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Rhodium Tolane Complex and Cyclotrimerization of Substituted Acetylenes Catalyzed by Transition Metal Complexes

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Cyclotrimerization of tolane and phenylacetylene has been studied from the viewpoint of the reaction intermediates and the composition of reaction products. $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ have been found to catalyze the trimerization of tolane and phenylacetylene to yield some substituted benzenes. By the reaction of $Rh_4(CO)_{12}$ with tolane, an unknown complex was obtained. The triphenyl phosphine derivative of this complex has been determined to be $Rh_2(CO)_3(C_6H_5C\equiv CC_6H_5)_2P(C_6H_5)_3$. From infrared spectroscopic study, it was concluded that the two tolane molecules in the complex are connected to rhodium atoms separately without completion of dimerization. On the basis of the ratio of 1,2,4-triphenylbenzene to 1,3,5-triphenylbenzene, the reaction course of trimerization is discussed.

Trimerization of acetylenes using transition metal catalysts has been studied by many investigators. Hübel and Krüerk[1] have described the cobalt complex in which three substituted acetylenes are involved. Hagihara and his coworker[2] have suggested a *cis*-butadiene type structure as an intermediate complex of cyclotrimerization reaction. However, evidence for the proposed structure of these intermediates does not seem to be conclusive. There remains the question whether acetylene completed trimerization in the complex or during the course of leaving the metal.

Rhodium Tolane Complex. Several rhodium complexes having acetylene as a ligand were obtained by the reaction of $Rh_4(CO)_{12}$ with acetylene in *n*-hexane. However, they were unstable even at low temperature and rapidly decomposed to give benzene. In order to obtain the stable complex, the reaction of $Rh_4(CO)_{12}$ with tolane was carried out at 50°C in *n*-hexane.

At the first stage of the reaction, the infrared spectrum of the solution (Fig. 1-I) was very similar to that of $CH\equiv CHCo_4(CO)_{10}$[1] (Fig. 2), and the formed complex is considered to be $(C_6H_5C\equiv CC_6H_5)$

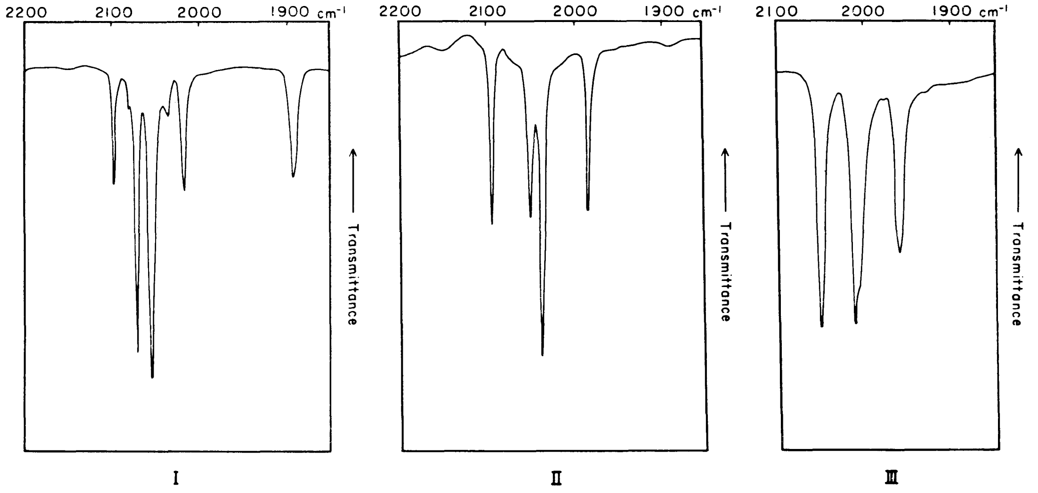

Fig. 1. Infrared spectra of reaction mixture: $Rh_4(CO)_{12}$ and tolane in *n*-hexane.

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[1] U. Krüerk und W. Hübel, *Chem. Ber.*, **95**, 2829 (1961).

