

displaced from the metal by treating the organometallic complex with a Ce(IV) salt (see Scheme II). The potent reactivity of **10** is due to two enamide units. The two pyrrole rings in compound **10** are now equivalent, which can be derived from the ^1H NMR spectrum. The ^1H NMR spectrum shows a singlet at 5.31 ppm due to the two former imine protons. The four methoxy groups give rise to two singlets at 3.63 and 3.89 ppm. Also, the ^{13}C NMR spectrum shows the high degree of symmetry of **10**. The four methoxy carbon atoms resonate at 164.5 and 164.0 ppm. The olefinic carbon atoms now give rise to only two signals at 155.7 and 96.5 ppm, from which it becomes clear that all four olefinic carbon atoms are sp^2 -hybridized. These frequencies are comparable to those of the olefinic and the methoxy carbon atoms of the uncoordinated pyrrole ring of complex **9**. From this can be concluded that the metal does not influence the uncoordinated pyrrole ring. This reaction is another example for an expansion of the synthetic potential of 1,3-dipolar additions in metal-promoted organic synthesis.

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Supplementary Material Available: A summary of crystal data and details of X-ray data collection and tables of atomic fractional coordinates, thermal parameters, and selected interatomic distances and angles (12 pages); a list of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Cyclization of 5-Hexyn-1-yllithiums

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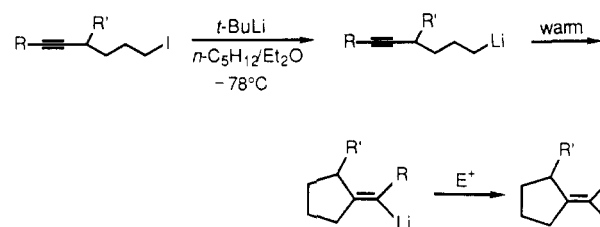
Summary: The kinetics of the 5-exo-dig cyclization of 5-decyn-1-yllithium (**1**) to (1-cyclopentylidene)pent-1-yl-lithium (**2**) are characterized by $\Delta H^\ddagger = 23.0 \pm 0.9$ kcal/mol and $\Delta S^\ddagger = +4.8 \pm 3.3$ eu ($E_a = 23.6 \pm 0.9$ kcal/mol; $\ln A = 32.9 \pm 3.5$). The phenyl-substituted analogue (6-phenyl-5-hexyn-1-yl)lithium (**5**) cyclizes much more rapidly than the alkyl-substituted systems: $k = (1.97 \pm 0.08) \times 10^{-3}$ at -50.6 °C ($t_{1/2} = 6$ min).

We recently reported that 5-alkyn-1-yllithiums undergo clean 5-exo-dig cyclization via syn addition of CH_2Li to the carbon-carbon triple bond upon warming to room temperature.¹ As shown below, this anionic cyclization provides a convenient regiospecific and stereoselective route to functionalized cyclopentylidene-containing products:¹⁻³

(1) Bailey, W. F.; Ovaska, T. V.; Leipert, T. K. *Tetrahedron Lett.* **1989**, *30*, 3901.

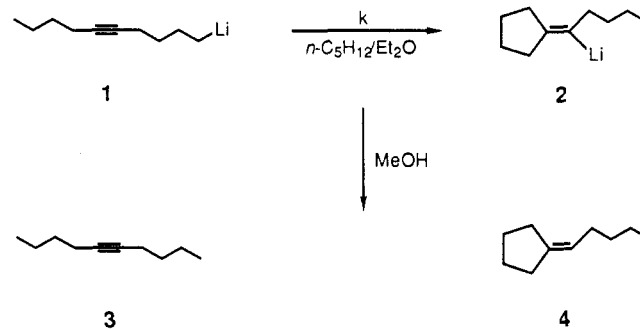
(2) Bailey, W. F.; Ovaska, T. V. *Tetrahedron Lett.* **1990**, *31*, 627.

(3) For the sake of pictorial clarity, organolithiums are represented as monomeric. The degree of aggregation of the acetylenic alkyllithiums **1**, **2**, **5**, and **6** under the reaction conditions is unknown.



While limited kinetic data for the sluggish cyclization of 5-hexynyl Grignard reagents have been reported in pioneering studies by Richey's group,⁴ activation parameters for the rather facile cyclization of 5-hexyn-1-yl-lithiums are unavailable. Prompted by the potential synthetic utility of the isomerization of acetylenic alkyllithiums, we have investigated the kinetics of the cyclization of 5-decyn-1-yllithium (**1**) to (1-cyclopentylidene)pent-1-yl)lithium (**2**). The results of these experiments are summarized in Table I.

