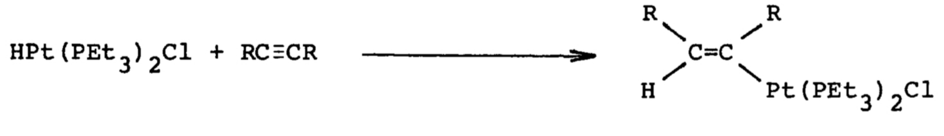
CHEMISTRY LETTERS, pp. 1351-1354, 1977. Published by the Chemical Society of Japan

REACTION OF ORGANOMETALLIC COMPOUNDS UNDER HIGH PRESSURE. I. THE EFFECT OF PRESSURE ON THE INSERTION REACTIONS OF ALKYNES INTO *trans*-CHLOROHYDRIDO-BIS(TRIETHYLPHOSPHINE)PLATINUM(II)

Takashi JOH and Nobue HAGIHARA
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka 565

The influence of pressure on the insertion reactions of alkynes into *trans*-chlorohydrido-bis(triethylphosphine)platinum(II) was investigated under high pressures up to 10,000 kg/cm^2. It was found that the insertion reactions of alkynes into H-Pt(II) bond were generally accelerated with increasing pressure and the influence of pressure was remarkable in the reactions which proceeded via an ionic intermediate. In some cases change of reaction mechanisms by the pressure changes was observed.

It has recently been shown by several workers$^{1,2)}$ that the use of very high pressures is valuable for synthetic organic chemistry. We have undertaken to investigate the reactions of organo-transition-metal compounds under high pressures up to 10,000 kg/cm^2. We would like to report here on the effects of pressure observed in the insertion reactions of alkynes into *trans*-chlorohydrido-bis(triethylphosphine)platinum(II).



(1)

The following is a typical procedure for reactions under high pressure. In an appropriate solvent *trans*-chlorohydrido-bis(triethylphosphine)platinum(II) (1 mole equiv.) and alkyne(2 mole equiv.) were dissolved. The capsule was filled with the solution under nitrogen atmosphere. The cylindrical capsule was made of Teflon (1.6 cm i.d., 3 cm long) with a snug-fitting lid. The capsule was placed in a 2 cm diameter hole in a special tungsten carbide cylinder and was compressed with tungsten carbide piston by 200 ton press. Reaction pressure was calibrated by use of phase-transition point of ammonium fluoride. Reaction temperature was controlled by an external heating bath. The yields of products were determined by measurement of the intensity of ν_{Pt-H}, $\nu_{C=O}$, and $\nu_{C=C}$ in the reaction mixture.

Firstly we examined the effect of pressure in the reaction of methyl phenyl acetylene and *trans*-chlorohydrido-bis(triethylphosphine)platinum(II) in methanol under various pressures. This reaction has been reported to take place under atmospheric pressure.[3)] The result is shown in Fig. 1. The reaction was linearly accelerated with increasing pressure and the reaction rate at 5,000 kg/cm^2 pressure was about 10 times faster than that at atmospheric pressure. When acetone or toluene was used as solvent, the reaction did not proceed even at 10,000 kg/cm^2 pressure as well as at atmospheric pressure.

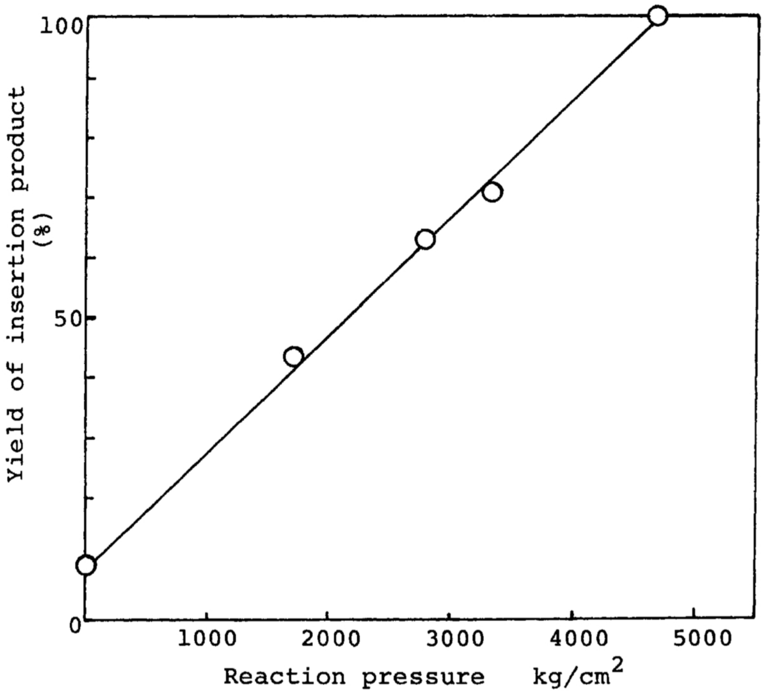


Fig. 1. The pressure effect on the reaction of *trans*-HPt(PEt$_3$)$_2$Cl and CH$_3$C≡CPh in MeOH.
HPt(PEt$_3$)$_2$Cl, 0.05 mmole; CH$_3$C≡CPh, 0.1 mmole; MeOH, 4 ml; reaction temp., 24°C; reaction time, 1 hr.

