[C_4$-$(COOCH_3)_4]$-(NBD)	$RuCl_2$-$(C_6H_5NH_2)_2$-(NBD)
M	Pd	Co	Co	Ir	Pd	Ru
Q_1	Cl	(CO)	(CO)	PMe_2Ph		$C_6H_5NH_2$
Q_2	Cl	(CO)	(CO)	PMe_2Ph		$C_6H_5NH_2$
Q_3		$SnCl_2^-$	(CO)	$SnCl_3$		Cl_2
Reference	13	14	15	16	Present structure	17
a	2.049	2.050	2.049	2.068	2.189	2.066
b	2.056	1.959	2.056	2.123	2.177	2.066
c	1.366(10)	1.396(15)	1.373(8)	1.400(9)	1.352(4)	1.385(6)
d	1.553(6)	1.550(15)	1.525(8)	1.528(10)	1.531(5)	1.537(6)
e	1.547(6)	1.560(14)	1.547(9)	1.525(10)	1.545(4)	1.524(12)
a-b	71.0	72.1	71.3	67.6	67.5	70.0
c-d	107.0(4)	106.7(9)	106.7(5)	105.7(6)	106.8(3)	105.9(1)
d-d	100.3(3)	99.5(8)	101.2(7)	99.5(5)	104.9(2)	100.9(5)
d-e	100.0(4)	100.6(9)	100.3(5)	101.9(6)	99.7(2)	101.0(5)
e-e	94.5	94.2(7)	93.4(4)	93.6(5)	92.8(2)	93.9(5)

π-bound NBD molecules and is equal to that in free NBD.[19)] Thus the structural results are completely consistent with the spectroscopic evidence for electron transfer from the olefin to the metallocycle.

3. 3. 4. *The Cyclocotrimerization Catalyzed by (V)*

The high stability of the cyclic diolefin complexes VIIIa and VIIIb suggested to us the possibility of a successful cyclocotrimerization between two molecules of DMAD and one molecule of an electron-rich olefin in the reverse sense in the electron demands to the previously reported cycloadditions with electron-deficient olefins mediated by the transition metal catalysts.[6~8)]

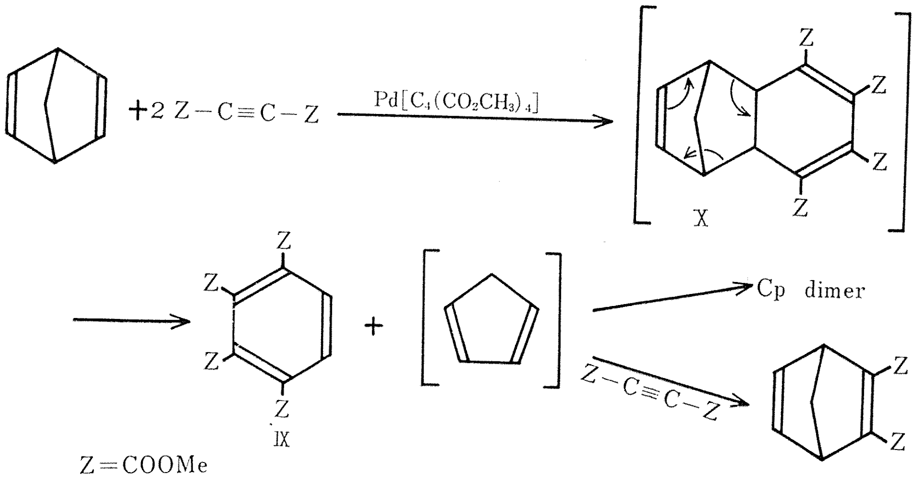
When a benzene solution of DMAD and NBD (in 2/1 molar ratio) was kept at

45° for four days in the presence of the catalytic amount of $Pd[C_4(CO_2CH_3)_4]$ (V), 1, 2, 3, 4-tetrakis(methoxycarbonyl)benzene (IX) was isolated in 35% yield. The formation of hexamethyl mellitate, the cyclic trimer of DMAD, was completely inhibited as expected from the fact that $Pd[C_4(CO_2CH_3)_4]$(DMAD) proved too unstable to isolate. The compound IX has Mp 127-128°. Anal. Calcd for $C_{14}H_{14}O_8$: C, 54.20 ; H, 4.55. Found: C, 53.77, H, 4.51. NMR($CDCl_3$) : δ3.81 and 3.83 (two s, 12H, CH_3O), 7.88 (s, 2, aromatic).

The thinlayer chromatogrphy (silicagel-benzene then chloroform) of the residual oil indicated the presence of dicyclopentadiene and 2, 3-bis(methoxycarbonyl)norbornadiene with the remaining IX, all of which were unequivocally assigned by comparison with authentic samples.

The formation of IX is explained reasonably in terms of a subsequent cycloreversion[20, 21] of the intermediate cyclic cotrimer (X).

This view is supported by the presence of dicyclopentadiene and 2, 3-bis(methoxycarbonyl)norbornadiene in the reaction mixture, suggestive of the generation of cyclopentadiene.

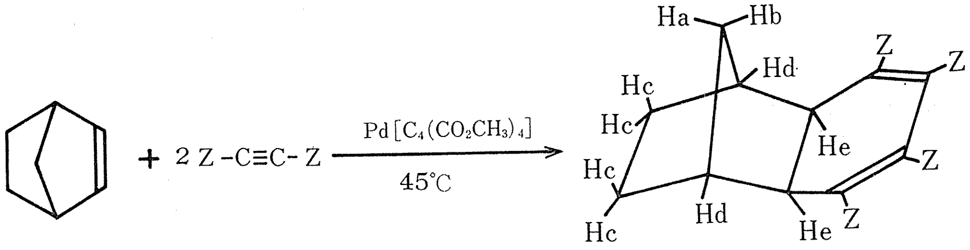


(4)

When the norbornadiene complex VIIIa was treated with a twice molar amount of DMAD in $CDCl_3$ for one hour at 55°, IX was formed in a quantitative yield (estimated by the characteristic aryl proton at δ7.88) with the concurrent precipitation of V in nearly 80% yield. This result indicates strongly that VIIIa is the correct intermediate of the catalytic cyclocotrimerization followed by the cycloreversion process.

In order to avoid the cycloreversion process in the above catalytic reaction with norbornadiene, norbornene was selected as an electron-rich olefin component.

When a benzene solution of norbornene, DMAD, and the catalytic amount of $Pd[C_4(CO_2CH_3)_4]$ was kept at 45° for 20 hr, the expected cycloadduct from two molecules of DMAD and norbornene, (XI), was isolated in 94% yield based on DMAD. No trace of hexamethyl mellitate was present. When added DMAD was consumed, palladium mirror appeared. The adduct XI has Mp 66.5-68.0°. Anal. Calcd for $C_{19}H_{22}O_8$: C, 60.31 ; H, 5.86. Found: C, 60.44 ; H, 5.83. IR (Liquid film) 1733 and 1720 cm^{-1} ($\nu C{=}O$). NMR($CDCl_3$) : δ1.30(m, 1, Ha), 1.54 (m, 4, Hc), 1.68 (m, 1, Hb), 2.34 (d of t, 2, J=0.75Hz, 1.50Hz, Hd), 2.92 (d, 2, J=0.75Hz, He), 3.71 and 3.68 (two s, 12, ester CH_3).



XI (5)

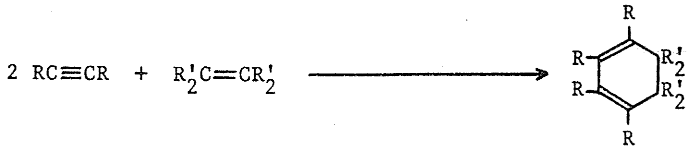
Z=COOMe

The cycloadduct XI, formed in an excellent yield, is the exo-adduct in the stereoselective manner, because the chemical shift difference between Ha (δ1.30) and Hb (δ1.68) was evidently large, and the coupling constant between Hd and He is small enough (J=0.8 Hz).

3. 4. *A Selective Palladium-catalyzed Cyclotrimerization of Dimethyl Acetylenedicarboxylate with Olefins.*

3. 4. 1. *Introduction*

The catalysis of the cyclotrimerization of acetylenes by transition metal complexes[3)] has been extensively studied but few examples of the cyclotrimerization of acetylenes with olefins as in Eq. (6) has been noted.[6~8, 22, 23)]

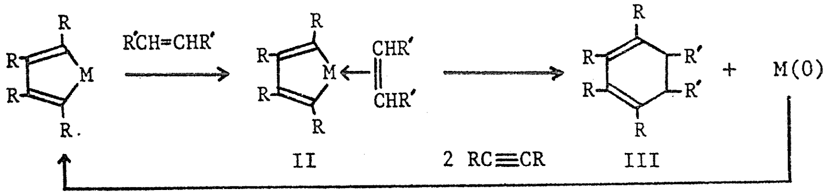


(6)

The cyclotrimerization of alkynes was suggested to proceed through the intermediacy of metallocyclopentadiene, in fact, metallocyclopentadiene have been shown to react with acetylenes to give substituted benzene as in Eq. (7).[2,24~27)]

[A] (7)

In the presence of an olefin it is expected to intercept [A] with a Diels-Alder reaction as in Eq. (8)



(8)

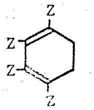
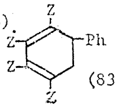
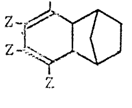
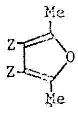
In this chapter, the cyclotrimerization of dimethyl acetylenedicarboxylate (DMAD) and olefin catalyzed by tetrakis(methoxycarbonyl)palladiacyclopentadiene (V) is described.

3. 4. 2. *Cyclotrimerization of two DMAD and Olefin Catalyzed by* $[Pd(DMAD)_2]n$

A solution of DMAD (0. 291 g, 2. 05 mmol) and $[(DMAD)_2Pd]_n$ (0. 011 g, 0. 028 mmol) in 40 ml of dry benzene was heated in a glass autoclave for 15 hr at 45℃ under 2 atm of ethylene. The ethylene was vented, and the solvent was removed under reduced pressure yielding a brown oil, which was purified by column chromatography on silica gel (11 g) in chloroform to give yellow crystals (0. 308 g, 96 %). Recrystallization from CCl_4-*n*-hexane gave 1, 2, 3, 4-tetrakis (methoxycarbonyl) cyclohexa-1, 3-diene as colorless needles in 62 % yield. Mp 94. 5-95. 0℃. Found: C, 53. 58; H, 5. 42 %. Calcd: C, 53. 86; H, 5. 16%. IR (in KBr) 1729 and 1720 cm^{-1}. ^1H NMR (in CCl_4) τ7. 34 (4H, s) and 6. 25 (12H, s).

