mmol) was added to a solution of alcohol **21b** (42 mg, 0.15 mmol) in dry CH_2Cl_2 (8 mL). The resulting suspension was stirred at rt overnight and then filtered through a Celite path. The solution was concentrated to give a residue which was flash chromatographed (1 × 14 cm, 3% EtOAc/hexanes) to afford 38 mg of ketone **6** (91%) which shows ^1H NMR and ^{13}C NMR identical to those of the compound obtained above.

Preparation of [1*S*-(1α,3aβ,4α,7aα)]-Octahydro-1,4-dihydroxy-7a-methyl-1*H*-indene (22) from 4 through 17 and 23. [1*S*-(1α,3aβ,7aα)]-Octahydro-1-[(*tert*-butyldimethylsilyl)oxy]-7a-methyl-4*H*-inden-4-one (17). PDC (140 mg, 0.53 mmol) was added to an ice–water-cooled solution of alcohol **4** (100 mg, 0.35 mmol) in dry CH_2Cl_2 (20 mL). The resulting suspension was stirred at rt for 4 h, filtered through Celite, and concentrated to give a residue which was dissolved with EtOAc (100 mL). This solution was washed with an aqueous saturated solution of $NaCHO_3$ (2 × 50 mL), dried, filtered, and concentrated to give a brown viscous liquid which was flash chromatographed (5% Et_2O/hexanes) to afford 98 mg of **17** (98%; R_f 0.55, 15% EtOAc/hexanes; colorless liquid): IR (film) 1710 cm^{-1}; ^1H NMR δ 3.84 (1 H, t, J = 8.5 Hz, H-3a), 0.88 (9 H, s, *t*-BuSi), 0.67 (3 H, s, Me-7a), 0.04 and 0.03 (6 H, 2 s, Me_2Si). Anal. Calcd for $C_{16}H_{30}O_2Si$: C, 68.01; H, 10.72. Found: C, 67.86; H, 10.53.

[1*S*-(1α,3aβ,4α,7aα)]-Octahydro-1-[(*tert*-butyldimethylsilyl)oxy]-7a-methyl-1*H*-inden-4-ol (23). (23). $NaBH_4$ (30 mg, 0.79 mmol) was added to an ice–water-cooled solution of **17** (109 mg, 0.39 mmol, prepared from **4** as above) in absolute EtOH (4 mL). The resulting mixture was stirred for 1 h at rt, and then H_2O (5 mL) was added. The mixture was concentrated to a small volume, and the residue was extracted with Et_2O (2 × 5 mL). The combined organic phases were dried, filtered, and concentrated to give a residue which was flash chromatographed (1 × 15 cm, 5% EtOAc/hexanes) to afford 94 mg of **23** (84%; R_f 0.7, 30% EtOAc/hexanes; colorless oil) and 18 mg of **4** (15%; R_f 0.6, 30% EtOAc/hexanes; white solid): ^1H NMR δ 4.03 (1 H, m H-4), 3.52 (1 H, t, J = 7.8 Hz, H-1), 0.95 (3 H, m, Me-7a), 0.88 (9H, s, *t*-Bu), 0.01 (3 H, s, Me_2Si); ^{13}C NMR δ 81.8, 69.3, 47.3, 42.2, 37.5, 33.8, 29.9, 25.8, 21.8, 18.0, 17.1, 12.6, −4.6, −5.0.

[1*S*-(1α,3aβ,4α,7aα)]-Octahydro-1,4-dihydroxy-7a-methyl-1*H*-indene (22). An aqueous solution of HF (48%, 17 drops) was added to a solution of **23** (91 mg, 0.32 mmol) in CH_3CN (5 mL). The resulting solution was stirred overnight at rt. After concentration, an aqueous saturated solution of $NaHCO_3$ (15 mL) was added and the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried, filtered, and concentrated. The residue was flash chromatographed (1 × 10 cm, 20% EtOAc/hexanes) to give 44 mg of **22** (81%: R_f 0.15, 30% EtOAc/hexanes; white solid; mp 135–7 °C): ^1H NMR δ 4.08 (1 H, m, H-4), 3.61 (1 H, t, J = 8.5 Hz, H-1), 1.00 (3 H, s, Me-7a); ^{13}C NMR δ 81.9, 69.0, 47.6, 41.9, 37.1, 33.7, 29.6, 21.7, 17.0, 12.2.

Alternative Route for Preparation of 22 from 6 through 21b. $NaBH_4$ (20 mg, 0.53 mmol) was added to an ice–water-cooled solution of **6** (43 mg, 0.15 mmol) in absolute EtOH (3 mL). The resulting mixture was stirred for 1 h at rt, and then H_2O (5 mL) was added. The mixture was concentrated to a small volume. The residue was extracted with Et_2O (2 × 5 mL), and the combined organic phases were dried, filtered, and concentrated to give 42 mg of **21b** (97%; R_f 0.3, 15% EtOAc/hexanes; white solid), which shows ^1H NMR and ^{13}C NMR identical to those of the compound obtained above. An aqueous solution of HF (48%, five drops) was added to a solution of **21b** (34 mg, 0.12 mmol) in CH_3CN (2 mL). The solution was stirred for 20 h. After concentration, an aqueous saturated solution of $NaHCO_3$ (10 mL) was added and the mixture was extracted with Et_2O (4 × 10 mL). The combined organic phases were dried, filtered, and concentrated, and the resulting residue was flash chromatographed (1 × 10 cm, 20% EtOAc/hexanes) to give 16 mg of **22** (80%; R_f 0.15, 30% EtOAc/hexanes; white solid, mp 134–6 °C). The ^1H NMR and ^{13}C NMR spectra were identical to those of the compound obtained from **23** as above.

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Supplementary Material Available: ^1H NMR spectra of **4, 6, 7a, 7b, 8, 9a, 9b, 10–14, 15a, 16, 17, 18b, 19, 20, 21a, 21b, 22,** and **23** and ^{13}C NMR spectra of **4, 6, 9a, 9b, 10, 11, 16, 19, 20, 21a, 21b, 22,** and **23** (35 pages). Ordering information is given on any current masthead page.

Transmetalation Reactions of Alkenylalanes: Copper-Catalyzed Conjugate Addition to Enones

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An improved synthetic strategy for the in situ preparation of vinyl cuprates from alkynes is presented and used for the stereospecific synthesis of di-, tri-, and tetrasubstituted olefins. Hydroalumination or Cp_2ZrCl_2-catalyzed carboalumination of alkynes, followed by in situ transmetalation to bis-alkynyl-copper complex $[(C_4H_9C{\equiv}C)_2CuCN]Li_2$ and addition of enones, led to the isolation of 1,4-addition products in high yields. Stoichiometric or catalytic amounts of copper complex gave similar results. However, in the presence of less than 10 mol % of Cu(I) complex, side products were formed and a significant drop in the yield of the desired conjugate addition product was observed. An ate-transfer mechanism is postulated for the rapid exchange of vinyl ligands from Al(III) to Cu(I) at low temperatures.

Introduction

The development of the chemistry of organocuprates has resulted in many important applications in organic synthesis, such as conjugate additions to α,β-unsaturated carbonyl compounds,[1] nucleophilic displacements on halides,[2] sulfonates,[3] and allylic acetates,[4,5] epoxide ring openings,[6] and additions to acetylenes.[7] However, the vast

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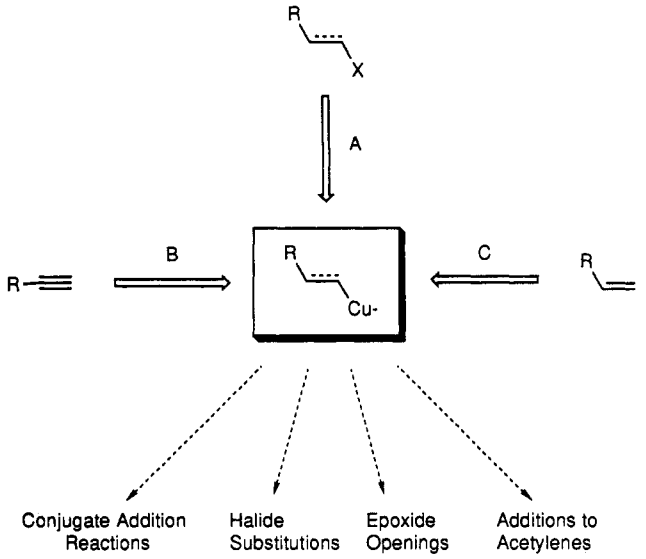
0022-3263/92/1957-3178$03.00/0

