atom is bonded.[14] This order of the chemical shift is also consistent with the trend in Mo–O bond lengths.[15] The ^{95}Mo and ^{103}Rh nuclei in the clusters are separately equivalent in $CDCl_3$ (^{95}Mo NMR, δ 176 for **1**, 191 for **2**; ^{103}Rh NMR, δ 4079 for **1**).[16] The ^{1}H and ^{13}C NMR spectra indicate that all four Cp* rings in both clusters are magnetically equivalent.[17] These NMR data confirm that the triple cubane structure is preserved in $CDCl_3$.

The oxygen atoms in the clusters do not exchange with H_2O in $CDCl_3$. Clusters **1** and **2** in solid decompose only at high temperatures such as 275 and 290 °C, respectively, indicating that the triple cubane structure is very stable. Reaction of $[WO_4]^{2-}$ with $[RhCp^*Cl_2]_2$ gave a similar cluster $[RhCp^*WO_4]_4$, and its properties are now under investigation.

Acknowledgment. We thank Professors Shinichi Kawaguchi of Kinki University and Martin A. Bennett (a visiting professor of IMS) for valuable discussions.

Supplementary Material Available: ORTEP diagram of **2**, listings of fractional coordinates with equivalent isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for **1** and **2** (7 pages); listings of observed and calculated structure factors for **1** and **2** (15 pages). Ordering information is given on any current masthead page.

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(15) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G. *Inorg. Chem.* **1985**, *24*, 4055–4062.
(16) The ^{95}Mo and ^{103}Rh NMR chemical shifts were referenced to 1 M Na_2MoO_4 in D_2O at 25 °C and Ξ(^{103}Rh) of 3.16 MHz, respectively (lower field positive).
(17) ^{1}H NMR ($CDCl_3$) C_5Me_5 δ 1.75 s (for **1**), 1.67 s (for **2**); ^{13}C NMR ($CDCl_3$) C_5Me_5 δ 9.33 s (for **1**), 9.60 s (for **2**); C_5Me$_5$ δ 90.15 d (for **1**, J_{C-Rh} = 8.8 Hz), 81.35 s (for **2**).

The "Gilman Reagent" Ph_2CuLi and "Higher Order" Ph_3CuLi_2: ^{13}C and ^{6}Li NMR in Dimethyl Sulfide[1]

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Higher order organocuprates[2a] have recently joined the classical Gilman reagents[2b] at the forefront of synthetic methodology. While "Me_3CuLi_2" had been postulated as a reactive intermediate, Lipshutz et al. showed by means of ^{1}H and ^{7}Li NMR that the addition of MeLi to Me_2CuLi does not form a higher order species, i.e., the reagent is merely Me_2CuLi + MeLi.[4] In contrast, to within the limits of NMR detection, free MeLi is not present in the higher order cyanocuprate $Me_2Cu(CN)Li_2$,[5] the stability of which has been attributed to dπ-backbonding.[6] On the basis of chemical reactivity, House et al. conjectured the existence of "Ph_3CuLi_2";[7] however, this reagent has not been confirmed spectroscopically. We find that Ph_3CuLi_2 in dimethyl sulfide (DMS)[8] is a novel, identifiable reagent. When prepared from