The results obtained in the reactions of *trans*-chlorohydrido-bis(triethylphosphine)platinum and dimethyl acetylenedicarboxylate in various solvents are shown in Fig. 2. Although the reaction was greatly accelerated in methylene chloride with increasing pressure, the influence of pressure was not so remarkable

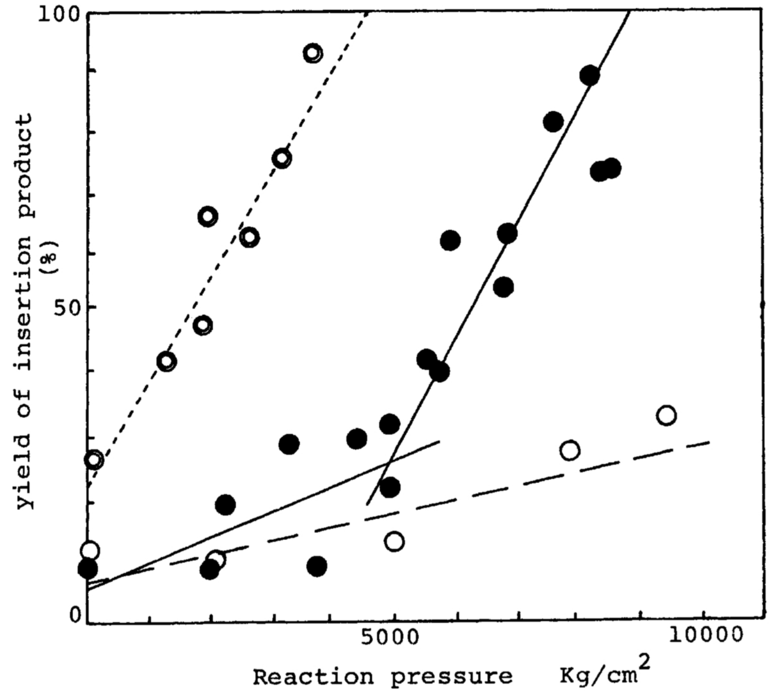
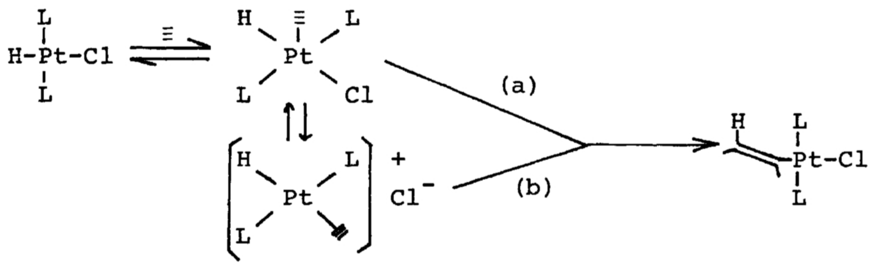


Fig. 2. The effect of pressure on the reaction of *trans*-$HPt(PEt_3)_2Cl$ and $CH_3O_2CC{\equiv}CCO_2CH_3$. $HPt(PEt_3)_2Cl$, 0.05 mmole; $CH_3O_2CC{\equiv}CCO_2CH_3$, 0.1 mmole; solv., 4 ml.

--------- CH_2Cl_2(15°C, 1hr)
———— toluene(25°C, 2hr)
— — — hexane(30°C, 2hr)

in the reaction in hexane solution. This suggests that these two reactions would proceed via different mechanistic pathways. H. C. Clark *et al*[3)] pointed out the insertion reactions of unsaturated compounds into hydrido-platinum complexes can proceed at least via two different mechanistic pathways (a and b) depending on reaction conditions (eq. 2).



(2)

It is considered that our results may correspond to this situation. When the reaction is carried out in hexane , the reaction would proceed via direct insertion process (a), while the reaction would proceed through an ionic intermediate in a polar solvent such as methylene chloride. It is reasonable that the influence of pressure is remarkable in the reaction which proceeds via an ionic process, because it is well known that reactions in which the transition state is more highly ionic, and hence more extensively solvated, than the initial state are greatly accelerated by pressure4).

It was also observed that the reaction in toluene was gradually accelerated with increasing pressure up to about 5,000 kg/cm^2 and was greatly accelerated with increasing pressure over the pressure of 5,000 kg/cm^2. This suggests that the change of reaction mechanisms would take place with increasing pressure.

Further investigations are now in progress.

References

1) D. Bieniek and F. Korte, Naturwissenschaften, 59, 529 (1972).
2) W. G. Dauben and H. O. Krabbenhoft, J. Amer. Chem. Soc., 98, 1992 (1976).
3) H. C. Clark, C. R. Jablonski and C. S. Wong, Inorg. Chem., 14, 1332 (1975), and references cited therein.
4) J. Buchanan and S. D. Hamann, Trans. Faraday Soc., 49, 425 (1953).

(Received September 10, 1977)