with no classical analogues. There is ample evidence from dynamic NMR,[18,19] kinetic data,[20] and inelastic neutron scattering[21] that the labile hydrogen nuclei in related systems exhibit quantum mechanical behavior at the temperatures involved ($T > 170$ K). Exchange couplings are well-known in ESR.[9-12] The formal mathematical description of the exchange interaction is in fact the same for any pair of indistinguishable spin 1/2 particles be they electrons, protons, or ^{3}He nuclei. The effect of the exchange interaction is to add a pseudo-magnetic coupling term to the spin Hamiltonian of the required form $-2\mathbf{J}\mathbf{I}_1\cdot\mathbf{I}_2$ where $2\mathbf{J}$ is the difference in energy of the symmetrical and antisymmetrical two particle orbital wave functions, i.e.

$$2\mathbf{J} = E_S - E_A = \langle\Psi_S(1,2)|\mathcal{H}(1,2)|\Psi_S(1,2)\rangle - \langle\Psi_A(1,2)|\mathcal{H}(1,2)|\Psi_A(1,2)\rangle \quad (1)$$

$\mathcal{H}(1,2)$ is given by

$$\mathcal{H}(1,2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(1) + V(2) + v(1,2) \quad (2)$$

where $V(1)$, $V(2)$ are single particle potentials, and $v(1,2)$ is the pairwise potential between the particles.[13]

The observation that the ^{3}T spectrum of **3** displays J_{HT}'s that are only 24 and 29 Hz, 20 times less than expected, is a direct consequence of this model. If the J_{HH} coupling is largely an exchange coupling, it is expected to disappear in the partially tritiated isotopomer as the configurations H_AT_B and T_AH_B are not degenerate in energy. The small couplings observed in the tritium spectrum are then principally the usual magnetic scalar couplings. The same situation must hold for the deuterium isotopomers as well. However the smaller J_{HD} values, now known to be ca. 4 Hz on the basis of the above result, will invariably be unresolved due to the short ^{2}D T_1's. While exchange couplings are familiar to chemists in the context of ESR,[9] such effects have not been identified before in solution NMR. It has been recognized for some time that the NMR of solid ^{3}He is dominated by nuclear exchange couplings[13] which can be as large as 10 MHz. The size of this coupling is a very sensitive function of the amplitude of the ^{3}He lattice vibrations. This is borne out by the fact that $\mathbf{J}$ varies three orders of magnitude in solid ^{3}He, from 10^{-2} to 10 MHz, over the molar volume range of 17–24 cm^3. It is reasonable to assume that the potential the protons experience in the trihydrides considered here is fairly flat given their fluxional nature. Thus the required large amplitude motion is quite plausible. To estimate the size of these couplings, Landesman's model[13b,c] for exchange has been applied with parameters suitable for a pair of protons. In this model, which assumes a hard spheres potential, $\mathbf{J}$ is given by

$$\mathbf{J} \approx -\frac{3}{4}\sqrt{\frac{3}{\pi}}\frac{\hbar}{m}\left(\frac{a}{\delta^3}\right)\exp-\left\{\frac{3}{4}\frac{a^2+\lambda^2}{\delta^2}\right\} \quad (3)$$

where a is the internuclear distance, δ the amplitude of the vibrational motion, λ the range of the interaction potential between the two protons, and m the proton mass. Preliminary solid-state NMR line shape[22] data for **2** give the AB distances as both 1.65 ± 0.05 Å and the BB distance as 2.20 ± 0.15 Å. Assuming λ the order[23] of 1 Å, J can be estimated for various values of δ. In a simple harmonic approximation, the zero-point motion amplitude δ (Å) for reasonable vibration frequencies of 410, 460, and 560 cm^{-1} are 0.35, 0.33, and 0.30 Å, respectively.[24] For these values J is calculated as 7200, 760, and 3 Hz in qualitative agreement with the observed range of such couplings. In addition when a is increased to the BB distance of 2.2 Å, J decreases by over a factor of 10^6. As the above rough calculation indicates, the value of J is an extremely sensitive function of the vibrational amplitude δ. At elevated temperatures there will also be thermally activated contributions to δ. In the temperature range in question $\langle\delta^2\rangle$ is expected to be directly proportional[24] to T. For small changes in T the observed exponential dependence is easily seen to be qualitatively predicted as a consequence of eq 3. Furthermore, fits of the temperature dependence are consistent with the above structural parameters and choice of λ.[25]

The ^{3}T NMR data reported here provides the first conclusive experimental evidence for pseudo-magnetic exchange couplings in solution ^{1}H NMR. A simple theory has been put forward which qualitatively accounts for the magnitude, temperature dependence, and isotope dependence of these couplings. Experiments are in progress to further test predictions of this model. Further theoretical work is also in progress to provide a better quantitative understanding of these couplings.