The requisite organolithium was prepared by our general protocol for low-temperature lithium-iodine interchange.^{1,5,6} Thus, treatment of a 0.05 M solution of 1-iodo-5-decyne⁷ in *n*-pentane-diethyl ether (3:2 by volume) with 2.1 equiv of *tert*-butyllithium (*t*-BuLi) at -78 °C under argon affords **1** in essentially quantitative yield.⁸ The isomerization of **1** to **2** was monitored at four temperatures⁹ between 0 and $+28.8$ °C by rapid removal of aliquots and quench of the organolithiums with dry, deoxygenated methanol to give 5-decyne (**3**) and pentylidene-cyclopentane⁷ (**4**). The relative proportions of hydro-



carbons **3** and **4** were determined by GC (25 m \times 0.2 mm HP-1 capillary column; 80 °C for 8 min, then 20 °C/min to 250 °C) with use of *n*-decane as an internal standard.

The isomerization of **1** to **2** is a cleanly first-order process when care is taken to exclude moisture and oxygen from the system. There was no evidence of products derived from prototropic rearrangement of **1**, and no trace of allene was observed in any of the reaction mixtures. Cyclizations were followed through 3-8 half-lives by monitoring both the disappearance of **1** (assayed as **3**) and the appearance

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(5) (a) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (b) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

(6) (a) Bailey, W. F.; Nurmi, T. T.; Patricia, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 2442. (b) Bailey, W. F.; Rossi, K. *J. Am. Chem. Soc.* **1989**, *111*, 765.

(7) Crandall, J. K.; Michaely, W. J. *J. Org. Chem.* **1984**, *49*, 4244.

(8) Lithium-iodine interchange between *t*-BuLi and a primary alkyl iodide invariably results in the formation of a small but non-negligible amount of hydrocarbon formally derived from the reduction of the halide. As noted elsewhere,⁸ formation of the hydrocarbon is an unavoidable consequence of the rapid reaction of RLi with the cogenerated *t*-BuI to give RH, 2-methylpropene, and LiI.

(9) The temperature of samples used in the kinetic experiments was maintained at ± 0.2 °C with a Braun Model 1495 refrigerated constant-temperature bath.

Table I. First-Order Rate Constants^a and Activation Parameters^b for the Cyclization of 5-Decyn-1-yllithium (1) to (1-Cyclopentylidene-pent-1-yl)lithium (2)

temp, °C	10 ⁴ k, s ⁻¹	ΔH [‡] , kcal/mol	ΔS [‡] , eu
10.0	1.08 ± 0.01	23.0 ± 0.9	+4.8 ± 3.3
14.6	2.61 ± 0.04		
19.0	3.60 ± 0.07		
28.8	15.9 ± 0.7		

^aErrors are reported as standard deviations. ^bErrors in the activation parameters are reported as maximum errors; see: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; pp 377-379.

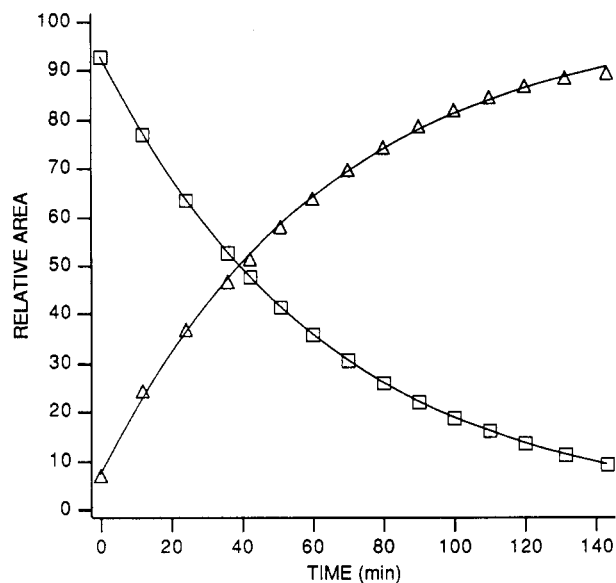
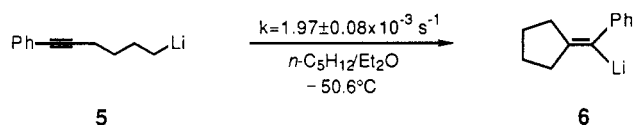


