

# Organic Syntheses by Means of Noble Metal Compounds. XXXVI.<sup>1</sup> Reactions of Carbanions with Cyclooctadienepalladium and -platinum Halide Complexes and Tetraphenylcyclobutadienepalladium Chloride Complex

Hidetaka Takahashi and Jiro Tsuji

Contribution from The Basic Research Laboratories, Toyo Rayon Co.,  
Kamakura, Japan. Received December 12, 1967

**Abstract:** The possibility of carbon-carbon bond formation by the reaction of dienepalladium and -platinum halide complexes with carbanions has been investigated. Malonate and acetoacetate react smoothly at room temperature with cyclooctadienepalladium and -platinum halide complexes to give new complexes, which contain  $\sigma$  and  $\pi$  bonds with metals. These complexes were treated with various bases. Reaction of the complexes with methylsulfinyl carbanion produced bicyclo[6.1.0]nonene derivatives. Malonate attacked the complexes to give 2,6-disubstituted bicyclo[3.3.0]octane rings. The reaction of tetraphenylcyclobutadienepalladium chloride complex with malonate has also been studied.

It is well known that olefin-palladium chloride complexes react with various nucleophiles, offering an interesting possibility for organic syntheses. Hydroxy, acetoxy, and alkoxy anions are known to attack the olefins coordinated to palladium to form carbonyl or vinyl compounds.<sup>2</sup> In these reactions, new carbon-oxygen bonds are formed, and this type of reaction is extremely useful for preparing vinyl compounds from olefins. It seemed interesting for us to investigate the possibility of a carbon-carbon bond formation by the reaction of the olefin complexes with carbanions. We have already shown that  $\pi$ -allylpalladium chloride reacts with typical carbanions such as malonate or enamines to form allyl derivatives.<sup>3</sup> The reaction of the carbanions has now been extended to cyclooctadienepalladium halide complexes I, corresponding platinum halide complexes II, and tetraphenylcyclobutadienepalladium chloride complex (XII). It was confirmed that the reaction of malonate and acetoacetate with these complexes proceeds smoothly to form the carbon-carbon bond. Part of the work has already been reported<sup>4</sup> and the details of the reaction are presented in this paper. It is known that these diene complexes I, II, and XII undergo oxypalladation and oxyplatination reactions with methanol to give methoxy-substituted complexes.<sup>5</sup>

## Results and Discussion

**Complex Formation.** Since complex I is difficultly soluble in organic solvents, the reaction was carried out under heterogeneous conditions. When a mixture of complex Ia, an excess of ethyl malonate, and anhydrous sodium carbonate powder in ether was stirred at room-temperature for 15 hr, the yellow complex Ia turned gradually into yellowish white. The newly formed complex IIIa was isolated by filtration. Complex

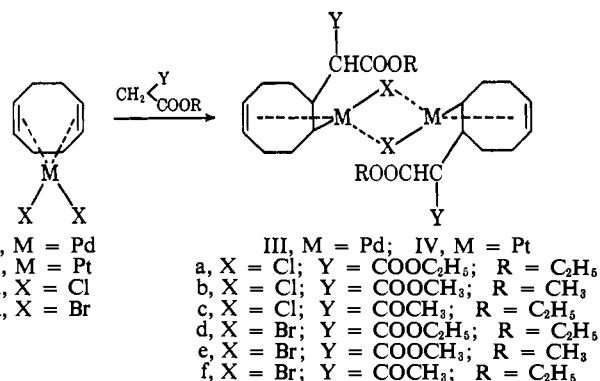
(1) Part XXXV: K. Ohno and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 99 (1968).

(2) A. Aguiló, "Advances in Organometallic Chemistry," Vol. V, Academic Press Inc., New York, N. Y., 1967, p 321.

(3) J. Tsuji, H. Takahashi, and M. Morikawa, *Tetrahedron Letters*, 4387 (1965); *Kogyo Kagaku Zasshi*, **69**, 920 (1966).

(4) J. Tsuji and H. Takahashi, *J. Am. Chem. Soc.*, **87**, 3275 (1965).

(5) (a) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957); (b) *ibid.*, 3413 (1957).



IIIa is soluble in chloroform and can be recrystallized from ethyl acetate. Methyl malonate and ethyl acetoacetate react similarly to form IIIb and IIIc. In addition to the chlorine-bridged complexes, the bromine-bridged ones were also prepared from Id. The infrared band of the malonate ester in complex IIIa was observed at 1730  $\text{cm}^{-1}$ , indicating that the carbonyl band was shifted from 1750 and 1740  $\text{cm}^{-1}$  of free ethyl malonate by incorporation into the complex. The properties of the palladium complexes III are shown in Table I.

Cyclooctadieneplatinum halide complexes II behaved similarly forming similar complexes IV. It is known that olefin-platinum chloride complexes are less reactive than the corresponding palladium complexes toward the nucleophilic attack. For example, ethyleneplatinum complex (Zeise salt) reacts with water much slower than the palladium complex.<sup>6-8</sup> On the other hand, the platinum complexes II reacted with malonate as smoothly as the palladium complexes I. The complexes II are white, and the newly formed complexes IV are also white. However, clear differences in solubility in organic solvents made the separation of IV from II easy. The properties of the platinum complexes IV are shown in Table II.