Acknowledgment. K. W. Zilm would like to acknowledge partial support of this work by a grant from the Exxon Education Foundation and the National Science Foundation under Grant CHE-8517584. J. M. Millar acknowledges support by an Exxon postdoctoral fellowship during a portion of this work. D. M. Heinekey acknowledges support from the National Science Foundation under Grant CHE-8814191. We acknowledge stimulating discussions with J. W. Faller, J. M. McBride, and S. Neshyba during the course of this work. A special acknowledgment is given J. C. Duchamp for providing spectral simulations and aiding in preparation of the manuscript.

Note Added in Proof. A similar exchange mechanism has been proposed by Jones et al. to explain these NMR observations. See paper in this issue.

Registry No. 1, 113161-52-7; **2**, 113161-54-9; **3**, 113180-40-8; **4**, 119326-87-3.

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Carbon–Carbon Bond-Forming Reactions of Organotransition Metals with α- or γ-Haloorganolithium Reagents[1]

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Received November 21, 1988

Migratory insertion is one of a very limited number of fundamentally different patterns of organometallic transformations permitting the formation of carbon–carbon and carbon–heteroatom bonds, some of the others being reductive elimination, carbo-

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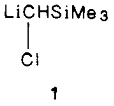
† On leave from Okayama University, Okayama, Japan.

(1) Migratory Insertion Reactions of Organometallics. 3. Part 2: Negishi, E.; Swanson, D. R.; Miller, S. R. *Tetrahedron Lett.* **1988**, *29*, 1631.

0002-7863/89/1511-3089$01.50/0 © 1989 American Chemical Society

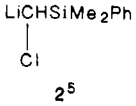
metalation, and nucleophilic attack on π-ligands.[2] And yet, the migratory insertion chemistry has been dominated by those involving a small number of reagents, such as carbon monoxide and isocyanides.[3,4]

In search for new C–C bond-forming reactions of organotransition metals that might proceed via migratory insertion, we have examined reactions of organometals containing a wide variety of transition metals with various α- and γ-haloorganolithiums and have indeed found that all eight metals of the first transition series as well as some others, such as Zr and Hf, can promote C–C bond formation between organometals containing these metals and α- and γ-haloorganolithiums, such as **1–5**. Although mechanistic details of these reactions still remain to be further clarified, the product before quenching is organometallic in every case that was examined by D_2O quenching (>95% D incorporation).



$$\underset{\text{Cl}}{\text{LiCHSiMe}_3}$$

1

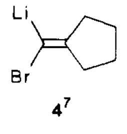


$$\underset{\text{Cl}}{\text{LiCHSiMe}_2\text{Ph}}$$

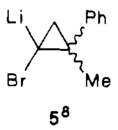
2[5]

$LiCHCl_2$

3[6]

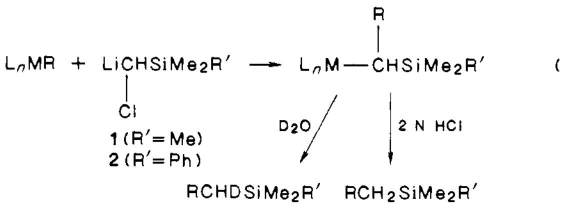


4[7]



5[8]

We have recently reported[9] that organometals containing various main group metals, such as Al, Mg, Zn, and Cd, react with $LiCH(Cl)SiMe_2Ph$[5] to undergo C–C bond formation, some of which have been shown to proceed via migratory insertion. In view of these favorable results, we reacted a wide variety of organotransition metals with **1** and **2** and indeed observed the desired C–C bond formation according to the general equation shown below (eq 1).



