the precursor does survive in solution at room temperature as indicated by the persistence of yellow coloration. The reaction course was followed semiquantitatively by means of both ^1H NMR and UV spectroscopy. When the photolysis of a sample in deuteriomethylcyclohexane containing a standard substance, 2,2,3,3-tetramethylbutane, was periodically interrupted and the photolysate, after being warmed to room temperature, was subjected to exclusion of air and moisture from the reaction system),[12] spectral measurements, a new NMR singlet at δ 1.37 appeared at the expense of the signals due to **3** (see above). The maximum height of this new signal was attained (29% yield of **2**) at 74% consumption of **3**. The intensity of two new UV absorptions [λ_{max} 305 (ϵ 5200), 433 nm (2800)] also increased in parallel (see Figure 1). Fractional distillation of the photolysate at 5×10^{-6} torr at 30 °C raised the purity of **2** to ca. 40%.[14]

Compound **2** is very reactive as already described in the above trapping experiments with methanol and water. In addition, after complete photolysis, quenching of **2** with 2,3-dimethylbutadiene provides the Diels–Alder adduct **7**[7] (4% yield) and the ene adduct **8**[7] (15%) in addition to **6** (5.7%). The disilene **2** in methylcyclohexane (ca. 10^{-2} M) has a half-life of 4–10 h.

The UV absorption maximum of **2** at 433 nm is located at a rather unexpectedly long wavelength, even compared with tetrakis(2,6-dimethylphenyl)disilene (422 nm).[2] This red shift observed for **2** coupled with its extraordinarily high reactivity suggests that the four quaternary carbon atoms of the bulky substituents in **2** may not attain coplanarity due to steric repulsion.[15] This inference has indeed led us to attempt the synthesis of tetrakis(1-ethylpropyl)disilene (**1b**), the silicon–silicon double bond of which, according to molecular models, is well "shielded" against external attack (and also polymerization) and yet can take a conformation of D_{2h} or C_{2h} symmetry.[15] Indeed, compound **1b** exhibits a UV maximum at 390 nm.[16,17] Details of the chemistry of this compound will be reported in due course.

Acknowledgment. We thank the National Science Foundation and Yoshitomi Pharmaceutical Industries, Ltd., Japan, for financial support. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Registry No. **1b**, 86766-28-1; **2**, 86766-29-2; **3**, 86766-30-5; **4**, 18395-90-9; **5**, 86766-31-6; **5a**, 86766-35-0; **6**, 86766-32-7; **7**, 86766-33-8; **8**, 86766-34-9.

Supplementary Material Available: A listing of physical properties of new compounds (2 pages). Ordering information is given on any current masthead page.

(14) The purity of **2** is equated to the ratio of the intensity of the singlet δ 1.37 to the total intensity of the signals between δ 0 and δ 4.

(15) The geometry of $H_2Si{=}SiH_2$ and $H_2Ge{=}GeH_2$ has been a subject of numerous recent calculations. See: Trinquier, T.; Malrieu, J.-P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529 and references quoted therein. The stable conformations of these species appear to be of C_{2h} symmetry rather than D_{2h}. No experimental data have yet been available.

(16) Masamune, S.; Tobita, H.; Murakami, S. unpublished results. Details of this chemistry will be reported in due course.

(17) The carbon analogue of **2**, tetra-*tert*-butylethylene still remained unsynthesized. For a recent attempt, see: (a) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563. For reviews, see: (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

Phosphine-Induced Reductive Elimination from *cis*-Arylmethylnickel(II) Complexes Having a 1,2-Bis(dimethylphosphino)ethane Ligand

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Summary: A series of *cis*-arylmethyl(1,2-bis(dimethylphosphino)ethane)nickel(II) complexes, *cis*-Ni(C_6H_4X)(Me)(dmpe) (X = *p*-OMe, *p*-Me, H, *p*-F, *o*-Me), has been prepared by the ligand exchange reaction of *trans*-Ni(C_6H_4X)(Me)(PEt_3)$_2$ with a stoichiometric amount of dmpe at low temperature. Addition of phosphorus ligands such as PEt_3, P(aryl)$_3$, dmpe, P(OEt)$_3$, and PCy_3 to the complexes induces facile reductive elimination of MeC_6H_4X.