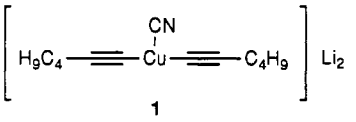
Scheme I



majority of protocols for the preparation of organocuprates use alkyl or alkenyl halides as starting materials and involve organolithium or Grignard reagents as intermediates (Scheme I, pathway A).[8-11]

The involvement of highly reactive and strongly basic first and second column derivatives in the preparation of cuprates complicates the experimental protocol. It also considerably limits the range of functionality that is tolerated in the starting material. Not surprisingly therefore, recent research in organocuprate chemistry has been targeting alternative preparations of both alkyl- and alkenyl–copper complexes. Since only highly activated copper metal allows the direct synthesis of copper organometallics from halides,[12] a number of transmetalation procedures have been investigated.[13] As early as 1977, Schwartz and co-workers established the copper triflate catalyzed 1,4-addition of vinyl zirconates to enones.[14,15] In 1988, Knochel and co-workers reported on the synthesis and reactivity of copper reagents RCu(CN)ZnI obtained from primary and secondary alkyl zinc iodides by a transmetalation with the soluble salt, CuCN·2LiCl.[16,17] The transmetalation of cyanocuprates and vinyl-, silyl-, and certain allylstannanes was demonstrated by Lipshutz and co-workers.[18] Cahiez and Alami applied organomanganese reagents for the copper-catalyzed conjugate addition,[19] Rieke and co-workers used organocalcium precursors for the preparation of calcium cuprate reagents,[20] and Comasseto and Berriel investigated the transmetalation of vinylic tellurides and cyanocuprates.[21] Recently, Nakamura and co-workers used organotitanium complexes in the copper-catalyzed S_N2' substitution of allylic chlorides and phosphates.[22]

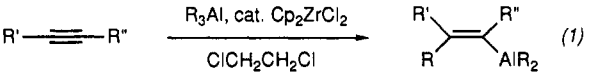
We have previously shown that alkylzirconocenes[23] and alkylsamarium reagents[24] readily undergo conjugate addition to enones in the presence of catalytic or stoichiometric amounts of copper(I) salts. In a preliminary study, we have also demonstrated that vinylic alanes undergo a highly efficient in situ exchange process with a bis-alkynyl–copper complex.[25] These procedures have established novel one-step preparations of alkyl- and alkenylcuprates from olefinic and acetylenic precursors without involving traditional halide starting materials or highly reactive organometallic intermediates (Scheme I, routes B and C). We now report further studies of the in situ cuprate formation from alkenylalanes by transmetalation with bis-alkynyl–copper complex **1**.



1

Results and Discussion

Substituted vinylic alanes are readily available by carbo- or hydroalumination of alkynes.[26-28] The Cp_2ZrCl_2-catalyzed carboalumination of alkynes represents a reasonably general and often highly selective route to vinylalanes (eq 1).[29,30] Various functional groups, such as alcohols, silyl



(1)

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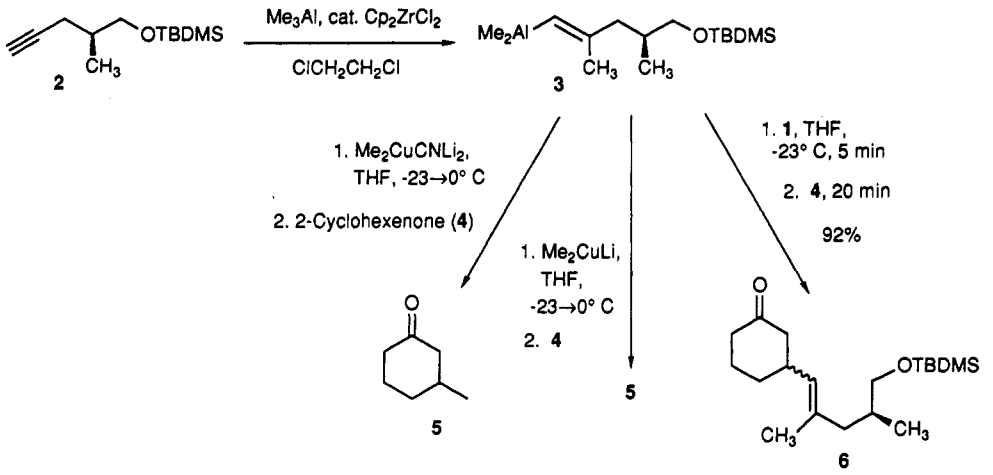
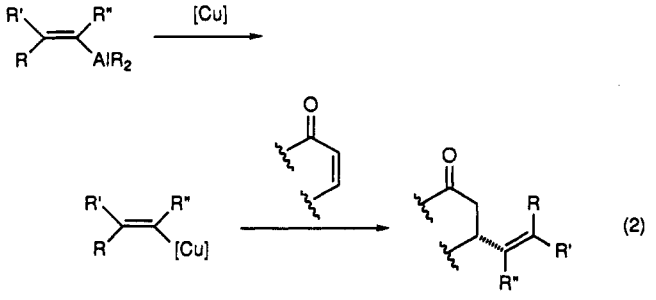
Scheme II



ethers, sulfides, halogens, alkenes, and arenes, are tolerated in this process.[31] The chemistry of organoaluminum derivatives is dominated by the high Lewis acidity and oxophilicity of the monomeric species.[32]

A direct preparation of cuprates from alkenylalanes significantly expands the scope of both organoaluminum and organocopper chemistry: Conjugate addition reactions of the relatively weakly nucleophilic alanes to enones are very narrow in scope,[33] and the preparation of vinylic cuprates from alkynes via carbocupration is essentially limited to terminal alkynes and does not tolerate halogens or other reactive functionality.[34] Additionally, methylcupration requires a large excess of cuprate over alkene and involves extremely long reaction times.[35] A transmetalation from alkenylalanes to Cu(I) salts, i.e., the combination of both Al and Cu in the reaction sequence, overcomes the limitations of the monometallic systems and thus results in a new synthetic pathway (eq 2).



(2)

The selection of the ligands on the copper complex proved to be crucial for the successful realization of the envisioned transmetalation protocol. Alane **3** was readily prepared from alkyne **2** and 3 equiv of Me_3Al in the presence of 20 mol % of Cp_2ZrCl_2. Treatment of crude **3** with $[Me_2CuCN]Li_2$,[36] followed by 2-cyclohexenone (**4**), led to methyl-group transfer to give ketone **5** (Scheme II). The same major product was observed with Me_2CuLi.[37] The use of a cyanocuprate **1** with two nontransferable[38] alkyne ligands, however, led to the formation of the trisubstituted olefin **6** in 92% yield! Both transmetalation and conjugate addition of the alkenyl substitutent occurred rapidly at −23 °C.

Control experiments with vinylalane **3** and the corresponding trimethylalkenyl-ate complex led only to traces of addition product **6** even in the presence of $Ni(acac)_2$ (eq 3). Moreover, attempted methylcupration of alkyne **2** with

$$3 \xrightarrow[\text{rt}]{\text{THF, 4}} 6\ (<5\%) \xleftarrow[\text{rt}]{\text{THF, 4, cat. Ni(acac)}_2} 3$$

$$3 \xrightarrow[\text{2. 4, rt}]{\text{1. MeLi, THF, −78 °C}} 6\ (<5\%) \xleftarrow[\text{2. 4, cat. Ni(acac)}_2\text{, rt}]{\text{1. MeLi, THF, −78 °C}} 3$$

$$2 \xrightarrow[\text{Et}_2\text{O/Me}_2\text{S, −25 °C, 5 days}]{\text{MeMgBr, CuBr·Me}_2\text{S}} \text{NR} \qquad (3)$$

MeCuMgBr[39] failed to produce any metalated alkene even after 5 d reaction time at −25 °C. This series of experiments clearly demonstrated the advantage of the in situ transmetalation sequence involving both aluminum and appropriate copper intermediates.