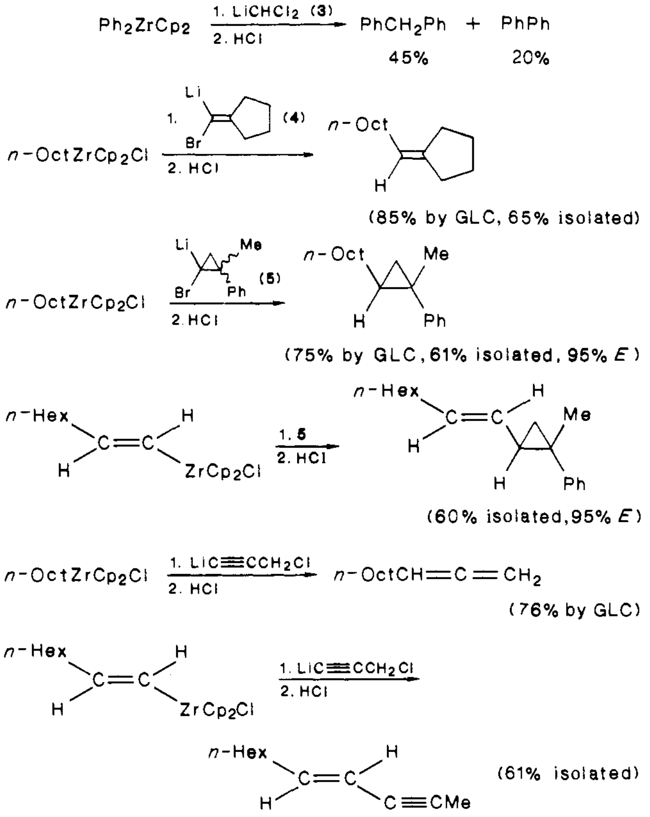
(1)

L_nM = metal group containing Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, or Cu

R = *n*-Bu, *n*-Oct, Ph, *p*-Tol, or (*E*)-1-octenyl

The experimental results are summarized in Table I. All starting substrates except Cp_2ZrCl(Octyl-*n*) and Cp_2ZrCl(Octenyl-1-*E*) were prepared by treating the corresponding halo derivatives with an organolithium reagent, and the molecular formula primarily indicate the stoichiometry of the reactants. In each case, however, complete consumption of the organolithium reagent was established by either ^1H NMR or disappearance of the pink color of $LiCPh_3$ used as an indicator. To the reagent **1** or **2** generated in THF at −78 °C was added an organometallic substrate. After 1 h at −78 °C the reaction mixture was warmed to 25 °C over 1 h and quenched with 2 N HCl in most cases. In some cases, quenching was performed at −78 °C. It is striking to note that the desired products, i.e., RCH_2SiMe_2R', were obtained in high yields using a wide range of organotransition metals including Zr, Hf, V, Cr, and Mn. On the other hand, the results obtained with organometals containing Ti, Fe, Co, Ni, and Cu were rather disappointing. With late transition metals, the major side reaction was the formation of dimers (RR). Biphenyl was obtained in high yields even when monophenyl derivatives, such as $(Et_3P)_2Ni(I)Ph$, were used.

Some remarkably high reaction rates were indicated by the formation of the desired products in high yields even when the reaction mixtures were quenched after 1 h at −78 °C. For example, the reaction of $Mn(Bu\text{-}n)_2$ with **2** (1.5 equiv) was quenched with 2 N HCl after 1 h at −78 °C to give *n*-$BuCH_2SiMe_2Ph$ in 88% isolated yield. Quenching with D_2O under the same conditions gave *n*-$BuCHDSiMe_2Ph$ in 52% isolated yield with nearly 100% D incorporation. Similarly, the yield and the extent of D incorporation for the reaction of $Cp_2Zr(Tol\text{-}p)_2$ with **1** (1 equiv) were 60 and >95%, respectively. The nearly complete D incorporation clearly indicates that, at least in these cases, the initial products were organometallic. Unfortunately, however, the high reaction rates have so far prevented us from further clarifying mechanistic details.



The scope of the carbon–carbon bond formation via reactions of organotransition metals with α-haloorganolithiums appears to be broad, as indicated by the following additional examples. The cyclopropane derivatives are isomerically ≃ 95% pure *E* isomers by ^{13}C and 2D NOESY ^1H NMR. Finally, the reactions of 3-chloropropynyllithium[10] represent examples of the use of γ-haloorganolithiums. Whereas the reaction with *n*-$OctZrCp_2Cl$ led to clean formation of an allenic product, the corresponding reaction with (*E*)-(*n*-HexCH=CH)$ZrCp_2Cl$ provided an 85:15 mixture of (*E*)-4-undecen-2-yne[11] and an apparently isomeric allenic compound (IR 1940 cm^{-1}) in 95% GLC yield, from which

