

## CATALYSIS BY METAL COMPLEXES. XI.\*

SELECTIVE HYDROSILYLATION OF STYRENE CATALYSED  
BY DI- $\mu$ -CARBONYLDI- $\pi$ -CYCLOPENTADIENYLDINICKEL

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( $\pi$ -C<sub>5</sub>H<sub>5</sub>(CO)Ni)<sub>2</sub> was found to be very effective catalyst for the addition of trichlorosilane to styrene. The reaction proceeds smoothly at room temperature to give exclusively 1-trichlorosilyl-1-phenylethane in a high yield. A mechanism of the reaction is suggested.

Within the framework of a study of selective hydrosilylation of conjugated dienes homogeneously catalysed by group VIII transition metal complexes<sup>1,2</sup> we have also investigated catalytic activity of some nickel complexes, including di- $\mu$ -carbonyldi- $\pi$ -cyclopentadienylnickel<sup>3</sup> (*I*). A comparatively high effectiveness of this complex led us to examine its behaviour in hydrosilylation of styrene. The reaction of this olefin with silicon hydrides is known to proceed with chloroplatinic acid as catalyst non-selectively, yielding a mixture of 1- and 2-silyl-substituted 1-phenylethanes<sup>4</sup>. An increased selectivity of the reaction towards 1-silyl-substituted derivatives, achieved recently by Bennett and Orenski<sup>5</sup> by the use of pyridine and phosphine nickel(II) complexes, was accompanied by slower reaction rates. In a recent report, Kumada and coworkers<sup>6</sup> described selective addition of trichlorosilane to styrene first effected at room temperature. As observed in this laboratory<sup>7</sup>, the catalyst employed, a menthyl-diphenylphosphine palladium(II) complex, is unique in that related phosphine palladium(II) complexes, such as *e.g.* bis(triphenylphosphine)-palladium dichloride, were ineffective under otherwise identical conditions.

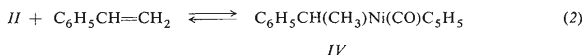
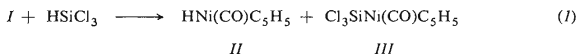
We now report the first example of highly selective hydrosilylation of styrene catalysed by a nickel complex under very mild conditions. Thus, a mixture of trichlorosilane (5 mmol), styrene (5 mmol), and complex *I* ( $5 \cdot 10^{-3}$  mmol) was allowed to stand in a sealed glass ampoule under nitrogen atmosphere at room temperature for 2.5 h, yielding 1-trichlorosilyl-1-phenylethane as a sole reaction product (82% yield, determined by g.l.c.). Similar yields were also obtained on preparative scale in the absence of an inert atmosphere. Methyl-dichlorosilane turned out to be much less reactive. Only slight yield (3%) of an adduct was obtained under the above conditions.

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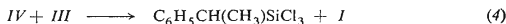
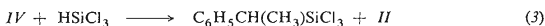
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Concerning mechanism of the reaction, similarities in the structure and chemical behaviour of complex *I* and formally isoelectronic dicobalt octacarbonyl suggested that also hydrosilylations catalysed by both complexes may proceed *via* similar pathways. We made therefore several experiments aimed at verification of this assumption. We found that, contrarily to the  $\text{Co}_2(\text{CO})_8$ -catalysed addition<sup>8</sup>, the course of the reaction is not so strongly dependent on the order in which the reaction components are added. Thus, the same yields were obtained irrespective of whether the silane or styrene were added first to the catalyst over a period of 15 min. Only on longer standing with trichlorosilane in the absence of the olefin (1 h) did complex *I* become ineffective. The decrease in the activity of the catalyst during this period roughly paralleled an increase in the intensity of the  $\nu(\text{CO})$  band at  $2062\text{ cm}^{-1}$ , assigned previously<sup>9</sup> to the silyl complex  $\text{Cl}_3\text{SiNi}(\text{CO})\text{C}_5\text{H}_5$ . The addition of the latter compound, prepared according to Jetz and Graham<sup>9</sup>, to an equimolar mixture of starting compounds induced no reaction. On the other hand, when a mixture of styrene and complex *I* was set aside for 1 h and then an equimolar amount of the silane was added, strongly exothermic reaction took place, which subsided in several minutes, giving almost quantitative yield of the 1-silyl derivative.

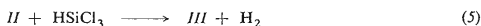
These results, which shed some light on initial phase of the reaction, may be rationalized in terms of a mechanism formally analogous to that proposed by Harrod and Chalk<sup>8,10</sup> for the  $\text{Co}_2(\text{CO})_8$ -catalysed hydrosilylation:



The product may result either from the reaction of complex *IV* with trichlorosilane (Eq. (3)) or from its reaction with complex *III* (Eq. (4)). No evidence in favour of either of these possibilities has so far been obtained in this laboratory *cf.*<sup>10</sup> Other



route to the product, which comprises the addition of complex *III* to the olefin, seems unlikely, as trichlorosilyl nickel complex *III*, formed presumably by reaction (5) in the absence of the olefin, was found to be catalytically inactive.



## EXPERIMENTAL

*Di- $\mu$ -carbonyldi- $\pi$ -cyclopentadienylnickel (I)* was prepared according to Fischer and Palm<sup>11</sup>, m.p. 135–136°C ( $\nu(\text{CO})$  1872 and 1835  $\text{cm}^{-1}$  (solid phase); lit.<sup>12</sup> records  $\nu(\text{CO})$  1879 and 1838  $\text{cm}^{-1}$ ). Styrene (containing less than 0.5% ethylbenzene), trichlorosilane (containing less than 1% tetrachlorosilane), and methylchlorosilane were commercial products. All experiments on millimole scale were performed in sealed glass ampoules under nitrogen (5 mmol of each reactant,  $5 \cdot 10^{-3}$  mmol of the catalyst) and the yields of reaction products were determined by g.l.c. A column (3 m) containing 16% Trifluoro Propyl Methyl Silicone FS 1 (Pye & Co. Ltd., England) on 30–60 mesh Chromosorb W, 190°C oven temperature, 30 ml per min nitrogen flow rate were used. Isomeric 1,2-trichloro- and methylchloro-1-phenylethanes, prepared by published literature procedures, were used as standards.

*Reaction of styrene with trichlorosilane.* To 21.9 g (0.21 mol) of styrene and 61 mg (0.25 mmol) of complex I were added 28.5 g (0.21 mol) of trichlorosilane and the mixture was stirred at room temperature for 3 h. Distillation afforded 41.7 g (0.17 mol, 82.5%) of 1-trichlorosilyl-1-phenylethane, b.p. 98°C/10 Torr. The NMR spectrum (neat): CH proton  $\tau$  7.3 p.p.m. (quartet),  $\text{CH}_3$  protons  $\tau$  8.6 and 8.7 p.p.m., aromatic absorption at  $\tau$  2.6 p.p.m. (hexamethyldisilane used as internal standard).

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