The structure of complex IIIa was determined as di- $\mu$ -chloro-bis(8-diethoxycarbonylmethyl)-4-cyclo-

(6) I. Leden and J. Chatt, *ibid.*, 2936 (1955).

(7) J. R. Joy and M. Orchin, *Z. Anorg. Allgem. Chem.*, **305**, 236 (1960).

(8) R. Jira, J. Sedlmeier, and J. Smidt, *Ann.*, **693**, 99 (1966).

**Table I.** Di- $\mu$ -halo-bis(8-substituted 4-cyclooctenyl)dipalladium

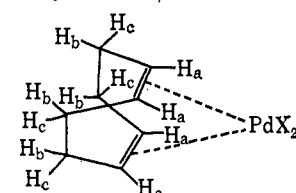
No.	X	Y	R	Mp (dec pt), °C	Mol wt	Found (calcd), %				$\nu_{C=O}$ , $cm^{-1}$
						C	H	X	Pd	
IIIa	Cl	COOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(155–156)	771 (819)	43.84 (43.99)	5.70 (5.66)	8.73 (8.66)	25.3 (26.0)	1730
IIIb	Cl	COOCH <sub>3</sub>	CH <sub>3</sub>	(155–156)		41.25 (40.93)	4.91 (5.02)	9.76 (9.30)	28.4 (28.0)	1735
IIIc	Cl	COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	(157–158)	719 (759)	44.23 (44.31)	5.49 (5.57)	9.36 (9.34)	27.8 (28.1)	1730 1715
III d	Br	COOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	148		39.78 (39.69)	5.31 (5.11)	17.85 (17.60)	19.8 (21.3)	1735
IIIe	Br	COOCH <sub>3</sub>	CH <sub>3</sub>	156–157		36.90 (36.66)	4.50 (4.50)	18.48 (18.76)	26.0 (25.1)	1735
III f	Br	COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	146–147		39.63 (39.65)	4.97 (4.99)	18.80 (18.85)	25.2 (24.6)	1730 1715

**Table II.** Di- $\mu$ -halo-bis(8-substituted 4-cyclooctenyl)diplatinum

No.	X	Y	R	Mp (dec pt), °C	Found (calcd), %				$\nu_{C=O}$ , $cm^{-1}$
					C	H	X	Pd	
IVa	Cl	COOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	195–197	36.30 (36.18)	4.66 (4.66)	7.11 (7.12)	39.4 (39.2)	1730
IVb	Cl	COOCH <sub>3</sub>	CH <sub>3</sub>	(195–200)	33.27 (33.23)	4.09 (4.08)	7.65 (7.55)	41.7 (41.5)	1735
IVc	Cl	COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	(203–208)	35.65 (35.94)	4.46 (4.52)	7.69 (7.58)	41.5 (41.7)	1730 1715
IVd	Br	COOC <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	(178–189)	33.12 (33.22)	4.24 (4.28)	14.76 (14.73)	36.3 (36.0)	1735
IVe	Br	COOCH <sub>3</sub>	CH <sub>3</sub>	(200–220)	30.54 (30.36)	3.77 (3.72)	15.84 (15.54)	37.5 (37.9)	1735
IVf	Br	COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	(194–200)	32.85 (32.82)	4.11 (4.13)	15.70 (15.60)	38.5 (38.1)	1730 1715

octenyl)dipalladium. The molecular weight determination showed that the complex has a chlorine-bridged dimeric structure. The presence of one double bond is distinctly shown by the nmr spectrum. Also, a band assignable to one active hydrogen of the malonate was observed as a doublet at  $\tau$  6.67 ( $J = 10$  cps). The degradative studies shown later also confirmed the carbon-carbon bond formation between malonate and cyclooctadiene. Thus this complex has both palladium-carbon  $\sigma$  and  $\pi$  bonds with the remaining double bond. In general, palladium-carbon  $\sigma$  bonds are not stable without other stabilizing ligands. Certainly, suitable geometry of the coordinating double bond in this complex is attributed to the stability of the  $\sigma$  bond. Complex IIIa showed a sharp decomposition point, and the nmr spectrum shows that the complex is not a mixture. There are two possible structures for IIIa, depending on the direction of the malonate attack, but the stereochemistry of the complex was not studied.

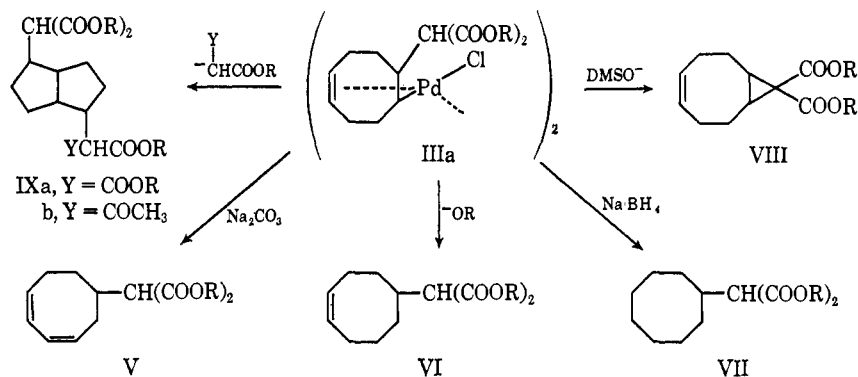
Several interesting observations have been made on the nmr spectra of complexes I, III, and IV. In general, the different shielding effect of halogens on neighboring protons is well known in alkyl halides. For example,  $\beta$ -protons in alkyl chlorides have higher chemical shifts than in corresponding bromides. The cyclooctadiene-