In order to determine the scope of the carboalumination/transmetalation process, a series of functionalized terminal and internal alkynes was converted to the corresponding alkenylalanes by Cp_2ZrCl_2-catalyzed carboalumination with Me_3Al or hydroalumination with DIBALH and subjected to reaction with 1 equiv of copper complex **1** and various enones (Tables I–III).

Zirconocene dichloride catalyzed carboalumination of alkynes with Me_3Al or uncatalyzed hydroalumination with DIBALH, followed by in situ transmetalation to cyanocuprate complex $[(C_4H_9C{\equiv}C)_2CuCN]Li_2$ (**1**), and addition of enones at −23 °C led to the isolation of 1,4-addition products in moderate to high yields. Isolation or purification of the intermediate air- and moisture-sensitive alanes is not necessary, and therefore these transformations do not require any glovebox techniques. Excess Me_3Al is

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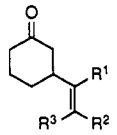
Table I. Carboalumination of Terminal Alkynes Followed by in Situ Cuprate Formation and Conjugate Addition Reactions with Stoichiometric 1 and Cyclohexenone 4

	alkyne		product					
entry	structure	no.	structure	no.	R^1	R^2	R^3	yield[a] (%)
1	$HC{\equiv}C(CH_2)_3CH_3$	7		8	H	*n*-Bu	CH_3	95
2	$HC{\equiv}CPh$	9		10	H	Ph	CH_3	45
3	$HC{\equiv}CSi(CH_3)_3$	11		12a	TMS	H	CH_3	64
				12b	TMS	CH_3	H	7
4	$HC{\equiv}C(CH_2)_2I$	13		14	H	$(CH_2)_2I$	CH_3	85
5	$HC{\equiv}CCH_2SPh$	15		16	H	CH_2SPh	CH_3	35
6	$HC{\equiv}C(CH_2)_3OBDPS$[b]	17		18	H	$(CH_2)_3OBDPS$	CH_3	70

[a] Yields are not optimized and are based one enones. Generally, a slight to moderate excess of alkyne over enone was used: alkyne: Me_3Al:Cp_2ZrCl_2:1:enone = 1.1–1.5:3–4.5:0.2:1:1. [b] BDPS = *tert*-Butyldiphenylsilyl.

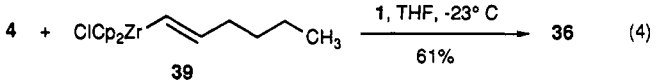
easily removed in vacuo before addition of complex 1 and enone. The actual transmetalation process is very rapid even at −23 °C; however, below −50 °C no ligand exchange reaction seems to occur, as added enone is recovered under these conditions.

As expected, functionalization of the alkyne with aromatic rings, silyl groups, thioethers, and silyl ethers did not interfere with cuprate formation and conjugate addition (Table I, entries 2, 3, 5, and 6). Remarkably, even iodide **13** was successfully carried through the methylalumination/transmetalation/conjugate addition sequence, and iodo ketone **14** was isolated in 85% yield (Table I, entry 4). The selective preparation of halide-substituted vinylcuprates from iodides such as **13** clearly demonstrates the wide range of functionality that is within the reach of transmetalation protocols that circumvent organolithium or Grignard reagents.

The reactivity of the cuprate reagents that result from equilibration of alkenylalanes with bis-hexynyl–copper complex **1** is slightly reduced compared to standard[40] cyanocuprate reagents;[41] optimal reaction temperatures range from −30 to −5 °C, and conjugate additions to enoates proceed only sluggishly.[42] With both cyclic and acyclic enones, however, the desired trisubstituted olefins were obtained in high yield even with sensitive substrates such as methyl vinyl ketone (**29**) or cyclopentenone **19** (Table II). The addition of the vinyl organometallic to cyclic enones occurs in an axial fashion, as exemplified by the highly stereoselective reaction with 4-*tert*-butylcyclohexenone **23** and spiroketal **32** (Table II, entries 3 and 8).[43] The regioselectivity of both the (generally syn-) addition process to the alkyne and the transmetalation is very high. Selectivities in the 95–100% range are typical for the Cp_2ZrCl_2-assisted methylalumination.[29] Transmetalation and conjugate addition occur with retention of configuration at the olefinic carbon, as determined by analysis of the ^{13}C NMR resonances of the olefinic methyl substituents.[44] Ketone **12** was isolated as a 9.5:1 mixture of alkene isomers due to formation of anti-addition products in the carboalumination of TMS–acetylene.[45]

The carboalumination/transmetalation of internal alkynes led, after the addition of enones, to the stereoselective formation of tetrasubstituted alkenes. Methyl ketone **35** was isolated in 48% yield (Table II, entry 9). Whereas the transmetalation of alkenylalanes from internal alkenes does not seem to present any difficulties, the scope of this process is presently limited by the poor regioselectivity in the carboalumination of unsymmetrically substituted alkynes.[29]

Trans-disubstituted olefins were obtained by hydroalumination of terminal alkynes with DIBALH,[46] followed by treatment with bis-hexynyl–cyanocopper complex **1** and enones. Conjugate addition products **36** and **38** were isolated in 72 and 75% yield, respectively (Table III). Ketone **36** was also prepared from zirconocene derivative **39** by transmetalation with **1** (eq 4).[47] Analogous to alkenyl-



(4)

alanes, alkenylzirconocenes are readily available by hydrozirconation of alkynes with Cp_2ZrHCl[48] and are therefore also useful reagents for the preparation of vinyl cuprates via hydrometalation of alkynes.[49] Since zirconocene dichloride is used as a carbometalation catalyst, this observation raises the question of a direct involvement of zirconocene derivatives in the transmetalation of alanes.

In this regard, the ease of ligand transfer of alkenylalanes prepared by thermal hydroalumination procedures to copper complex **1** has important mechanistic implications. No Cp_2ZrCl_2 is used in this hydroalumination/transmetalation sequence. It appears therefore unlikely that traces of zirconocene derivatives are critically involved in the carboalumination/transmetalation sequence, even though a transfer of ligands from R_3Al to Cp_2ZrCl_2 is certainly feasible as a side process in this reaction.[28,50]

Mechanistic studies of the transmetalation scheme and the nature of the resulting cuprate reagent are still in process. Interestingly, the addition of HMPA to the reaction mixture or the use of a vinylalane ate complex with copper reagent **1** led to a sharp decrease in both the yield

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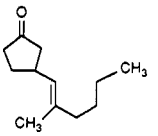
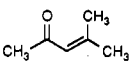
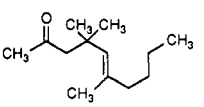
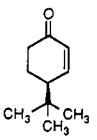
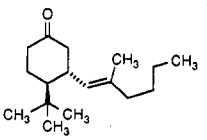
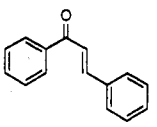
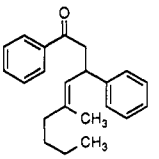
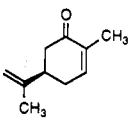
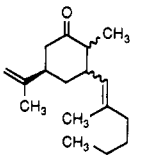
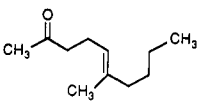
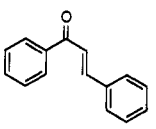
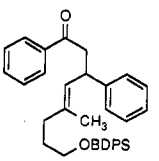
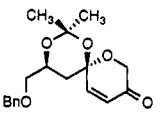
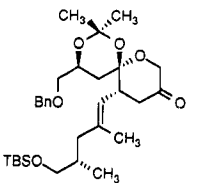
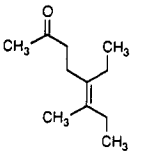
(41) Mixed alkynyl organocuprates are generally of lower reactivity than bis-alkylcuprates: Mandeville, W. H.; Whitesides, G. M. *J. Org. Chem.* **1974**, *39*, 400.
(42) Wipf, P. Unpublished results.
(43) For a detailed analysis of the stereochemistry of **33**, see ref 25, footnote 16.
(44) For assignments of *E*- and *Z*-stereochemistry, see: (a) Jones, T. K.; Mills, S. G.; Reamer, R. A.; Askin, D.; Desmond, R.; Volante, R. P.; Shinkai, I. *J. Am. Chem. Soc.* **1989**, *111*, 1157. (b) Ragan, J. A.; Nakatsuka, M.; Smith, D. B.; Uehling, D. E.; Schreiber, S. L. *J. Org. Chem.* **1989**, *54*, 4267.
(45) Eisch, J. J.; Manfre, R. J.; Komar, D. A. *J. Organomet. Chem.* **1978**, *159*, C13.
(46) Wilke, G.; Müller, H. *Chem. Ber.* **1956**, *89*, 444.
(47) Wipf, P. Unpublished results.
(48) Kautzner, B.; Wailes, P. C.; Weigold, H. *J. Chem. Soc., Chem. Commun.* **1969**, 1105.
(49) See ref 14b and 15 for alternative protocols for the preparation of cuprate reagents from vinylzirconocenes.
(50) For a discussion of transmetalations between Al and Zr, see: Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, p 692.

