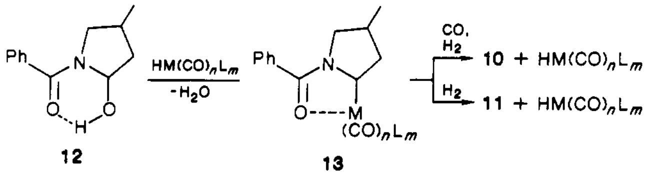
kyl–metal complex (**13**), which is generated from **12** (eq 4). Namely, the two reactions are competing processes: The carbon monoxide insertion is the predominant process for rhodium catalysts while the hydrogenolysis is almost exclusive for $Co_2Rh_2(CO)_{12}$.



12 **13**

M = Rh or CoRh (4)

Further studies on the mechanisms and applications of chelation-controlled hydrocarbonylations and novel double carbonylation (a new intramolecular amidocarbonylation) including asymmetric synthesis are in progress.

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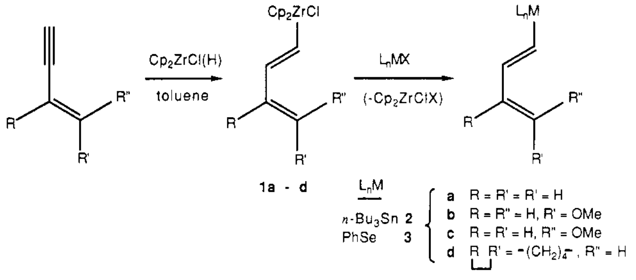
Transition Metal Dienyls in Organic Synthesis. Dienyl Transfer Reactions from Zirconium to Phosphorus and to Boron

Summary: The stereoselective preparation of 1,3-dienylphosphines and boranes, via a transfer process from zirconium, proceeds smoothly in excellent yields. The analogous reaction does not occur for silicon.

Sir: The preparation of heterosubstituted 1,3-dienes with oxygen-, nitrogen-, and sulfur-bonded functional groups has greatly enhanced the scope of the Diels–Alder reaction.[1] Not only do these substituents activate the diene, thereby extending the range of usable dienophiles, but they can also serve as focal points for subsequent synthetic elaboration.

Our continuing interest in the preparation of transition metal and metalloid substituted 1,3-dienes has already provided examples of zirconium dienyls **1a–d** prepared by hydrozirconation of conjugated enynes, which can be subsequently used to generate tin[2] (**2a–d**) and selenium[3] (**3a–d**) dienes via transmetalation (eq 1). In this paper, we further establish the synthetic utility of these zirconium dienyl reagents in the general preparation of functionalized 1,3-dienes substituted in the 1-position with organophosphorus[4] and boron[5] derivatives. A similar strategy to generate main group heterocycles has been reported recently.[6]



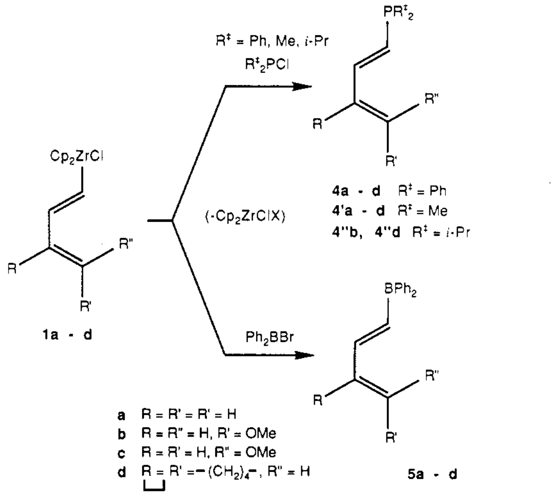
1a - d

L$_n$M	
n-Bu$_3$Sn	**2**
PhSe	**3**

a R = R' = R' = H
b R = R'' = H, R' = OMe
c R = R' = H, R'' = OMe
d R R' = -(CH$_2$)$_4$-, R'' = H

equation 1

Reaction of the zirconium dienyls **1a–d** with 1 equiv of either Ph_2PCl or Me_2PCl in toluene proceeds rapidly at room temperature to generate the corresponding stereoisomerically pure dienylphosphines **4a–d** and **4′a–d** (eq 2), respectively, in quantitative yields (by ^1H NMR spectroscopy). Isolated yields of 80–90% are easily obtained by extraction with hexanes and filtration through alumina (to remove Cp_2ZrCl_2). The analogous reaction with the more sterically crowded diisopropylchlorophosphine (i-Pr_2PCl) requires heating to 80 °C for several hours to generate the expected products (**4″b** and **4″d**) as mixtures of rotamers. A more detailed description of the latter reaction will appear in a future publication. The coordination chemistry of these new tertiary phosphines is now under investigation.[7]