**Table III.** Nmr Spectra of Cyclooctadienepalladium Halide Complexes (I) in CDCl<sub>3</sub> at 100 Mc/sec<sup>a</sup>


	a	b	c
(1,5-COD)PdCl <sub>2</sub>	3.79	7.10	7.40
(1,5-COD)PdBr <sub>2</sub>	3.55	7.15	7.45

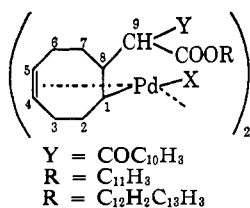
<sup>a</sup> (CH<sub>3</sub>)<sub>4</sub>Si as internal standard; values in  $\tau$  units.

palladium chloride (Ia) and bromide (Id) showed appreciable differences in the nmr spectra, as shown in Table III. The olefinic protons in the chloride Ia have higher chemical shifts ( $\tau$  3.79) than the bromide Id ( $\tau$  3.55). The chemical shifts of complexes III are shown in Table IV, and the similar difference between the chlorine- and bromine-bridged complexes was observed. Again the olefinic protons of the bromine-bridged complexes (for example, III d) showed smaller  $\tau$  values (3.91 and 4.27) than those of the chlo-



Five-bridged ones IIIa (4.03 and 4.47). The same effect of the halogens was observed with the protons on the carbon (C<sub>1</sub>)  $\sigma$  bonded to the palladium in complexes IIIa and d (6.56 and 6.34). The similar effect of halogens on the chemical shifts of neighboring protons has been reported with alkylmercury halides.<sup>9</sup>

**Table IV.** Nmr Spectra of Di- $\mu$ -halo-bis(8-substituted 4-cyclooctenyl)dipalladium (III) in CHCl<sub>3</sub> at 100 Mc/sec<sup>a</sup>



	C <sub>5</sub>	C <sub>4</sub>	C <sub>12</sub>	C <sub>11</sub>	C <sub>1</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>13</sub>	C <sub>2,3,6,7,8</sub>
IIIa	4.03	4.47	5.83	...	6.56	6.67	...	8.76	7.0-8.9
IIIb	4.03	4.47	...	6.30	6.58	6.64	...	...	7.0-8.9
IIIc	4.03	4.46	5.84	...	6.54	6.64	7.78	8.76	7.0-8.9
III d	3.91	4.27	5.82	...	6.34	6.66	...	8.73	7.0-8.9
III e	3.88	4.24	...	6.28	6.40	6.64	...	...	7.0-8.9
III f	3.88	4.24	5.82	...	6.37	6.62	7.78	8.74	7.0-8.9

<sup>a</sup> (CH<sub>3</sub>)<sub>4</sub>Si as internal standard; values in  $\tau$  units.

Different from complex I, the two olefinic protons in the complexes III are not equivalent, and accordingly, two separated peaks were observed as a diffused multiplet at  $\tau$  4.03 and 4.47 for IIIa. The higher peak can be assigned to the proton at C<sub>4</sub> which is located closer to the palladium than the proton at C<sub>5</sub>. The olefinic protons in the platinum complexes IV also showed two separate peaks. Different from the palladium complexes, no different effect of the halogens on the chemical shift of the neighboring protons was observed with the platinum complexes IV. The peak assignable to the methyl protons of the acetyl group (C<sub>10</sub>) in complexes IIIc, f, IVc, and f was observed as clearly separated two singlets and the proton at C<sub>9</sub> as superposed two doublets, as shown in Figure 1. This result indicates that the acetyl group in the complexes takes two different fixed orientations with respect to the cyclooctene ring.

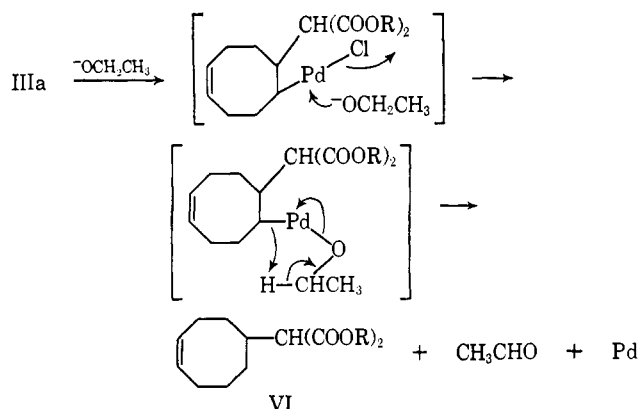
It is rather surprising that the new carbon-carbon bonds were introduced at the double bond of cyclo-

octadiene by the reaction of malonate and other esters under extremely mild conditions in the presence of such a weak base as sodium carbonate. The result clearly indicates that olefinic carbons suitably coordinated with palladium or platinum are extremely susceptible to the nucleophilic attacks. In addition, the  $\sigma$  and  $\pi$  bonds in these complexes are expected to be susceptible to further attacks of the nucleophiles. Thus the reactions of the complexes with various bases have been carried out as described in the following section.