The analogous catalytic process took place in the reaction between two molecules of DMAD and styrene with the catalytic amount of the complex V, resulting 1, 2, 3, 4-tetrakis(methoxy-carbonyl)-3-phenylcyclohexa-1, 4-diene (Mp. 105. 0-107. 0 ℃. Found: C, 61. 77; H, 5. 26%. Calcd. for $C_{20}H_{20}O_8$: C, 61. 84; H, 5. 19 %) in 83 % yield. The catalytic reaction of various electron-donating olefin with two moles of DMAD are summarized in Table 4.

Table 4.

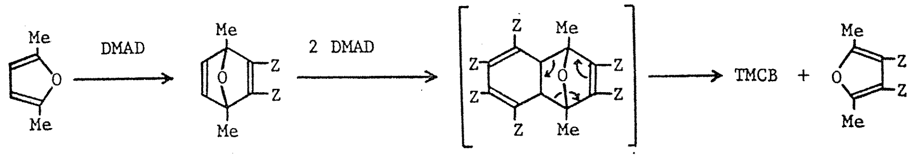
Olefin	Reaction Conditions[a)]					Products (yield;%)
	Olefin (mmol)	DMAD (mmol)	Cat. (mmol)	Temp. (°C)	Time (hr)	
C_2H_4	2 atm[b)]	3.15	0.044	50	150	 (96) (TMCB)
C_6H_5-CH=CH_2	1.99	4.23	0.043	45	139	 (83)
Norbornene	3.30	3.37	0.10	45	40	 (94)
Norbornadiene	1.50	3.00	0.10	45	96	TMCB (35) + Cp-dimer
Et-O-CH=CH_2	1.00	4.67	0.037	45	45	TMCB (64) + EtOH
2,5-Dimethylfuran	1.36	3.11	0.031	45	48	TMCB (69) +  (86)

a) in benzene (3~4 ml). b) in autoclave.

In the case of the reaction of ethylvinylether, the 2 : 1 adduct, 1, 2, 3, 4-

tetrakis(methoxycarbonyl)-5-ethyl-1, 3-cyclohexadiene, decomposed into ethanol and 1, 2, 3, 4-tetramethoycarbonyl)benzene, as shown in the Table 4.

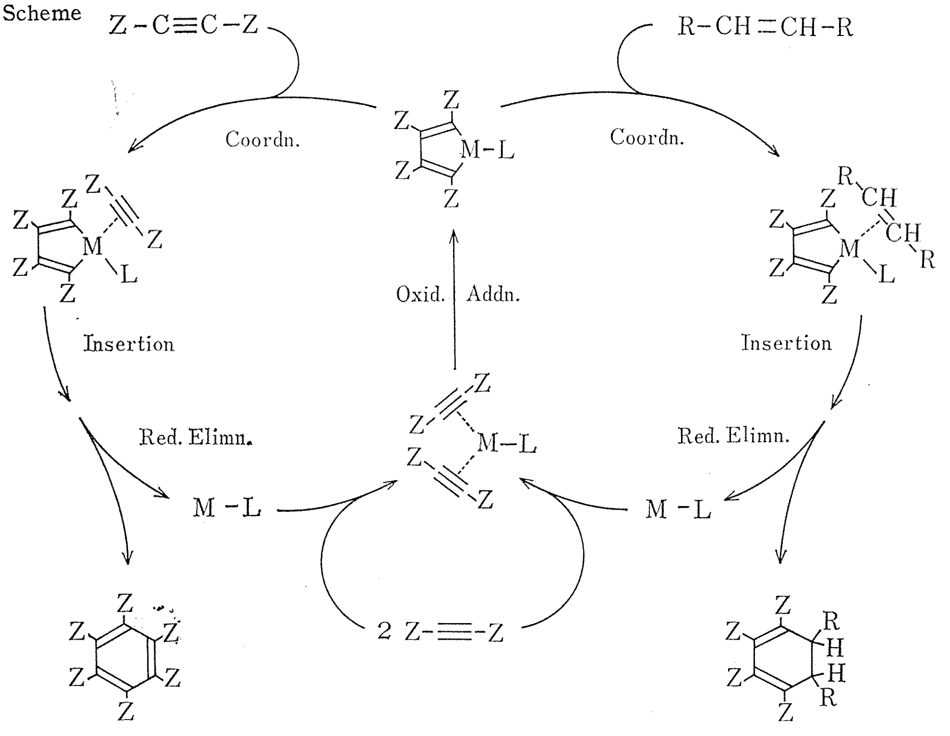
In the reaction with furan or 2, 5-dimethylfuran, 1, 2, 3, 4-tetrakis (methoxycarbonyl) benzene is concluded to be formed *via* 7-oxa-norbornadiene which is Diels-Alder adduct of furan and DMAD, because 3, 4-bis(methoxycarbonyl)furan was isolated as a by-product (Eq. (9)).



(9)

These catalytic processes can be explained by the following scheme.

Scheme



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4. Novel Rhodium and Palladium Complexes with Activated Isocyanates or Isothiocyanates as Ligand.

4. 1. *Introduction*

In this chapter, a variety of new type of complexes are introduced in the reactions of benzoyl isocyanate or isothiocyanate with activated group with low valent organo-transition metal complex, for example, $RhCl(PPh_3)_3$, $Pd_2(DBA)_3$.

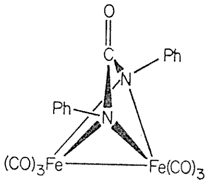
As an extension of our other study on the reaction between organosilicon and organtin compounds and benzoyl isocyanate, we were much interested in the reaction of these activated isocyanate compounds with Pd(0) and Rh(I) complexes.

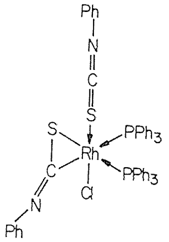
As shown in the latter part of this chapter, amazing complexes with unusual ligands were disclosed.

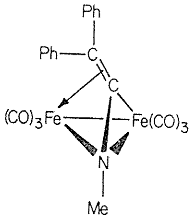
4. 2. *Novel Rhodium and Palladium Complexes from Benzoyl and Thiobenzoyl Isocyanates*

4. 2. 1. *Introduction*

No systematic investigations of the coordinating properties of benzoyl and thiobenzoyl isocyanates with low-valent transition metals have been reported, although some transition metal complexes of simple heterocumulene compounds were known.[1~5] Manuel originally reported $[(CO)_3Fe(PhNCO)]_2$ in the reaction of phenyl isocyanate with $Fe_3(CO)_{12}$;[1a] however, later structural investigations[1b-1d] concluded that the original complex was a diphenylurea complex of diiron hexacarbonyl. Similar types of urea complexes were isolated recently in the case of arylsulfonyl isocyanates.[1e] Baird and Wilkinson[2] prepared π- and S-bonded phenyl isothiocyanate complexes of nickel, palladium. platinum, rhodium, and iridium. The preparation and X-ray study of ketenimine complexes of iron were achieved by Otsuka.[3, 4] Bycroft and Cotton[5] obtained carbodiimide-palladium(II) complexes with the formula $(RN{=}C{=}NR')_2PdX_2$. The representative structures of some transition metal complexes induced from simple heterocumulene compounds are shown below.

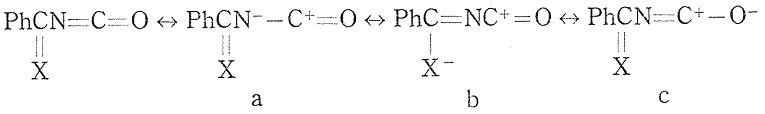






On the other hand, the five-membered metallocyclic complexes containing heteroatoms as the ring member have attracted much attention in recent years.[6~9] In particuar, *N*-acylhydrazine or diazenes were found to be an excellent precursor to generate various five-membered metallocyclic systems (M-O-C-N-N), for instance, $[(PhCON{=}N)_2Cu]^+$ [6], $MoCl_2(NAr)(ArCON{=}NAr)(PhMe_2P)$,[7] $[(diphos)_2WCl(N{=}N\text{-}COR)]$,[8] and $Pt(Ph_3P)_2(PhCON{=}NCOPh)$.[9] The five-membered structure was definitely concluded by Ittel and Ibers[9] for the final complex by means of X-ray structural derermination.

The following canonical structures (X=O or S) can be represented for (thio) benzoyl isocyanate and are corresponding to three possible modes of coordination.



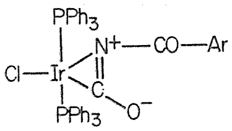
$$\underset{\begin{array}{c}\|\\ \mathrm{X}\end{array}}{\mathrm{PhC}}\mathrm{N{=}C{=}O} \leftrightarrow \underset{\begin{array}{c}\|\\ \mathrm{X}\end{array}}{\mathrm{PhC}}\mathrm{N^{-}{-}C^{+}{=}O} \leftrightarrow \underset{\begin{array}{c}|\\ \mathrm{X^{-}}\end{array}}{\mathrm{PhC}}\mathrm{{=}NC^{+}{=}O} \leftrightarrow \underset{\begin{array}{c}\|\\ \mathrm{X}\end{array}}{\mathrm{PhC}}\mathrm{N{=}C^{+}{-}O^{-}}$$

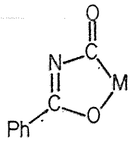
a b c

Our studies on the addition-elimination reactions of benzoyl and thiobenzoyl isocyanates with group IVb oranometallic compounds disclosed a lot of interesting results indicative of the occurrence of the 1, 4 addition of these heterocumulene systems (mode b),[10] which had stimiulated us to investigate the interaction of these heterocumulene systems with low-valent transition metals.

In this context, Collman, *et al.*,[11] obtained $IrCl(Ph_3P)_2(ArCONCO)$ in the reaction between Vaska's complex and aroyl azide and proposed the following structure in which nitrogen and carbon atoms of the isocyanate group coordinated to the iridium atom (mode a). Another probability, the 1, 4 addition of (thio) benzoyl isocyanate by mode b, should induce a new five-membered metallocyclic complex containing two heteroatoms. (N and O or S).

In this chapter, the results of reactions between benzoyl or thiobenzoyl isocya-





nate and various rhodium(I) or palladium(0) complexes are described.