1a - d

4a - d R‡ = Ph
4'a - d R‡ = Me
4"b, 4"d R‡ = i-Pr

5a - d

a R = R' = R' = H
b R = R" = H, R' = OMe
c R = R' = H, R" = OMe
d R = R' = -(CH$_2$)$_4$-, R" = H

equation 2

The dienyl unit can also be transferred from zirconium to boron. The addition of diphenylbromoborane (Ph_2BBr) to the zirconium reagents (in the dark[8]), in the same way as described for phosphorus, generates the corresponding diphenylboron-substituted dienes **5a–d** stereoisomerically pure (by ^1H NMR spectroscopy) and in excellent isolated yields. While this two-step method may not be as convenient or as tolerant of other functional groups as the hydroboration of enynes,[5] there is the advantage that less hindered boranes can be used since the regiochemistry is

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(1) (a) Grayson, J. I.; Petrzilka, M. *Synthesis* **1981**, 753. (b) Everhardus, R. H.; Grafting, R.; Brandsma, L. *Ibid.* **1983**, 623. (c) Reglier, M.; Ruel, R.; Lorne, R.; Julia, S. A. *Ibid.* **1983**, 624. (d) Akermark, B.; Nystrom, J.-E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719.

(2) Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537.

(3) Fryzuk, M. D.; Bates, G. S.; Stone, C. *J. Org. Chem.* **1987**, *52*, 2334.

(4) For the preparation of some 1,3-dienylphosphines (via a five-step process), see: Mathey, F.; Mercier, F.; Santini, C. *Inorg. Chem.* **1980**, *19*, 1813.

(5) For reports on the preparation of other 1,3-dienylboranes, see: (a) Clark, G. M.; Hancock, K. G.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 1308. (b) Vaultier, M.; Truchet, F.; Carboni, B.; Hoffmann, R. W.; Denne, I. *Tetrahedron Lett.* **1987**, *28*, 4169.

(6) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(7) Reference 4 contains examples of 1,3-dienylphosphines bound to Ni, Mn, and Fe.

(8) Compounds **5** appear to be photochemically labile, for photolysis of 1,3-dienylboranes see: Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192.

defined by the hydrozirconation step. Also, to our knowledge, the direct hydroboration of 1-buten-3-yne to generate dienyls of type **5a** has not been achieved.

These dienyl transfer processes, also referred to generally as transmetalation reactions, operate for a wide variety of metal and metalloid $\mathrm{L_nMX}$ species.[9] *One notable exception is* $\mathrm{Me_3SiCl}$ *for which no reaction is observed even at high temperatures.* Attempts to make the silicon center more electrophilic by the use of better leaving groups (e.g. 1-(trimethylsilyl)imidazole or trimethylsilyl trifluoromethanesulfonate) also failed to generate the corresponding 1,3-dienylsilanes. On thermodynamic grounds, it would appear that the Si–X bond energy is too similar to the corresponding Zr–X bond energy[10] and thus there is no strong driving force for transfer from Zr to Si.[11]

These highly functionalized 1,3-dienes are now being evaluated in the Diels–Alder reaction, particularly with respect to stereospecificity and regiochemistry. This and the photolability of these new dienes will be reported in due course.

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Supplementary Material Available: Experimental details, analytical and spectroscopic data for compounds **4a–d**, **4′a–d**, and **5a–d**, and ^{1}H NMR spectra of **4″b** and **4″d** (8 pages). Ordering information is given on any current masthead page.

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[9] We have observed similar transfer reactions from Zr to S, Ge, Ga.

[10] The average bond dissociation energy^{10b} for Zr–Cl ($\mathrm{ZrCl_4}$) is 117 kcal mol^{-1} and the Si–Cl bond dissociation energy in $\mathrm{Me_3SiCl}$ is calculated^{10c} to be 97.4 kcal mol^{-1}. (b) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; p 846. (c) Pilcher, G. Thermochemistry of Organometallic Compounds Containing Metal–Carbon Linkages. *International Review of Science, Physical Chemistry, Series 2*; Butterworths: London, 1975; Vol. 10, Chapter 2, p 45.

[11] A similar lack of reactivity in the transfer reaction from Zr to Si was observed even with use of $\mathrm{SiCl_4}$, see ref 6.

Additions and Corrections

Vol. 53, 1988

Giovanni Palmisano,* Bruno Danieli, Giordano Lesma,* Federica Trupiano, and Tullio Pilati. Oxidation of β-Anilinoacrylate Alkaloids Vincadifformine and Tabersonine by Fremy's Salt. A Mechanistic Insight into the Rearrangement of *Aspidosperma* to *Hunteria* Alkaloids.

Page 1057, ref 1. We regret having overlooked the following references to relevant synthesis of *Aspidosperma* alkaloids vindorosine and vindoline when writing our paper and are grateful to Dr. Y. Langlois for calling them to our attention: Andriamialisoa, R. Z.; Langlois, N.; Langlois, Y. *J. Org. Chem.* **1985**, *50*, 961. Gênin, D.; Andriamialisoa, R. Z.; Langlois, N.; Langlois, Y. *Heterocycles* **1987**, *26*, 377.