

Preliminary communication

Interaction of silanes with bis(triphenylphosphine)ethyleneplatinum(0); Hydrosilylation of olefins with this complex

KEIJI YAMAMOTO, TAMIO HAYASHI and MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)
(Received December 31st, 1970; in revised form March 1st, 1971)

Various silanes react with phosphine complexes of nickel¹, palladium^{2,3}, and platinum⁴, which have been found to be effective catalysts for the hydrosilylation of olefins.

Current interest in facile oxidative additions of simple molecules to bis(triphenylphosphine)ethyleneplatinum(0)⁵, $[\text{PtL}_2(\text{C}_2\text{H}_4)]$ (L = PPh_3 throughout this paper), prompted us to study the reaction of this complex with various silanes, as well as its effectiveness as hydrosilylation catalyst of olefins.

Reaction of 1-hexene with MeCl_2SiH in the presence of $[\text{PtL}_2(\text{C}_2\text{H}_4)]$ as catalyst gave $n\text{-C}_6\text{H}_{13}\text{SiMeCl}_2$ in almost quantitative yield. With a sufficient amount of the complex (100–200 mg), fine white crystals were formed from the reaction mixture, and these were found to be $[\text{PtH}(\text{SiMeCl}_2)_2\text{L}_2]$ (probably *cis*) (70% yield), m.p. 210–215°; IR (KBr): 2110 m ($\nu(\text{Pt}-\text{H})$), 1240 m ($\delta(\text{Si}-\text{CH}_3)$), 790 m and 775 m ($\delta(\text{Pt}-\text{H})/\delta(\text{Si}-\text{CH}_3)$), and 450 m ($\nu(\text{Pt}-\text{P})$, doublet). This hydridosilylplatinum(II) complex was too insoluble for its configuration to be assigned beyond doubt by NMR. Recently, several hydridosilylplatinum(II) complexes of the formula $\{\text{PtH}[\text{Si}(\text{C}_6\text{H}_4\text{X})_3]_2\text{L}_2\}$ (X = *m*- and *p*-F or CF_3) have been prepared by Chatt, Eaborn and Kapoor⁶ using $[\text{PtL}_4]$.

Under our conditions but without 1-hexene, another platinum complex was formed and this was identified as $[\text{Pt}(\text{SiMeCl}_2)_2\text{L}_2]$ (probably *cis*) (50% yield), m.p. 200–210°; IR (KBr): 1240 m ($\delta(\text{Si}-\text{CH}_3)$), 800 m ($\delta(\text{Si}-\text{CH}_3)$, doublet), and 450 m ($\nu(\text{Pt}-\text{P})$). The complex was sparingly soluble in benzene and gave a poor NMR spectrum; it was very unstable in CHCl_3 and CH_2Cl_2 .

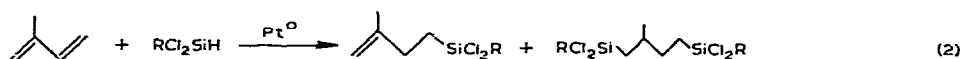
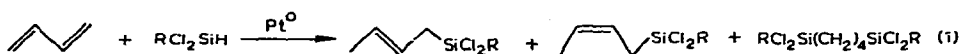
When HSiCl_3 was used instead of MeCl_2SiH , the last-mentioned type of complex, *i.e.*, $[\text{Pt}(\text{SiCl}_3)_2\text{L}_2]$ was the only product, regardless of whether 1-hexene was present or not. This complex has been obtained by treatment of $[\text{PtL}_4]$ with HSiCl_3 at 35°⁶. It is likely that HSiCl_3 is so reactive towards the intermediate hydridosilylplatinum(II) that it readily gives the observed $[\text{Pt}(\text{SiCl}_3)_2\text{L}_2]$.

In cases where $(\text{EtO})_2\text{MeSiH}$, Me_2ClSiH , Me_3SiH , or Me_2EtSiH were used, hydrosilylation of simple olefins such as 1-hexene and $\text{Me}_3\text{SiCH}=\text{CH}_2$ was effectively catalyzed by $[\text{PtL}_2(\text{C}_2\text{H}_4)]$. However, with these silanes, the platinum(0) complex was immediately converted into red-brown crystals which were very soluble in benzene, and analyzed as $[\text{PtL} \cdot \text{C}_6\text{H}_6]_x$, m.p. > 280°. Although this complex cannot be fully characterized at present,

a cluster structure of Pt^0 complex may be suggested. Gillard *et al.*⁷ have briefly described the preparation of $[\text{PtL}]_4$ and $[\text{PtL}_2]_3$.

On the basis of these observations, it can be said that the order of the stabilities of the silylplatinum complexes formed by treatment of $[\text{PtL}_2(\text{C}_2\text{H}_4)]$ with silanes is the same ($\text{SiCl}_3 > \text{SiMeCl}_2 > \text{SiMe}_3$) as that observed for the adducts of silanes to $[\text{RhClL}_3]^{8,9}$.

Another important feature of the present catalyst became evident when conjugated dienes were used as substrates for hydrosilylation (eqn. 1 and 2). Of interest are the facts that in the case of isoprene the only mono-adduct formed was the 1,2-addition product, and that even when excess diene was present the di-adduct was also obtained in considerable amounts.



As $[\text{PtL}_2(\text{C}_2\text{H}_4)]$ cannot catalyze the addition of silanes to inner olefins such as 2-hexene and cycloolefins at least at 80° , and as isomerization of 1-hexene to 2-isomers is slow under the conditions used, the absence of the 1,4-adduct of isoprene may be ascribed to a less favorable reaction of the conjugated diene with the platinum catalyst than that of simple olefins. This may also account for the favored di-adduct formation. Phosphine complexes of nickel^{1a} and palladium³ catalyze 1,4-addition of silanes to isoprene, which fact suggests the intervention of π -allylic metal intermediates. Such π -allylic platinum complexes are known to be rather unusual.

REFERENCES

- 1 M. Kumada, Y. Kiso and M. Umeno, *Chem. Commun.*, (1970) 611.
- 1a Y. Kiso, K. Sumitani, K. Maeda, K. Tamao and M. Kumada, *Symposium on Organometallic Compounds, Kiryu, Japan, 1970; Abstr.*, p. 154.
- 2 S. Takahashi, T. Shibano and N. Hagihara, *Chem. Commun.*, (1969) 161.
- 3 M. Hara, K. Ohno and J. Tsuji, *Symposium on Organometallic Compounds, Kiryu, Japan, 1970; Abstr.*, p. 164.
- 4 K. Yamamoto, H. Okinoshima and M. Kumada, to be published.
- 5 C.D. Cook and G.S. Jauhal, *J. Amer. Chem. Soc.*, 90 (1968) 1464.
- 6 J. Chatt, C. Eaborn and P.N. Kapoor, *J. Organometal. Chem.*, 13 (1968) P21; *J. Chem. Soc. (A)*, (1970) 881.
- 7 P.D. Gillard, R. Ugo, F. Cariati, S. Cenini and F. Bonati, *Chem. Commun.*, (1966) 869.
- 8 F. de Charentenay, J.A. Osborn and G. Wilkinson, *J. Chem. Soc. (A)*, (1968) 787.
- 9 R.N. Haszeldine, R.V. Parish and D.J. Parry, *J. Organometal. Chem.*, 9 (1967) P31; *J. Chem. Soc. (A)*, (1969) 683.