

## Preliminary communication

### Asymmetric hydrosilylation with a chiral phosphine–nickel(II) complex

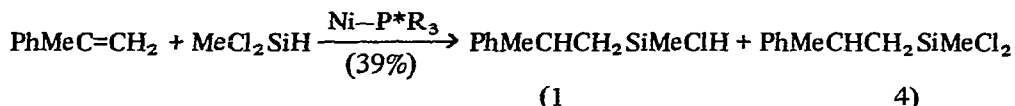
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(Received June 29th, 1971)

Recently we have reported<sup>1</sup> the first example of asymmetric hydrosilylation of  $\alpha$ -methylstyrene catalyzed by *cis*-dichloro(ethylene) [(*R*)-benzylmethylphenylphosphine] platinum(II), which leads to at best a 5% excess one enantiomer in the addition product. In view of the effectiveness of phosphine complexes of nickel as hydrosilylation catalysts<sup>2,3</sup>, it seemed likely that asymmetric addition of a silicon hydride to olefins might be better realized by use of a nickel(II) complex having chiral phosphine ligands.

We now report that the addition of methyldichlorosilane to  $\alpha$ -methylstyrene catalyzed by *trans*-dichlorobis[(*R*)-benzylmethylphenylphosphine] nickel(II) (red-brown crystals, m.p. 132–133° (sealed tube)) yields 2-phenylpropylmethyldichlorosilane with a 17.6% enantiomeric excess of the *R* isomer. A mixture of  $\alpha$ -methylstyrene (5.3 g, 45 mmoles), methyldichlorosilane (5.1 g, 45 mmoles) and the catalyst (10 mg,  $1.8 \times 10^{-2}$  mmole) was heated at 90° in a de-gassed sealed glass tube for 60 h. Fractional distillation gave two products: (i) PhMeCHCH<sub>2</sub>SiMeClH, b.p. 51–52°/0.8 mm (95+% pure), 0.7 g (8% yield),  $[\alpha]_D +6.43^\circ$  (neat) and (ii) PhMeCHCH<sub>2</sub>SiMeCl<sub>2</sub><sup>4</sup>, b.p. 66.0–66.5°/0.6 mm, 3.3 g (31% yield),  $[\alpha]_D +6.50^\circ$  (neat). The latter was methylated to give 2-phenylpropyltrimethylsilane<sup>4</sup>,  $[\alpha]_D +4.10^\circ$  (neat), which was found to be of 17.6% optical purity based on authentic (+)-(*R*)-PhMeCHCH<sub>2</sub>SiMe<sub>3</sub>,  $[\alpha]_D +23.3^\circ$  (neat)<sup>1</sup>.



[P\*R<sub>3</sub> = (+)-(*R*)-(PhCH<sub>2</sub>)MePhP (81% optical purity)]

Clearly use of the nickel complex gives a product of much improved optical purity. Although the exact nature of the catalytically active species is still uncertain, it is likely that the presence of two chiral phosphines in the nickel complex compared with the one in the platinum complex is advantageous.

It is also noteworthy that the two adducts obtained have almost the same degree of rotation, despite the different addends, MeCl<sub>2</sub>SiH and MeClSiH<sub>2</sub>. (The latter

arises from a redistribution of Cl/H on silicon catalyzed by the nickel complex during the course of hydrosilylation<sup>2</sup>.) Since any change in substituents on silicon will have a relatively minor effect on the optical rotation of the resulting structures<sup>5</sup>, the optical yields of the two products must be substantially the same.

Further studies on other chiral phosphine-nickel complexes as hydrosilylation catalysts are in progress.

#### REFERENCES

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