(Trimethylstannyl)vinyl Cuprates: Generation and Conjugate Addition Reactions

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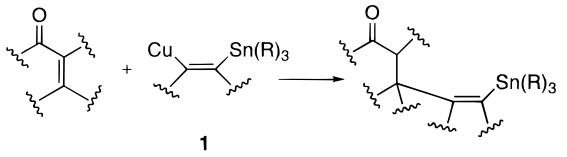
A new convenient route to the bis[(trimethylstannyl)vinyl] cuprate reagent **9** is described. Its addition to α,β-unsaturated ketones has been studied. Bis(trimethylsilyl)acetamide (BSA) was found to activate 1,4-conjugate addition of **9** to α,β-unsaturated ketone esters without concomitant reduction of the double bond.

Introduction

Organostannanes have enjoyed considerable use in organic synthesis recently, especially as new, mild, and efficient methods for their preparation have been developed.[1a] In particular, the deployment of vinylstannanes[2,3] as geometrically defined, latent vinyl anions has been reported in several recent accounts of natural product synthesis including rapamaycin,[4] taxol,[5] and avermectins.[6]

A useful method of preparing vinylstannanes is to use vinylstannyl cuprates **1** as the precursors. Reactions of **1** with diverse electrophiles give readily vinylstannanes. Of particular interest is the reaction of **1** with α,β-unsaturated ketones to give regioselectively the 1,4-conjugate adducts (eq 1).[7] Recently, Marino[8] and Pulido/

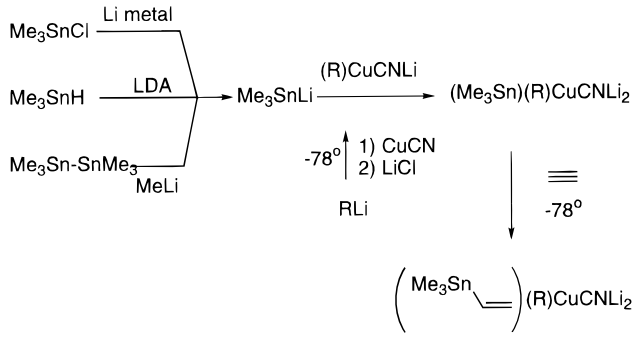


1 Eq 1

Fleming[9] have independently described the addition of tri-n-tributylstannyl cuprates to acetylene as a way to afford the *cis*-tri-*n*-butylstannyl)vinyl cuprate reagents.

We became interested in the use of various *cis*-(trimethylstannyl)vinyl cuprate reagents because of the greater ease of manipulation and spectral simplicity of the trimethyltin moiety relative to the tri-*n*-butyltin reagents. We have recently reported[10] in preliminary form a novel preparation of various (trimethylstannyl)-vinyl cuprates. We report here full experimental details and a study of the conjugate addition of these reagents with α,β-unsaturated ketones and keto esters.

Scheme 1



Results and Discussion

(1) Generation of Mixed (Trimethylstannyl)vinyl Cuprates. The conventional methods[11] of generating mixed stannyl cuprate via trimethylstannyl lithio species, when applied to the addition to acetylene in order to obtain the vinylstannyl reagents (Scheme 1), gave low yields (ca. < 10%). We thus adopted the Lipshutz protocol[12] by starting from different organolithium reagents according to Scheme 2. Addition of 2 equiv of trimethyltin hydride to the cuprate reagents **2** gave the mixed trimethylstannyl cuprates **3** in good yields. Acetylene was then passed slowly into the mixture at −78 °C to give mixed (trimethylstannyl)vinyl cuprates **4**. The mixed cuprates **4** were then reacted with cyclohex-2-enone in the presence of Et_3SiCl, and the products were analyzed. It is clear from results summarized in Table 1 that in the case of **4a** (entry 1), **4b** (entry 2), and **4c** (entry 3), incomplete addition to acetylene occurred, leading to addition products **5** (derived from **3**, R = Me, or Ph or tBu) and **6** (derived from **4a**, **4b**, or **4c**). In the case of **4d** (R = nBu), little addition product **5** was obtained, indicating that the addition of **4d** to acetylene was complete. Ratios of the trimethylstannyl versus (trimethylstannnyl)vinyl versus alkyl adducts **5**, **6**, and **7**, respectively, were readily determined from the integral values of the respective enolic protons that characteristically occurred at 4.5−6.0 ppm. However, for most of the enones examined, transfer of the *n*-butyl group competed

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(3) Lipshutz, B. H.; Lee, J. I. *Tetrahedron Lett.* **1991**, 7211−7214.