Reductive elimination of alkyl and aryl ligands is the key step in nickel- or palladium-catalyzed cross-coupling reactions of aryl or alkenyl halides with alkylmagnesium halides, a process which is believed to proceed as shown in Scheme I.[1] For the reductive elimination to proceed in a concerted, nonradical pathway, the alkyl and aryl groups attached to nickel must be brought into adjacent positions, in a square-planar or tetrahedral configuration. Recent studies on thermolysis of square-planar cis-dialkyl complexes of nickel, palladium, and platinum clarified some of the reductive elimination mechanisms,[2-9] but the arylalkylnickel complexes so far isolated are only those of trans configuration[6,7] and no report is available, to our knowledge, concerning the preparation and behavior of a *cis*-arylalkylnickel complex, one which would have direct relevance to the catalytic cross-coupling reactions. We now report the preparation of the first *cis*-arylmethylnickel complexes that contain a 1,2-bis(dimethylphosphino)ethane (dmpe) ligand and the pronounced enhancement of the reductive elimination of the methyl and aryl groups by added tertiary phosphine ligands.

Preparation of *cis*-Arylmethylnickel(II) Complexes. Treatment of a homogeneous solution of *trans*-arylmethylbis(triethylphosphine)nickel(II),[7] **1**, in ether with a stoichiometric amount of 1,2-bis(dimethylphosphino)ethane (dmpe) below 0 °C resulted in immediate precip-

(1) (a) Corriu, R. J.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144. (b) Tamao, K.; Sumitani, K.; Kiso, Y.; Zenbayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958 and references cited therein.

(2) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

(3) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265.

(4) (a) Gille, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Moravsky, A.; Stille, J. K. *Ibid.* **1981**, *103*, 4182. (c) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.

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(6) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360.

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(9) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255; **1977**, *99*, 8840.

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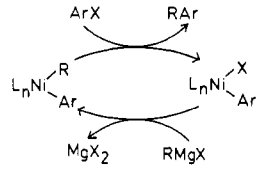
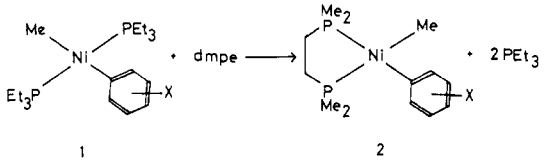
Scheme I. A Mechanism for Ni-Catalyzed Cross-Coupling Reaction



itation of yellow *cis*-arylmethyl(1,2-bis(dimethylphosphino)ethane)nickel(II), **2**, which could be recrystallized from a mixture of benzene and hexane (eq 1).



(1)

1 2

X = p-OMe(2a), p-Me(2b), H(2c), p-F(2d), o-Me(2e)

Complexes **2a–e** are extremely air sensitive but thermally moderately stable. Because of their extreme air sensitivity elemental microanalysis of **2a–e** was not feasible and they were characterized on the basis of ^1H and $^{31}P\{^1H\}$ NMR spectral data and chemical reactions.[10] The doublet of doublets for Ni–Me protons of **2a–e** in the ^1H NMR spectra and the AB quartet pattern in $^{31}P\{^1H\}$ NMR indicate the square-planar cis configuration of these complexes. Acidolysis of complexes **2** with dry HCl afforded methane and C_6H_5X in quantitative yields, supporting the above composition of **2**. Attempts to prepare *cis*-Ni(aryl)$_2$(dmpe) by the ligand exchange of *trans*-Ni(aryl)$_2$(PEt$_3$)$_2$ with dmpe were unsuccessful due to the occurrence of rapid reductive elimination to produce biaryls.