Table II. Carboalumination of Terminal and Internal Alkynes Followed by in Situ Cuprate Formation and Conjugate Addition Reactions with Stoichiometric 1. Variation of Enone

		enone		product		
entry	alkyne	structure	no.	structure	no.	yield[a] (%)
1	7		19		20	63
2	7		21		22	64
3	7		23		24	65
4	7		25		26	87
5	7		27		28	67
6	7		29		30	88
7	17		25		31	90
8	2		32		33	72
9	3-hexyne (34)		29		35	48[b]

[a] Yields are not optimized and are based on enones. Generally, a slight to moderate excess of alkyne over enone was used: alkyne: Me_3Al:Cp_2ZrCl_2:1:enone = 1.1–1.5:3–4.5:0.2:1:1. [b] Alkyne:Me_3Al:Cp_2ZrCl_2:1:enone = 2:6:0.2:1:1.

and the rate of addition of alane 3 to cyclohexenone. No acceleration of conjugate addition to sterically hindered enones was observed in the presence of BF_3[51] or TMSCl.[52]

These observations led us to the conclusion that an initial ligand transfer[53] from copper–ate complex 1 to the Lewis acidic alane is followed by a second ligand exchange between the newly-formed aluminum–ate complex 40 and copper derivative 41 (Scheme III).[54] The exchange of vinyl ligands is kinetically strongly favored over alkyl-group exchange.[55] Overall, ate-transfer processes establish an equilibrium that involves the presence of some vinylic

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(52) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349, and references cited therein.
(53) Collman, J.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(54) Lewis acid induced abstraction of ligands has been documented for several types of cuprate reagents: (a) Lipshutz, B. H.; Ellsworth, E. L.; Dimock, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 5869. (b) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 1351. (c) Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J.; Shirazi, A. *Tetrahedron Lett.* **1988**, *29*, 6677.
(55) Alexakis, A.; Hanaizi, J.; Jachiet, D.; Normant, J.-F. *Tetrahedron Lett.* **1990**, *31*, 1271, and references cited therein.

Scheme III

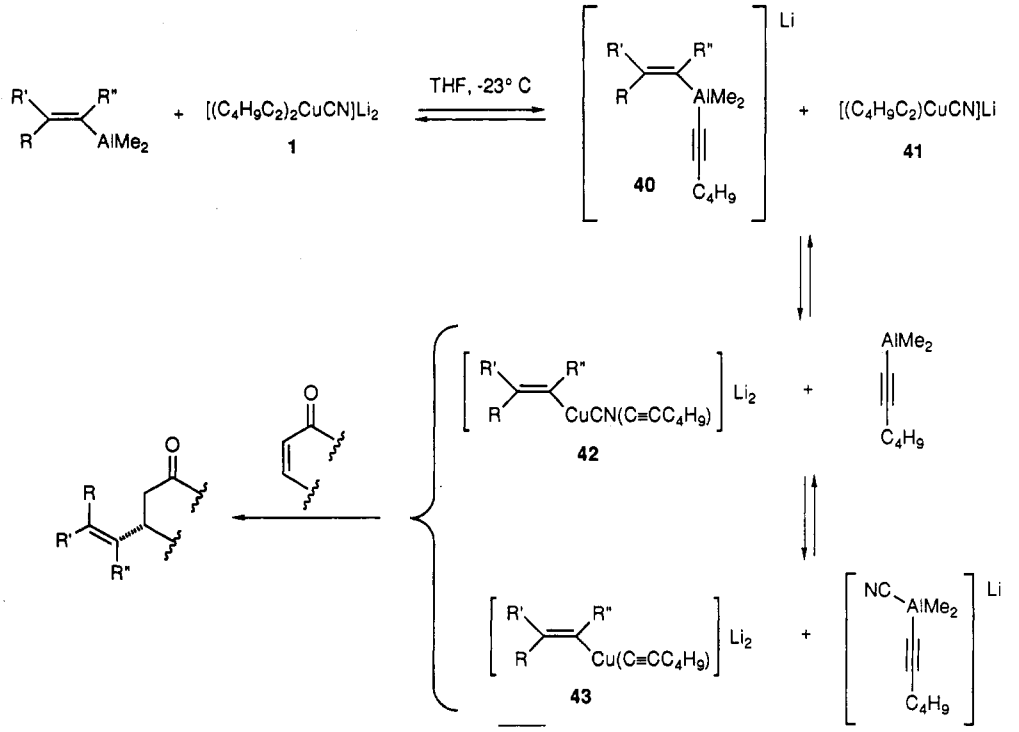
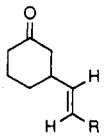


Table III. Hydroalumination of Terminal Alkynes Followed by in Situ Cuprate Formation and Conjugate Addition Reactions with Stoichiometric 1 and Cyclohexenone 4

entry	alkyne structure	alkyne no.	product structure	product no.	R	yield[a] (%)
1	$HC{\equiv}C(CH_2)_3CH_3$	7		36	*n*-Bu	72
2	$HC{\equiv}C(c\text{-}C_6H_{11})$	37		38	$c\text{-}C_6H_{11}$	75

[a] Yields are not optimized and are based on enones. An excess of alkyne over enone was used: alkyne:DIBALH:1:enone = 1.5:1.5:1.5:1.

Scheme IV

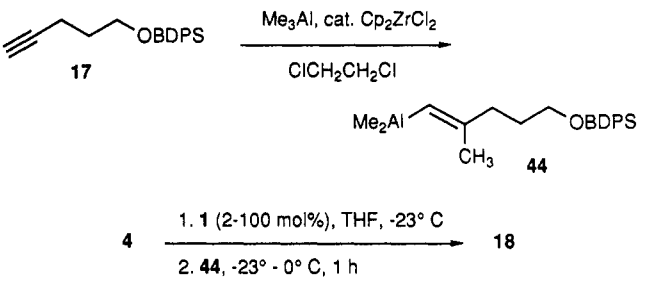


Table IV. Carboalumination of Alkyne 17 Followed by in Situ Cuprate Formation and Conjugate Addition Reactions with Enones 4 and 25 with Catalytic 1. Comparison of Standard (SA) and Inverse Addition (IA) Protocols

1 (mol %)	18 (%) (SA)	18 (%) (IA)	31 (%) (SA)
100	70	67	90
50	41	58	89
10	26	52	90
2		27	75
0	14		40

cyanocuprate **42** and/or mixed cuprate **43**, which undergo irreversible addition to appropriate acceptor systems. The presence of alanes and aluminum ate complexes in the reaction mixture reduces the catalytic efficiency of Lewis acid additives. An open coordination site on the alkenylalane is essential for establishing an equilibrium with copper ate complex **1**. As long as the rate of conjugate addition of **42** or **43** exceeds the rate of side reactions of any other species in the reaction mixture, ligand transfer from weakly nucleophilic vinylorganometallics to copper complexes with non-transferable ligands such as **1** does not need to be thermodynamically favorable.

When stoichiometric quantities of bis-hexynyl–copper complex **1** were used, a solution of the enone in THF was usually added last after a short equilibration of alane and copper complex at −23 °C (= standard addition, SA). Additionally, an alternative protocol was investigated for the application of catalytic amounts of **1** in the transmetalation scheme. In the inverse addition (IA) protocol 1 equiv of alane **44** was added to a mixture of enone **4** and catalytic quantities of bis-hexynyl–cyanocopper complex in THF at −23 °C (Scheme IV). Whereas no differences between these experimental protocols were noticeable with stoichiometric **1**, at substoichiometric levels the IA procedure clearly prevailed (Table IV).

