tion proceeds with retention of the configuration present in the alkenylborane.[12]

Thus, the hydroboration–mercuration of alkynes provides a major new stereospecific route to the alkenylmercurials, which have proven invaluable for the synthesis of other alkenylmetallics.[3]

(12) Retention had previously been observed in the mercuration of alkenylboronic acids. See ref 4 and 6.

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Asymmetric Homogeneous Hydrosilylation with Chiral Phosphine–Palladium Complexes

Sir:

Recently we have reported the first example of asymmetric hydrosilylation of α-methylstyrene catalyzed by (R)-benzylmethylphenylphosphine complexes of platinum(II)[1] or nickel(II),[2] which, respectively, lead to a 5 or 17.6% excess of one enantiomer in the addition product, 2-phenylpropylmethyldichlorosilane. Experiments with the similar phosphine complex of palladium(II) showed it to be only slightly useful for the asymmetric synthesis in hydrosilylation of olefins, despite other studies on the effectiveness of tertiary phosphine complexes of palladium.[3,4]

Instead of using tertiary phosphines which are asymmetric at phosphorus, Morrison and coworkers[5] have reported that a chiral rhodium complex from neomenthyldiphenylphosphine ligands is very effective as an asymmetric homogeneous hydrogenation catalyst. The fact that a complex with ligands that are dissymmetric remote from phosphorus does fulfill the necessary condition for asymmetric catalysis[5,6] prompted us to investigate the asymmetric hydrosilylation using complexes with this type of chiral phosphine.

We wish to report that a palladium(II) complex of menthyldiphenylphosphine (MDPP)[7] or epimeric neomenthyldiphenylphosphine (NMDPP)[8] is especially useful to induce asymmetry in hydrosilylation of styrene and some cyclic conjugated dienes.

Thus, addition of trichlorosilane (60 mmol) to styrene (30 mmol) was carried out in the presence of dichlorobis(benzonitrile)palladium(II) (6×10^{-2} mmol) and MDPP (1.2×10^{-1} mmol) in a degassed sealed glass tube at room temperature over a period of 5 hr. The reaction mixture was distilled to give α-phenylethyltrichlorosilane[9] as a sole addition product (87% yield), $[\alpha]^{20}\text{D}$ +2.72° (neat). The adduct was methylated to give α-phenylethyltrimethylsilane[10] ($[\alpha]^{20}\text{D}$ −5.30° (neat); $[M]^{20}\text{D}$ −9.44°), a 5.1% enantiomeric excess (ee) of the S isomer, which was estimated on the basis of predicted molecular rotations in a series of (S)-α-phenylethyl derivatives.[11]

When the NMDPP–palladium complex was used as catalyst, the enantiomeric R addition product (3.3% asymmetric bias) was obtained, as indicated in Table I.

Table I. Asymmetric Hydrosilylation of Styrene and Cyclic Dienes with $HSiCl_3$ Catalyzed by Chiral Phosphine–Palladium(II) Complexes[a]

Olefin	Catalyst Pd(II) plus[b]	Yield, %	$[\alpha]^{20}\text{D}$, deg, of product[c]	$[\alpha]^{20}\text{D}$, deg, of methylated	Confign[d]
$PhCH{=}CH_2$	MDPP	87	+2.72	−5.30	S
$PhCH{=}CH_2$	NMDPP	87	−1.51	+3.38	R
$PhCH{=}CH_2$	R_3P^*[e]	70	−0.13	+0.25	R
Cyclopentadiene	MDPP	69	f	−11.84	S
Cyclopentadiene	NMDPP	81	f	−7.54	S
1,3-Cyclohexadiene	MDPP	64	f	−11.08	S
1,3-Cyclohexadiene	NMDPP	56	f	−3.66	S

[a] All new compounds gave satisfactory elemental analyses, and have correct structures assigned on the basis of infrared and nmr spectra. [b] $PdCl_2(PhCN)_2$–chiral phosphine (1:2); the molar ratio of the catalyst/olefin = 2×10^{-3}. [c] α-Phenylethyltrichlorosilane,[9] 2-cyclopentenyltrichlorosilane (bp 60–70° (23 mm)), and 2-cyclohexenyltrichlorosilane (bp 88–90° (23 mm)), respectively, from styrene, cyclopentadiene, and 1,3-cyclohexadiene. [d] Configuration of the predominant isomer. [e] R_3P^* = (R)-(+)-$(PhCH_2)MePhP$ (K. Neuman, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7102 (1969)) (67% optical purity). *trans*-$[PdCl_2(R_3P^*)_2]$ (mp 166°) was used as catalyst (unpublished results by R. Ito of this laboratory). [f] Not determined.