[2] H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, 22 (1967).

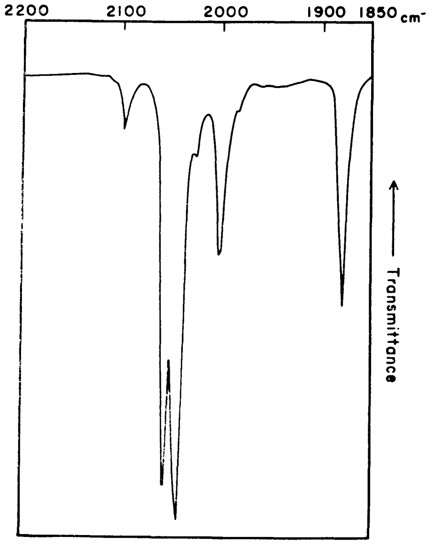

Fig. 2. Infrared spectrum of $CH\equiv CHCo_4(CO)_{10}$.

$Rh_4(CO)_{10}$.

After a while, the absorption due to the bridging carbonyls of the complex vanished (Fig. 1-II). When the reaction continued further at 50°C, the precipitation of hexaphenylbenzene was observed in the reaction vessel. Since the complex was too unstable to be isolated, it was transformed into a triphenylphosphine substituted complex. The same complex was also obtained from the reaction using aromatic solvents, although they show different powder X-ray patterns. When the formed complex was accompanied by some aromatic solvents such as benzene, toluene, *etc.*, the complex was washed by *n*-hexane, and recrystallized from ether. Thus, red-brown prisms decomposing at 115°C, were obtained.

The 100 MHz NMR spectrum of the complex shows the signals of triphenylphosphine protons[3] and tolane protons at separate positions in a perchloroethylene solution. The ratio of triphenylphos phine to tolane in the complex was then determined by the integration of spectrum. Molecular weight measurement failed because of decomposition. In the infrared spectrum of the complex, three strong bands at 2052.0, 2013.0 and 1954.5cm⁻¹ were observed in terminal carbonyl stretching region (Fig. 1-III). The above-described spectroscopic data and elemental analysis are coincident with the molecular formula $Rh_2(CO)_3P(C_6H_5)_3(C_6H_5C\equiv CC_6H_5)_2$.

The course of the reaction may be expressed by the following equation :

$$Rh_4(CO)_{12} + C_6H_5C\equiv CC_6H_5 \rightarrow (C_6H_5C\equiv CC_6H_5)Rh_4(CO)_{10} + 2CO$$

$$(C_6H_5C\equiv CC_6H_5)Rh_4(CO)_{10} + 3C_6H_5C\equiv CC_6H_5 \rightarrow 2Rh_2(CO)_4(C_6H_5C\equiv CC_6H_5)_2 + 2CO$$

$$Rh_2(CO)_4(C_6H_5C\equiv CC_6H_5)_2 + P(C_6H_5)_3 \rightarrow Rh_2(CO)_3P(C_6H_5)_3(C_6H_5C\equiv CC_6H_5)_2 + CO$$

Infrared Spectra of the Coordinated Tolane. In order to separate the infrared absorption bands due to tolane from those due to triphenylphosphine moiety, the perdeuterio triphenylphosphine $P(C_6D_5)_3$[4] substituted complex was prepared. Assignment of the infrared spectrum was done on the basis of a comparison with its deuterated compound (Table 1). In the region between 1600 cm⁻¹ and 800 cm⁻¹, the bands attributed to the coordinated tolane have positions and intensities similar to those of free tolane molecule.