The catalytic process provided good yields of addition products only if the reaction time was increased and the temperature of the reaction mixture was gradually raised from −23 to 0 °C over 1 h. Whereas the conjugate addition of alane **44** to enone **4** experienced only a slight drop in yield with 50 and 10 mol % copper complex under IA conditions, the drop was significant with the SA protocol. With 2 mol % copper complex, side reactions diminished the yield of the desired product **18**. Chalcone (**25**), however, provided good yields of trisubstituted olefin **31** even in presence of as little as 2 mol % complex **1**. In the absence of any copper catalyst, the yield of alane addition products dropped to 14% and 40%, reflecting the weakly nucleophilic character of these vinylorganometallics. Isolation of **18** and **31** was also complicated by the formation of several side products under the latter conditions.

These experiments clearly demonstrate that the catalytic efficiency of the in situ carboalumination/transmetalation sequence strongly depends both on the reactivity of the substrate enone and on the order of addition of the reagents. In general, best results are achieved by the use of

10 mol % or more copper complex 1 and addition of the alane to a mixture of enone and catalyst.[56]

Conclusions

Alkenylalanes, available via Cp_2ZrCl_2-catalyzed carboalumination or hydroalumination of alkynes, are readily transmetalated in situ to vinylic cuprates by treatment with bis-alkynyl–copper complex 1. After conjugate addition to enones, the overall sequence allows the highly stereoselective preparation of di-, tri-, and, with internal alkynes, tetrasubstituted olefins. A wide range of functionality such as silanes, silyl ethers, sulfides, and iodides is compatible with this process. No halide intermediates or traditional organolithium or organomagnesium reagents are involved, and transmetalation/conjugate addition occurs readily in the presence of both stoichiometric and catalytic amounts of copper complex. The mechanism of the transmetalation sequence is likely to involve consecutive ate-transfer ligand exchanges between Cu(I) and Al(III). Further applications of the transmetalation methodology for the in situ preparation of cuprates will be reported in due course.

Experimental Section

General. Unless otherwise noted, all starting materials were commercially available[57] and were used without further purification. All reactions were run under a positive pressure of dry N_2 or Ar. Ether and THF were distilled from either sodium or potassium/benzophenone ketyl under Ar or N_2 immediately prior to use. CuCN was dried in vacuo with periodic heating prior to use. NMR spectra were recorded at 300 MHz for ^1H and at 75 MHz for ^{13}C in $CDCl_3$ unless noted otherwise. High-resolution mass spectra were obtained by peak matching with reference peaks of known m/z. Chromatography was performed on silica gel according to the Still protocol.[58]

General Procedure for the Carboalumination/Transmetalation/Conjugate Addition of Alkynes: 3-[(1*E*,4*S*)-5-[(*tert*-Butyldimethylsilyl)oxy]-2,4-dimethyl-1-pentenyl]-cyclohexanone (6). A suspension of Cp_2ZrCl_2 (28 mg, 0.10 mmol) in dry 1,2-dichloroethane (2 mL) was treated at 0 °C with a 2.0 M solution of trimethylaluminum in toluene (0.71 mL, 1.42 mmol), followed by addition of a solution of (4*R*)-5-[(*tert*-butyldimethylsilyl)oxy]-4-methyl-1-pentyne (2, 100 mg, 0.47 mmol) in 1,2-dichloroethane (0.3 mL). The reaction mixture was stirred at room temperature for 3 h, the solvent was removed in vacuo, and dry Et_2O (2 mL) was added. The solution of the alkenylalane was added at −23 °C to a mixture of flame-dried CuCN (45 mg, 0.51 mmol) in THF (4 mL) and a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (2.2 mL, 1.1 mmol). The reaction mixture was stirred for 5 min at −23 °C, and a solution of 2-cyclohexenone (4, 38 mg, 0.40 mmol) in THF (1 mL) was added dropwise. Stirring at −23 °C was continued for another 20 min. The mixture was quenched into a cold (0 °C) solution of saturated ammonium chloride/ammonium hydroxide (9:1) and extracted three times with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered through silica gel, and chromatographed (EtOAc/hexane (1:5)) to yield 119 mg (92%) of 6 as a clear oil: IR (neat) 2940, 2920, 2850, 1705, 1450, 1380, 1245, 1215, 1080, 1027, 830, 770 cm^{-1}; ^1H NMR δ 4.99 (d, 1 H, J = 8.7 Hz), 3.50–3.30 (m, 2 H), 2.80–2.60 (m, 1 H), 2.40–2.00, 1.90–1.40 (2m, 11 H), 1.57 (s, 3 H), 0.88 (s, 9 H), 0.82–0.78 (m, 3 H), 0.21, 0.20 (2s, 6 H); ^{13}C NMR δ 211.9, 134.4, 129.7, 68.4, 48.6, 44.0, 41.7, 38.7, 34.1, 32.3, 26.4, 25.8, 18.8, 16.8, 16.5, −4.9; MS (CI) m/z (rel intensity) 325 ([M + 1]$^+$, 100).

3-[(*E*)-2-Methyl-1-hexenyl]cyclohexanone (8). Prepared from 1-hexyne (7) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:5)) gave 95% of 8 as a clear oil: IR (neat) 2950, 2915, 2845, 1700, 1440, 1305, 1245, 1212 cm^{-1}; ^1H NMR δ 4.96 (dq, 1 H, J = 8.7, 1 Hz), 2.70–2.60 (m, 1 H), 2.40–1.20 (m, 14 H), 1.55 (d, 3 H, J = 1 Hz), 0.85 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 211.9, 136.1, 127.9, 48.6, 41.7, 39.6, 38.6, 32.2, 30.4, 25.8, 22.6, 16.5, 14.4; MS (CI) m/z (rel intensity) 195 ([M + 1]$^+$, 100). Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.47; H, 11.42.

3-[(*E*)-2-Phenyl-1-propenyl]cyclohexanone (10). Prepared from phenylacetylene (9) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:6)) gave 45% of 10 as a clear oil: IR (neat) 3070, 3020, 2950, 2890, 1710, 1500, 1450, 1320, 1210, 750, 700 cm^{-1}; ^1H NMR δ 7.45–7.25 (m, 5 H), 5.65 (d, 1 H, J = 8.9 Hz), 2.95–2.85 (m, 1 H), 2.50–2.10 (m, 4 H), 2.07 (s, 3 H), 1.95–1.55 (m, 4 H); ^{13}C NMR δ 211.1, 143.2, 134.9, 131.0, 128.2, 127.0, 126.8, 47.9, 41.3, 38.9, 32.7, 25.6, 16.1; MS (EI) m/z (rel intensity) 214 (M$^{\bullet+}$, 77), 199 (35), 181 (15), 171 (28), 157 (48), 143 (79), 129 (100), 118 (62), 105 (85), 91 (55), 77 (31), 71 (18), 65 (12), 55 (23); HRMS m/z calcd for $C_{15}H_{18}O$ 214.1358, found 214.1358.

3-[(*E*)-1-(Trimethylsilyl)-1-propenyl]cyclohexanone (12a) and 3-[(*Z*)-1-(Trimethylsilyl)-1-propenyl]cyclohexanone (12b). Prepared from (trimethylsilyl)acetylene (11) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:5)) gave 71% of a 9.5:1 mixture[59] of 12a and 12b as a clear oil: IR (neat) 3020, 2940, 1780, 1690, 1510, 1480, 1320, 1290, 900, 820 cm^{-1}; ^1H NMR (12a, major isomer) δ 6.06 (q, 1 H, J = 7.2 Hz), 2.45–2.20 (m, 5 H), 2.05–1.95 (m, 1 H), 1.85–1.75 (m, 1 H), 1.78 (d, 3 H, J = 7.2 Hz), 1.65–1.55 (m, 1 H), 1.50–1.40 (m, 1 H), 0.14 (s, 9 H); ^{13}C NMR (12a, major isomer) δ 212.2, 142.8, 134.8, 48.5, 43.5, 41.2, 32.7, 25.4, 18.0, 0.0; MS (EI) m/z (rel intensity) 210 (M$^{\bullet+}$, 10), 195 (90), 181 (8), 167 (25), 137 (20), 120 (7), 91 (12), 73 (100), 59 (35), 45 (50); HRMS m/z calcd for $C_{11}H_{19}OSi$ (M − CH_3) 195.1205, found 195.1205.