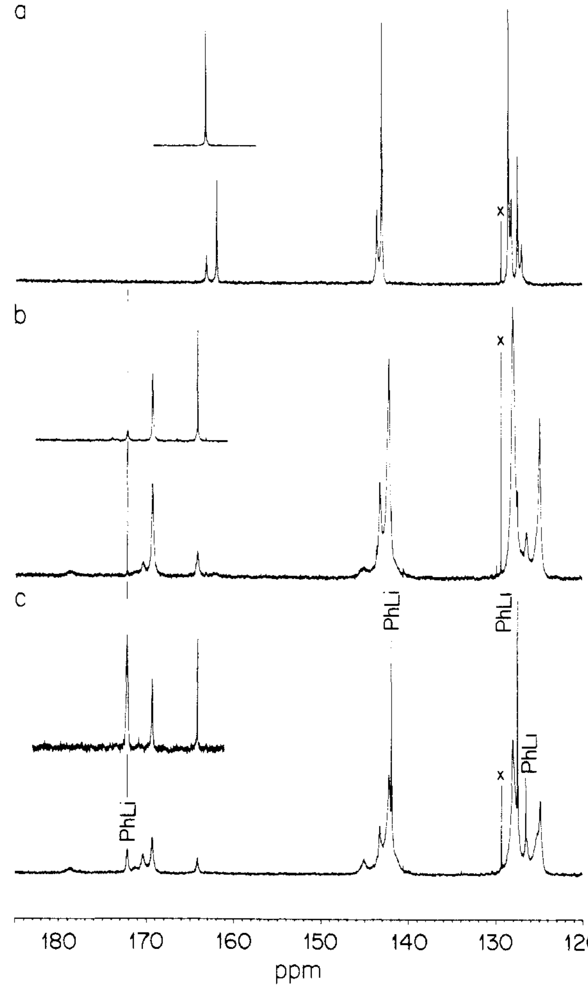

Figure 1. ^{13}C NMR spectra (173 K) of (a) Ph_2CuLi, (b) Ph_3CuLi_2, and (c) Ph_3CuLi_2 + PhLi prepared from CuI in DMS (10% $C_6{}^2H_{12}$ for internal lock). Benzene (δ 129.3) is indicated by X. The scale places $C_6{}^2H_{12}$ at δ 26.4 ppm. Insets are for reagents prepared from CuBr.

CuI in DMS, Ph_2CuLi exists primarily as a halide-containing cluster. By using CuBr, we obtain halide-free Ph_2CuLi.

At −100 °C in DMS, the ^{13}C NMR spectrum (Figure 1a) of Ph_2Cu^6Li, prepared from CuI and 2 equiv of Ph^6Li,[9a] consists of eight lines: four major (δ 161.9, ipso; 143.0, ortho; 128.5, meta; 127.4, para)[9b] and four minor (163.1, 143.6, 128.1, 127.0 ppm), due to two kinds of Ph groups. The two sets coalesce to one set of four lines at ca. −80 °C (δ 162.1, 143.1, 128.3, 127.2, see Figure 3, Supplementary Material). By substituting CuBr for CuI, "halide-free" Ph_2CuLi is obtained, owing to the precipitation of LiBr from DMS. The four peaks in the ^{13}C NMR spectrum of this material are at precisely the same positions as the peaks of the minor Ph_2CuLi species from CuI (e.g., see Figure 1a, inset). Thus, as far as the iodocuprate is concerned, the major species at low temperature (70% by integration of the ^{13}C NMR spectrum) contains LiI.

The ^{6}Li NMR spectra of Ph_2CuLi prepared from CuI and from CuBr (Figure 2a) are in harmony with the ^{13}C NMR results. The

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(8) For the preparation of organocuprates in DMS, see: Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1974**, 1713. House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.
(9) (a) Ph^6Li was prepared by the method of Schlosser and Ladenberger (Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193). All Li used was ^{6}Li unless otherwise specified. The organocopper reagents were prepared by adding a cold (≤0 °C) solution of PhLi in DMS to a cold solution of CuI in DMS in a 10-mm NMR tube and bringing the resulting solution (~0.2 M) to 0 °C before cooling it in the probe of a Bruker AM360. Ca. 10% [$^2H_{12}$]cyclohexane was included for the internal ^{2}H lock. (b) The assignment of the ^{13}C NMR spectrum is based on an analysis of the coupling constants $J_{CCH} \approx 0$ and $J_{CCCH} \approx 6$ Hz. The same order is observed for PhLi (see ref 13).

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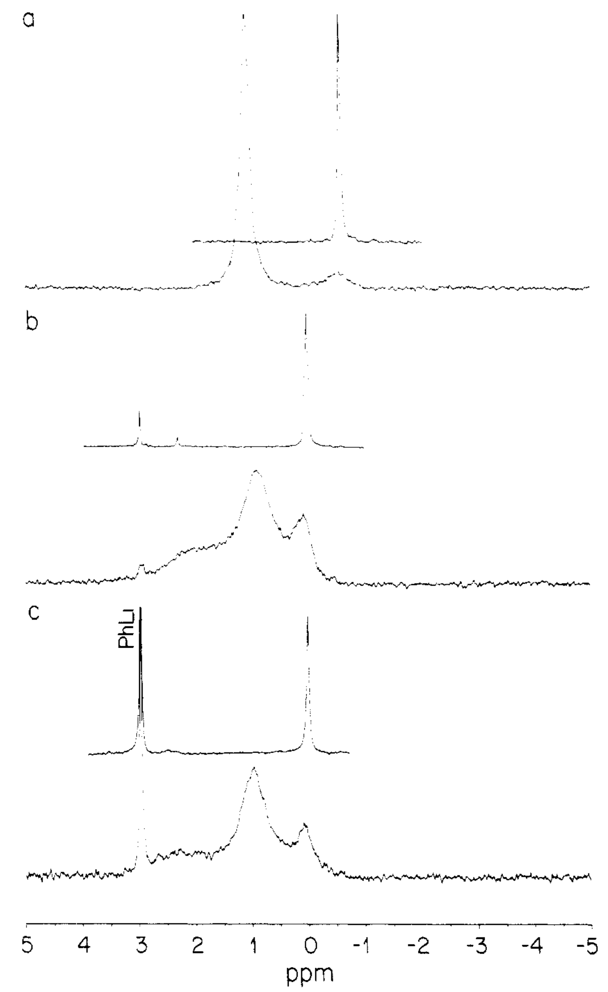