4. 2. 2. Reactions of Benzoyl Isocyanate with Rhodium(I) *Complexes*

$[RhCl(Ph_3P)_2(PhCONCO)]_2$(I). To a benzene (20 ml) solution of chlororhodium tris(triphenylphosphine), $RhCl(Ph_3P)_3$ (870 mg, 0.94 mmol), an excess of benzoyl isocyanate (410 mg, 2.50 mmol) was added with stirring. The color of the solution changed gradually from deep red to yellow, and a yellow crystalline product started to precipitate in 1 hr. The mixture was stirred for 6 hr at room temperature. Then a yellow precipitate of bis (μ-(benzoyl isocyanate))-dichlorotetrakis (triphenylphosphine)dirhodium, $[RhCl(Ph_3P)_2(PhCO\text{-}NCO)]_2$ (I), was isolated by filtration and followed by recrystallization from methylene chloride-ethyl ether mixed solvent as yellow needles (638 mg, 89%). Melting points, analytical results, and $\nu(C=O)$ bands of products including I are summarized in Table I.

From large lower frequency shifts of infrared absorptions, ν(NCO) 1710 and ν(CO) of benzoyl group 1400 cm^{-1} (absorptions of the free ligand were 2240 and 1690 cm^{-1}, respectively), both of the isocyanate and the benzoyl carbonyl groups of benzoyl isocyanate may coordinate to rhodium atom, just like the ketenimine group coordination to cobalt in the case of $\pi\text{-}C_5H_5Co(Ph_2C=C=NMe)$[3] (with a change of ν(CCN) from 1998 to 1565 cm^{-1} on coordination). Complex I is very stable in air and in solvent. When I was heated up to 200° under reduced pressure, benzoyl isocyanate was recovered quantitatively.

Evidence for the structure of I was supplemented by the following reaction. When excesses of sodium tetraphenylborate and bipyridine (bipy) were added to I in $CH_2Cl_2\text{-}CH_3OH$ at room temperature, pale yellow platelike crystals of $[(bipy)Rh\text{-}(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (IIa) were isolated in 72% yield. The ν(CO) absorption of IIa (1623 cm^{-1}) implies the acyl-type bonding with rhodium metal as a five-membered ring structure: Rh—O—C=N—C as depicted in Scheme 1. The conversion from I to IIa could be followed by recording the infrared spectrum of the reaction mixture at different times (Figure 1). As shown in Figure 1, ν(CO) of I at 1710 cm^{-1} began to disappear gradually, in accordance with the increase of ν(CO) of IIa at 1623 cm^{-1}, which means that bipyridine displaces the bridging oxygen atom and the nitrogen atom of I, followed by the bond formation between Rh metal and benzoyl oxygen with simultaneous liberation of chloride anion which was trapped by sodium cation, to yield the more stable 1, 4-metallocyclic complex (IIa).

The cationic complex (IIa) could be prepared independently by the reaction of $[(bipy)Rh(cyclooctadiene)]^+BPh_4^-$[13] with benzoyl isocyanate under excess of triphenylphosphine in refluxing CH_2Cl_2 in lower yield (34%).

An analogous cationic complex (IIb) which involves *o*-phenanthroline (*o*-phen) as a stabilizing ligand instead of bipy was obtained in 73% yield from I, *o*-phen, and sodiun tetraphenylborate [ν(CO) 1628 and 1379 cm^{-1}]. In contrast to the reaction with bipy or *o*-phen, the reaction between I and pyridine in CH_2Cl_2 produced a reversible change to $[(py)_2Rh(PPh_3)_2(PhCONCO)]^+Cl^-$ [ν(CO) at 1625 cm^{-1}] (IIc)

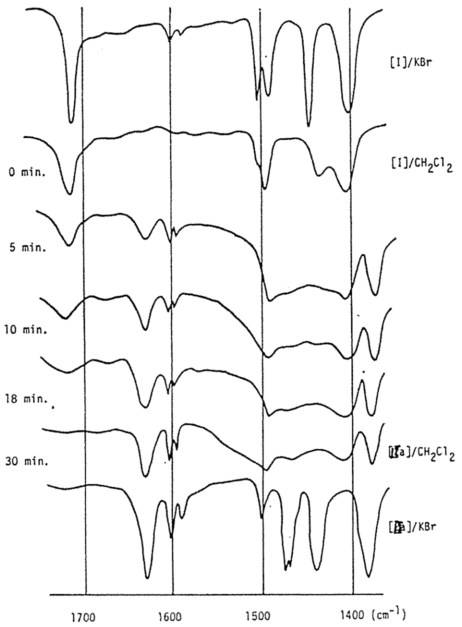
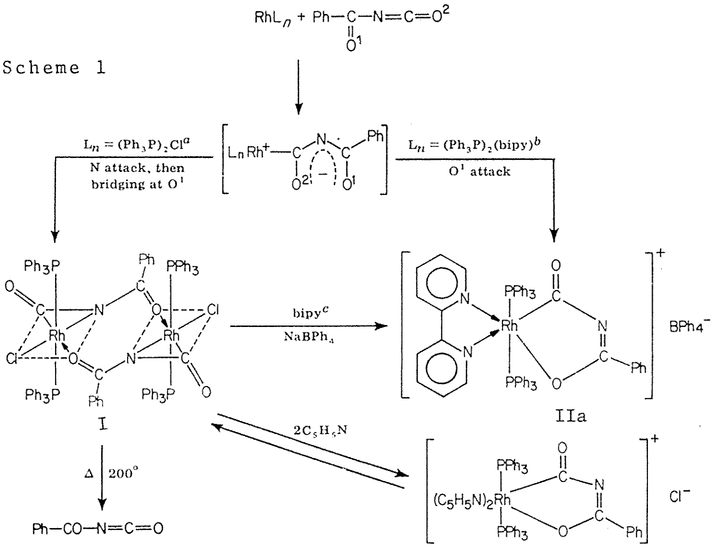


Fig 1. Variation of infrared spectrum with time for the conversion from $[RhCl(Ph_3P)_2(PhCONCO)]_2$ (I) to $[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (IIa) by bipyridine and sodium tetraphenylborate in CH_2Cl_2-CH_3OH.

Scheme 1



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[a] $Rh(Ph_3P)_3Cl - Ph_3P$. [b] $[(bipy)Rh(cyclooctadiene)]^+ + 2Ph_3P -$ cyclooctadiene.

[c] When *o*-phenanthroline was used instead of bipyridine $[(o\text{-phen})Rh(PhCONCO)]^+BPh_4^-$ (IIb) was obtained.

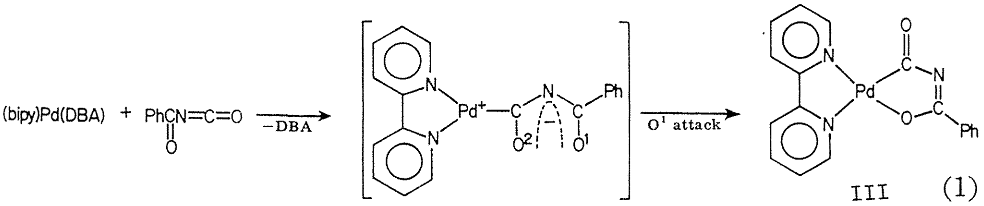
instantaneously, which returned to I on recrystallization from CH_2Cl_2-$(C_2H_5)_2O$.

These reactions were summarized in Scheme 1. The nucleophilic attack of rhodium(I) complexes on the carbon atom of the isocyanate group may be the primary step, followed by N, O^1 attack (more precisely, at first N attack and the following O^1 bridging to dimerization) in the case of $RhCl(PPh_3)_3$ or by O^1 attack on the $[(bipy)Rh(PPh_3)_2]^+$ species. Due to dissociation of one molecule of triphenylphosphine from $RhCl(PPh_3)_3$, the resulting coordinatively unsaturated $RhCl(PPh_3)_2$ may accept benzoyl isocyanate as a tridentate ligand (C, N, and O^1) [modes a and b] to complete six-coordination around Rh(III), while $[(bipy)Rh(PPh_3)_2]$ has a coordination number of 4 and benzoyl isocyanate behaves as a bidentate ligand (C and O^1) [mode b]. Because the metal basicity of $Rh(CO)(Ph_3P)_2Cl$ or $Rh^+(Ph_3P)_2$(cyclooctadiene) is lower than that of $RhCl(Ph_3P)_3$ or $Rh^+(Ph_3P)_2$(bipy), the former did not react with benzoyl isocyanate.

4. 2. 3. Reactions of Benzoyl Isocyanate with Tris(dibenzylideneacetone) dipalladium

(bipy)Pd(PhCONCO) (III). Bipyridine (526 mg, 3.30 mmol) and benzoyl isocyanate (0.5 ml) were added to an ether (20 ml) suspension of tris(dibenzylideneacetone)dipalladium, $Pd_2(DBA)_3$ (500 mg, 0.55 mmol), at room temperature. After 5 hr the dark red crystals had disappeared and orange crystals appeared, which were collected by filtration and were recrystallized from CH_2Cl_2-Et_2O mixed solvent to give yellow needle crystals of III as a half-solvate of methylene chloride. They were dried under vacuum to give orange crystals of (bipy)Pd(PhCONCO)·$^1/_2CH_2Cl_2$ (III) in 75% yield (340 mg). The presence of methylene chloride as solvate was confirmed by a nmr spectrum and analyses.

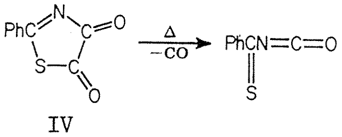
In this case, benzoyl isocyanate acts as a bidentate ligand (C and O^1) to form stable 1, 4 coordination of benzoyl isocyanate to square-planar palladium [mode b; ν(CO) 1630 cm^{-1}]. No stable complex was obtained when an excess of triphenylphosphine was used instead of bipyridine in the above-mentioned reaction.



