

is inferior to the Norit-A/silica gel because, with the former, packing is more difficult and cracking of the stationary phase occurs easily. Molecular sieves (13X pellets ground to a fine powder and packed in a column) were used as a stationary phase and proved to be inadequate for C_{60} purifications.

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Preparation and Use of Vinylic Lithiocyanocuprates Containing an ω -Electrophilic Center

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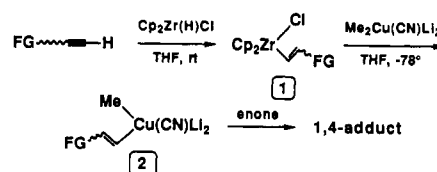
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Traditional cuprate formation, as originally prescribed by Gilman,¹ bears a fundamental limitation in its reliance on organolithium precursors (i.e., $2RLi + CuX$). Thus, lithiocuprates of either the lower order (LO , R_2CuLi) or higher order (HO , $R_2Cu(CN)Li_2$) persuasion which contain electrophilic centers (e.g., an ester or nitrile group) in R are presently unknown.² To circumvent the incompatibility of a highly reactive organolithium containing such a useful functionality, more stable organometallics have been developed, most notably from the Knochel,³ Riecke,⁴ and Piers⁵ groups. However, the price paid for switching from lithium to other gegenions³ is the lowering of cuprate reactivity, a general observation characteristic of both neutral species (i.e., " $RCu \cdot LiX$ ")⁵ as well as *ate* complexes ($R_2CuM^{6a}/R_2Cu(CN)MM^{6b}$). In this report, we now describe the first method for generation of vinylic lithiocuprates which contain internal electrophiles utilizing a transmetalation strategy based on readily available zirconium intermediates **1**⁷ (Scheme I).

Treatment of a vinylzirconate **1**, easily prepared from 1-alkynes using $Cp_2Zr(H)Cl$ in THF (room temperature, 15 min),⁸ with the trivial HO cuprate $Me_2Cu(CN)Li_2$ at low temperatures ($-78^\circ C$, 15 min) leads directly to the mixed cuprate **2**. Introduction of an α,β -unsaturated ketone, neat or in THF, to the newly generated cuprate at this temperature affords the expected 1,4-

Scheme I



Scheme II

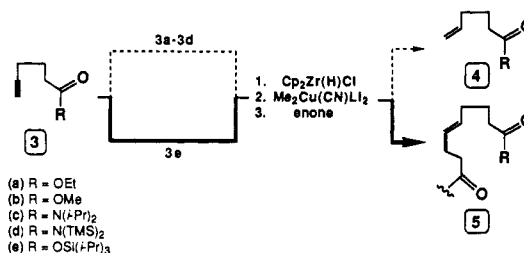


Table I. Formation and Reactions of Functionalized Lithiocuprates

Entry	1-Alkyne	Enone	Product ^a	Yield(%) ^b
1				75
2				75
3				71 ^c
4				93 ^c
5				83 ^{c,d}
6				82 ^c
7				71 ^{c,e}
8				76 ^{c,d}

^a Fully characterized by IR, NMR, MS, and HRMS data. ^b Isolated yields. ^c $BF_3 \cdot Et_2O$ (1 equiv) was added to the cuprate prior to introduction of the enone. ^d One isomer by capillary GC. ^e Yield was 35% without $BF_3 \cdot Et_2O$.

adduct in good isolated yields. This simple, one-pot process can be applied to acetylenes which possess a nitrile, ester, or chloride residue (Table I). It is especially noteworthy that β,β -disubstituted enones react readily at $-78^\circ C$, a clearly distinguishable feature between these lithiocuprates and, for example, zinc halide-containing reagents.⁹ Moreover, the rapidity and simplicity associated with this hydrozirconation-transmetalation-Michael addition sequence are also attractive elements, as there is no major time commitment to prior generation of activated organometallics (i.e., $RZnX^2$ or $Cu(0)^3$).