Reductive Elimination of MeC_6H_4X from *cis*- and *trans*-Ni(C_6H_4X)(Me)(L)$_2$. Thermolysis of cis complexes **2** in benzene gave predominantly intramolecular reductive elimination products, MeC_6H_4X, similar to those obtained with the *trans* compound **1** with triethylphosphine ligands as reported by Parshall[6] and Kochi.[7] Small amounts of methane and C_6H_5X also were formed. Rates of the reductive elimination were followed by ^1H NMR and found to be first order in the concentration of **2**.

$$\text{Ni(aryl)(Me)(dmpe)} \xrightarrow[k_{obsd}]{} \text{aryl–Me}$$

$$d[2]/dt = -k_{obsd}[2]$$

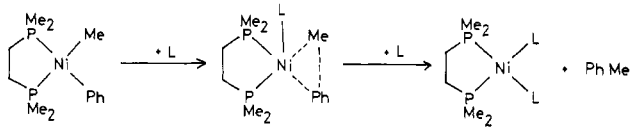
The rate constants, k_{obsd}, for thermolysis of **2** under various conditions are listed in Table I. All of the cis-arylmethyl complexes **2a–e** decompose much faster than the trans complex **1**. Thus **2** decomposes at room temperature in benzene at a considerable rate, while **1** shows no sign of decomposition under the same conditions. An electron-withdrawing para substituent such as fluorine on the phenyl group slightly retards the reductive elimination, the trend being consistent with the theoretical expectation.[8]

Addition of phosphorus ligands such as dmpe, PEt_3, P(aryl)$_3$, PCy_3, and P(OEt)$_3$ greatly accelerates the selective reductive elimination of MeC_6H_4X from **2**. The resulting Ni product was found to be NiL_2(dmpe) as confirmed by NMR and IR spectroscopy. For example, 6 molar equiv of dmpe added to the solution of **2a** at 10 °C immediately afforded toluene and Ni(dmpe)$_2$ and no methane and benzene were formed. Under these conditions, **2** itself decomposed with a half-life of 10 h. Triphenylphosphine ligand had a moderate accelerating effect on the reductive elimination, and the rate increases linearly with increasing the concentration of free PPh_3. Substituents on the phenyl group in the PPh_3 ligand had little effect on the rate of reductive elimination. On the other hand, the more sterically demanding tricyclohexylphosphine showed no accelerating effect on the reductive elimination. The accelerating effect of the unidentate phosphorus ligands is in the order of P(OEt)$_3$ ≈ PEt_3 > P(aryl)$_3$ > PCy_3, reflecting the order of steric bulkiness of the ligands. N donors such as pyridine and triethylamine showed no acceleration effect. The observation of the pronounced *accelerating* effect of the phosphorus ligands on thermolysis of **2** is in sharp contrast to the *retarding* effect of PEt_3 on the thermolysis of the trans complex **1**.[7] While a dissociative mechanism has been assumed in the thermolysis of **1** as well as in that of *cis*-PdR_2L_2[4] and AuR_3L,[9] an associative mechanism involving a five-coordinate intermediate seems to be operative here (eq 2). An analogous associative mechanism has been postulated in the reductive elimination of *cis*-Pt(aryl)$_2$L$_2$.[5]

Table I. First-Order Rate Constants k_{obsd} for the Reductive Elimination from **2** in C_6D_6

compd	additive (mol/L)	temp, °C	$10^4 k_{obsd}$, s^{-1}
2a[a]	none	38	1.1
2b	none	38	3.8
2c	none	40	2.7
	none	10	0.18
	PPh_3 (0.98)	10	3.3
	$P(C_6H_4$-*p*-F$)_3$ (0.87)	10	2.3
	$PPh_2(C_6H_4$-*p*-OMe) (0.86)	10	2.3
	$P(C_6H_4$-*p*-OMe$)_3$ (0.49)	10	1.7
	PEt_3 (0.45)	10	ca. 20
	CPy_3 (0.89)	10	ca. 0.2[b]
	P(OEt)$_3$ (1.7)	10	>50
	dmpe (0.51)	10	>50
2d	none	38	0.63
2e	none	30	1.0

[a] Considerable amounts (ca. 0.4 mol/Ni) of HC_6H_4X were also detected in the thermolysis. [b] Accurate value was not obtained by overlap of the toluene peak with large peaks due to the PCy_3 ligand.