(1)

4. 2. 4. Reaction of 2-Phenylthiazoline-4, 5-dione with Rh(I) Complexes

2-Phenylthiazoline-4, 5-dione (IV) is a precursor of thiobenzoyl isocyanate which was generated by heating IV in refluxing methylcyclohexane.[14)]

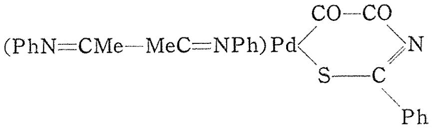


IV

(2)

In the reaction between $RhCl(Ph_3P)_3$ and an excess of IV in benzene at room

Table 1. Analytical Results for Benzoyl or Thiobenzoyl

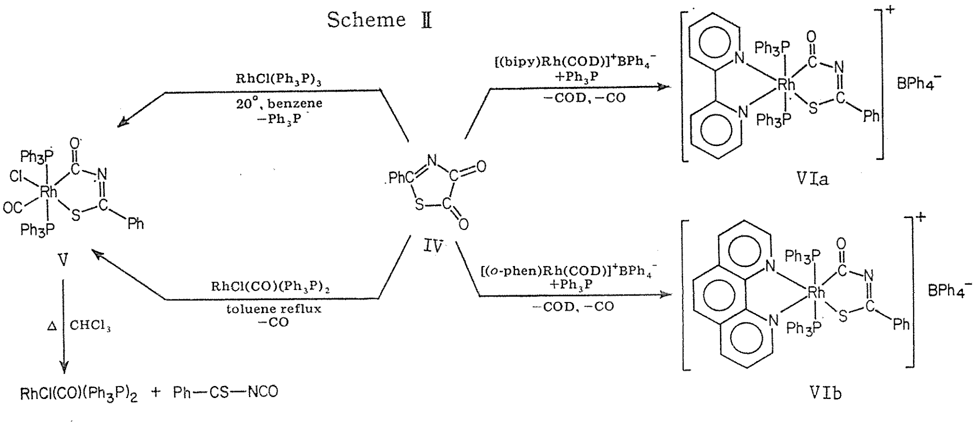
Complex	Yield %	Mp, °C
$[RhCl(Ph_3P)_2(PhCONCO)]_2$ (I)	89	206-208 dec
$[(bipy)Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (IIa)	72	187-188
$[(o\text{-phen})Rh(Ph_3P)_2(PhCONCO)]^+BPh_4^-$ (IIb)	71	212-214 dec
$(bipy)Pd(PhCO{\cdot}NCO)\,{}^1/_2CH_2Cl_2$ (III)	75	202-207 dec
$RhCl(CO)(Ph_3P)_2(PhCSNCO)$ (V)	50	210-212 dec
$[(bipy)Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (VIa)	69	197-199 dec
$[(o\text{-phen})Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (VIb)	85	217-219 dec
$(bipy)Pd(PhCSNCO)$ (VIIa)	63	185-190 dec
$(o\text{-phen})Pd(PhCSNCO)$ (VIIb)	84	200-205 dec
 (VIII)	76	159-163 dec

temperature under nitrogen, a precipitate of yellow crystals of $RhCl(CO)(Ph_3P)_2$-(PhCSNCO) (V) was obtained in 50% yield. The infrared spectrum of V shows the acyl carbonyl absorption at 1623 and an Rh-CO band at 2070 cm^{-1}.

The same complex V could also be prepared in 64% yield in the reaction of IV with $RhCl(CO)(Ph_3P)_2$ in refluxing toluene with the evolution of carbon monoxide. On heating V in refluxing chloroform, decomposition to thiobenzoyl isocyanate and $RhCl(CO)(Ph_3P)_2$ was observed.

On the other hand, the reaction of IV with $[(bipy)Rh(COD)]^+BPh_4^-$ or $[(o$-phen$)Rh(COD)]^+BPh_4^-$ in the presence of excess triphenylphosphine in refluxing mixed solvent (CH_2Cl_2 : toluene = 1 : 2) for 6 hr gave yellow needlelike crystals of $[(bipy)$-$Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (VIa; 69% yield) or yellowish prismlike crystals of $[(o\text{-phen})Rh(Ph_3P)_2(PhCSNCO)]^+BPh_4^-$ (VIb; 85% yield), respectively. Their structures were identified by analysis and the ν(CO) absorption bands (VIa, 1620 cm^{-1};

Scheme II



Isocyanate Complexes of Rhodium and Palladium

Color	Analysis, %						IR (KBr) ν (C=0) cm^{-1}
	C		H		N		
	Calcd	Found	Calcd	Found	Calcd	Found	
Yellow	65.24	65.18	4.36	4.24	1.73	1.76	1710
Pale yellow	74.95	74.64	5.08	5.25	3.36	3.50	1623
Pale yellow	75.45	75.55	4.99	5.25	3.38	3.18	1628
Orange	49.14	48.36	3.24	3.12	9.29	9.34	1630
Yellow	63.28	63.41	4.13	4.11	1.64	1.62	1623
Yellow	74.00	73.82	5.02	5.08	3.32	3.21	1620
Yellow	74.48	74.24	4.92	4.88	3.26	3.32	1615
Red	50.78	50.44	3.08	3.20	9.87	9.79	1620
Red	53.41	53.59	2.91	2.81	9.34	9.31	1630
Brown	56.24	55.77	3.96	4.19	7.87	8.05	1660

VIb, 1615 cm^{-1}) indicative of a five membered metallocyclic structure (mode b).

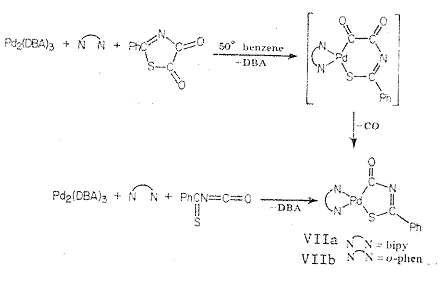
These results are summarized in Scheme II.

4. 2. 5. *Reactions of 2-Phenylthiazoline-4, 5-dione with Tris(dibenzylideneacetone)dipalladium*

When the benzene solution of $Pd_2(DBA)_3$ with an excess of bipyridine and IV was heated to 50°, evolution of carbon monoxide occurred violently. The product was reddish needlelike crystals of (bipy)Pd(PhCSNCO)(VIIa) in 92% yield. The same complex VIIa was also obtained in 63% yield in the reaction of $Pd_2(DBA)_3$ with thiobenzoyl isocyanate, generated *in situ* from IV, in the presence of bipyridine. When *o*-phenanthroline was used instead of bipyridine in the reaction of IV with $Pd_2(DBA)_3$, (*o*-phen)Pd(PhCSNCO) (VIIb) was obtained in 84% yield.

However, when biacetyldianil was used in the analogous reaction, no evolution of carbon monoxide was observed. The sole product was brownish needlelike crystals of the complex with the composition of [(PhN=CMe—MeC=NPh)Pd($C_9H_5NO_2$-S)] (VIII) in 76% yield. In the infrared spectrum, a broad absorption band at 1660 cm^{-1} is quite different from those of either VIIa or VIIb. Consequently VIII may correspond to the unidentified reaction intermediate shown in brackets in Scheme III. Complex VIII did not evolve carbon monoxide upon heating, only causing decomposition to metallic palladium.

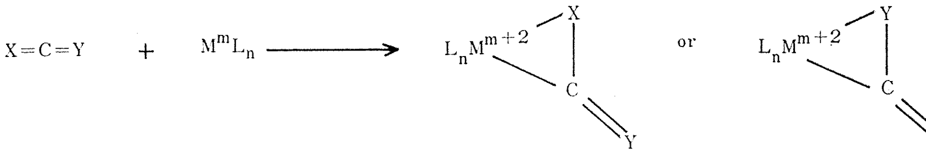
Schemel Ⅲ



4. 3. Novel Tridentate Carbene Rhodium Complexes by the Condensation of Activated Isothiocyanates and the Related Palladium Complexes

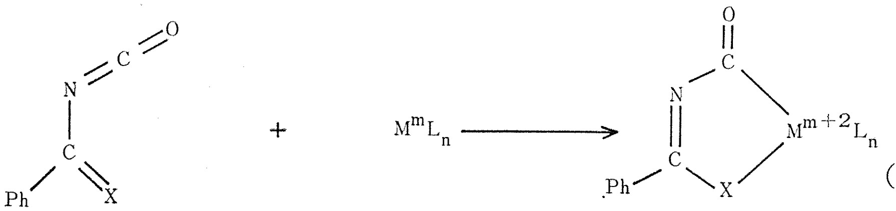
4. 3. 1. Introduction

The coordinating behavior of various heterocumulene compounds to transition metals have been investigated in the last decade for carbon dioxide,15~19) carbon disulfide,2,20, 21) carbodiimide,5) and isothiocyanate.2) The most popular coordination of these heterocumulene components in the formation of three-membered metallocyclic structures is given by the η^2-coordination of the one carbon-heteroatom bond via a formal oxidative addition.



(3)

The reaction of isothiocyanates, however, was different and more complex from the above heterocumulene acceptors.1) For example, phenyl isocyanate induced a decarbonylative dimerization of two isocyanate ligands to lead a N, N'-urea complex in the reaction with iron carbonyls.1b, 1d) In the chapter 4. 2., the reaction of benzoyl or thiobenzoyl isocyanates with rhodium(I) and palladium(0) complexes led to the five-membered rhodia- or palladia-cyclic complexes *via* an 1, 4-addition of activated isocyanates.



(4)

X=O and S M^m=Rh(I) and Pd(0)

This chapter describes firstly that a molecular condensation of four activated isothiocyanates in the presence of $ClRh(PPh_3)_3$ yields novel tridentate planar carbene rhodium (III) complexes. Secondly, the mechanistic aspects on this new carbenoid formation are discussed by diverting the possible intermediates to model complexes which coordination modes are related to the corresponding palladium (II) analogues.

4. 3. 2. Synthesis and Spectroscopies of a new Tridentate Carbene Rhodium Complex (IXa) by the Condensation of two Benzoyl Isothiocyanate.

Benzoyl,22) toluyl,22) ethoxycarbonyl,23), 24) and N, N-dimethyl-carbamonyl25 isothiocyanates were prepared according to the reported methods.

Preparation of $RhCl(Ph_3P)_2(C_6H_5CONCS)_2$ (IXa). A suspension of $RhCl(Ph_3P)_3$ (300 mg; 0. 325 mmol) in a benzene (10 ml)-n-hexane (10 ml) mixed solvent was added benzoyl isothiocyanate (460 mg; 2. 84 mmol) under vigorous stirring. The mixture was refluxed for 1 hr, and turned gradually to orange. The pale orange product precipitated from the reaction mixture. The stirring was continued for 14 hr at room temperature. The filtration of the crude solid product gave IXa (268 mg; 84 % yield), which was recrystallized by dissolving in dichloromethane followed by the addition of ether to yield reddish orange prisms of IXa. Mp. 174.5-175.5° dec. IR : 1617 (νCO). Anal. Calcd for $C_{52}H_{40}ClN_2O_2P_2RhS_2$: C, 63.03; H, 4.08; N, 2.83. Found : C, 63.03; H, 4.32; N, 2.89.

The infrared spectrum of IXa is also consistent with the unusual structure, which was revealed in the X-ray structural determination of IXa in *4. 3. 3.*, since the $\nu(C=O)$ band appears at 1617 cm^{-1} which is lower than that of the common acid amides, and the $\nu(C=N)$ band falls below 1500 cm^{-1} and these results suggest the intensive electron delocalization within nearly planar carbene ligand connected to the $RhCl(PPh_3)_2$ moiety.