Figure 2. ^{6}Li NMR spectra (173 K) of (a) Ph_2CuLi, (b) Ph_3CuLi_2, and (c) Ph_3CuLi_2 + PhLi prepared from CuI in DMS (10% $C_6{}^2H_{12}$ for internal lock). The scale places 1 M ^{6}LiCl/[$^2H_4$]methanol at 0 ppm. Insets are for reagents prepared from CuBr.

spectrum of the reagent prepared from CuI consists of two peaks, the major one at 1.09 ppm and the minor one at –0.57 ppm, whereas the spectrum of the reagent from CuBr (inset) contains a single peak at –0.57 ppm, which is thus assigned to the halide-free species.

The ^{13}C NMR spectrum of Ph_3CuLi_2 prepared from CuI (Figure 1b) contains seven major peaks (δ 169.3, 164.1, 143.2, 142.2, 128.0, 126.4, 124.9), attributable to at least two kinds of phenyl groups, which coalesce to four lines (δ 168.3, 142.4, 127.8, 125.6) as the temperature is increased from –80 °C to 0 °C. For both Ph_2CuLi (second paragraph) and Ph_3CuLi_2 the changes are reversible, and upon recooling to –100 °C, the more complex patterns reappear. An unidentified peak ($\sim$11%) is present at 170.4 ppm (vide infra). Ph_3CuLi_2 prepared from CuBr gives rise to the same principal lines, but they are much narrower, and the relative intensities are different (e.g., see Figure 1b, inset). In addition, more free PhLi (δ 172.2, 141.9, 127.4, 126.5) is present in the product from CuBr than from CuI (10% versus 2% by integration of the ^{13}C NMR spectra).

The ^{6}Li spectrum of Ph_3CuLi_2 prepared from CuI (Figure 2b) contains three broad peaks ($\sim$0.08, 0.90, 2.0 ppm) which span the region from free LiI (δ 2.3) to halide-free Ph_3CuLi_2 (0.03 ppm, see product from CuBr, inset). Intermolecular exchange of Li between Ph_3CuLi_2 and LiI apparently causes broadening in both ^{13}C and ^{6}Li NMR spectra even at –100 °C.

While no free PhLi is detectable in the Ph_2CuLi solutions and only a small amount of it is present in the solution of Ph_3CuLi_2 prepared from CuI (see ^{13}C δ 172.2, ^{6}Li δ 2.97), substantial PhLi ($\sim$17% of total Ph) appears in the spectrum of Ph_3CuLi_2 + PhLi prepared from CuI (Figure 1c), and no new peaks appear. Nevertheless, the relative intensity of the 170.4-ppm peak increases from 11% to 22%. This peak is not due to "Ph_4CuLi_3" as it does not appear in the spectrum of halide-free Ph_3CuLi_2 + PhLi (Figure 1c, inset). The 170.4 ppm ^{13}C NMR peak may be due to a cluster that contains LiI.

In THF, addition of PhLi to Ph_2CuLi (from CuI) does not afford a higher order reagent but simply a mixture of the two initial species, as observed in the methyl case.[4] In ether, the preparation of Ph_2CuLi from CuI or CuBr results in considerable dark precipitate and biphenyl, and the NMR spectra (e.g., see Figures 3–5, Supplementary Material) are not nearly as "clean" as those of DMS solutions, which are yellow and homogeneous. Nevertheless, two major species appear to be present in $Ph_2CuLi{\cdot}LiI$ and only one in $Ph_2CuLi{\cdot}LiBr$ in ether. Unfortunately, the ipso-C peaks are very broad and not as informative as they are in DMS. Upon addition of a third equivalent of PhLi to CuBr in ether,[7] the ^{13}C NMR spectrum reveals that the reagent consists of the mixture Ph_2CuLi + PhLi and not higher order Ph_3CuLi_2 (Figure 5, Supplementary Material).