An unexpected observation was made in the case of 5-hexynoic acid ethyl or methyl ester (**3a,b**), where the sequence described

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(2) There is an example of an LO lithiocuprate containing a primary chloride, see: Piers, E.; Roberge, J. Y. *Tetrahedron Lett.* **1991**, *32*, 5219. Piers, E.; Yeung, B. W. A. *J. Org. Chem.* **1984**, *49*, 4567. Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* **1983**, 935.

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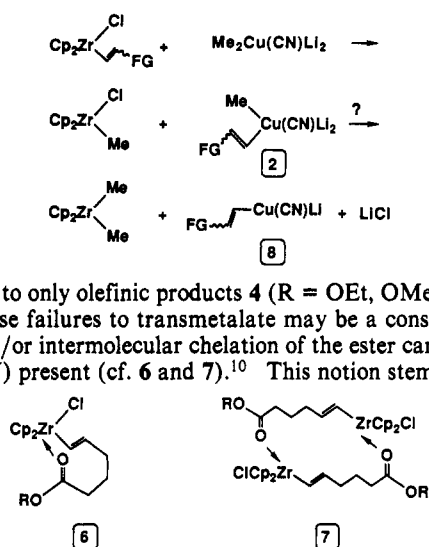
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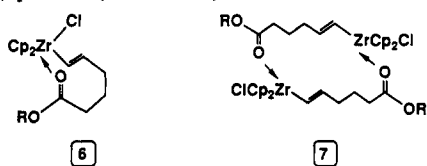
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Scheme III



above led to only olefinic products 4 ($\text{R} = \text{OEt}, \text{OMe}$) (Scheme II). These failures to transmetalate may be a consequence of intra- and/or intermolecular chelation of the ester carbonyl with the Zr(IV) present (cf. 6 and 7).¹⁰ This notion stems from the



observation that for all known HO cyanocuprate-based transmetalations (involving Sn,¹¹ Te,¹² Al,¹³ Zr^{8,13}), whatever the mechanism involved, the common denominator is the Lewis acidic nature of the participating organometallic. Thus, occupation of the remaining coordination site as in 6/7 shuts down ligand exchange with $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ and, hence, vinylcuprate formation. However, replacement of $\text{R} = \text{OEt}$ or OMe in 3a,b with $\text{R} = \text{OSi}(i\text{-Pr})_3$ (OTIPS), on steric¹⁵ or stereoelectronic grounds (or both),¹⁶ completely restores the transmetalation pathway. In support of the argument above, we also find that (1) introduction of ethyl heptanoate to reactions of 3e completely inhibits formation of 5 ($\text{R} = \text{OTIPS}$) and (2) all attempts to effect the sequence with amides 3c,d likewise produced the alkene 4 rather than the desired Michael adducts 5.

The true nature of the species formed in the transmetalation process has yet to be established. Although formulated here initially as a HO cuprate (cf. Scheme I), it is possible that 2 reacts to some degree with the presumed $\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}$ byproduct of the transmetalation to produce an LO lithiocyanocuprate 8 (Scheme III). Spectroscopic studies are anticipated to elucidate this issue.

In summary, the extreme mildness and rapidity with which vinylzirconates undergo transmetalations with HO cyanocuprates have led to the first examples of functionalized lithiocuprates.¹⁷ Applications, in particular to polyene macrolide chemistry, are currently in progress and will be reported in due course.

(10) See, for examples: Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Organomet. Chem.* **1985**, *285*, 31. Buchwald, S. L.; Nielsen, R. B.; Dawan, J. C. *Organometallics* **1988**, *7*, 2324.

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(15) Use of the corresponding *t*-BuMe₂Si ester gave low (15–20%) yields.