The NMR spectrum of the complex IXa in $CDCl_3$ shows no sign of diethyl ether or methylene chloride. However, when the crude complex was recrystallized slowly, over few days, from methylene chloride-diethyl ether, reddish orange prismatic crystals, Mp. 176-177°, were obtained which contained incorporated diethyl ether, as seen in the NMR spectrum (τMe 8.8). NMR and infrared studies of the product did not lead to a ready formulation of the nature of the complex. Accordingly an X-ray diffraction investigation was undertaken.

4. 3. 3. X-ray Structural Determination of the Complex IXa, RhCl(PPh$_3$)$_2$(PhCONCS)$_2$.

$RhCl(PPh_3)_2(PhCONCS)_2 \cdot Et_2O$ ($Ph=C_6H_5$, $Et=C_2H_5$) crystallizes in the space group C^5_{2h}-$P2_1/n$ with four formula units of the complex and four solvent molecules in a cell of dimensions $a=21.184$ (3) Å, $b=19.963$ (2) Å, $c=12.226$ (2) Å, $\beta=100.03$ (1)°, and $V=5091.56$ Å^3. The experimental and calculated densities are 1.39 (1) and 1.387gcm^{-3}, respectively.

Data were collected on a Picker X-ray diffractometer, using nickel-filtered Cu Kα radiation. Of the 8248 unique reflections measured, 6266 were significantly above background ($F_0^2 > 3\sigma(F_0^2)$). The absorption-corrected data have been refined by full-matrix least-squares methods to an R of 0.061 and R_W of 0.079. The diethyl ether molecule was found to be severely disordered.

The Rh atom has a slightly distorted octahedral coordination with trans PPh_3 groups in the axial positions. The four equatorial sites are occupied by a chloro ligand and the tridentate ligand $(PhCONCS)_2$. Figure 2 shows the molecule viewed in the isothiocyanate ligand plane, with relevant bond lengths and angles shown. The PPh_3 groups, approximately perpendicular to this plane, are omitted for the sake of clarity.

This tridentate ligand is an interesting and unexpected consequence of the aforementioned reaction. Although the five-membered ring formed by Rh, O(1), C(2), N(1), and C(1) is not surprising, on the basis of the previous work on benzoyl and thiobenzoyl isocyanates,2) the condensation of the two ligands at C(3)-S(1) is without precedent. This sulfur-carbon bond joining the two ligands is a regular S-C single bond agreeing well with the distance of 1.77 Å based on the sums of the C and S covalent radii.28), 29)

The Rh-C(1) bond is believed to be the shortest Rh(III)-C(carbene) bond yet observed, being, for example, significantly shorter than the distances of 1.968 and

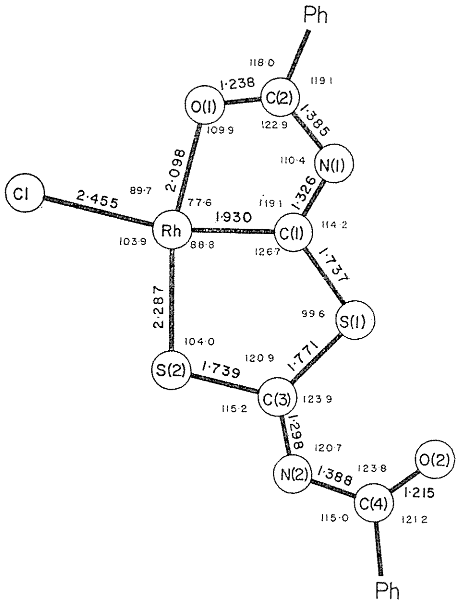


Fig. 2. A drawing of $\mathrm{RhCl(PPh_3)_2(PhCONCS)_2}$ viewed in the isothiocyanate ligand plane, showing important bond distances and angles. $\mathrm{PPh_3}$ groups, approximately perpendicular to this plane, are omitted for clarity. Standard deviations in the bond lengths (in Å×10^3) are: Rh-Cl, 2; Rh-O, 2; Rh-C, 6; Rh-S, 2; C-O, 8; C-N, 8; S-C, 7.

1.961 Å observed in $\overline{\mathrm{RhI_3(CO)CPhN}}\mathrm{MeCPhNMe}$,[30] and $\mathrm{RhCl_3(CHNMe_2)(PEt_3)_2}$,[31] respectively. It is also significantly shorter than other Rh(III)-C(alkyl) single bond distances (2.05-2.08 Å)[32)~35)] even allowing for the change in covalent radius from C(sp^2) to C(sp^3). The shortness of the Rh-C bond may result from increased back-donation from metal d to the p_z orbital on the trigonal carbon atom. It may also result from ligand constraints. Although short, this Rh-C distance is still longer than the Rh(III)-C(carbonyl) distance (1.89 Å) observed in the rhodium carbonyl complex mentioned above.[30]

The carbene carbon atom has the expected high trans influence, observed when chlorine is trans to another chlorine ligand[36] (2.34 Å) or to pyridine[32] (2.339 Å). However, it is shorter than the Rh-Cl distance of 2.531 Å observed when a benzyl carbon atom is the trans ligand.[32]

Within the metallocyclic rings there is some delocalization evident as witnessed by the C(2)-O(1) and C(1)-N(1) bonds being longer than the double bond values (compare C(4)-O(2) and C(3)-N(2)). Similarly N(1)-C(2) is shorter than a C-N single bond (1.43 Å). In the ring involving Rh, C(1), S(1), C(3), and S(2) the C(1)-S(1) and C(3)-S(2) bonds are both intermediate between single and double bonds so here again the possibility of delocalization exists.

The ring involving Rh, C(1), N(1), C(2), and O(1) is essentially planar with only C(2) being displaced by 0.015 Å from the mean plane. The Rh-S(2)-C(3)-S(1)-C(1) ring is slightly puckered with C(3) and C(1) deviating from the mean plane by 0.032 and −0.039 Å, respectively. The stability of this complex may arise in part from resonance stabilization resulting from the extended π system on the ligand and on the nearly coplanar phenyl groups.

Analogous reactions involving benzoyl isocyanate in place of benzoyl isothiocyanate yield five-membered metallocyclic structures, as determined in a routine matter spectroscopically. The present results illustrate the striking differences that may be expected between reactions of isocyanates and isothiocyanates with low-valent transition metal systems.

4. 3. 4. *Similar Carbene-Rhodium Complexes formed by the Condensation of each two Molecules of p-Toluyl-and N, N-Dimethylcarbamoyl-isothiocyanates*

Analogous tridentate carbene rhodium complexes; $RhCl(Ph_3P)_2(p\text{-}CH_3\text{-}C_6H_4\text{-}CONCS)_2$ (IXb) and $RhCl(Ph_3P)_2[(CH_3)_2NCONCS]_2$ (IXc) are similarly prepared by reacting $RhCl(Ph_3P)_3$ with the corresponding activated isothiocyanates in 77 and 76% yields, respectively.

Preparation of $RhCl(Ph_3P)_2(p\text{-}CH_3\text{-}C_6H_4CONCS)_2\cdot 0.5CH_2Cl_2$(IXb). A mixture of $RhCl(Ph_3P)_3$ (300 mg; 0.325 mmol), $p\text{-}CH_3\text{-}C_6H_4CONCS$ (440 mg; 2.49 mmol), benzene (10 ml); and n-hexane (10 ml) was refluxed for 1 hr, and stirred for 2 hr at room temperature. The precipitated pale orange powder was filtered and recrystallized directly from dichloromethane and ethyl ether to give IXb (255 mg; 77% yield). M.p. 169-173° dec. NMR ($CDCl_3$): τ2.0-3.0 (m, 30), 4.77 (s, 1, CH_2Cl_2), 7.63 (s, 3, CH_3), and 7.67 (s, 3, CH_3). IR: 1615, 1607 cm^{-1} (νCO).

Anal. Calcd for $C_{54.5}H_{45}Cl_2N_2O_2P_2RhS_2$: C, 61.76; H; 4.28; N, 2.64. Found: C, 61.58; H, 4.26; N, 2.80.

Preparation of $RhCl(Ph_3P)_2[(CH_3)_2N\text{-}CONCS]_2$ (IXc). A mixture of $RhCl(Ph_3P)_3$ (250 mg; 0.27 mmol) and N, N-dimethylcarbamoyl isothiocyanate (440 mg; 3.38 mmol) in benzene (10 ml) and n-hexane (15 ml) was refluxed for 30 min. to result orange precipitates of IXc (210 mg; 76% yield), which was recrystallized from dichloromethane-ethyl ether. Mp 175-176°dec. IR: 1631 (νCO), 1594 and 1586 CM^{-1} (νCN). NMR($CDCl_3$): τ2.1-3.0 (m, 30, aromatic), 7.19 (s, 6, two CH_3), 7.22 (s, 3, CH_3) and 7.54 (s, 3, CH_3).

Anal. Calcd for $C_{44}H_{42}N_4ClO_2P_2RhS_2$: C, 57.24; H, 4.58; N, 6.07. Found: C, 57.09; H, 4.60; N, 6.11.

The infrared spectrum of IXb showed the $\nu(C=O)$ bands at 1615 and 1607 cm^{-1} and the NMR spectrum indicated the two nonequivalent aroyl methyl protons at τ7.63 and 7.67, suggestive of the analogous structure of IXb to IXa. The infrared spectrum of IXc, however, indicated a $\nu(C=O)$ band at 1631 cm^{-1}, as well as two broad $\nu(C=N)$ bands at 1594 and 1586 cm^{-1}, which were higher than those of IXa or IXb. This suggests that the carbonyl function of the N, N-dimethylcarbamoyl group delocalizes electrons in the carbene ligand to a lesser extent than IXa or IXb. In consistent with the above conclusion, the NMR spectrum of the $N\text{-}CH_3$ proton signal appeared as a set of two singlets at τ7.22 and 7.54 (each 3H) suggestive of restricted rotation around the $C=N^+(CH_3)_2$ located at the remote position from the carbene center, as well as a sharp singlet of the freely rotating dimethylamino group (connected directly to the ligand plane) at τ7.19 (6H).

4. 3. 5. *Novel Tridentate Rhodium-Carbene Complex by the Condensation of Three Molecules of Ethoxycarbonyl Isothiocyanate*

The reaction of $RhCl(Ph_3P)_3$ with an excess of ethoxycarbonyl isothiocyanate, however, yields a surprising novel complex; $RhCl(Ph_3P)_2(C_2H_5OCONCS)_3$ (X) in which three molecules of the isothiocyanate are involved.