Hydrosilylation of cyclic conjugated dienes with trichlorosilane catalyzed by a palladium(II) complex either with MDPP or with NMDPP required much higher reaction temperature. However, of particular interest was that the reaction always gave 2-cycloalkenyltrichlorosilanes with an enantiomeric excess of the S-(−) isomer,[12] regardless of the phosphine epimer used in the catalyst. This is not the case with styrene (see Table I).

Thus, addition of trichlorosilane (90 mmol) to cyclopentadiene (45 mmol) catalyzed by Pd(II)–NMDPP at 120° for 58 hr yielded almost exclusively 2-cyclopentenyltrichlorosilane (81% yield), which was not contaminated

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(1) K. Yamamoto, T. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, **93**, 5301 (1971).

(2) K. Yamamoto, Y. Uramoto, and M. Kumada, *J. Organometal. Chem.*, **31**, C9 (1971).

(3) S. Takahashi, T. Shibano, and N. Hagihara, *Chem. Commun.*, 161 (1969).

(4) H. Hara, K. Ohno, and J. Tsuji, *ibid.*, 247 (1971).

(5) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, **93**, 1301 (1971).

(6) T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971).

(7) Prepared from the reaction of lithium diphenylphosphide with neomenthyl chloride [$[\alpha]^{20}\text{D}$ +48.5° (neat), $[\alpha]^{20}\text{D}$ +48.0° (c 1.40, n-octane); the maximum rotation in the literature, $[\alpha]^{25}\text{D}$ +53.7° (c 1.27, n-octane): N. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968)]; $[\alpha]^{20}\text{D}$ −95.7° (c 1.07, CH_2Cl_2). The reaction proceeds much more readily than that with menthyl chloride (*cf.* ref 5).

(8) Prepared according to a procedure by J. D. Morrison, *et al.*,[5] using menthyl chloride [$[\alpha]^{20}\text{D}$ −45.5° (neat); 86% epimeric purity based on a maximum rotation reported, $[\alpha]^{20}\text{D}$ −53.0°; E. D. Hughes, C. K. Ingold, and J. B. Rose, *J. Chem. Soc.*, 3839 (1953)]; $[\alpha]^{20}\text{D}$ +82.9° (c 1.20, CH_2Cl_2).

(9) A. D. Petrov, V. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, *Dokl. Akad. Nauk SSSR*, **97**, 687 (1954).

(10) J. W. Ryan and J. L. Speier, *J. Org. Chem.*, **24**, 2052 (1959).

(11) D. D. Davis and F. R. Jensen, *ibid.*, **35**, 3410 (1970); (S)-(−)-$PhMeCHSiMe_3$, $[M]^{20}\text{D}$ −184° (±5%).

with the 3 isomer but a trace of the cyclopentadiene dimer. The adduct was methylated to give 2-cyclopentenyltrimethylsilane: bp 99–100°; $n^{20}\text{D}$ 1.4485; $d^{20}{}_4$ 0.8131; $[\alpha]^{20}\text{D}$ $-7.54°$ (neat).[12,13] Similarly, hydrosilylation of 1,3-cyclohexadiene (25 mmol) with excess trichlorosilane catalyzed by Pd(II)–MDPP gave two isomeric cyclohexenyltrichlorosilanes (9:1 by glpc analysis) (71% yield), which led, upon methylation, to 2-cyclohexenyltrimethylsilane, $n^{20}\text{D}$ 1.4629, $d^{20}{}_4$ 0.8361; $[\alpha]^{20}\text{D}$ $-11.08°$ (neat),[12] as the major component.

The significant feature of the present results is twofold. First, it will be reasonable to conclude that a catalyst involves the intervention of π-allylic metal intermediates, since the catalytic action of palladium (and nickel) complexes in hydrosilylation of 1,3-dienes distinctly differs from that of platinum for which π-allylic complexes are rather unusual.[14] Furthermore, it has recently been reported that even aromatic ring carbons can be contained in the formation of a π-benzyl complex with palladium.[15] The formation of α-phenylethyltrichlorosilane as a sole product in the palladium complex catalyzed hydrosilylation[16] may be ascribed to the incorporation of a silyl group exclusively into a benzylic position of π-α-methylbenzyl–metal bonding, which in turn must exhibit diastereomeric interactions with the chiral phosphine ligands[17] (partial asymmetric induction, *vide infra*).

A second important feature follows from the first: the effect on stereoselectivity given by variation in configuration at the chiral center C-3 of the menthyl system resulted in the formation of enantiomeric (*S*)-(+)- and (*R*)-(−)-α-phenylethyltrichlorosilane (5.1 and 3.3% ee, respectively). However, this regularity was not observed in 2-cycloalkenylsilane formation.[18] It is difficult at present to ascertain the pattern of addition with respect to stereoselectivity in the product as functions of olefins used and phosphine ligands having multiple chiral centers. Nevertheless, the finding of an asymmetric induction in hydrosilylation of cyclic conjugated dienes has some interesting mechanistic implications.