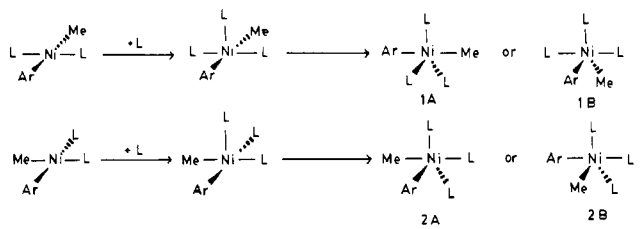


(2)

The striking difference in the reductive elimination behavior of the *trans*- and *cis*-arylmethylnickel complexes may be associated with the kinetic stability of five-coordinate, trigonal bipyramidal intermediates toward intramolecular pseudorotation. If one assumes pseudorotation of the trigonal-bipyramidal intermediates causing the isomerization is a slow process, the difference in the thermolysis behavior may be accounted for consistently by postulating the following trigonal-bipyramidal intermediates (Scheme II).[11] In intermediates 2A or 2B, possibly formed from *cis*-Ni(aryl)(Me)L$_2$ on interaction with L, the methyl and aryl groups are situated in adjacent

(10) Supplementary data of yields, decomposition points, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy are deposited as supplementary material.

Scheme II. Five-Coordinate Intermediates in Reductive Elimination from *cis*- and *trans*-Arylmethylnickel Complexes



equatorial and apical positions in the trigonal bipyramid and thus reductive elimination is symmetry allowed,[13] whereas in 1A or 1B the aryl and the methyl ligands are either in the trans positions[14] or in the equatorial cis positions (1B), from which reductive elimination of the aryl and methyl ligands is not allowed.[13] Thus the reductive elimination from the trans complex may be forced to take another course, a dissociative pathway[7] through the formation of unsaturated three-coordinate species that may be isomerized by a polytopal rearrangement to the cis form, from which the methylarene can be reductively eliminated.[8]

In relation to the catalytic system, addition of aryl halide to the benzene or THF solution of **2** has some promotion effect on the reductive elimination, but the reaction is accompanied by formation of scrambled biaryls Ar–Ar, Ar′–Ar, and Ar′–Ar′ arising from NiArMe(dmpe) and the aryl halide Ar′X in agreement with the similar observation by Kochi concerning the reaction of **1** with aryl halides.[7] The accelerating effect of aryl halide, however, is much less pronounced than the effect of the tertiary phosphine addition to the cis complex **2**, and the *main* catlytic cross-coupling reaction may be proceeding by the phosphine-promoted reductive elimination pathway of the cis complex of type **2**.

Registry No. **1a**, 86823-38-3; **1b**, 86823-39-4; **1c**, 57811-74-2; **1d**, 52242-81-6; **1e**, 57811-73-1; **2a**, 86823-40-7; **2b**, 86823-41-8; **2c**, 86823-42-9; **2d**, 86823-43-0; **2e**, 86823-44-1; PPh_3, 603-35-0; $P(C_6H_4\text{-}p\text{-}F)_3$, 18437-78-0; $PPh_2(C_6H_4\text{-}p\text{-}OMe)$, 896-89-9; $P(C_6H_4\text{-}p\text{-}OMe)_3$, 855-38-9; PEt_3, 554-70-1; PCy_3, 2622-14-2; $P(OEt)_3$, 122-52-1; dmpe, 23936-60-9.

Supplementary Material Available: A table of yields and NMR data for compounds **2a–e** (1 page). Ordering information is given on any current masthead page.