Preparation of $RhCl(Ph_3P)_2(C_2H_5OCONCS)_3\cdot(CH_3)_2CO$ (X). A benzene (20 ml) solution of $RhCl(Ph_3P)_3$ (400 mg; 0.432 mmol) and ethoxycarbonyl isothiocyanate (480 mg; 3.66 mmol) was stirred for 30 min. at room temperature, and was refluxed for 2 hr. After the solvent and the excess ethoxycarbonyl isothiocyanate was removed under reduced pressure, n-hexane (30 ml) was added to the oily residue, from which reddish orange powder of $RhCl(Ph_3P)_2(C_2H_5OCONCS)_3$ precipitated quantitatively. The crude product was dissolved to the minimal amount of acetone and evaporated. Ethyl ether was added to the remaining oil dropwise until few microcrystals appeared (nearly twice volume of ethyl ether to the oil was required). The mixture was kept in refrigerator for 24 hr to yield X as reddish orange prisms. Mp. 115-119° IR: 1785, 1761 ($\nu C=O$), 1711 (acetone) cm^{-1} NMR-($CDCl_3$): τ2.1-2.9 (m, 30, aromatic), 8.76 (t, 6, CH_3; J=7.5Hz), 5.87 (q, 4, CH_2; J=7.5Hz), 8.79 (t, 3, CH_3; J=6.8Hz), 6.04 (q, 2, CH_2, J=6.8Hz).

Anal. Calcd for $C_{51}H_{51}N_3ClO_7P_2RhS_3$: C, 54.96; H, 4.61; N, 3.77. Found: C, 54.94; H, 4.69; N, 3.78.

The two kinds of ethoxycarbonyl proton signals occur in 2:1 intensity ratio at τ8.76t, 5.87q (J=7.5 Hz) and τ8.79t, 6.04q (J′=6.8 Hz) in the NMR spectrum of X. The infrared spectrum of X also showed the corresponding $\nu(C=O)$ bands at 1785 and 1765cm^{-1}. These spectroscopic observations clearly indicated that two ethoxy carbonyl groups of the three are different from the another. The presence of one molecule of acetone solvate is supported by the NMR (τ7.95, s, 6H) and the infrared spectra ($\nu C=O$ 1711 cm^{-1}). These routine spectroscopic information, however, did not suggest an unambiguous formulation of X involving a ligand composed of the unusual three molecular condensation of ethoxycarbonyl isothiocyanate. Consequently, an X-ray diffraction study is indispensable, and is described in the following section.

The conclusive structure of X is well consistent with the spectral information discussed before. The presence of the two equivalent ethoxycarbonyl groups requires an ethoxycarbonyl group migration during the condensation process.

Although many carbene transition metal complexes were reported [23), 27)] from various precursors, the formation of such a tridentate and planar carbene ligand in IX and X from the formal oxidative addition of the condensed heterocumulene linkage is an amazing one.

4. 3. 6. *The X-ray Determination of the Structure of the Complex X, $RhCl(PPh_3)_2(EtOCO\text{-}NCS)_3$*

The compound $RhCl(PPh_3)_2(EtOCONCS)_3\cdot(CH_3)_2CO$ crystallizes with four formula units in the triclinic space group C_i^1-$P\bar{1}$ in a cell of dimensions $a=15.214(6)$, $b=27.571(9)$, c 12.857(6) Å, $\alpha=103.12(2)$, $\beta=90.24(2)$, $\gamma=100.03(2)°$, $V=5166$ Å^3, $d_{cald}=1.432$ g cm^{-3}, $d_{obs}=1.35(3)$ g cm^{-3}, $\mu(CuK\alpha)=53.56$ cm^{-1}. Data were collected on a Picker X-ray diffractometer using Ni-filtered $CuK\alpha$ radiation out to $2\theta(CuK\alpha_1)$ of 94°. A total of 7375 unique reflections having $F_0^2>3\sigma(F_0^2)$ was used in the ensuing calculations. The fact that the cell is indeed triclinic was established through extensive photographs, through a cell reduction, and by comparison of F_0^2 values of low-order planes. The presence of two formula units per asymmetric unit necessitates the location of 64 individual atoms and 12 rigid phenyl groups. Refinement of the resultant 401 variables (isotropic model) by full-matrix least-squares methods has converged to values of 0.072 and 0.091 for the conventional R and R_w indices, respectively.

The two independent nonsolvent molecules in the asymmetric unit differ somewhat in conformations of their terminal groups; they are otherwise equivalent. In Figure 3 we show a projection of molecule X onto the ligand plane. The trans PPh_3 groups

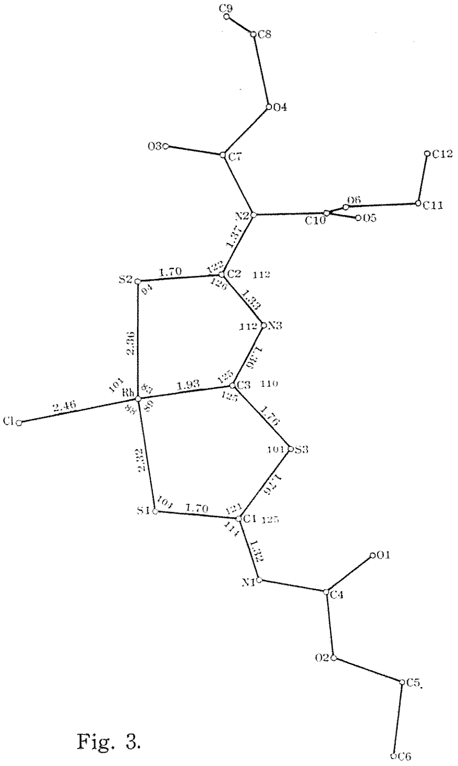


Fig. 3.

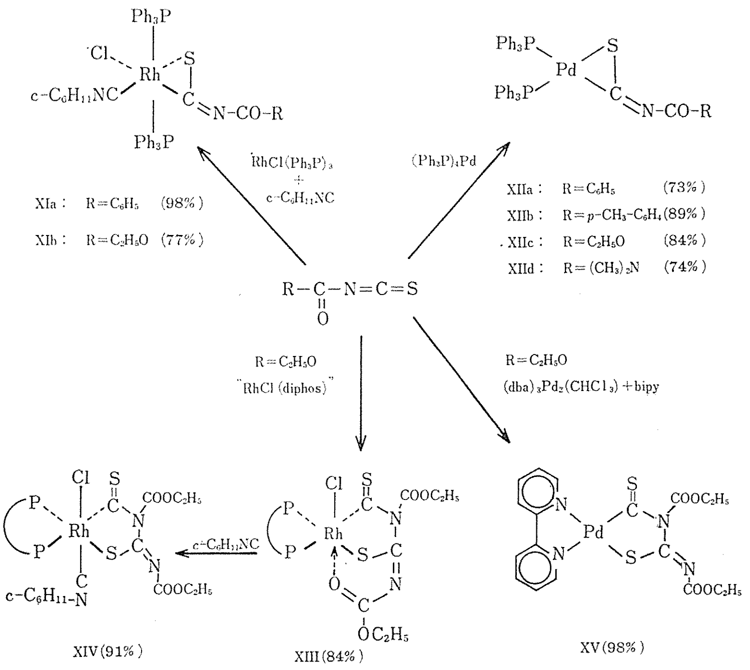
in axial positions, approximately above and below the Rh atom, have been omitted for the sake of clarity. The Rh atom has a slightly distorted octahedral coordination with trans PPh_3 groups. The four equatorial sites are occupied by the chloro ligand and by the tridentate ligand $(EtOCONCS)_3$. Two former EtOCONCS molecules can be thought of as C(6)-C(5)-O(2)-C(4)O(1)-N(1)-C(1)-S(1) and C(9)-C(8)-O(4)-C(7)O(3)-N(2)-C(2)-S(2) ; the two fragments of the third EtOCONCS molecule consist of C(12)-C(11)-O(6)-C(16)O(5) attached to N(2) and of N(3)-C(3)-S(3) joining C(2) and C(1) to form a fused system of two five-membered rings. The tridentate ligand is attached to Rh through two S linkages (S(1) and S(2)) and one carbene C linkage (C(3)). The fused ring system closely resembles that found earlier for $(PhCONCS)_2$ attached to Rh(III), with the exception that an O atom in that system has been replaced by S(2). With the exception of the geometrical changes brought about by this substitution, the geometries of the two ring systems are very similar. In particular, the present ring system is again essentially planar with some evidence for delocalization of bonding. The Rh(III)-C(3) (carbene) bond is again 1.93 Å, and the carbene again exerts a large trans influence on the trans chloro ligand.

4. 3. 7. *The Primary Step of the Condensation of Activated Isothiocyanates. The Formation of η^2-Isothiocyanate Rhodium (III) and Palladium (II) Complexes*

In order to elucidate a reasonable mechanism on the formation of the new tridentate carbene rhodium (III) complexes IX and X arose by the condensation of two or three activated isothiocyanate molecules, several reactions summarized in Scheme IV were carried out.

When cyclohexyl isocyanide was present in the reaction of RhCl $(Ph_3P)_3$ with benzoyl or ethoxycarbonyl isothiocyanates, the formation of the tridentate carbene complexes was completely inhibited. The elemental analysis of the isolated pale yellow powder in both cases suggested the composition of the corresponding six-coordinate complexes involving one molecule of the isothiocyanate ligand; $RhCl(Ph_3P)_2(c\text{-}C_6H_{11}NC)(RCONCS)$, XIa for $R=C_6H_5$; XIb for $R=C_2H_5O$. The complexes XIa and XIb were unstable in solution and decomposed with dissociating phenyl or ethoxycarbonyl isothiocyanate ligands. The infrared spectrum of XIa showed a $\nu(C=O)$ band at 1668 cm^{-1} as well as $\nu(C=N)$ band at 1530 cm^{-1}. The corresponding absorptions were observed at 1700 and 1605 cm^{-1} in the case of XIb. The appearance of these two bands in the infrared spectra is consistent with the depicted structure involving a η^2-coordination was reported by Wilkinson *et al.*[2] for the common isothiocyanate complexes of rhodium and palladium. An alternative structure of the five-membered metallocyclic skeleton similar to the benzoyl or thiobenzoyl isothiocyanate complexes is unlike, since the $\nu(C=O)$ band should disappear for that structure. The reference complexes of XIa and XIb are prepared by treating four activated isothiocyanates with tetrakis(triphenylphosphine)palladium(0).