TABLE 1. VIBRATIONAL FREQUENCIES AND ASSIGNMENT OF $(C_6H_5C\equiv CC_6H_5)_2Rh_2(CO)_3\cdot P(C_6H_5)_3$

2052.0	v.s	C≡O		849	w	P	
2013.0	v.s	C≡O		803	w	N	
2007	sh			754	m	T	
1953.5	v.s	C≡O		749	m	P	
1598	v.w	T		729	s	N	
1591	w	P		702	s	P	
1570	w	P		699	sh	T	
1565	v.w	T		646	w	N	
1490	v.w	T		636	w	N	
1479	m	P		622	w	P	
1438	m	P	T	610	w	N	
1320	w	P		574	m	N	
1310	w	P	T	567	s	N	
1280	v.w	P	T	540	w	P	T
1186	m	P	T	520	s	P	
1159	w	P	T	507	m	T	
1118	w	N		501	m	P	
1089	m	P		483.0	w	N	
1071	m	P		469.0	w	T	
1028	m	P	T	444.0	w	P	
1000	m	P		430.0	w	P	
878	w	N					

N : The bands could not be assigned to tolane or triphenylphosphine. T : $C_6H_5C\equiv CC_6H_5$, P : $P(C_6H_5)_3$, v.s : very strong, s : strong, m : medium, w : weak, v.w : very weak, sh : shoulder

If the two coordinated tolane molecules take the form of *cis*-butadiene, the change of intensities and positions of absorptions should be observed.[5] Therefore, the two tolane molecules must be connected with the rhodium atoms independently. Several bands in far-infrared region which could not be assigned to tolane or triphenylphosphine may be due to rhodium-tolane[4] stretching, rhodium-(C≡O) stretching and Rh-(C≡O) bending vibrations. The

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[3] Y. Iwashita, F. Tamura and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

[4] Y. Iwashita and A. Hayata, *J. Amer. Chem. Soc.*, **91**, 2525 (1969).

[5] W. Keim, *J. Organometal. Chem.*, **16**, 191 (1969).

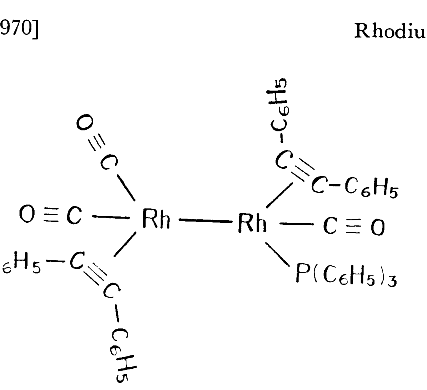


Fig. 3. The proposed structure of $(C_6H_5C\equiv CC_6H_5)_2Rh_2(CO)_3P(C_6H_5)_3$.

proposed structure of the complex is illustrated in Fig. 3.

Cyclotrimerization of Phenylacetylene. The $Rh_4(CO)_{12}$ or $Co_4(CO)_{12}$ catalyzed cyclotrimerization reaction of phenylacetylene was carried out in a benzene solution at 60°C. The products were identified by IR, E.A. and molecular weight measurements. The ratio of 1,2,4-triphenylbenzene to 1,3,5-triphenylbenzene was determined by gas chromatography. The results are given in Table 2. When $Co_4(CO)_{12}$ was used as a catalyst, the product was almost composed of 1,2,4-triphenylbenzene and when $Rh_4(CO)_{12}$ was used as a catalyst, the amount of 1,2,4-triphenylbenzene was twice as much as that of 1,3,5-triphenylbenzene.

In a transition state, three *cis*-butadiene type intermediates may be assumed (Fig. 4). Form III seems to be the most stable because of the lack of steric repulsion between phenyl groups and the metal carbonyl moiety. If the structure of the intermediate is supposed to be form III, the subsequent reaction to a phenylacetylene molecule should give 1,2,4-triphenylbenzene. In the $Rh_4(CO)_{12}$ catalyzed reaction, since rhodium atom has a larger covalent bond radii[6] than that of cobalt atom, the contribution of form II, which gives 1,3,5-triphenylbenzene, might be larger.

When the infrared spectra of the solution indicate the existence of $C_6H_5C\equiv CCHCo_4(CO)_{10}$ type complex only, half of triphenylbenzene is formed as a result of cyclotrimerization.