(11) This assumption is not unreasonable since most of the ligand displacement reactions of the square-planar d^8 metal complexes take place with stereochemical retention of the initial configuration and are generally believed to proceed through trigonal-bipyramidal intermediates that do not rearrange to other isomers by the pseudorotation during the displacement reactions.[12]

(12) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions", 2nd ed.; Wiley: New York, p 1967.

(13) (a) Tatsumi, K., private communication. Extended Hückel calculation revealed appropriate symmetry requirements for the reductive elimination and a higher energy barrier for interconversion between 1A and 2A (1B and 2B) than that for the symmetry-allowed reductive elimination in trigonal-bipyramid intermediates. The full paper will be published elswhere. (b) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *188*, 59.

(14) The presence of stable, trigonal-bipyramidal, trans complexes of formula $NiMe_2L_3$ (L = PMe_3, PMe_2Ph) has been spectroscopically observed: (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1972**, *105*, 2628. (b) Jeffery, E. A. *Aust. J. Chem.* **1973**, *26*, 219.

General Synthesis of Alkylalkenylalkynylboranes via Haloboranes

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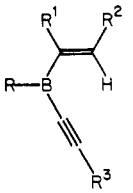
Summary: Methyl alkylalkenylborinates, obtained via hydroboration of alkynes with alkylbromoboranes, followed by methanolysis, react with alkynyllithium reagents in THF to form the corresponding "ate" complexes, which, on treatment with 1.33 equiv of $BF_3\cdot OEt_2$, produce the desired alkylalkenylalkynylboranes, thus providing a convenient and simple synthesis of these hitherto inaccessible organoboranes.

It has long been the dream of organoborane chemists to synthesize and study the chemistry of organoboranes containing three different groups on boron. Recently we have developed[2] a rational synthesis of mixed dialkylhaloboranes (**1**) and trialkylboranes (**2**), via stepwise hydroboration (eq 1), thus providing a solution to this

$$RBBr_2\cdot SMe_2 \xrightarrow{^1/_4LiAlH_4} \underset{\mathbf{3}}{RBHBr\cdot SMe_2} \xrightarrow{\text{alkene 1}} \underset{\mathbf{1}}{RR^1BBr} \xrightarrow[\text{MeOH}]{\text{NaOMe}} RR^1BOMe \xrightarrow[\text{alkene 2}]{^1/_3LiAlH_4} \underset{\mathbf{2}}{RR^1R^2B} \quad (1)$$

long-standing problem in organoborane chemistry. The synthesis of alkylalkenylalkynylboranes (**4**) constitutes



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another such unsolved long-standing problem in organoborane chemistry. A convenient synthesis of such valuable organoboranes would not only help in understanding the chemistry of those molecules but also further expand the scope and application of the versatile organoboranes. We herein report a general and simple synthesis of the hitherto inaccessible alkylalkenylalkynylboranes (**4**).

The importance of organoboranes in organic synthesis has been well documented, and a variety of methods via organoboranes are now becoming available for stereo- and regioconstruction of carbon–carbon bonds.[3,4] A general synthesis of thexyldiorganoboranes via the reaction of alkyl- or alkenyllithium reagents on thexylalkenylchloroboranes (eq 2) has recently been reported by Zweifel and Pearson.[5] Therefore, we first examined the utility of these

(1) (a) Postdoctoral research associate on Grant GM 10937-20 from the National Institutes of Health. (b) Postdoctoral research associate on Grant CHE 79-18881 from the National Science Foundation.

(2) Kulkarni, S. U.; Basavaiah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212.

(3) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(4) Brown, H. C. *Pure Appl. Chem.* **1976**, *47*, 49.

(5) Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919. For thexylallenic and thexylpropargylic borane intermediates, see: Zweifel, G.; Pearson, N. R. *J. Org. Chem.* **1981**, *46*, 829.

0276-7333/83/2302-1468$01.50/0