**Reaction of the Complexes III.** The degradative studies of the complexes III were carried out with various bases as summarized in the following scheme.

At first the reaction with weak bases was carried out. When the complex IIIa was treated with triethylamine or anhydrous sodium carbonate in boiling benzene, black metallic palladium separated gradually to yield diethyl 3,5-cyclooctadienylmalonate (V). The ultraviolet absorption spectrum of V showed an absorption maximum in methanol at 229  $m\mu$  ( $\epsilon$  4900), indicating the presence of a conjugated diene system.<sup>10</sup> Also the nmr spectrum supports the structure. The ester was converted into the known cyclooctylmalonic acid by hydrogenation, followed by hydrolysis, and identified. The ester is presumably formed by the removal of the element of H-Pd-Cl from the complex IIIa, and the double bond migrated into the conjugated position after the main reaction.

The decomposition of the complex IIIa with sodium ethoxide in ethanol formed diethyl 4-cyclooctenylmalonate (VI) with the reductive cleavage of the carbon-palladium  $\sigma$  bond. The reduction presumably occurred by the concomitant oxidation of ethoxide anion to aldehyde as shown below.



(9) J. V. Hatton and W. G. Schneider, *J. Chem. Phys.*, **39**, 1330 (1963).

(10) A. C. Cope and L. C. Ester, Jr., *J. Am. Chem. Soc.*, **72**, 1128 (1950).

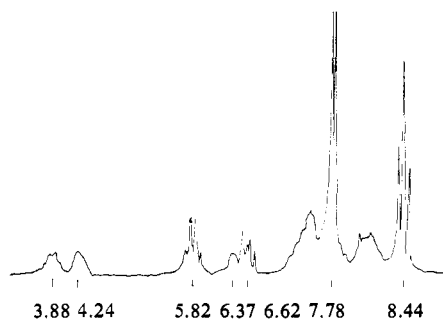
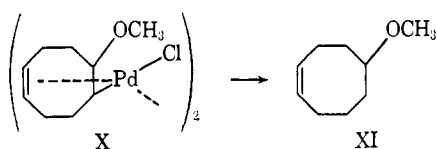


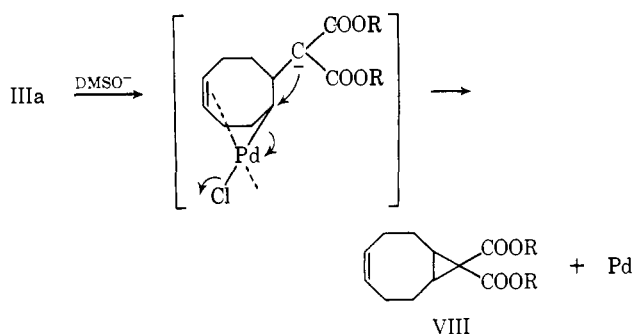
Figure 1. Nmr spectrum of di- $\mu$ -bromo-bis(8-acetyl(ethoxycarbonyl)methyl-4-cyclooctenyl)dipalladium (III f).

Similar degradative reactions were carried out with the known methoxy complex X with methoxide, and 5-methoxycyclooctene (XI) was obtained by the reductive cleavage.



On the other hand, the reduction of complex IIIa with sodium borohydride in ether produced diethyl cyclooctylmalonate (VII). Thus, sodium carbonate and triethylamine afforded the diene systems, ethoxide the cyclooctenyl derivatives, and sodium borohydride produced the saturated compounds.

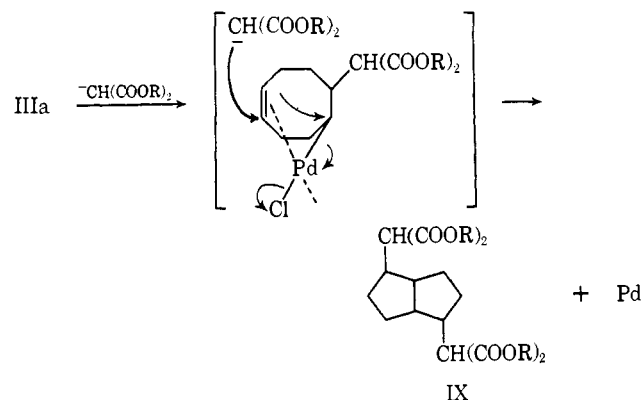
A stronger base, methylsulfinyl carbanion,<sup>11</sup> was then used for the degradation of IIIa, for the stronger base could be expected to abstract the active hydrogen of the malonate group to cause a reaction different from that of the weak bases. The degradation of IIIa with the base proceeded even at room temperature and was completed with slight warming. The product obtained was found to be diethyl bicyclo[6.1.0]non-4-ene-9,9-dicarboxylate (VIII), which was converted into the known bicyclo[6.1.0]nonane-9,9-dicarboxylic acid by hydrogenation and hydrolysis. The formation of the bicyclo[6.1.0]nonane system can be explained in the following way. The base abstracts the hydrogen from the malonate to give the anion which attacks the carbon  $\sigma$  bonded to the palladium to form the cyclopropane ring. It should be noticed that cyclopropane rings are formed usually by the reaction of double bonds with an electrophile such as carbene. On the contrary, the cyclopropane ring was formed by the attack of the nucleo-



(11) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

phile on the double bond in the palladium-complexed reaction.