Scheme IV



As expected, bis-(triphenylphosphine) (η^2-isothiocyanate) palladium complexes, XIIa~XIId are prepared without difficulty, and they readily dissociate the parent isothiocyanate in solution in similar to XIa, XIb and the common isothiocyanate complexes reported earlier.2) The $\nu(C=O)$ band of XIIa at $1658cm^{-1}$ and XIIc at $1700 cm^{-1}$ corresponds well to the related rhodium(cyclohexyl isocyanide) complexes, XIa ($1668 cm^{-1}$) and XIb ($1700 cm^{-1}$) involving the presumed η^2-coordination of isothiocyanate ligands. The similar palladium complexes XIIb and XIId showed the apparent $\nu(CO)$ and $\nu(CN)$ bands, therefore, the complexes XII all have η^2-isothiocyanate ligands coordinating at the C=S bond.

In addition, when a large excess of ethoxycarbonyl isothiocyanate was reacted with $(Ph_3P)_4Pd$, a dithiocarbamate palladium complex; $(Ph_3P)_2Pd(S_2C=NCOOC_2H_5)$ was accidentally isolated. The structural similarity of XIa and XIb to the corresponding palladium complexes XIIa and XIIc suggests that the primary step of the condensation reaction of phenyl or ethoxycarbonyl isothiocyanate molecules to lead the tridentate carbene complexes IXa and X is the η^2-coordination of these acceptors to the rhodium metal at their C=S bonds. The subsequent step should be the lone pair coordination of the second isothiocyanate molecules to the sixth coordination site, which was occupied by cyclohexyl isocyanide in the case of the model complexes XIa and XIb. The X-ray structure of IXa indicated that the carbon-sulfur bond formation between the sulfur atom of the firstly coordinated benzoyl isothiocyanate and the most electrophilic central carbon atom (its electrophilicity may be greatly enhanced by the coordination to the cationic rhodium atom) of the second one. Thus the initial problem on the formation of a tridentate carbene complex; $RhCl(Ph_3P)_2(C_6H_5CONCS)_2$ (IXa) becomes clear by understanding the coordination mode of the first isothiocyanate molecules in XIa.

Preparation of $RhCl(Ph_3P)_2(c\text{-}C_6H_{11}NC)(C_6H_5CONCS)$ (XIa). A benzene (10 ml) solution of $RhCl(Ph_3P)_3$ (300 mg; 0.324 mmol) and cyclohexyl isocyanide (36.5 mg; 0.335 mmol) was stirred for 15 min. at room temperature to result a red-brown solution to which benzoyl isothiocyanate (310 mg; 1.30 mmol) was added. The reaction completed immediately to give pale yellow suspension. After the mixture was stirred for 3 hr at room temperature, the crude complex XIa was filtrated and washed by ethyl ether (20 ml). The complex XIa was isolated in 98% yield (296 mg) and was unstable in solution. Therefore, the recrystallization of XIa was achieved by dissolving dichloromethane containing few drops of benzoyl isothiocyanate followed by adding ethyl ether to give pale yellow prisms of XIa: Mp. 160-162° dec. IR: 2180($\nu N\equiv C$), 1668($\nu C=O$), 1572 and 1530 cm^{-1} ($\nu C=N$).

Anal. Calcd for $C_{51}H_{46}N_2ClOP_2RhS_2$: C, 65.49; H, 4.96; N, 3.00. Found: C, 65.57; H, 4.87; N, 3.03.

Preparation of $RhCl(Ph_3P)_2(c\text{-}C_6H_{11}NC)(C_2H_5OCONCS)\cdot CH_2Cl_2$ (XIb). The procedure was analogous to that of XIa with $RhCl(Ph_3P)_3$ (350 mg; 0.378 mmol), cyclohexyl isocyanide (53.2 mg; 0.488 mmol), ethoxycarbonyl isothiocyanate (355 mg; 2.71 mmol), and benzene (20 ml). The complex XIb was isolated in 77% yield as pale yellow powder, which was recrystallized from dichloromethane-ethyl ether-acetone (2/1/1 vol.) containing few drops of ethoxycarbonyl isothiocyanate: Mp. 121-125° dec. IR: 2190 ($\nu N\equiv C$), 1700 ($\nu C=O$) and 1605 ($\nu C=N$). NMR($CDCl_3$): $\tau 2.0$-3.0 (m, 30, aromatic), 4.98 (s, 2, CH_2Cl_2), 6.36 (q, 2, CH_2; J=6.3 Hz), 8.95 (t, 3, CH_3; J=6.3 Hz) and eleven proton multiplets around $\tau 9$ for cyclohexyl group. Anal. Calcd for $C_{48}H_{48}N_2Cl_3OP_2RhS$: C, 58.34; H, 4.90; N, 2.83. Found: C, 58.62; H, 5.16; N, 3.05.

Preparation of $Pd(Ph_3P)_2(C_6H_5CONCS)$ (XIIa). After tetrakis(triphenylphosphine) palladium was synthesized *in situ* from $(DBA)_3Pd_2(CHCl_3)$ (200 mg; 0.193 mmol), triphenylphosphine (400 mg; 1.53 mmol), and ethylether (15 ml) by stirring for 1 hr at room temperature, benzoyl isothiocyanate (449 mg, 2.75 mmol) was added dropwise. The reaction mixture turned to yellow homogeneous solution, from which the complex **XIIa** precipitated as pale yellow powder (225 mg) in 73% yield: Mp 111-116° dec. IR: 1658 (νC=O), 1562 cm^{-1} (νC=N). The NMR($CDCl_3$) indicated only the presence of phenyl protons. Anal. Calcd for $C_{44}H_{35}NOP_2PdS$: C, 66.54; H, 4.44; N, 1.76. Found: C, 66.42; H, 4.43; N, 1.83.

Preparation of $Pd(Ph_3P)_2$(*p*-CH_3-C_6H_4CONCS) (XIIb). This was prepared similarly to XIIa with $(DBA)_3Pd_2(CHCl_3)$ (300 mg, 0.290 mmol), triphenylphosphine (600 mg, 2.23 mmol) and p-toluyl isothiocyanate (220 mg, 1.24 mmol) in benzene (20 ml), to obtain **XIIb** in 89% yield (424 mg) as pale yellow needles: Mp. 119-121° dec. IR: 1659 (νC=O), 1551 br (νC=N). NMR ($CDCl_3$): τ2.6-3.2 (m, 34, aromatic), 7.71 (s, 3, CH_3). Anal. Calcd for $C_{45}H_{37}NOP_2PdS$: C, 66.88; H, 4.62; N, 1.73. Found: C, 67.00; H, 4.49; N, 1.63.

Preparation of $Pd(Ph_3P)_2(C_2H_5OCONCS)$ (XII**c**). The reaction condition was similar to XII**a** with $(DBA)_3Pd_2(CHCl_3)$ (400 mg, 0.386 mmol), triphenyl phosphine (800mg, 3.05 mmol), ethoxycarbonyl isothiocyanate (163 mg; 1.24 mmol) in benzene (20 ml) at room temperature. After the removal of low-boiling materials under reduced pressure, ethyl ether (20 ml) was added to cause precipitation of XII**c** (472 mg; 80% yield) as pale yellow prisms. Recrystallization was similarly performed from dichloromethane containg few drops of ethoxycarbonyl isothiocyanate and ethyl ether: Mp. 108-112° dec. IR: 1700 (νC=O), 1625 (νC=N). NMR ($CDCl_3$): τ2.8 (m, 30, aromatic) 6.07 (q, 2, CH_2), 8.87 (t, 3, CH_3): J=7.0Hz. Anal. Calcd for $C_{40}H_{35}NO_2P_2PdS$: C, 63.4; H, 4.63; N, 1.84. Found: C, 62.98; H, 4.67; N, 1.83.

When ethoxycarbonyl isothiocyanate was added 5-7 times of the palladium(0) complex, unexpected formation of the complex $Pd(Ph_3P)_2(S_2C{=}N{-}COOC_2H_5)$ was observed: Mp. 200-202°dec. IR: 1706(νC=O), 1535 (νC=N). Anal. Calcd for $C_{40}H_{35}NO_2P_2PdS_2$: C, 60.49; H, 4.44; N,1.84; P, 8.13. Found: C, 60.14; H, 4.67; N, 1.97; P, 8.01.

Preparation of $Pd(Ph_3P)_2[(CH_3)_2NCONCS]$ (XIId). A mixture of $(DBA)_3Pd_2(CHCl_3)$ (300mg, 0.290mmol) and triphenylphosphine (600 mg, 2.29 mmol) in benzene (20 ml) was stirred for 1 hr at room temperature. To this solution, N,N-dimethyl-carbamoyl isothiocyanate (187mg; 1.44 mmol) was added to give yellow homogeneous solution which was stirred for additional 2 hr. The low-boiling materials were removed under reduced pressure, and ethyl ether (25 ml) was added to the residual oil to precipitate XII**d** (324 mg) in 74% yield: Mp. 96-106° dec. IR: 1674(νC=O), 1646, 1616 (νC=N). NMR ($CDCl_3$): τ2.85 (m, 30, aromatic), 7.13 (s, 3, CH_3), 7.81 (s, 3, CH_3). Anal. Calcd for $C_{40}H_{36}N_2OP_2PdS$: C, 63.12; H, 4.77; N, 3.68. Found: C, 63.39; H, 4.77; N, 3.84.