(4) Nicolaou, K. C.; Chakraborty, A. D.; Piscopio, A. D.; Minowa, N.; Bertinato, P. *J. Am. Chem. Soc.***1993**, 115, 4419−4420.

(5) Queneau, Y.; Krol, W. J.; Bornmann, W. G.; Danishefsky, S. J. *J. Org. Chem.* **1992**, *57*, 4043−4047.

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(7) Kozlowski, J. A.; *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergammon Press: New York, 1991; Vol. 1, p 169.

(8) Marino, J. P.; Emonds, V. M.; Stengel, P. J.; Oliveira, A. R. M.; Simonelli, F.; Ferreira, J. T. B. *Tetrahedron Lett.* **1992,** *33*, 49−52.

(9) Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 351.

(10) Pereira, O. Z.; Chan, T. H. *Tetrahedron Lett.* **1995**, *36*, 8749−8752.

(11) Sato, T. *Synthesis* **1990**, 259−270 and references cited therein.

(12) Lipshutz, B. H.; Ellworth, E. L.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065−2068.

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Scheme 2

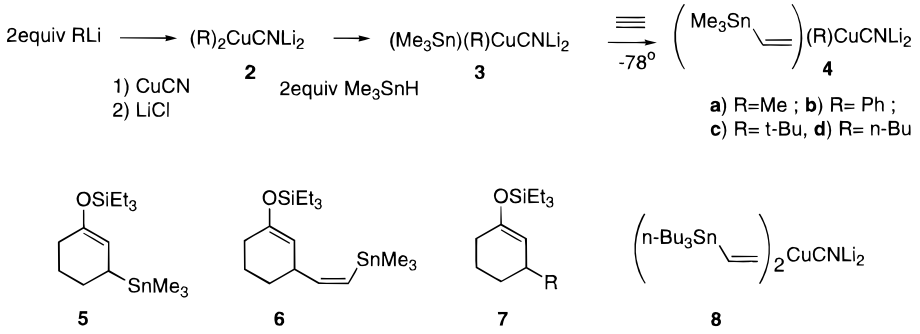


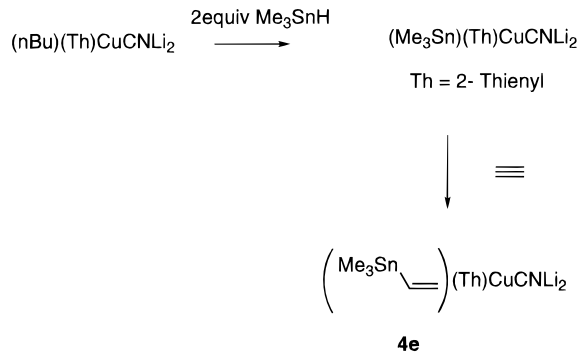
Table 1. Addition of Cuprates 4 and 9 to α,β-Unsaturated Enones

Entry	Cuprate	Enone/Cond	Product	Ratio/Yield
1	(Me)CuCNLi2 (**4a**)	-78	**5** : **6**: Me	1 : 1 : 1
2	(Ph)CuCNLi2 (**4b**)	-78	**5** : **6** : Ph	4 : 1 : 5
3	(tBu)CuCNLi2 (**4c**)	-78	**5** : **6** : tBu	2 : 1 : 0.5
4	(nBu)CuCNLi2 (**4d**)	-100	**6** : **7**	79 % : 9 %
5	(**4d**)	$BF_3.OEt_2$/-78	SnMe3 + a nBu	12% : 61%
6	(**4d**)	-78, 1 h	Et3SiO SnMe3 + Et3SiO Bu; ca 1:1 inseparable mixture	1 : 1, 62%
7	(**4d**)	-78	Et3SiO SnMe3 + Et3SiO Bu	52 % : 15 %
8	(Th)CuCNLi2 (**4e**)	-60, 45 min	**6**	82%
9	2CuCNLi2 (**9**)	-78	**6**	89 %
10	(**9**)	-78	Et3SiO SnMe3	65 %
11	(**9**)	EtO2C CO2Et -78	Et3SiO SnMe3 EtO2C CO2Et	78 %