3-[(*E*)-4-Iodo-2-methyl-1-butenyl]cyclohexanone (14). Prepared from 4-iodobutyne (13) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:5)) gave 85% of 14 as a clear oil: IR (neat) 2950, 2900, 1710, 1620, 920, 730 cm^{-1}; ^1H NMR δ 5.06 (d, 1 H, J = 9.0 Hz), 3.20 (t, 2 H, J = 7.4 Hz), 2.70–2.60 (m, 1 H), 2.45 (t, 2 H, J = 7.4 Hz), 2.35–2.00 (m, 4 H), 1.85–1.40 (m, 4 H), 1.58 (s, 3 H); ^{13}C NMR δ 211.1, 133.8, 130.9, 47.8, 43.2, 41.2, 38.2, 31.5, 25.4, 15.6, 5.1; MS (EI) m/z (rel intensity 292 (M$^{\bullet+}$, 41), 270 (10), 249 (42), 235 (27), 195 (15), 165 (67), 147 (59), 137 (40), 123 (12), 107 (70), 95 (41), 81 (50), 67 (53), 55 (70); HRMS m/z calcd for $C_{11}H_{17}OI$ 292.0324, found 292.0324.

3-[(*E*)-3-(Phenylthio)-2-methyl-1-propenyl]cyclohexanone (16). Prepared from 3-(phenylthio)propyne (15) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:6)) gave 35% of 16 as a clear oil (a minor impurity could not m/z removed by chromatography or distillation): IR (neat) 3070, 2940, 2830, 1710, 1580, 1490, 1440, 1210, 1090, 1010, 910, 720 cm^{-1}; ^1H NMR δ 7.35–7.05 (m, 5 H), 4.89 (d, 1 H, J = 7.1 Hz), 3.37 (s, 2 H), 2.55–2.45 (m, 1 H), 2.30–1.50 (m, 6 H), 1.66 (s, 3 H), 1.30–1.15 (m, 2 H); ^{13}C NMR δ 211.1, 131.9, 131.6, 129.4, 128.9, 128.3, 126.9, 120.5, 47.4, 44.5, 41.3, 38.0, 31.2, 25.0, 15.5; MS (EI) m/z (rel intensity) 260 (M$^{\bullet+}$, 16), 164 (31), 150 (25), 135 (10), 110 (18), 97 (32), 81 (22), 69 (28), 55 (54); HRMS m/z calcd for $C_{16}H_{20}OS$ 260.1235, found 260.1235.

3-[(*E*)-5-[(*tert*-Butyldiphenylsilyl)oxy]-2-methyl-1-pentenyl]cyclohexanone (18). Prepared from 5-[(*tert*-butyldiphenylsilyl)oxy]pentyne (17) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:7)) gave 70% of 18 as a clear oil: IR (neat) 3080, 2955, 2880, 1708, 1439, 1452, 1417, 1106, 1007, 860, 741, 700 cm^{-1}; ^1H NMR δ 7.65–7.55 (m, 4 H), 7.30–7.25 (m, 6 H), 4.88 (d, 1 H, J = 8.2 Hz), 3.55 (t, 2 H, J = 7 Hz), 2.60–2.40 (m, 1 H), 2.25–1.80 (m, 5 H), 1.70–0.80 (m, 7 H), 1.46 (s, 3 H), 0.98 (s, 9 H); ^{13}C NMR δ 211.8, 135.4, 134.9, 134.7, 133.9, 129.4, 127.7, 127.5, 63.2, 47.9, 41.1, 38.0, 35.5, 31.6, 30.5, 26.8, 26.5, 25.2, 19.1, 16.0; MS (EI) m/z (rel intensity) 377 (1), 283 (2), 199 (100), 77 (12).

3-[(*E*)-2-Methyl-1-hexenyl]cyclopentanone (20). Prepared from 1-hexyne (7) and 2-cyclopentenone (19). Chromatography (EtOAc/hexane (1:5)) gave 63% of 20 as a clear oil: IR (neat) 2960, 2935, 2860, 1740, 1455, 1400, 1378, 1157, 1117 cm^{-1}; ^1H NMR

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(59) Determined by integration of the ^1H resonances of the vinyl protons at 6.06 and 5.87 ppm for 12a and 12b, respectively. See also: Eisch, J. J.; Foxton, M. W. *J. Organomet. Chem.* **1968**, *11*, P24.

δ 5.07 (d, 1 H, J = 8.7 Hz), 3.10–2.95 (m, 1 H), 2.40–1.80 (m, 6 H), 1.70–1.55 (m, 1 H), 1.64 (s, 3 H), 1.45–1.25 (m, 5 H), 0.89 (t, 3 H, J = 7.2 Hz); ^{13}C NMR δ 220.1, 137.2, 127.4, 46.1, 39.7, 38.9, 36.3, 30.8, 30.5, 22.8, 16.7, 14.4; MS (CI) m/z (rel intensity) 361 ([2M + 1]$^+$, 100), 181 ([M + 1]$^+$, 30). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.07; H, 11.24.

(*E*)-4,4,6-Trimethyl-5-decen-2-one (22). Prepared from 1-hexyne (7) and mesityl oxide (21). Chromatography (EtOAc/hexane (1:5)) gave 64% of **22** as a clear oil: IR (neat) 2950, 2920, 2850, 1700, 1450, 1345, 1190 cm^{-1}; ^{1}H NMR δ 5.17 (d, 1 H, J = 1 Hz), 2.51 (s, 2 H), 2.10 (s, 3 H), 1.92 (t, 2 H, J = 7.5 Hz), 1.70 (d, 3 H, J = 1 Hz), 1.40–1.20 (m, 4 H), 1.18 (s, 6 H), 0.88 (t, 3 H, J = 6.9 Hz); ^{13}C NMR δ 209.1, 135.7, 133.0, 56.4, 42.0, 35.2, 32.4, 30.9, 29.9, 22.7, 17.6, 14.4; MS (CI) m/z (rel intensity) 197 ([M + 1]$^+$, 100). Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.42; H, 12.26.

***trans*-4-*tert*-Butyl-3-[(*E*)-2-methyl-1-hexenyl]cyclohexanone (24).** Prepared from 1-hexyne (7) and 4-*tert*-butyl-2-cyclohexenone (23). Chromatography (EtOAc/hexane (1:6)) gave 65% of **24** as a clear oil: IR (neat) 2960, 2920, 2880, 1720, 1490, 1380, 1210 cm^{-1}; ^{1}H NMR δ 5.02 (d, 1 H, J = 9.8 Hz), 2.80–2.70 (m, 1 H), 2.45–2.00 (m, 5 H), 1.91 (t, 2 H, J = 7.0 Hz), 1.65–1.45 (m, 1 H), 1.57 (s, 3 H), 1.45–1.20 (m, 6 H), 0.92 (s, 9 H), 0.87 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 213.5, 132.5, 131.0, 50.2, 46.5, 39.9, 39.2, 36.3, 34.0, 30.0, 28.5, 24.8, 22.2, 15.9, 14.1; MS (EI) m/z (rel intensity) 250 (M$^{\bullet+}$, 10), 193 (45), 153 (15), 137 (18), 123 (12), 109 (48), 95 (49), 83 (52), 69 (70), 55 (92); HRMS m/z calcd for $C_{17}H_{30}O$ 250.2297, found 250.2297.

(*E*)-5-Methyl-1,3-diphenyl-4-nonen-1-one (26). Prepared from 1-hexyne (7) and chalcone (25). Chromatography (EtOAc/hexane (1:5)) gave 87% of **26** as a clear oil: IR (neat) 3025, 2970, 2850, 1690, 1460, 750, 700 cm^{-1}; ^{1}H NMR δ 7.95–7.90 (m, 2 H), 7.55–7.50 (m, 1 H), 7.50–7.40 (m, 2 H), 7.30–7.20 (m, 4 H), 7.20–7.10 (m, 1 H), 5.31 (d, 1 H, J = 9.3 Hz), 4.31 (dt, 1 H, J = 7.5, 8.7 Hz), 3.40–3.25 (m, 2 H), 1.93 (t, 2 H, J = 6.9 Hz), 1.61 (s, 3 H), 1.35–1.15 (m, 4 H), 0.83 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 198.8, 145.0, 137.2, 136.5, 132.8, 128.5, 128.1, 127.2, 126.8, 125.9, 45.9, 40.0, 39.4, 29.9, 22.2, 16.3, 14.0; MS (EI) m/z (rel intensity) 306 (M$^{\bullet+}$, 12), 249 (19), 221 (10), 186 (72), 157 (25), 143 (45), 131 (67), 105 (100), 91 (76), 77 (90), 69 (12), 55 (41); HRMS m/z calcd for $C_{22}H_{26}O$: 306.1984, found: 306.1984.