4. 3. 8. A Model Complex of the Intermediate Involving Two Molecules of Ethoxycarbonyl Isothiocyanate

The construction of the $RhCl(Ph_3P)_2(C_2H_5OCONCS)_3$ (X) which structure was unambiguously determined by a three-dimensional X-ray analysis as discussed in the earlier part of this chapter is more complex than that of IX, because (IX) an unusual condensation of the three molecules of isothiocyanate occurs around the rhodium atom resulting a carbene ligand and (X) the 1,3-shift of the one ethoxycarbonyl group is necessary to generate the final structure of X. An efficient inhibition of this complex condensation process with cyclohexyl isocyanide, to give $RhCl(Ph_3P)_2$

(c-$C_6H_{11}NC$)($C_2H_5OCONCS$) (XIb) suggested that the first η^2-coordination of the isothiocyanate followed by the lone pair coordination of the second isothiocyanate was the most possible passway in a similar manner to the formation of IX. The following step in the formation of X should be the carbon-nitrogen bond formation which is definitely made clear by X-ray structure determination and is different from that of IXa that occurred by the carbon-sulfur bond formation. It was therefore necessary to achieve a model reaction in order to understand the structure of the highly reactive intermediate complex involving two molecules of ethoxycarbonyl isothiocyanate, and to decide the stage of the ethoxycarbonyl group migration. The X-ray conclusion clearly indicated that X involves a tridentate carbene ligand and that two triphenylphosphine located up and down to this ligand plane. Consequently, it is highly probable that the objective model complex involving two isothiocyanate skeletons may be attainable if two phosphorus ligands occupy the cis position to leave only two planar coordination sites for ethoxycarbonyl isothiocyanate. Based on this view point, a reaction of "RhCl(diphos)", prepared *in situ* from [RhCl(1, 5-cyclooctadiene)]$_2$ with 1, 2-bis(diphenylphosphino)ethane, with ethoxycarbonyl isothiocyanate was undertaken. As expected, the isolated deep yellow product showed the composition of RhCl(diphos)($C_2H_5OCONCS$)$_2$ (XIII). The ν(C=O) bands appeared at 1770 and 1543cm^{-1}. The latter band indicates the presence of the intramolecular coordination of the one of the carbonyl oxygen to the sixth coordination site of the rhodium atom. The NMR spectrum of XIII indicated two ethyl methylene quartets at τ5. 80 and 5. 86. When XIII was reacted with cyclohexyl isocyanide for the purpose to cleave the intramolecular coordination, RhCl(diphos)(c-$C_6H_{11}NC$)($C_2H_5OCONCS$)$_2$ (XIV) was obtained in 91% as sparingly soluble yellow powder. The infrared spectrum of XIV showed the ν (C=O) bands at 1768 and 1694 cm^{-1} indicative of the presence of the one nonconjugating carbonyl and the one conjugating carbonyl groups, the latter of which took part in the intramolecular coordination in XIII. The most reasonable formulation of XIV is, therefore, the five-membered rhodiacyclic structure as depicted in scheme IV, and is induced simply by a carbon-nitrogen and a rhodium-sulfur bond formations from two ethoxycarbonyl isothiocyanate molecules. In order to obtain further confidence to the proposed structure of XIV, the corresponding palladium complex; Pd(bipy)($C_2H_5OCONCS$) (XV) was prepared from $(DBA)_3Pd_2(CHCl_3)$, bipyridine, and ethoxycarbonyl isothiocyanate in 98% yield. There are two carbonyl bands in the infrared spectrum of XV at 1771 and 1681cm^{-1} which were extremely close to these absorptions of the corresponding rhodium complex XIV. It is therefore reasonable to conclude that the three molecule condensation to the tridentate carbene complex X proceeds *via* an intermediate including a similar five-membered rhodiacyclic structure which is coordinatively unsaturated five-coordination to remain ethoxycarbonyl isothiocyanate. It is noteworthy to emphasize that the model complex XIV did not involve the 1, 3-shift of the ethoxycarbonyl group which will occur at the final stage of the reaction with the concurrent carbenoid formation.

Preparation of RhCl(diphos)($C_2H_5OCONCS$)$_2$ (XIII). To a benzene (4 ml) solution [RhCl(1, 5-COD)]$_2$ (100mg, 0. 41 mmol) and 1, 2-bis(diphenylphosphino)-ethane (diphos; 163 mg; 0. 4 mmol), ethoxycarbonyl isothiocyanate (112 mg, 0. 857 mmol) was added dropwise. The mixture turned from deep yellow to yellow orange suspension. The reaction was completed by stirring for 15 hr at room temperature. Ethyl ether (20 ml) was added to the above mixture to yield the deep yellow powder complex XIII (271 mg) in 84% yield. Recrystallization was achieved from dichloromethane-ethyl ether mixture: Mp. 212-216° dec. IR: 1770, 1543 (νC=O). NMR ($CDCl_3$): τ2.0-3.2 (m, 20, phenyl) 5.80 (q, 2, CH_2O) 5.86 (q, 2, CH_2O) 7.0-8.4 (m, 4, br, CH_2P) 8.74 (t, 6, two CH_3). Anal. Calcd for $C_{34}H_{36}N_2ClO_4P_2RhS_2$: C, 51.11; H, 4.29; N, 3.51. Found: C, 51.28; H, 4.49; N, 3.68.

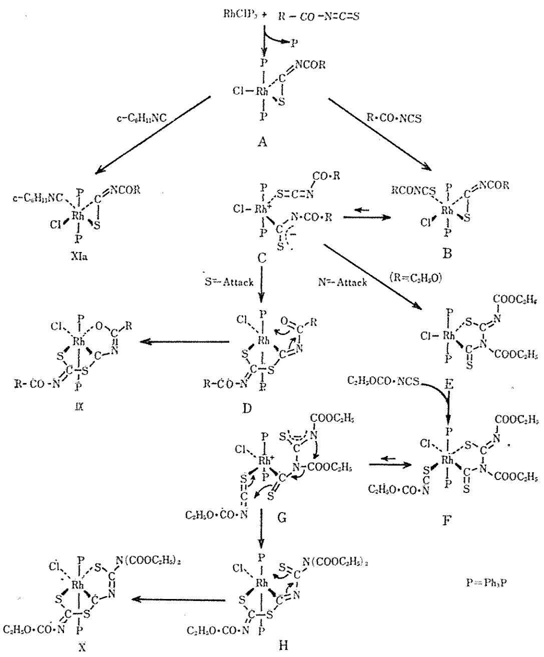
Preparation of RhCl(diphos)(c-$C_6H_{11}NC$)($C_2H_5OCONCS$) (XIV). To a dichloromethane (8 ml) solution of XIII (83.1 mg, 0.104 mmol) was added cyclohexyl isocyanide (29.6 mg, 0.272 mmol) to give gradually yellow homogeneous solution which was kept stirring for 17 hr at room temperature. After the low-boiling materials were removed under reduced pressure, ethyl ether (10 ml) was added to give XIV as yellow powder (86.5 mg) in 92% yield. Recrystallization of XIV was done from dichloromethane-ethyl ether: Mp. 165-168° dec. IR: 1768 (νC=O) 1694 (conjugating νC=O), 1611 (νC=N). The measurement of NMR spectrum of XIV was impossible because of the low solubility. Anal. Calcd for $C_{41.5}H_{46}N_3Cl_2P_2RhS_2$ involving 0.5 CH_2Cl_2 as a solvate: C, 52.43; H, 4.88; N, 4.42. Found: C, 52.37; H, 4.84; N, 4.63.

Preparation of Pd(bipy)($C_2H_5OCONCS$)$_2$ (XV). A benzene (20 ml) suspension of $(DBA)_3Pd_2(CHCl_3)$ (400mg, 0.386 mmol) and bipyridine(400 mg, 2.56 mmol) was stirred for 1 hr at room temperature, and ethoxycarbonyl isothiocyanate (420 mg, 3.20 mmol) was added dropwise to the above mixture. An orange suspension instantaneously turned to reddish brown suspension after 2 hr at room temperature. The low-boiling material was removed under reduced pressure, and the residue was mixed with n-hexane (20 ml). The resulting oil solidified to the crude XV as yellow brown powder (397 mg; 98%) which was recrystallized by dissolving to dichloromethane followed by the addition of ethyl ether: Mp. 149-153° dec. IR: 1771,1681 (νC=O). NMR ($CDCl_3$): τ1.9-2.8 (m, 8, bipy), 5.60 (q, 2, CH_2), 5.73 (q, 2, CH_2), 8.60 (t, 6, two CH_3) with J=7.0 Hz. Anal. Calcd for $C_{18}H_{18}N_4O_4PdS_2$: C, 41.19; H, 3.46; N, 10.67. Found: C, 41.22, H, 3.57; N, 10.38.

4. 3. 9. Mechanism of the Formation of two Novel Types of Rhodium Carbene Complexes: $RhCl(PPh_3)_2(C_6H_5CONCS)_2$ *and* $RhCl(PPh_3)_2(EtOCONCS)_3$

A reasonable mechanism for the formation of the new tridentate rhodium carbene complexes IX and X are proposed in scheme V based on the crystallographical results and the above-mentioned chemical evidence. The first step of the reaction is the formation of the five-coordinate complex A involving a η^2-coordination of the C=S bond of isothiocyanate ligand, to which the second isothiocyanate coordinates to complete the stable six coordination around the rhodium(III) atom. A similar complex to B which contained η^2-coordination at the C=S bond and the lone pair coordination of the two isothiocyanate molecules were mentioned by Baird and Wilkinson[2)] based on the infrared spectroscopy. The cyclohexyl isocyanide (η^2-isothiocyanate)rhodium complexes XIa and XIb and the bis(triphenylphosphine)(η^2-isothiocyanate)palladium complexes XIIa ~ XIId readily dissociate the coordinating isothiocyanate ligands as discussed earlier, therefore, the sulfur terminus of the η^2-ligand dissociates by the trans-influence of the sulfur lone-pair coordination of the entered second isothiocyanate to yield a zwitter-ionic intermediate C. The anionic part of this zwitter-ionic C is stabilized by the electron delocalization within the S-C-N-C-O- entity, and it behaves as an "ambident anion" to the nucleophilic attack towards the coordinating isothiocyanate, which electrophilicity is increased by the coordination to the cationic rhodium atom. When the sulfur atom

Scheme V



of the anionic part in C attacks the central carbon atom of the second isothiocyanate a five-coordinate imidoyl intermediate (D) is produced, which induces an electron reorganization to form the tridentate carbene skelton of IX, in order to fulfil the stable six coordination intramolecularly. On the other hand, the anionic part of the zwitter-ion C cannot delocalize extensively in the case where R is ethoxy group, because the carbonyl group is strongly conjugating with the lone pair electrons on the ethoxy group. As a result, the electron density on the nitrogen terminus becomes high and forms a carbon-nitrogen bond with the second isothiocyanate to give a five-membered rhodiacyclic intermediate having a coordinative unsaturation. The model complex of E was actually isolated by controlling the stereochemistry of E in the case of XIII and XIV as well as the corresponding palladium complex XV, which had stable coordination number. The sixth coordination site of the intermediate E then accepts the third ethoxycarbonyl isothiocyanate to complete the stable six coordination to give F. The generation of the another zwitter-ionic intermediate in a similar manner to the passway B → C, the sulfur terminus of the five-membered rhodiacyclic intermediate dissociates to G, then the most nucleophilic nitrogen atom in G becomes a "trigger" to the 1, 3-shift of the ethoxycarbonyl group and the concurrent sulfur-carbon bond formation in a depicted "charge-relay system" giving directly an imidoyl intermediate H, which readily fulfils the coordinative unsaturation intramolecularly similar to D → IX to generate the tridentate carbene rhodium complex X. A molecular model consideration of the intermediate F indicated that the distance between the attacking nitrogen atom and the rearranging ethoxycarbonyl group was too remote to exhibit the 1, 3-shift.

Therefore, the bond-breaking at the rhodium-sulfur bond prior to the rearrangement is indispensable.

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