[a] See ref 13a.

with the transfer of the (trimethylstannyl)vinyl moiety to the enone. With cyclohexenone, under careful control of reaction conditions (−100 °C, Table 1, entry 4), adduct **6** was obtained in 79% yield versus the butyl transfer adduct **7** (R = nBu) obtained in 9% yield. Changing Et_3SiCl to BF_3OEt_2 as the promoting reagent served only to promote transfer of the butyl group (Table 1, entry 5). Similar transfer of the butyl group from **4d** was observed

Scheme 3

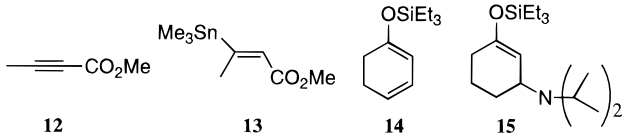


4e

for other α,β-unsaturated ketones such as 4-methylpent-3-en-2-one (Table 1, entry 6) and 4,4-dimethylcyclohex-2-enone (Table 1, entry 7).

Since the thienyl group was reported[13b] to not compete with the tributylstannyl group, we prepared the mixed thienyl (trimethylstannyl)vinyl cuprate reagent **4e** according to Scheme 3. When **4e** was reacted with cyclohex-2-enone under similar conditions, **6** (Table 1, entry 8) was obtained as the only product in 82% yield.

(2) Generation of Bis[(trimethylstannyl)vinyl] Cuprate 9. In his work on hindered enones, Marino[8] reported best results with homo bis[(tri-*n*-butylstannyl)-vinyl] cuprate **8** and attributed this outcome to its superior reactivity. Given the results from the mixed (trimethylstannyl)vinyl cuprates **4**, we decided to explore the reactivity of the trimethylstannyl analog **9**. After considerable experimentation, we found the protocol delineated in Scheme 4 to give synthetically useful yields of the reagent **9**. LDA was added to CuCN and LiCl in THF at −78 °C to generate a deep royal blue solution of **10**. Trimethyltin hydride was then added to give an intense yellow solution of **11**. The formation of **11** was confirmed by its reaction with an activated alkyne, methyl 2-butynoate (**12**), at −78 °C to give the addition product **13** in 94% yield. Addition of **11** to acetylene did not occur at −78 °C but at −50 °C, when formation of the reagent **9** as a bright yellow solution took place. Addition of **9** to cyclohex-2-enone, 4,4-dimethylcyclohex-2-enone, and 4,4-bis(ethoxycarbonyl)cyclohex-2-enone (Table 1, entries 9−11) gave transfer of the (trimethylstannyl)vinyl moiety in good yields.



12 **13** **14** **15**

Formation of the amidocuprate **10** has not previously been reported in the literature. Its existence in the present case is strongly implicated by the observation that when cyclohex-2-enone and Et_3SiCl were added to the deep royal blue solution of **10**, the 1,3-diene **14** could be obtained in 60% unoptimized yield. Jung[14] has demonstrated that 1,3-dienes of type **14** are not available through simple base-mediated deprotonation at the γ-position of cyclohex-2-enones under either kinetic or thermodynamic conditions. In all probability, **14** arose through silica-catalyzed Hoffmann elimination of the initially formed amide adduct **15**, although direct γ-deprotonation by cuprate **10** cannot be excluded. This result has also led us to prepare the mixed (trimethylstannyl)-vinylamide cuprate **16** via the mixed reagent **17** formed by the addition of only 1 equiv of trimethyltin hydride to **10**. Indeed, the mixed cuprate **16** reacted at −35 °C with cyclohexenone with complete selective transfer of the (trimethylstannyl)vinyl residue (63%) but, as expected, with somewhat poorer reactivity (over 2 h) than the homo reagent **9**.

(3) Conjugate Addition Reactions to α,β-Unsaturated Keto Esters. In contrast to enones, cuprate addition to α,β-unsaturated ketoesters has received little attention despite the increasing use of these Michael acceptors as useful building blocks in synthesis.[15] Specifically, conjugate cuprate addition of vinylstannanes to these substrates has not been studied. As part of our program on the synthesis of highly functionalized decalin systems,[16] we examined the conjugate addition of (trimethylstannyl)vinyl cuprate **9** to α,β-unsaturated keto esters.