(5*R*)-2-Methyl-3-[(*E*)-2-methyl-1-hexenyl]-5-(1-methylethenyl)cyclohexanone (28). Prepared from 1-hexyne (7) and L-carvone (27). Chromatography (EtOAc/hexane (1:6)) gave 67% of a 7.4:1:1 mixture[60] of stereoisomers **28** as a clear oil: IR (neat) 3025, 2960, 2860, 2850, 1705, 1680, 1600, 1590 cm^{-1}; ^{1}H NMR (major isomer) δ 4.80 (d, 1 H, J = 9.9 Hz), 4.66 (d, 2 H, J = 9.6 Hz), 3.05–2.95 (m, 1 H), 2.60–2.15 (m, 4 H), 1.95–1.85 (m, 2 H), 1.80–1.75 (m, 2 H), 1.64 (s, 3 H), 1.52 (s, 3 H), 1.35–1.15 (m, 6 H), 0.92–0.76 (m, 6 H); ^{13}C NMR (major isomer) δ 212.8, 147.9, 138.2, 122.5, 109.5, 48.0, 46.9, 42.0, 41.0, 39.7, 37.3, 30.2, 22.0, 20.5, 16.0, 14.0, 12.2; ^{13}C NMR (minor isomers) δ 212.7, 212.0, 147.6, 146.9, 136.1, 135.9, 127.9 (2 C), 112.1, 109.6, 50.5, 50.0, 45.2, 44.5 (2 C), 41.2, 41.0, 39.3 (2 C), 38.0, 34.1, 22.2 (2 C), 20.1, 16.4, 16.2, 12.5, 11.9 (6 C missing); MS (EI) m/z (rel intensity) 248 (M$^{\bullet+}$, 37), 205 (15), 191 (18), 177 (100), 165 (15), 150 (50), 135 (20), 121 (61), 107 (70), 93 (74), 81 (51), 67 (53), 55 (90), 43 (93); HRMS m/z calcd for $C_{17}H_{28}O$: 248.2140, found: 248.2140.

(*E*)-6-Methyl-5-decen-2-one (30). Prepared from 1-hexyne (7) and methyl vinyl ketone (29). Chromatography (EtOAc/hexane (1:5)) gave 88% of **30** as a clear oil: IR (neat) 2950, 2920, 2890, 1710, 1390, 1290 cm^{-1}; ^{1}H NMR δ 5.07–5.00 (m, 1 H), 2.42 (t, 2 H, J = 7.3 Hz), 2.25 (q, 2 H, J = 7.3 Hz), 2.09 (s, 3 H), 1.92 (t, 2 H, J = 7.3 Hz), 1.53 (s, 3 H), 1.40–1.20 (m, 4 H), 0.84 (t, 3 H, J = 7.1 Hz); ^{13}C NMR δ 208.8, 136.7, 122.2, 43.7, 39.3, 30.0, 29.9, 22.4, 22.3, 15.8, 13.9; MS (EI) m/z (rel intensity) 168 (M$^{\bullet+}$, 10), 150 (10), 110 (38), 95 (20), 81 (30), 68 (31), 58 (10), 55 (32), 43 (100); HRMS m/z calcd for $C_{11}H_{20}O$: 168.1514, found: 168.1514.

(*E*)-8-[(*tert*-Butyldiphenylsilyl)oxy]-5-methyl-1,3-diphenyl-4-octen-1-one (31). Prepared from 5-[(*tert*-butyldiphenylsilyl)oxy]pentyne (17) and chalcone (25). Chromatography (EtOAc/hexane (1:6)) gave 90% of **31** as a clear oil: IR (neat) 3095, 3055, 2980, 2960, 2925, 2880, 1695, 1608, 1592, 1501, 1480, 1455, 1435, 1396, 1368, 1270, 1210, 1192, 1118, 1007, 828, 747, 710 cm^{-1}; ^{1}H NMR δ 7.98 (d, 2 H, J = 7.4 Hz), 7.75–7.70 (m, 4 H), 7.60–7.55 (m, 1 H), 7.50–7.40 (m, 8 H), 7.35–7.30 (m, 4 H), 7.25–7.20 (m, 1 H), 5.42 (d, 1 H, J = 9.6 Hz), 4.38 (q, 1 H, J = 7.8 Hz), 3.69 (t, 2 H, J = 6.3 Hz), 3.46–3.28 (m, 2 H), 2.13 (t, 2 H, J = 7.6 Hz), 1.72–1.60 (m, 2 H), 1.66 (s, 3 H), 1.13 (s, 9 H); ^{13}C NMR δ 198.7, 144.9, 137.2, 135.8, 135.5, 134.0, 132.8, 129.5, 128.5, 128.0, 127.5, 127.2, 126.0, 63.4, 45.9, 39.8, 35.8, 30.7, 26.8, 19.2, 16.4; MS (EI) m/z (rel intensity) 489 ([M – *tert*-butyl]$^+$, 15), 369 (100), 291 (10), 199 (55), 171 (25), 91 (70); HRMS m/z calcd for $C_{33}H_{33}O_2Si$ (M – *tert*-butyl) 489.2250, found 489.2250.

(1*R*,5*S*,11*R*)-5-[(Benzyloxy)methyl]-11-[(1*E*,4*S*)-5-[(*tert*-butyldimethylsilyl)oxy]-2,4-dimethyl-1-pentenyl]-3,3-dimethyl-2,4,7-trioxaspiro[5.5]undecan-9-one (33). Prepared from (4*S*)-5-[(*tert*-butyldimethylsilyl)oxy]-4-methyl-1-pentyne (2) and (1*R*,5*S*)-5-[(benzyloxy)methyl]-3,3-dimethyl-2,4,7-trioxaspiro[5.5]undec-10-en-9-one[61] (32). Chromatography (EtOAc/hexanes (1:5)) gave 72% of **33** as a clear oil: IR (neat) 2940, 2920, 2840, 1715, 1450, 1365, 1246, 1198, 1142, 1080, 998, 831, 770 cm^{-1}; ^{1}H NMR δ 7.40–7.30 (m, 5 H), 5.06 (d, 1 H, J = 10.2 Hz), 4.60, 4.56 (AB, 2 H, J = 12.3 Hz), 4.40–4.30 (m, 2 H), 4.17, 3.93 (AB, 2 H, J = 16.5 Hz), 3.55–3.30 (m, 4 H), 3.02, 2.18, 2.92 (ABC, 3 H, J_{AB} = 15.8, J_{AC} = 5.9, J_{BC} = 3 Hz), 2.25–2.10 (m, 1 H), 1.85–1.45 (m, 3 H), 1.63 (s, 3 H), 1.59 (s, 3 H), 1.43 (s, 3 H), 0.88 (s, 9 H), 0.77 (d, 3 H, J = 6.3 Hz), 0.26, 0.08 (2s, 6 H); ^{13}C NMR δ 208.5, 139.1, 138.0, 128.8, 128.1, 128.0, 123.8, 99.9, 97.3, 73.8, 73.5, 68.8, 68.5, 65.7, 45.1, 44.2, 41.2, 34.5, 34.2, 31.2, 26.4, 23.8, 18.5, 16.9, 16.7, –4.9; MS (CI) m/z (rel intensity) 547 ([M + 1]$^+$, 100). Anal. Calcd for $C_{31}H_{50}O_6Si$: C, 68.09; H, 9.22. Found: C, 68.13; H, 9.29.

(*E*)-5-Ethyl-6-methyl-5-octen-2-one (35). Prepared from 3-hexyne (34) and methyl vinyl ketone (29). Chromatography (EtOAc/hexane (1:5)) gave 48% of **35** as a clear oil: IR (neat) 2995, 2960, 2900, 1727, 1465, 1365, 1170 cm^{-1}; ^{1}H NMR δ 2.47–2.40 (m, 2 H), 2.27–2.20 (m, 2 H), 2.13 (s, 3 H), 2.05–1.95 (m, 4 H), 1.60 (s, 3 H), 0.93 (t, 6 H, J = 7.7 Hz); ^{13}C NMR δ 209.4, 132.1, 131.1, 42.8, 29.9, 26.9, 26.1, 24.6, 17.4, 13.8, 13.2; MS (CI) m/z (rel intensity) 169 ([M + 1]$^+$, 25), 151 (30), 110 (38), 75 (100).