In the light of current views of the mechanisms of metal-catalyzed hydrosilylation,[19,20] the following processes may be involved: (a) insertion of the palladium center into the silicon–hydrogen bond; (b) addition of the resulting hydridopalladium to the cyclic diene to convert it into a π-alkenyl metal bonding; and (c) transfer of the silicon from the metal center to the π-enyl carbon to give the product. Since cyclic π-enyl–palladium bonding has a local plane of symmetry and cannot induce asymmetry, the last process (c) must involve diastereomeric transition states or intermediates (including catalyst complexes), which control the stereochemical course of the present reaction.

Related experiments in regard to platinum-catalyzed hydrosilylation will be reported elsewhere.

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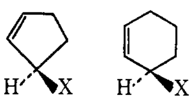
[12] J. H. Brewster, *J. Amer. Chem. Soc.*, 81, 5493 (1959). Conformational asymmetry of endocyclic olefinic compounds is successfully predicted. For such a configuration of compounds as shown below the molecular rotation at 589 nm will have a positive sign.



[13] None of the metal-catalyzed hydrosilylation of cyclopentadiene has been recorded so far in the literature.

[14] K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organometal. Chem.*, 28, C37 (1971).

[15] R. R. Stevens and G. D. Shier, *ibid.*, 21, 495 (1970).

[16] M. Hara, K. Ohno, and J. Tsuji, Symposium on Organometallic Compounds, Kiryu, Japan, 1970, Abstracts, p 164.

[17] For a review: G. Paiaro, *Organometal. Chem. Rev., Sect. A*, **6**, 319 (1970).

[18] For a related illustration, see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 140.

[19] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 87, 16 (1965).

[20] L. H. Sommer, J. E. Lyons, and H. Fujimoto, *ibid.*, **91**, 7051 (1969).

Selective Carbon–Carbon Bond Formation by Cross-Coupling of Grignard Reagents with Organic Halides. Catalysis by Nickel–Phosphine Complexes

Sir:

We report here a new and useful preparative method of synthesizing unsaturated compounds which involves the selective cross-coupling of a Grignard reagent with a vinyl or aryl halide, *catalyzed* by a nickel–phosphine complex.[1]

The cross-coupling of organic groups by the reaction of Grignard reagents with organic halides is induced by a variety of transition metal halides.[4,5] These reactions are, however, seldom employed in synthetic practice, due to the formation of homo coupling products and a variety of disproportionation products in substantial amounts.

Tamura and Kochi[6] recently demonstrated that "soluble catalysts" consisting of silver, copper, or iron in tetrahydrofuran were extremely effective for the coupling of Grignard reagents with alkyl halides: the first of these was useful for homo coupling and the last two for cross-coupling, especially the iron catalyst, being only for alkenyl halides.[7]

We were primarily interested in two independent facts concerning σ-organonickel complexes. First, two organic groups on a nickel complex are released by the action of an organic halide to undergo coupling, while

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[1] It has been reported that dichlorobis(triphenylphosphine)nickel(II) catalyzed the coupling of Grignard reagents with allylic alcohols[2] and hydrosilanes.[3,3a]

[2] C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *Chem. Commun.*, 1604 (1968).

[3] R. J. P. Corriu and J. P. Masse, *ibid.*, 213 (1970).

[3a] Note Added in Proof. After submission of this paper, a communication (R. J. P. Corriu and J. P. Masse, *Chem. Commun.*, 144 (1972)) dealing with similar cross-coupling reactions to those reported here using nickel catalysts such as Ni(acac)$_2$ reached us.

[4] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, pp 122–137, 1056–1059.

[5] M. Tamura and J. Kochi, *J. Amer. Chem. Soc.*, **93**, 1483 (1971), and references cited therein.

[6] M. Tamura and J. Kochi, *Synthesis*, 303 (1971), and references cited therein.

[7] Although, from the standpoint of the selective cross-coupling of organometallic compounds and organic halides, a π-allylnickel compound and lithium diorganocuprate, first developed by Corey and his group[8,9] and subsequently studied by others,[10] may be cited as excellent reagents, our interest centers on a transition metal *catalyst*.

[8] E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, **89**, 2755 (1967).

[9] E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967); **90**, 5615 (1968). This copper method has been extended to the similar reagents containing other metals of the first transition series, involving nickel iodide; see E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, 315 (1970).

[10] G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).