Then complex IIIa was treated with another malonate anion in dimethyl sulfoxide; the attack was expected to be at the  $\pi$ -bonded carbon. The product IX was a crystalline substance which contains two molecules of malonate, and its nmr spectrum shows no double bond. Apparently a transannular reaction took place to form a bicyclo[3.3.0]octane system. The formation of this ring system can be explained by the following scheme.

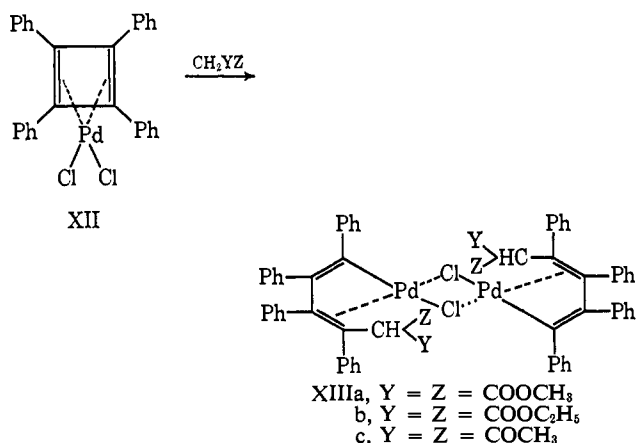


The formation of bicyclo[3.3.0]octane systems from cyclooctenyl derivatives by the transannular reaction under certain conditions is an established reaction.<sup>12</sup> The exact stereochemistry of this transannular reaction of IIIa cannot be determined. However, it seemed likely that the reaction proceeded stereospecifically to give a single product, which was easily crystallizable. When the complex IIIa was treated with ethyl malonate, a symmetrically substituted product IXa was obtained. An unsymmetrically substituted product IXb was formed by the reaction of IIIb with ethyl acetoacetate. The formation of the above shown degradation products through the complex formation followed by the degradation can be carried out as a one-step reaction starting from complex I. Thus the reaction of I with ethyl malonate and 2 equiv of methylsulfinyl carbanion in dimethyl sulfoxide afforded diethyl bicyclo[6.1.0]non-4-ene-9,9-dicarboxylate (VIII) as a main product, accompanied by a small amount of diethyl 3,5-cyclooctadienylmalonate (V). Similarly, complex I reacted with 2 equiv of ethyl malonate anion to give mainly tetraethyl bicyclo[3.3.0]octane-2,6-dimalonate (IXa).

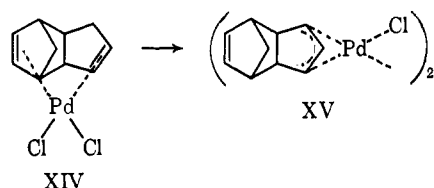
**Reactions of Other Diene Complexes.** Tetraphenylcyclobutadienepalladium chloride complex (XII) is another stable dienepalladium chloride complex. When complex XII was treated with methyl malonate under heterogeneous conditions as before, the red complex XII turned gradually into yellow. The new complex XIIIa is slightly soluble in chloroform, dichloromethane, and ethyl acetate, and can be recrystallized. An infrared spectrum showed carbonyl bands at 1740 and 1760  $\text{cm}^{-1}$ . In a nmr spectrum, the peak assignable to the active methylene proton of the malonate in complex XIIIa was observed as superposed two singlets. These results indicate that the malonate was incorporated into the new complex. The following structure has been assigned to the complex, considering the

(12) A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **81**, 1650 (1959).

similar structure proposed for the complex obtained by the reaction of complex XII with methanol.<sup>13</sup> The ultraviolet spectrum of complex XIII is similar to the corresponding methoxy complex<sup>13</sup> as shown in Figure 2. Ethyl malonate and acetylacetone react similarly to form XIIIb and XIIIc.



It is known that dicyclopentadienylpalladium chloride complex (XIV) can be converted into the methoxy complex containing  $\sigma$  and  $\pi$  bonds as had been done with complex I.<sup>5b</sup> When complex XIV was treated with malonate and anhydrous sodium carbonate, however, it was converted into a new complex XV without incorporating the malonate. The same complex was obtained by the treatment of complex XIV with anhydrous sodium carbonate in acetone-ether mixture. The analysis indicated that one of the chlorine atoms was removed. The lack of solubility did not allow us to take a nmr spectrum, and the following  $\pi$ -allylic structure has been proposed as a provisional structure.



## Experimental Section

**Materials.** Cyclooctadienylpalladium halide complexes I, methoxy complex X, and dicyclopentadienylpalladium chloride (XIV) were prepared by the known method.<sup>5b</sup> Cyclooctadienylplatinum halide complexes II were prepared in a similar way.<sup>5a</sup> Tetraphenylcyclobutadienylpalladium chloride (XII) was prepared by the known procedure.<sup>14</sup> Molecular weights were determined using a Mechrolab vapor pressure osmometer, or by mass spectroscopy.