It is generally believed that organocopper reagents exist as aggregates or clusters. Trimeric Ph_2CuLi has been characterized in the solid state by X-ray crystallography;[10] however, no evidence has been adduced for cuprate trimers in solution. Although the solid trimer has been prepared from both CuCN and CuI,[10b] neither counterion has been found in the solid. Cryoscopy indicates that di-*p*-tolylcopper(I)lithium diethyl etherate is dimeric in benzene solution.[11] A monomeric diphenylcuprate has been characterized in the solid state[12] but not in solution. Phenyllithium clusters tend to be smaller in solvents of higher coordinating power,[13] and the coordination of Cu(I) by DMS is thought to be especially strong due to dπ–dπ interaction.[14] Nevertheless, our ^{13}C chemical shifts for Ph_2CuLi (prepared from CuI or CuBr) measured in DMS are very close to those measured for Ph_2CuLi (from CuI) in dichloromethane-d_2 by Hallnemo and Ullenius,[11b] who assigned the structure as a dimer based upon the agreement of their ^{1}H NMR spectrum with that of the dimer studied by van Koten et al.[11a]

Treatment of 2-cyclohexenone with Ph_3CuLi_2/DMS at 0 °C yielded 90% of 1,4-addition product (3-phenylcyclohexanone) but only traces (<0.05% by GLC) of 1,2-addition products (1-phenylcyclohex-2-en-1-ol and two dienes derived from it by elimination of water), as expected considering the fact that free PhLi is not an important constituent. Remarkably, Ph_3CuLi_2 + PhLi/DMS and Ph_3CuLi_2 + 2PhLi/DMS afforded only minor amounts (3% and 10%, respectively) of 1,2-products and good yields of 1,4-product (85% and 65%, respectively). Apparently, 1,4-addition of Ph_3CuLi_2 is much faster than 1,2-addition of PhLi in DMS.[15] In agreement with the ^{13}C NMR results in THF (vide supra), Ph_2CuLi + PhLi/THF yielded 36% 1,2-addition and 64% 1,4-addition. In contrast, Ph_2CuLi + PhLi/ether gave but 3% 1,2-addition and 88% 1,4-addition.[15] These reactions were run with copper reagents prepared from CuI.

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(11) (a) Koten, G. van; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Organomet. Chem.* **1977**, *140*, C23. (b) Hallnemo, G.; Ullenius, C. *Tetrahedron* **1983**, *39*, 1621. The ^{13}C chemical shifts reported by these authors are 162.3, 142.2, 128.4, and 126.8 ppm for solutions in dichloromethane-d_2 which "sometimes contained traces of diethyl ether".

(12) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337. See, also: Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23.

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To summarize our work, we have discovered that the phenyl Gilman reagent contains LiI incorporated in the cuprate cluster and should be represented as $Ph_2CuLi{\cdot}LiI$ or $Ph_2Cu(I)Li_2$,[16] just as the cyanocuprates have been represented as $R_2CuLi{\cdot}LiCN$[17] or more commonly as $R_2Cu(CN)Li_2$.[2a] Furthermore, Ph_3CuLi_2 in DMS is not merely a mixture of Ph_2CuLi and PhLi as it is in THF or ether, but rather it is a new "higher order" reagent, the first without CN. In this regard, chemical evidence and X-ray crystallography are not as reliable as NMR for the characterization of organocopper reagents.

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Registry No. CuI, 7681-65-4; CuBr, 7787-70-4; Ph_2Cu^6Li, 113811-10-2; Ph_2CuLi, 23402-69-9; $Ph_2Cu^6Li{\cdot}^6LiI$, 113811-11-3; Ph^6Li, 92382-42-8; PhLi, 591-51-5; $Ph_3Cu^6Li_2$, 113811-12-4; ^6Li, 14258-72-1; 2-cyclohexenone, 930-68-7; 3-phenylcyclohexanone, 20795-53-3; 1-phenylcyclohex-2-en-1-ol, 60174-90-5.

Supplementary Material Available: ^{13}C and ^6Li spectra of diphenylcopperlithium-6 at 195 K and ^{13}C spectra of $Ph_2CuLi{\cdot}LiBr$, $Ph_2CuLi{\cdot}LiBr$ + PhLi, and PhLi in ether at 173 K (3 pages). Ordering information is given on any current masthead page.