We first examined the reaction of ketoester **18** toward the mixed stannyl cuprate **4d**. Not unexpectedly, exposure of keto ester **18** to **4d** in the presence of Et_3SiCl at −78 °C afforded products of both butyl and vinylstannyl transfer. Unlike the case of cyclohex-2-enone though, preferential transfer of the butyl group occurred, affording the butyl adduct **19** in 42% yield versus 31% of the vinylstannyl adduct **20** (Table 2, entry 1). The use of the mixed thienyl cuprate **4e** afforded a marginally better yield (46%, Table 2, entry 2) of the desired product **20**. To our surprise, in both cases, there was present in the products a small amount of 1,4-reduction product **21**. Of greater concern was the fact that when the reaction was carried out on a longer running, larger scale (700 mg) run with **4e**, the yield of the reduction product **21** was increased substantially to 35% (Table 2, entry 3).

The mechanism by which this reduction occurs remains unclear at present. However, it is perhaps noteworthy that treatment of keto ester **18** with the bisbutyl cuprate **22a** under similar conditions yielded the expected butyl adduct **19** in 93% yield. No reduction product was observed. This tends to preclude reduction of the α,β-unsaturated unit via a mechanism involving β-elimination of the butyl ligand, followed by reductive elimination with concomitant hydride transfer.

More significantly, the bis[(trimethylstannyl)vinyl] cuprate reagent **9** showed an even greater propensity to effect 1,4-reduction. In the reaction of **9** with **18** under the same reaction conditions, an almost 1:1 ratio of the stannylvinyl adduct **20** to the reduced product **21** (Table 2, entry 5) was obtained. The presence of the reduction product appeared to be quite sensitive to the nature of the substituents at the 4-position. With the unsubstituted keto ester **22**, the stannylvinyl adduct **23** was obtained exclusively, albeit in lower yield (52%, Table 2, entry 6). On the other hand, with the sterically more demanding keto ester **24**, only the reduction product **25**

(13) (a) Wang, Y.; Gladysz, J. A. *J. Org. Chem.* **1995**, *60*, 903−909. (b) Lipshutz, B. H. *Synlett* **1989**, 119−128 and references cited therein. (c) Lipshutz, B. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 4617.

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(15) (a)Liu, H.-J.; Ngooi, T. K. *Can. J. Chem.* **1984**, *62*, 2676. (b) Deslongchamps, P.; Lavallee, J. F. *Tetrahedron Lett.* **1988**, *29*, 5117. (c) Lejeune, J.; Lallemand, J. Y. *Tetrahedron Lett.* **1991**, *32*, 2621−2624.

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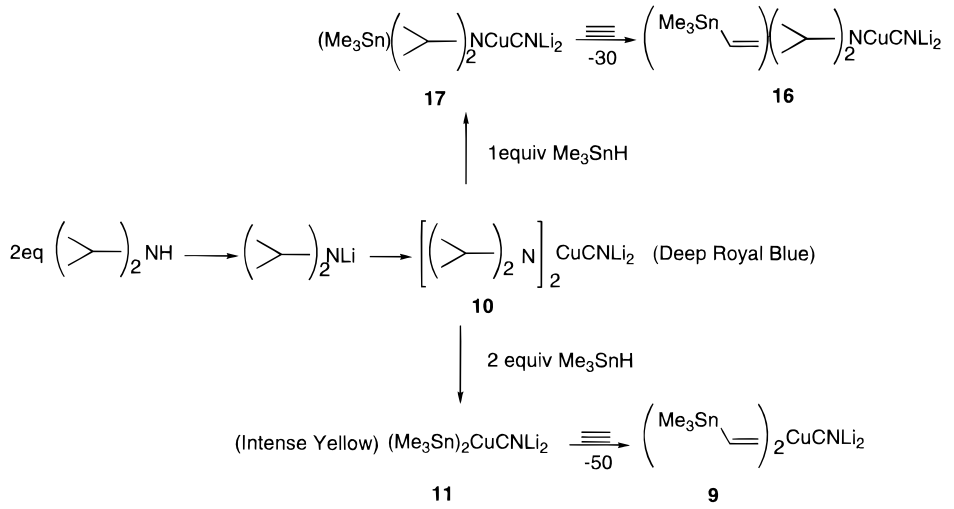
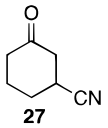
Scheme 4



was obtained (65%, entry 7), after 24 h at −50 °C, with no detectable amount of the stannylvinyl adduct.