**Preparation of the Complex IIIa.** A mixture of the complex Ia (0.5 g), anhydrous sodium carbonate (0.5 g), and ethyl malonate (1.0 g) in an excess of ether was stirred magnetically at room temperature for 15 hr, during which time the yellow complex Ia turned into yellowish white. The yellowish white complex was collected by filtration, washed with water and ether, and dried in a desiccator. Crystallization from a mixture of ethyl acetate-hexane gave needles, mp 155–156° dec. The infrared spectrum showed main peaks at 2980, 2930, 1730, 1470, 1450, 1370, 1330, 1305, 1245, 1195, 1170, 1145, 1135, 1080, 1070, 1035, 855, and 770 cm<sup>-1</sup>. IIIb, IIIc, and the bromine-bridged palladium complexes IIId-f were prepared similarly. The properties of the complexes III are shown in Table I.

**Preparation of the Complex IVa.** The complex IIa (0.7 g), anhydrous sodium carbonate (1.5 g), and ethyl malonate (3 ml) in an

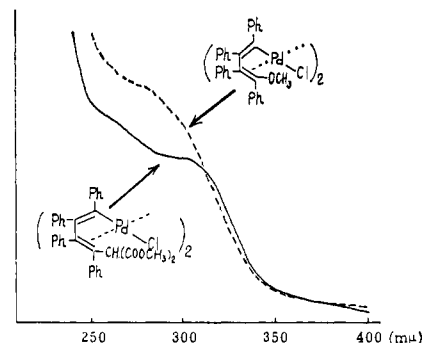


Figure 2. Uv spectrum of complex IIIa.

excess of ether were allowed to react at room temperature for 24 hr with stirring. The complex formed was collected by filtration, washed with water and ether, and dried in a desiccator. The chloroform-insoluble complex IIa was removed, and the crystallization of IVa from a mixture of chloroform and ether produced needles, mp 195–197°. IVb, IVc, and the bromine-bridged platinum complexes IVd-f were prepared similarly. The properties of the complexes IV are shown in Table II.

**Degradation of the Complex III.** 1. **Treatment with Anhydrous Sodium Carbonate.** The complex IIIa (2.0 g) was suspended in benzene (20 ml) with anhydrous sodium carbonate (4.0 g), and the mixture was refluxed for 50 hr. Separated metallic palladium was removed by filtration and benzene was evaporated. The residue was distilled under reduced pressure (4 mm) at 165–170° (bath temperature) to give diethyl 3,5-cyclooctadienylmalonate (V, 1.1 g). *Anal.* Calcd for C<sub>15</sub>H<sub>22</sub>O<sub>4</sub>: C, 67.64; H, 8.33; mol wt, 266. Found: C, 67.48; H, 8.31; mol wt, 266. Spectral data were as follows: nmr spectrum ( $\tau$  values): 8.74 (6 H, triplet), 8.47 (3 H, multiplet), 7.78 (4 H, multiplet), 6.81 (1 H, doublet), 5.85 (4 H, quartet), and 4.30 (4 H, multiplet); ir spectrum: 3000, 2940, 1750, 1730, 1445, 1365, 1290, 1235, 1170, 1145, 1090, 1030, 860, 810, and 680 cm<sup>-1</sup>; uv spectrum:  $\lambda_{\text{max}}^{\text{MeOH}}$  229 m $\mu$  ( $\epsilon$  4900). The ester was hydrogenated using palladium on carbon and then hydrolyzed by refluxing in 10% ethanolic potassium hydroxide for 10 hr. The hydrolyzed product was recrystallized from a mixture of ethyl acetate-hexane to give cyclooctylmalonic acid, mp 123–124°, undepressed by mixing with an authentic sample, prepared by the reaction of cyclooctyl bromide with ethyl malonate, followed by hydrolysis.<sup>15</sup> Cyclooctylmalonic acid (400 mg) was heated in a glass tubing at 180° for 10 min, and cyclooctylacetic acid was obtained as an oil. Chlorination with oxalyl chloride followed by the treatment with ammonia afforded cyclooctylacetamide (250 mg), mp 132–133° (lit.<sup>16</sup> 130°). Treatment of complex IIIa (2.0 g) with triethylamine (3.0 g) in boiling benzene for 4 hr produced the same product.

2. **Treatment with Sodium Ethoxide.** The complex IIIa (2.0 g) was suspended in ethanol (15 ml), and sodium ethoxide solution (0.2 g of sodium in 10 ml of ethanol) was added. The mixture was heated at 65° for 2 hr. Separated palladium was removed by filtration, and ethanol was evaporated. The residue was distilled under reduced pressure to give 1.2 g of diethyl 4-cyclooctenylmalonate (VI, 130–140° (bath temperature) (3 mm)). *Anal.* Calcd for C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>: mol wt, 268. Found: mol wt, 268. Spectral data were as follows: nmr spectrum ( $\tau$ ): 8.79 (6 H, triplet), 8.48 (7 H, multiplet), 7.83 (4 H, multiplet), 6.79 (1 H, doublet), 5.87 (4 H, quartet), and 4.37 (2 H, multiplet); ir spectrum: 2930, 2880, 1750, 1730, 1465, 1450, 1390, 1370, 1290, 1270, 1225, 1210, 1170, 1150, 1110, 1095, 1035, 860, and 725 cm<sup>-1</sup>. Hydrogenation, followed by hydrolysis, afforded cyclooctylmalonic acid.

