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Preliminary communication

Asymmetric hydrosilylation of ketones catalyzed by chiral phosphine-platinum(II) complexes

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In the last few years several asymmetric homogeneous hydrogenation catalysts, all of which are rhodium complexes, have been described[1], but their utility has been limited to the reduction of unsaturated carbon–carbon bonds. We have previously reported[2] that the catalytic asymmetric hydrosilylation of olefins is effected by platinum complexes with chiral phosphines as ligands. We now find that the same complexes, dichlorodiphosphine-μ,μ'-dichlorodiplatinum(II), in which the phosphine is either (*R*)-(+)-benzylmethylphenylphosphine (I)[3] or (*R*)-(–)-methylphenyl-n-propylphosphine (II)[3], also catalyze the addition of methyldichlorosilane to a series of alkyl phenyl ketones at room temperature to give optically active silyl ethers of alkylphenylcarbinols.

$$\mathrm{RCOPh} + \mathrm{MeCl_2SiH} \xrightarrow{[\mathrm{R_3\overset{*}{P}PtCl_2}]_2} \mathrm{RPh\overset{*}{C}HOSiMeCl_2} \xrightarrow[(2)\ \mathrm{H_3O^+}]{(1)\ \mathrm{MeLi}} \mathrm{RPh\overset{*}{C}HOH} \qquad (1)$$

(R = Me, Et, n-Pr, i-Pr, and t-Bu; $R_3\overset{*}{P}$ = chiral phosphine)

Addition of methyldichlorosilane (80 mmoles) to acetophenone (60 mmoles) in the presence of the platinum(II) complex $[(I)\text{–}PtCl_2]_2$ ($4 \cdot 10^{-2}$ mmole) gave α-phenylethyl methyldichlorosilyl ether (III) in 81% yield; b.p. 109°/18 mm, n_D^{20} 1.4920, d_4^{20} 1.1464, $[\alpha]_D^{20}$ –4.60° (neat). NMR (CCl_4): δ 7.26 (s, 5H, Ph), 5.24 (q, 1H, *J* 6.4 Hz, CH), 1.56 (d, 3H, *J* 6.4 Hz, Me), and 0.76 ppm (s, 3H, SiMe). Methylation of (III) with excess methyllithium followed by acid hydrolysis gave (*S*)-α-phenylethanol, with a rotation which indicated an optical purity of 6.0% for (III).

Hydrosilylation of acetophenone using $[(II)\text{–}PtCl_2]_2$ as a catalyst produced, after methylation, the same alcohol of lower optical purity (5.2%), but having an (*R*)-configuration.

The results for a series of alkyl phenyl ketones examined are summarized in Table 1. It is noteworthy that the platinum(II) complex containing chiral phosphine (I) catalyzes the addition reaction to give predominantly (*S*)-carbinols, whereas that containing

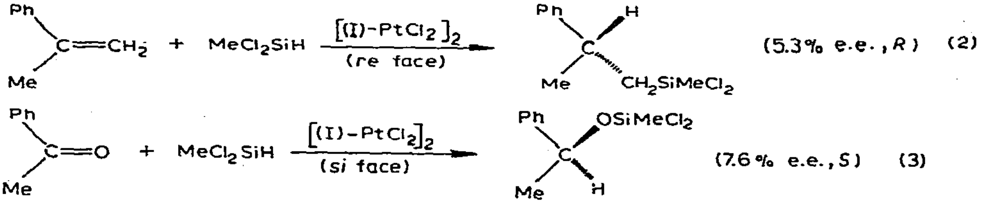
TABLE 1

ASYMMETRIC HYDROSILYLATION OF ALKYL PHENYL KETONES WITH $MeCl_2SiH$ CATALYZED BY $[R_3\overset{*}{P}PtCl_2]_2$ AT ROOM TEMPERATURE

Alkyl group in alkyl phenyl ketone	*Silyl ether* [a] *$[\alpha]_D^{20}$ (neat)*	*Yield (%)*	*Carbinol* [b] *$[\alpha]_D^{20}$*	*Configuration*	*Optical yield* [c] *(%)*
$R_3\overset{*}{P}$ = (*R*)-(+)-($PhCH_2$)MePhP–(I) (79% optical purity)					
Methyl	–4.60	81	–2.61	*S*	7.6
Ethyl	–6.11	81	–2.21	*S*	10.0
n-Propyl	–5.21	77	–3.0 [d]	*S*	8.4
i-Propyl	–	55 [e]	–1.7 [f]	*S*	4.5
t-Butyl [g]	–6.74	33	–3.8 [h]	*S*	18.6
$R_3\overset{*}{P}$ = (*R*)-(–)-MePh-n-PrP–(II) (93% optical purity)					
Methyl	+3.81	71	+2.24	*R*	5.5
Ethyl	+5.13	83	+1.94	*R*	7.4
n-Propyl	+3.82	74	+2.0 [d]	*R*	4.7
i-Propyl	–	57 [e]	+1.1 [f]	*R*	2.4
t-Butyl [g]	–2.62	24	–1.5 [h]	*S*	6.2

[a] Satisfactory elemental analyses, IR and NMR spectra were obtained for these silyl ethers. [b] Specific rotation was measured neat unless otherwise noted. [c] Optical yields are calculated from the specific rotations of the pure enantiomers which are reported in the literature (lit. 4), and calibrated for the optical purity of chiral phosphines used. [d] Specific rotation in benzene; maximum rotation $[\alpha]_D^{27}$ –45.9° (*c* 6, benzene) (lit. 5). [e] Contaminated with ca. 10% of $Ph(MeCl_2SiO)C{=}CMe_2$. [f] Specific rotation in ether. [g] Heated at 90° for 10 days. [h] Specific rotation in benzene.

phosphine (II) leads to the (*R*)-isomers, except in the case of t-butyl phenyl ketone. Further, it should be noted that asymmetric hydrosilylation of α-methylstyrene catalyzed by $[(I){-}PtCl_2]_2$ gives rise predominantly to the (*R*)-adduct, while the (*S*)-carbinyl silyl ether is the preferred enantiomer in the case of asymmetric addition of methyldichlorosilane to acetophenone, as mentioned above. These facts suggest that the stereoselectivity of addition of a hydrosilane to enantiotopic faces of an olefin, which is undoubtedly involved in π-coordination to the chiral catalyst, may be different from that of addition to a ketone (see Eqn. (2) and (3)).



(*re* refers to *rectus*, *si* to *sinister*, and e.e. to enantiomeric excess)

Schrock and Osborn[6] have reported that cationic rhodium complexes with more basic phosphines as ligands (*e.g.* $PPhMe_2$ instead of PPh_3) catalyze reduction of ketones and olefins under mild conditions. While we have not yet established the details of the mechanism of the catalytic processes, the results show clearly that the platinum complex is an effective catalyst for the hydrosilylation of both olefins and ketones.

REFERENCES

1 W.S. Knowles, M.J. Sabacky and S.D. Vineyard, *Chem. Commun.*, (1972) 10, and references cited therein.
2 K. Yamamoto, T. Hayashi and M. Kumada, *J. Amer. Chem. Soc.*, 93 (1971) 5301.
3 K. Neumann, G. Zon and K. Mislow, *J. Amer. Chem. Soc.*, 91 (1969) 7102.
4 R. MacLeod, F.J. Welch and H.S. Mosher, *J. Amer. Chem. Soc.*, 82 (1960) 876.
5 K. Mislow and C.L. Hamermesh, *J. Amer. Chem. Soc.*, 77 (1955) 1590.
6 R.R. Schrock and J.A. Osborn, *Chem. Commun.*, (1970) 567.