# Nickel(II) Complexes as Catalysts in the Hydrosilylation of Olefins

By M. KUMADA,* Y. KISO, and M. UMENO

*(Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan)*

*Summary* Nickel(II) chlorides complexed with a ditertiary phosphine catalyse not only the addition of silicon hydrides to olefins but also the interchange of hydrogen and chlorine on silicon.

DESPITE a vast number of publications concerning the hydrosilylation of olefins catalysed by platinum or its derivatives,[1] very little interest has been shown in nickel and its compounds as catalysts. To our knowledge, only two papers using nickel catalysts have been published previously; one concerns the addition of trichlorosilane to acrylonitrile catalysed by Raney nickel,[2] and the other deals with the same reaction in the presence of nickel chloride.[3] We now report that certain nickel(II) complexes with a ditertiary phosphine ligand are very effective as hydrosilylation catalysts and also quite unique in that they catalyse an interchange of hydrogen and chlorine on silicon during the course of the reaction.

A mixture of oct-1-ene (1 mole), methyldichlorosilane (2 moles), and dichloro[1,1′-bis(dimethylphosphino)ferrocene]nickel(II) [Ni(dmpf)$Cl_2$] ($10^{-3}$ mole) was placed in a glass tube. It was degassed with cooling in a liquid-nitrogen bath, sealed and heated at 120° for 20 hr. G.l.c. analysis of the reaction mixture showed that two products were formed, one being the expected octylmethyldichlorosilane (16% yield), another being the unexpected octylmethylchlorosilane (79% yield) which arose from an interchange of hydrogen and chlorine on silicon. The latter compound was isolated and characterized by elemental analysis and i.r. (2160 cm$^{-1}$, Si–H stretching). Some other terminal olefins reacted similarly (see Table).

With trichlorosilane, the extent of the hydrogen–chlorine interchange was lower than with methyldichlorosilane. Thus, the reaction of trichlorosilane (2 moles) with oct-1-ene (1 mole) under the same conditions as above gave octyldichlorosilane and octyltrichlorosilane, both in 50% yield. Trimethylsilane did not add to oct-1-ene at all with this catalyst.

*Addition of methyldichlorosilane to terminal olefins* ($C_nH_{2n}$) *catalysed by* Ni(dmpf)$Cl_2$[a]

| | Yield (%) | |
|---|---|---|
| $C_nH_{2n}$ | $C_nH_{2n+1}SiMeClH$ | $C_nH_{2n+1}SiMeCl_2$ |
| $n = 5$ | 80 | 18 |
| 6 | 87 | 18 |
| 7 | 55 | 28 |
| 8 | 79 | 16 |

[a] $HSiMeCl_2$ : olefin = 2; catalyst : olefin = $10^{-3}$; 120°, 20 hr.

The hydrogen–chlorine interchange accompanying hydrosilylation takes place also with cyclic olefins. Thus, the reaction of cyclo-octa-1,5-diene with methyldichlorosilane in the presence of Ni(dmpf)$Cl_2$ yielded (methylchlorosilyl)-cyclo-octene and (methyldichlorosilyl)cyclo-octene, each being a mixture of the three possible isomers.

Besides Ni(dmpf)$Cl_2$, other dichloro(ditertiary phosphine)-nickel(II) complexes, such as $Ni(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)Cl_2$ and $Ni(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)Cl_2$, also proved to be very effective catalysts for both hydrosilylation and hydrogen–chlorine interchange reactions, with the catalytic activity decreasing in this order. Nickel complexes with monodentate phosphines such as $Ni(PPh_3)_2Cl_2$ and those with amines such as $Ni(Me_2N{\cdot}CH_2{\cdot}CH_2NMe_2)Cl_2$ and Ni(dipy)$Cl_2$ were practically ineffective.

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[1] For a leading review, see C. Eaborn and R. W. Bott, in "Organometallic Compounds of the Group IV Elements," ed. A. G. MacDiarmid, Dekker, New York, 1968, vol. 1, part 1, ch.2.

[2] A. D. Petrov, V. F. Mironov, V. M. Vdovin, and S. I. Sadykh-Zade, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1956, 256; *Chem. Abs.*, 1956, **50**, 13,726.

[3] S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, 1956, **29**, 326.