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Table I. Reaction of Organotransition Metals with $LiCH(Cl)SiMe_2R'$[a]

L_nMR	R'[b] of $LiCH(Cl)SiMe_2R'$	RCH_2SiMe_2R' (%)[c]	Me_3SiR' (%)	RR (%)[d]
$Cp_2Ti(Bu\text{-}n)_2$	Ph (1)	13	67	*e*
$Cp_2Zr(Bu\text{-}n)_2$	Ph (1.5)	85 (65)	15	*e*
$Cp_2Zr(Cl)Oct\text{-}n$	Ph (1)	55	40	*e*
Cp_2ZrPh_2	Ph (1)	60	29	4
$Cp_2Zr(Tol\text{-}p)_2$	Me (1)	70 (54)	*e*	*e*
$Cp_2ZrCl(Octenyl\text{-}1\text{-}E)$	Me (1)	75[f]	*e*	*e*
$Cp_2Zr(Octenyl\text{-}1\text{-}E)_2$	Me (1)	45[f]	*e*	20
$Cp_2Hf(Bu\text{-}n)_2$	Ph (1)	55	22	*e*
Cp_2HfPh_2	Me (1.3)	65	*e*	2
VPh_3	Me (1.5)	56	*e*	22
$CrPh_2$	Me (1.5)	76 (53)	*e*	*e*
$MnPh_2$	Me (2)	82	*e*	4
$MnBu_2$	Ph (1.5)	97 (88)	*e*	*e*
$FePh_2$	Me (1.5)	39	*e*	29
$CoPh_2$	Me (1.5)	12	*e*	70
$(Et_3P)_2NiPh_2$	Me (1.5)	9	*e*	65
$LiCuPh_2$	Me (1.0)	35	*e*	*e*

[a] The reactants were mixed in THF at −78 °C. After 1 h the temperature was raised to 25 °C over 1 h. [b] The number in parentheses indicates the molar quantity of the reagent relative to L_nMR. [c] By GLC. The numbers in parentheses indicate isolated yields. [d] The % figure corresponds to the number of mmol of this byproduct per 100 mmol of L_nMR. [e] The yield was not determined. [f] A 1:1 mixture of (*E*)-1-(Nonenyl)$SiMe_3$ and (*E*)-2-(Nonenyl)$SiMe_3$.

the enyne was chromatographically isolated as a pure sample in 61% yield.

Acknowledgment. We thank the National Science Foundation (CHE-8503075) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (18710-AC1), for support of this research. We thank F. E. Cederbaum and Y. Zhang of our laboratories for their technical assistance in obtaining 2D NOESY ^1H NMR spectra.

Virtually Complete Diastereofacial Selectivity in the S_N2' Allylation of Organocopper Reagents

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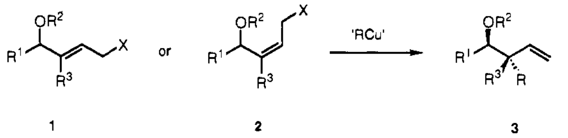
Diastereoselective carbon–carbon bond formation in acyclic systems continues to attract the interest of chemists. Numerous examples of 1,2-asymmetric induction involving nucleophilic additions to carbonyl compounds have been reported,[1] and considerable progress has been made for controlling the stereochemistry of chiral centers bearing a heteroatom. On the other hand, there have been only scattered reports on acyclic asymmetric induction involving additions to olefins,[2] a process which can be employed as a means for the stereoselective construction of tertiary and quaternary carbon centers. In this paper we describe a highly regio- and diastereoselective S_N2' reaction of organocopper reagents with 4-alkoxy allylic chlorides (**1** and **2**) that creates tertiary and quaternary carbon centers often with virtually complete diastereofacial selectivity (eq 1). To our knowledge, this reaction represents the first example where an S_N2' allylation reaction of carbon nucleophile[3] has been examined for its potential in asymmetric induction.