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(17) A typical procedure for the preparation of an ω -functionalized cyanocuprate is as follows: The vinyl zirconate is formed by treating a slurry of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (0.5 mmol) in anhydrous THF (2 mL) with the 1-alkyne (0.5 mmol, added neat) for 15 min at room temperature. The solution is then cooled to -78°C and treated for 10 min with a -78°C THF solution of $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ (prepared from 2MeLi (1 mmol) and CuCN (0.5 mmol) at -78°C in 2 mL of THF). If necessary, $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.5 mmol in 1 mL of Et_2O or THF) can be added at this time in a dropwise fashion. The enone (0.25 mmol, neat or in 0.5 mL of THF) is then introduced and the solution stirred at -78°C until the reaction is complete (5 min to 1 h), as determined by TLC. The mixture is then quenched by pouring it into saturated aqueous NH_4Cl /concentrated NH_4OH solution (9:1) and is extracted with Et_2O . Normal handling and chromatography affords the pure 1,4-addition product.

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Registry No. 1, 139461-23-7; 3a, 108545-38-6; 3b, 77758-51-1; 3c, 139461-32-8; 3d, 139461-33-9; 3 (R = OSiMe₂Bu-*t*), 139461-36-2; 4a, 54653-25-7; 4b, 2396-80-7; 4c, 139461-34-0; 4d, 139461-35-1; Cp₂Zr-(H)Cl, 37342-97-5; Me₂Cu(CN)Li₂, 80473-70-7; HC≡C(CH₂)₃CN, 14918-21-9; HC≡C(CH₂)₂OCOPh, 122471-85-6; HC≡C(CH₂)₂Cl, 51908-64-6; 2-cyclohexenone, 930-68-7; 2-methyl-2-cyclopentenone, 1120-73-6; 4-methylpent-3-en-2-one, 107-86-8; 3-methyl-2-cyclopentenone, 1193-18-6; (*R*)-4-(dimethyl-*tert*-butylsiloxy)-2-cyclopentenone, 61305-35-9; (*E*)-3-(5-cyano-1-pentenyl)cyclohexanone, 139461-24-8; (*E*)-3-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclohexanone, 139461-25-9; (*E*)-3-[4-(phenylcarbonyloxy)-1-butenyl]cyclohexanone, 139461-26-0; (*E*)-3-(4-chloro-1-butenyl)cyclohexanone, 139461-27-1; 2-methyl-3-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclopentanone, 139461-28-2; triisopropylsilyl (*E*)-7,7-dimethyl-9-oxodec-5-enoate, 139461-29-3; (*E*)-3-methyl-3-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclohexanone, 139461-30-6; (*E*)-2(*R*)-(dimethyl-*tert*-butylsiloxy)-3(*S*)-[6-(triisopropylsiloxy)-6-oxo-1-hexenyl]cyclopentanone, 139461-31-7.

Supplementary Material Available: Listings of spectral data for the products in Table I and ¹H and ¹³C NMR spectra for these and other products of the reactions of lithiocuprates (18 pages). Ordering information is given on any current masthead page.

Dynamics of Solute Motion: Photoisomerization Shows Linear Dependence on Solvent Mass

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In the general theory of solute motion based on Kramers' equation,¹ the control of reaction dynamics is divided into two limiting categories. At low friction (i.e., at low viscosity), the reaction rate is expected to increase with the number of collisions with solvent, as these supply the energy required to cross a potential barrier. At high viscosity, solvent will obstruct the path along the reaction coordinate and decrease the rate. Experiments have shown that Kramers' theory regularly fails when the potential barrier of the reaction is small (relative to kT) or no activation energy is required.² Several attempts have been made to account for behavior in this low-barrier regime.³ Grote and Hynes⁴ replaced the friction coefficient in Kramers' equation (ξ), with a frequency-dependent function, $\xi(\omega)$, which permits the viscosity to vary with the rate of the reaction. Velsko and Fleming² added a reaction coordinate-dependent sink function to Kramers' theory and obtained an improved fit to experimental observation. In an approach developed by Åkesson, Sundström, and Gillbro,⁵ the barrier height, large or small, is made to depend on the solvent. When this approach is applied to a homologous solvent series such as the *n*-alcohols, adjusting the barrier generates a good fit to experimental data. Dote, Kivelson, and Schwartz⁶ introduced "free spaces" in the solvent where rotation can take place unhindered

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