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A Total Synthesis of (±)-Forskolin†

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The labdane diterpene forskolin (**1**),[1] isolated from the roots of the Indian herb *Coleus forskohlii*, has been shown to be a hypotensive agent with spasmolytic, cardiotonic, and platelet aggregation inhibitory activity and also demonstrated to be a unique and potent stimulator of the enzyme adenylate cyclase in various tissues.[2] Owing to its therapeutic potential for glaucoma,[3] congestive heart failure,[4] and bronchial asthma[5] coupled with a substantial structural challenge, forskolin (**1**) has emerged as a highly attractive target for synthetic investigations.[6–9]

† Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.
‡ Visiting scientist from Yamasa Shoyu Co. Ltd., Choshi, Chiba, Japan, 1983–1985.

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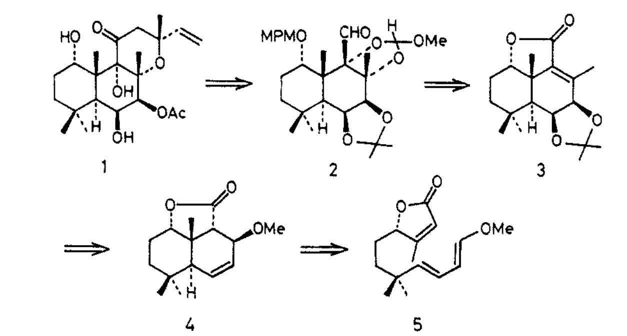
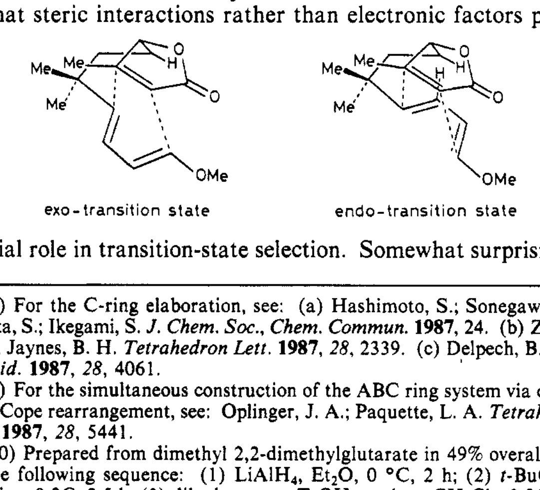
Scheme I



We report herein the total synthesis of (±)-forskolin, the strategy for which is outlined retrosynthetically in Scheme I.

The key intermediate **3** we envisaged became the same as Ziegler and co-workers reported,[7c] but the synthetic approach differs significantly from their efforts as detailed in Scheme II. The aldehyde **6**[10] was converted to the butenolide **7** by a series of routine manipulations in 56% overall yield. Subsequent addition of 3-methoxypropynyllithium (THF, −78 °C, 0.5 h) followed by sequential semihydrogenation over Lindlar catalyst (quinoline, benzene, 25 °C, 2 h), the allylic methyl carbonate formation (MeOCOCl, DMAP, CH_2Cl_2, reflux, 2 h), and palladium-catalyzed elimination[11] ($Pd(PPh_3)_4$ (0.1 equiv), Et_3N (2 equiv), THF, reflux, 5 h) afforded the desired *E*,*E*-diene **5** in 11% yield together with 35% yield of the *E*,*Z*-isomer. The key intramolecular Diels–Alder reaction[12] of **5** (toluene, 220–230 °C, sealed tube, 5 h) proceeded smoothly to give the desired trans fused decalin **4** in 85% yield. No evidence of the formation of any other isomeric cycloadducts was observed by 400 MHz ^1H NMR analysis of the crude reaction mixture. The relatively facile cyclization might be ascribed to the geminal dimethyl effect in favor of the proper orientation of the diene unit for cyclization[13] as well as the dominant HOMO–LUMO interaction in this highly activated system. The stereochemical outcome resulting from the exo transition state can be rationalized by the recently proposed nonsynchronous transition-state model,[12–14] in which bond formation between the olefinic termini with the largest FMO coefficients, the internal bond formation in this case, precedes bond formation at the other, so that steric interactions rather than electronic factors play a



exo-transition state endo-transition state

crucial role in transition-state selection. Somewhat surprisingly,

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