Figure 1. Typical plot of the relative areas of 5-decyn-1-yllithium (□, assayed as 3) and (1-cyclopentylidene-pent-1-yl)lithium (Δ, assayed as 4) as a function of time. Data are from the experiment at 14.6 °C. Solid lines represent the nonlinear least-squares fits of the data.

of 2 (assayed as 4). These data were fit by nonlinear least-squares analysis to the standard exponential form of the first-order rate expression (a typical plot is shown in Figure 1) to give the rate constants reported in Table I. In each instance the rate of disappearance of 1 was identical within experimental error with the rate of appearance of 2. Activation parameters were obtained by application of the Eyring equation: a plot of $\ln(k/T)$ versus $1/T$ was linear and gave $\Delta H^{\ddagger} = +23.0 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = +4.8 \pm 3.3$ eu. The corresponding Arrhenius parameters are $E_a = 23.6 \pm 0.9$ kcal/mol and $\ln A = 32.9 \pm 3.5$.

A less extensive kinetic analysis of the isomerization of (6-phenyl-5-hexyn-1-yl)lithium (5) to the vinylolithium 6 confirmed the qualitative observation¹ that cyclization of the phenyl-substituted acetylene is much more rapid than that of alkyl-substituted analogues. At -50.6 °C, the



first-order rate constant for the cyclization of 5 to 6 is $k = (1.97 \pm 0.08) \times 10^{-3} \text{ s}^{-1}$. Thus, the isomerization of 5 to 6, which has a half-life of ~6 min at -50.6 °C, is some 10⁶ times more rapid than is the cyclization of 1 to 2 at this temperature. The rather dramatic increase in the rate of cyclization on going from an alkyl-substituted 5-hexyn-1-yllithium to a phenyl-substituted substrate is most likely a consequence of a reduction in ΔH^{\ddagger} due to stabilization

of the incipient vinylolithium product by the phenyl group.

It is of interest to note that the 5-exo-dig cyclization of 1 to 2 (and presumably other alkyl-substituted 5-hexyn-1-yllithiums) is slower, at temperatures below ca. +40 °C, than is the corresponding 5-exo-trig isomerization of 5-hexen-1-yllithium to (cyclopentylmethyl)lithium (for which $\Delta H^{\ddagger} = 11.8 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -30 \pm 2$ eu).¹⁰ Indeed, the activation enthalpy for the intramolecular addition of CH_2Li to an alkyl-substituted acetylene ($\Delta H^{\ddagger} = 23.0 \pm 0.9$ kcal/mol, Table I) is about twice that for the analogous addition to an olefin. The small and unexpectedly positive ΔS^{\ddagger} value for the cyclization of 1 to 2 may be due to a decrease in the state of aggregation³ on attaining the transition state, and this, in turn, may reflect a lower state of aggregation of the product vinylolithium (2).

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Facile Addition of Alkynes to $(\text{CpCo})_3(\text{CO})_2$. General Method for the Synthesis of $(\text{CpCo})_3(\text{CO})(\text{RCCR}')$ Complexes

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Summary: Incorporation of alkynes into the framework of $(\text{CpCo})_3(\text{CO})_2$ occurs at room temperature to produce alkyne-carbonyl complexes of the form $(\text{CpCo})_3(\text{CO})(\text{RCCR}')$. The structure of the 3-hexyne adduct is described as well as preliminary observations on the dynamic properties of these complexes.

A wide variety of transition-metal complexes containing alkyne ligands now exists in which this ligand interacts with one or more metal atoms.¹ Although many examples of cluster complexes of the form $\text{M}_3(\text{CO})_n$ (alkyne) have been described, relatively few are known for the corresponding Cp_3M_3 ($\text{Cp} = \eta^5\text{-cyclopentadiene}$) systems. We recently described the synthesis and properties of a new series of 46-electron Fischer-Palm type trinuclear clusters $(\text{Cp}^*\text{M})_3(\text{CO})_2$ that readily react with two-electron ligands.² Here we describe a convenient, general method for the introduction of a wide variety of alkynes, diynes, and functionalized alkynes into the trinuclear framework of $(\text{CpCo})_3(\text{CO})_2$, 1. Two isomeric adducts (referred to as static and dynamic isomers) may be obtained depending

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