3. **Treatment with Sodium Borohydride.** The complex IIIa (1.0 g) was dissolved in a mixture of ethanol (20 ml) and dichloromethane (5 ml), and sodium borohydride (0.1 g) was added slowly at room temperature with stirring. After 2 hr, the palladium was removed by filtration, and diethyl cyclooctylmalonate (VII, 0.5 g) was obtained by the usual work-up.

4. **Treatment with Methylsulfinyl Carbanion.** Methylsulfinyl carbanion<sup>11</sup> prepared from sodium hydride (0.4 g) and dimethyl sulfoxide (30 ml) was added dropwise to a solution of complex IIIa

(13) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

(14) P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).

(15) W. U. Jones and D. S. Withey, *J. Chem. Soc.*, 3491(1954).

(16) F. F. Blicke and W. K. Johnson, *J. Am. Pharm. Assoc., Sci. Ed.*, **45**, 443 (1956).

(3.0 g) in dimethyl sulfoxide (20 ml) at room temperature with stirring under nitrogen. The mixture was stirred at room temperature for 2 hr and then warmed at 68° for 30 min. A large excess of water was added, and the solution was repeatedly extracted with ether. The ethereal solution was dried, and the ether was evaporated. The residue was subjected to distillation under reduced pressure (170–175° (bath temperature) (4 mm)) to give 1.0 g of diethyl bicyclo[6.1.0]non-4-ene-9,9-dicarboxylate (VIII). The structural assignment was carried out in the following way: nmr spectrum ( $\tau$ ): 8.79 (6 H, two triplets), 8.22 (6 H, multiplet), 7.87 (4 H, multiplet), 5.87 (4 H, two quartets), and 4.41 (2 H, multiplet). The ester was hydrogenated with palladium on carbon and purified by distillation. The nmr spectrum of the hydrogenated ester showed bands at 8.77 (6 H, two triplets), 8.47 (12 H, multiplet), 8.05 (1 H, multiplet), 7.93 (1 H, multiplet), and 5.88 (4 H, two quartets). The hydrogenated ester (2.0 g) was hydrolyzed by refluxing in 10 ml of 50% ethanol containing potassium hydroxide (4.0 g) for 40 hr. By the usual work-up of the hydrolyzed product, 1.0 g of bicyclo[6.1.0]nonane-9,9-dicarboxylic acid was obtained and recrystallized from ethyl acetate–hexane mixture, mp 208–209°, undepressed with an authentic sample. The authentic sample was prepared by the reaction of ethyl diazomalonnate with cyclooctene and hydrolysis by following the reported synthetic method of norcarenedicarboxylate.<sup>17</sup> *Anal.* Calcd for  $C_{11}H_{16}O_4$ : C, 62.31; H, 7.61. Found: C, 62.50; H, 7.55. The ir spectrum showed bands at 2980, 2920, 2840, 1715, 1690, 1465, 1425, 1325, 1285, 1235, 1220, 1180, 1110, 1090, 1065, 980, 930, 780, 750, 730, and 670  $cm^{-1}$ . The dicarboxylic acid (600 mg) was placed in glass tubing and heated in an oil bath kept at 230° for 10 min. After the decarboxylation, the solid in the glass tubing was recrystallized from an ethyl acetate–hexane mixture to give bicyclo[6.1.0]nonane-9-carboxylic acid (470 mg), mp 110–112°.

**5. Reaction of the Complex III with Malonate or Ethyl Acetoacetate.** The complex IIIa (2.0 g) was dissolved in a mixture of ethanol (10 ml) and dimethyl sulfoxide (30 ml). Also a solution of ethyl malonate (0.9 g) and sodium (0.15 g) in ethanol (10 ml) and dimethyl sulfoxide (10 ml) was prepared. The latter was added dropwise to the former, and the mixture was stirred at room temperature for 1 hr and then warmed at 65° for 1 hr. Separated palladium was removed by filtration and most of ethanol was evaporated. A large amount of water was added, and the solution was extracted repeatedly with ether. The ethereal solution was dried and evaporated. The residue was distilled under reduced pressure to give 0.7 g of tetraethyl bicyclo[3.3.0]octane-2,6-dimalonate (IX, 200–220° (3 mm)). The oil crystallized on standing, mp 38–39°. The nmr spectrum ( $\tau$ ) showed peaks at 8.75 (12 H, triplet), 8.0–9.0 (8 H, multiplet), 7.40 (4 H, multiplet), 6.80 (2 H, doublet), and 5.86 (8 H, quartet). The corresponding tetramethyl ester had mp 113–114° (needles from methanol). *Anal.* Calcd for  $C_{18}H_{26}O_8$ : C, 58.34; H, 7.08. Found: C, 58.44; H, 7.06. Spectral analyses gave the following results: nmr spectrum ( $\tau$ ): 8.0–9.0 (8 H, multiplet), 7.40 (4 H, multiplet), 6.67 (2 H, doublet), and 6.25 (12 H, singlet); ir spectrum: 2960, 2850, 1750, 1450, 1380, 1310, 1290, 1255, 1225, 1200, 1155, 1075, 1050, 1015, 995, 970, 915, 885, and 705  $cm^{-1}$ . Similarly, the reaction of complex IIIb with ethyl acetoacetate produced 2-dimethoxycarbonylmethyl-6-acetyl-(ethoxycarbonyl)methylbicyclo[3.3.0]octane (220–230° (2 mm)). *Anal.* Calcd for  $C_{19}H_{28}O_7$ : C, 61.94; H, 7.66. Found: C, 62.20; H, 7.61. Spectral results were as follows: nmr spectrum ( $\tau$ ): 8.77 (3 H, triplet), 8.1–9.1 (8 H, multiplet), 7.88 (3 H, singlet), 7.50

(4 H, multiplet), 6.80 (1 H, doublet), 6.72 (1 H, doublet), 6.39 (6 H, singlet), and 5.93 (2 H, quartet); ir spectrum: 2955, 2880, 1750, 1730, 1710, 1455, 1360, 1315, 1270, 1200, 1150, and 1025  $cm^{-1}$ .