This means that not only $(C_6H_5C\equiv CH)_2M_2(CO)_4$ (M = Co or Rh) but also $(C_6H_5C\equiv CH)M_4(CO)_{10}$ has catalytic activity. Therefore these complexes must be transformed into *cis*-butadiene type structure in the transition state.

Experimental

Rhodium Tolane Complex. To a solution (50 m*l*) of $Rh_4(CO)_{12}$ (108 mg) in *n*-hexane, tolane (103 mg) was added and warmed at 50°C for 5 hr and then $P(C_6H_5)_3$ (62 mg) was added. The reaction product was chromatographed on alumina. From the eluted solution, red-brown prisms were obtained; yield 38%, mp 115°C (decomposed).

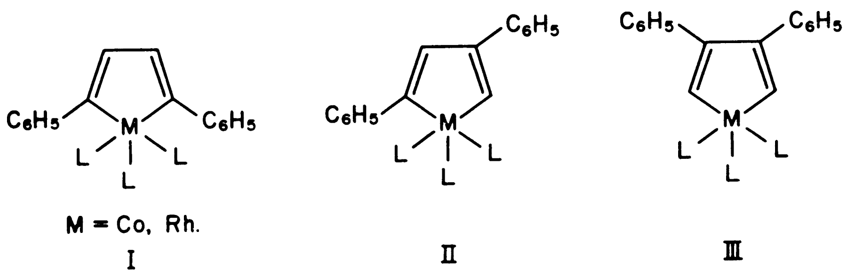
Found: C, 64.98; H, 4.36; Rh, 22.7%. Calcd for $C_{49}H_{35}O_3Rh_2P$: C, 64.77; H, 3.89; Rh, 22.65%.

The NMR spectrum was measured with a Varian HA-100 spectrometer in a tetrachloroethylene solution.

TABLE 2. CYCLOTRIMERIZATION OF PHENYLACETYLENE

Catalyst	$C_6H_5C\equiv CH$(mM) / Catalyst(mM)	1,2,4-TPB* (mM)	1,3,5-TPB (mM)	Total** yield	1,2,4-TPB / 1,3,5-TPB
$Rh_4(CO)_{12}$	0.675/0.019=35.5	0.066	0.032	43%	2.2
	1.349/0.018=74.9	0.123	0.050	38%	2.4
$Co_4(CO)_{12}$	1.22/0.034=35.9	0.056	0.008	16%	7.0
	2.44/0.034=71.8	0.079	0.009	11%	8.9

* 1,2,4-Triphenylbenzene.
** Total yield for used phenylacetylene.



I II III

Fig. 4. The possible intermediates of cyclotrimerization.

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[6] L. Pauling, " The Nature of the Chemical Bonds," 3rd Ed., Cornell University Press, Ithaca, New York (1960).

TMS was used as an internal reference. The multiplet at 725 Hz was assigned to phenyl protons of $P(C_6H_5)_3$ and the multiplet at 676 Hz was assigned to phenyl protons of tolane, respectively. Integration of the spectrum showed that this complex contained one $P(C_6H_5)_3$ and two tolane molecules.

The infrared spectra were measured with a Hitachi-225 spectrometer as paste and KBr pellets. The absorption was corrected by the known absorption of standard polystyrene film.

Cyclotrimerization of Tolane. A 200 m*l* Schlenk tube was charged with 130 mg of $Rh_4(CO)_{12}$, 620 mg of tolane and 100 m*l* of degassed benzene, and then heated to 60°C for 10 hr. The reaction mixture was chromatographed on alumina, and the eluted solution was condensed to dryness. The product was recrystallized by methanol and identified by means of IR spectrum. (Yield 28%)

Cyclotrimerization of Phenylacetylene. The reaction was carried out in a Schlenk tube under a nitrogen stream at 60°C, for 4 hr. The ratio of 1,2,4-triphenylbenzene to 1,3,5-triphenylbenzene was determined with a Shimadzu GC-2 gas chromatograph, operated with a 3.0 m column packed with 4% OV-1 coated on Diatoport at 245°C.

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