General Procedure for the Hydroalumination/Transmetalation/Conjugate Addition of Alkynes: 3-[(*E*)-1-Hexenyl]cyclohexanone (36). A solution of 1-hexyne (7, 123 mg, 1.50 mmol) in dry hexane (1 mL) was treated at 0 °C with a 1.0 M solution of DIBALH in hexane (1.5 mL, 1.50 mmol). The reaction mixture was stirred at 50 °C for 2 h, the solvent was removed in vacuo, and dry Et_2O (2 mL) was added. The etheral solution of the alkenylalane was added at –23 °C to a mixture of flame-dried CuCN (134 mg, 1.50 mmol) and a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (6 mL, 3.0 mmol). The reaction mixture was stirred for 5 min at –23 °C, and a solution of 2-cyclohexenone (4, 96 mg, 1.00 mmol) in THF (2 mL) was added dropwise. Stirring at –23 °C was continued for another 30 min. The mixture was quenched into a solution of saturated ammonium chloride/ammonium hydroxide (9:1) and extracted three times with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered through silica gel, and chromatographed (EtOAc/hexane (1:9)) to yield 120 mg (72%) of **36** as a clear oil: IR (neat) 2980, 2945, 2880, 1719, 1453, 1320, 1230, 978 cm^{-1}; ^{1}H NMR δ 5.40 (dt, 1 H, J = 15.5, 6.0 Hz), 5.34 (dd, 1 H, J = 15.5, 5.4 Hz), 2.50–1.80 (m, 9 H), 1.75–1.60 (m, 1 H), 1.55–1.40 (m, 1 H), 1.35–1.20 (m, 4 H), 0.87 (t, 3 H, J = 6.9 Hz); ^{13}C NMR δ 211.9, 133.4, 130.4, 48.2, 42.0, 41.7, 32.6, 32.0 (2 C), 25.4, 22.6, 14.4; MS (CI) m/z (rel intensity) 361 ([2M + 1]$^+$, 100), 181 ([M + 1]$^+$, 15). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.02; H, 11.19.

3-[(*E*)-2-Cyclohexylethenyl]cyclohexanone (38). Prepared from cyclohexylacetylene (37) and 2-cyclohexenone (4). Chromatography (EtOAc/hexane (1:7)) gave 75% of **38** as a clear oil: IR (neat) 2950, 2930, 1710, 1459, 1432, 1355, 1320, 1233, 976 cm^{-1}; ^{1}H NMR δ 5.40–5.20 (m, 2 H), 2.45–0.80 (m, 20 H); ^{13}C NMR δ 211.2, 135.6, 130.1, 47.5, 41.3, 41.0, 40.3, 32.8, 31.4, 25.9, 25.8, 24.7; MS (EI) m/z (rel intensity) 206 (M$^{\bullet+}$, 8), 148 (20), 124 (16), 123 (18), 110 (100), 97 (45), 81 (30), 67 (55), 55 (30); HRMS m/z calcd for $C_{14}H_{22}O$: 206.1671, found: 206.1671.

(60) Determined by integration of the ^{1}H resonances of the vinyl protons at 4.80 (major isomer) and 4.83 ppm (minor isomers).

(61) Ireland, R. E.; Wipf, P.; Miltz, W.; Vanasse, B. *J. Org. Chem.* **1990**, *55*, 1423.

3-[(*E*)-1-Hexenyl]cyclohexanone (36) by Hydrozirconation/Transmetalation/Conjugate Addition. A suspension of Cp_2ZrHCl (390 mg, 1.51 mmol) in THF (8 mL) was treated with 1-hexyne (7, 123 mg, 1.50 mmol). The reaction mixture was stirred at 22 °C for 30 min and added at −23 °C to a mixture of flame-dried CuCN (134 mg, 1.50 mmol) and a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (6 mL, 3.0 mmol). This mixture was stirred for 5 min at −23 °C, and a solution of 2-cyclohexenone (4, 96 mg, 1.00 mmol) in THF (2 mL) was added dropwise. Stirring at −23 °C was continued for another 30 min. The mixture was quenched into a solution of saturated ammonium chloride/ammonium hydroxide (9:1) and extracted three times with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered through silica gel, and chromatographed (EtOAc/hexane (1:9)) to yield 110 mg (61%) of **36**.

3-[(*E*)-5-[(*tert*-Butyldiphenylsilyl)oxy]-2-methyl-1-hexenyl]cyclohexanone (18) by Inverse Addition (IA) Protocol with 10 mol % CuCN. A suspension of CuCN (8.9 mg, 0.10 mmol) in THF (6 mL) was treated at −45 °C dropwise with a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (0.40 mL, 0.20 mmol). The reaction mixture was warmed to −23 °C, and a solution of 2-cyclohexenone (4, 96 mg, 1.0 mmol) in THF (1 mL) was added. After dropwise addition of a solution of alane **44** (approximately 1.5 mmol) in Et_2O (3 mL), stirring was continued for 30 min at −23 °C and for 30 min at 0 °C. Standard workup led to the isolation of 227 mg (52%) of **18**.

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Supplementary Material Available: ^{13}C NMR spectra for compounds **6**, **10**, **12a**, **14**, **16**, **18**, **24**, **26**, **28**, **30**, **31**, **35**, and **38** (14 pages). Ordering information is given on any current masthead page.

Highly Stereoselective 3 + 2 Annulations by Cyclopropanation of Vinyl Ethers with Rhodium(II)-Stabilized Vinylcarbenoids Followed by a Formally Forbidden 1,3-Sigmatropic Rearrangement

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A highly stereoselective 3 + 2 annulation has been developed by cyclopropanation of vinyl ethers with rhodium(II)-stabilized vinylcarbenoids to generate vinylcyclopropanes followed by a Et_2AlCl-catalyzed 1,3-sigmatropic rearrangement. The success of this methodology rests on the remarkably stereoselectivity that is exhibited in both the cyclopropanation step and also the Et_2AlCl-catalyzed vinylcyclopropane rearrangement.

The development of general synthetic strategies for the construction of five-membered rings has been a very active area of research in recent years.[1] Particularly impressive are a number of approaches which proceed by means of carbenoid intermediates. A major contribution to this area has been Hudlicky's 4 + 1 annulation approach[2] based on intramolecular cyclopropanation of dienes followed by a 1,3-sigmatropic rearrangement of the resulting vinylcyclopropanes. A complimentary 3 + 2 annulation strategy by reaction of 4-bromocrotonates with α,β-unsaturated ketones in the presence of base has also been developed.[3] Harsh thermal conditions were originally required for ring expansion of the vinylcyclopropanes to the cyclopentenes, but since then, a number of milder procedures[2-7] using catalysts such as $(C_2H_4)_2Rh(acac)$[2a] or Et_2AlCl[7] have been reported. In the thermal reaction, the level of stereocontrol is substrate dependent.[2,3] However, improved stereoselectivity is possible with $(C_2H_4)_2Rh(acac)$,[2a] while the two examples of Et_2AlCl-induced rearrangement involving stereocontrol were highly stereoselective.[7a,b] An alternative and highly stereoselective 4 + 1 annulation was reported by Danheiser[8] using an anion-accelerated vinylcyclopropane rearrangement. 3 + 2 annulations have also been achieved through reaction of a nucleophilic vinylcarbene with electron-deficient alkenes[9] and by means of Fisher carbenes.[7c,10] Another carbenoid approach to cyclopentanes has been the intramolecular C–H insertion reaction reported by Taber.[11]

For some time we have been engaged in developing general synthetic procedures based on rhodium(II)-stabilized vinylcarbenoid intermediates.[12] From our results on the tandem cyclopropanation/Cope rearrangement sequence that we have employed for the stereoselective construction of seven-membered rings, it was evident that cyclopropanation with vinylcarbenoids can be remarkably stereoselective.[12] Extending the chemistry of vinylcarbenoids to their reaction with vinyl ethers was expected to produce donor–acceptor-substituted vinylcyclopropanes[13] that would readily rearrange to highly functionalized cyclopentenes (eq 1). In this paper we will

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