**Decomposition Reaction of the Complex I with Malonate. 1. Treatment with an Excess of Methylsulfinyl Carbanion.** The complex Ia (5.7 g) was dissolved in dimethyl sulfoxide (30 ml), and a solution of ethyl malonate (3.2 g) and sodium hydride (0.5 g) in dimethyl sulfoxide (30 ml) was added slowly at room temperature with stirring under nitrogen. After 1 hr, methylsulfinyl carbanion prepared by the reaction of sodium hydride (0.5 g) and dimethyl sulfoxide (100 ml) was added. The mixture was stirred at room temperature for 3 hr and then warmed at 68° for 1 hr. After removing most of the dimethyl sulfoxide, a large amount of water was added to the residue, and the solution was extracted with ether. The ethereal solution was dried, and the ether was evaporated. The residue was distilled to yield diethyl bicyclo[6.1.0]nonane-9,9-dicarboxylate (VIII, 2.8 g) and a small amount of diethyl 3,5-cyclooctadienylmalonate (V).

**2. Treatment with an Excess of Malonate.** The complex Ia (2.8 g) was dissolved in dimethyl sulfoxide (30 ml) and a solution of ethyl malonate (3.2 g) and sodium hydride (0.48 g) in dimethyl sulfoxide (20 ml) was prepared. The latter solution was added dropwise to the former at room temperature with stirring under nitrogen. The mixture was stirred at room temperature for 1 hr and then warmed at 68° for 1 hr. After the usual work-up, tetraethyl bicyclo[3.3.0]octane-2,6-dimalonate (IX, 1.6 g) and diethyl bicyclo[6.1.0]nonane-9,9-dicarboxylate (VIII, 0.6 g) were obtained as the main products.

**Reaction of the Complex XII with Malonate.** A mixture of the complex XII (1.0 g), ethyl malonate (5 ml), anhydrous sodium carbonate (3.0 g), and ethyl ether (5 ml) was stirred at room temperature for 20 hr. The reaction mixture was filtered and washed with water and ether. The complex obtained was recrystallized from ethyl acetate to give 0.8 g of yellow crystals, mp 175–177° dec. *Anal.* Calcd for  $C_{33}H_{31}O_4PdCl$ : C, 63.91; H, 4.75; Cl, 5.39; ash, 16.2. Found: C, 63.77; H, 4.81; Cl, 5.27; ash, 17.5. The ir spectrum showed bands at 3060, 2990, 1760, 1730, 1600, 1500, 1445, 1370, 1310, 1250, 1215, 1195, 1150, 1030, 775, 765, and 700  $cm^{-1}$ . The corresponding methyl ester complex showed mp 165–168° dec (from a chloroform–ether mixture). *Anal.* Calcd for  $C_{33}H_{27}O_4PdCl$ : C, 62.91; H, 4.32; Cl, 5.63; ash, 16.9. Found: C, 63.05; H, 4.46; Cl, 5.57; ash, 16.7. Spectral results were as follows: ir spectrum: 3050, 3030, 2960, 1760, 1740, 1600, 1580, 1500, 1440, 1370, 1320, 1240, 1205, 1160, 1075, 1030, 780, 770, 750, and 700  $cm^{-1}$ ; nmr spectrum ( $\tau$ ): 6.62 (12 H, singlet), 6.01 (2 H, two singlets (superposed)), and 2.1–3.0 (40 H, multiplet). The ultraviolet spectrum is shown in Figure 2.

Although very satisfactory analysis of the acetylacetone complex similarly prepared was not obtained, it is clear that one molecule of acetylacetone and one molecule of tetraphenylcyclobutadiene are present per palladium or chlorine atom.

**Preparation of the Complex XV.** A mixture of dicyclopentadienepalladium chloride complex (1.0 g) and anhydrous sodium carbonate (2.0 g) in an acetone (10 ml)–ether (5 ml) mixture was stirred at room temperature for 24 hr. The complex was collected by filtration, washed with water and ether, and dried in a desiccator. Crystallization from a mixture of chloroform–ether gave yellow crystals. *Anal.* Calcd for  $C_{10}H_{11}PdCl$ : C, 43.99; H, 4.06; Pd, 38.97; Cl, 12.99. Found: C, 42.29; H, 4.40; Pd, 40.8; Cl, 14.32. The ir spectrum showed bands at 2970, 2900, 1450, 1375, 1340, 1320, 1295, 1280, 1265, 1235, 1195, 1150, 1110, 1065, 1040, 1015, 1005, 985, 975, 960, 920, 840, 780, 750, and 705  $cm^{-1}$ .

(17) H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).