In order for this allylation method to constitute a useful synthetic strategy, it is first necessary that the reaction be highly S_N2' selective.[4] Unfortunately, the reaction of a standard cuprate reagent, e.g., Bu_2CuLi, with *trans*-chloride **1** (R^1 = *i*-Pr, R^2 = benzyl, R^3 = H) in THF gave predominantly the S_N2 product[5] (Table I, entry 1). On the basis of our previous experience on the reactions of zinc alkyls,[4c] we next examined the reaction of the "zinc cuprate",[6] prepared by treatment of a Gilman reagent with 1 equiv of anhydrous $ZnCl_2$ prior to addition of the substrate. The reagent "$R_2CuZnCl$" reacted quantitatively with **1** at −70 °C to afford the desired S_N2' allylation product **3** with 98% regioselectivity and, more importantly, a single anti diastereomer[6c] (entry 2) was realized. No trace (≪0.2%) of the other diastereomer could be detected by capillary GLC analysis versus an authentic mixture of diastereomers. Excellent selectivities were also observed for the reaction of **1** with "$Me_2CuZnCl$" (entry 7), "$Bu_2CuTi(i\text{-}PrO)_3$" (entry 3),[6b] and $BuCu{\cdot}BF_3$[7] (entry 4). The moderately regioselective reaction of a vinyl cuprate reagent[4b] was also diastereoselective to give a 1,4-diene containing a chiral center between the olefins (entry 8). Not unexpectedly, the reaction of a lithium alkyl showed little selectivity.



(1)

A high level of anti selectivity has been consistently observed for **1** (R^3 = H) regardless of the nature of the R^1 substituent on the C(4) stereogenic center (entries 11 and 12), the R^2 protecting group on oxygen (entries 9 and 10), or the nature of the leaving group (entry 13). The reaction of the cis isomer **2** (R^3 = H) was also anti selective[6c] (entries 14 and 15).

We also found that a catalytic reagent generated in situ from a zinc alkyl and a catalytic amount of $CuBr{\cdot}Me_2S$[4c] can lead to results comparable to those observed with more elaborate stoichiometric reagents (entry 5). The advantages of the catalytic system follow from the characteristics of the reagent: (1) higher thermal stability that allows a >99% diastereoselective reaction to be performed at room temperature, (2) diverse and generally simpler preparation of organozinc reagents,[8] and (3) distinctively higher functional group tolerance, as has recently demonstrated.[8] This last point is illustrated by the reaction of a zinc homoenolate[9] (entry 6) which gives the S_N2' product **4** as a single diastereomer.

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(2) Cf.: Yamamoto, Y.; Nishii, S.; Ibuka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 464. Yamamoto, Y.; Nishii, S.; Ibuka, T. *J. Am. Chem. Soc.* **1988**, *110*, 617. Kruger, D.; Sopchik, A. E.; Kingsbury, C. A. *J. Org. Chem.* **1984**, *49*, 778. Salomon, R. G.; Miller, D. B.; Raychaudhuri, S. R.; Avasthi, K.; Lal, K.; Levison, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 8296. Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 1224.

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(4) Only a few, highly S_N2' selective allylations have been reported: (a) $RCu{\cdot}BF_3$: Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318. (b) $RCu(CN)MgBr$: Tseng, C. C.; Paisley, S. D.; Goering, H. L. *J. Org. Chem.* **1986**, *51*, 2884. (c) Sekiya, K.; Nakamura, E. *Tetrahedron Lett.* **1988**, *29*, 5155.

(5) The formation of 1:1 stereoisomeric S_N2 products from **2** indicates that the "S_N2" reaction of Bu_2CuLi is not a simple substitution reaction.

(6) (a) Presently, the nature of the "zinc cuprate" is totally unknown. Interestingly, $BF_3{\cdot}Et_2O$[4a,7a] and Me_3SiCl,[7b] which strongly assist conjugate addition of cuprates, were completely ineffective in the S_N2' reaction. For an excellent study on the nature of such reagents, see: Lipshutz, B. H.; Ellsworth, D. L.; Siahaan, T. *J. Am. Chem. Soc.* **1988**, *110*, 4834. (b) General procedure: To a suspension of $CuBr{\cdot}Me_2S$ (1.10 mmol) in 2 mL of THF is added BuLi in hexane (2.20 mmol) at −70 °C, and the clear solution was stirred at −40 °C for 40 min. Freshly fused $ZnCl_2$ (or $TiCl(^iPrO)_3$) (1.15 mmol) in THF is added, and, after 15 min, allylic halide **1** (1.00 mmol) in 1 mL of THF is added. After 15 h at −70 °C or at −40 °C, the reaction mixture is worked up, and the product is purified by chromatography. (c) The Masamune nomenclature is applied for the original carbon skeleton in **1** taken as the main chain: Masamune, S.; Ali, S. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557.

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0002-7863/89/1511-3091$01.50/0
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