In all probability, the low reduction potential of the α,β-unsaturated keto ester favors single electron transfer (SET) over ligand transfer from the presumed intermediate Cu(III) complex,[17] especially in the more sterically encumbered substrate such as **24**. The absence of reduction product in the case of the keto ester **22** for which the reaction was complete in 15−20 min tends to suggest that a combination of both steric and electronic factors is involved in promoting reduction.

(4) Bis(trimethylsilyl)acetamide (BSA) as a Novel Activating Agent. In order to circumvent the reduction reaction, activation of either the cuprate reagent or the enone−ester greater than that provided by Et_3SiCl is required. Lipshutz,[18] among others, has published extensively on the nature of such activation and has invoked σ-donation to explain the accelerated rate effect, observed in cuprate-mediated Michael addition. Furthermore, he found trimethylsilyl cyanide (TMSCN) to be superior in this respect and implicated π-donation to explain the enhanced yields. In our hands, TMSCN, regardless of the order of addition, reacted instead, in a 1,4-fashion, with ester **18** to give the cyanoester **26** in 65% yield (Table 2, entry 8). It should be noted that, under analogous conditions, the use of TMSCN in lieu of Et_3SiCl in the reaction of **9** with cyclohexenone did not lead to similar cyano adduct **27** (Scheme 3).



27

$(nBu)_2CuCNLi_2$

22a

Trimethyl phosphite has been used extensively in cuprate chemistry. We found, however, that under the present reaction conditions $P(OMe)_3$ did not have any observable effect on the reaction outcome.

Bis(trimethylsilyl)acetamide (BSA) is well recognized as a powerful silylating agent. As an amido enol ether, BSA has good potential as a π-donor. We found that the effect of this reagent on the conjugate addition of stannnyl cuprate **9** to keto esters is quite dramatic. Thus, with the keto ester **18**, a near-quantitative yield (92%, Table 2, entry 9) of the stannylvinyl adduct **28** was obtained with no trace of the reduction product **21**. Even with the hindered ketoester **24**,[19] a complete reversal of product selectivity was observed, affording the adduct **29** exclusively in 79% yield (Table 2, entry 10). It is interesting to observe that BSA activation toward enones is less pronounced. It is comparable to Et_3SiCl (Table 2, entries 11 and 12) and is otherwise not remarkable.

Conclusion

In conclusion, we have demonstrated a convenient route to the bis [(trimethylstannyl)vinyl] cuprate **9** through the intermediacy of the novel amido cuprate **10**. Additionally, cuprate **9** was found to be an effective reagent for the introduction, via conjugate addition, of the *cis*-(trimethylstannyl)vinyl unit to substituted cyclohex-2-enones. Finally we have illustrated BSA to be far superior to existing activating agents in the 1,4-addition of cuprate **9** to sterically encumbered keto esters, providing (trimethylstannyl)vinyl adducts in high yields.

Experimental Section

Distillation temperatures refer to short-path distillations. Melting points are uncorrected. THF was distilled from sodium/benzophenone ketyl. All other solvents when used dry were distilled under argon from calcium hydride. Prior to use, acetylene was passed through two −78 °C cooling towers (to remove acetone) separated by a $NaOH/CaCl_2$ drying tube and then allowed to pass over a column of Drierite before collection in an inverted burette over paraffin oil. BSA was used acetamide free. Copper cyanide and lithium chloride were dried at 120 °C in a vacuum oven(<1 mm) for 16 h prior to use. Chromatography was performed on Merck Kieselgel 60 (mesh 70−230) using distilled solvents. Unless otherwise indicated, ^1H NMR was recorded in $CDCl_3$ on 200, 270, or 500 MHz spectrometers. ^{13}C NMR spectra were recorded at 50,

(17) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergammon Press: New York, 1992; pp 5−27.

(18) (a) Lipshutz, B. H.; Dimock, S. H.; James, B. *J. Am. Chem. Soc.* **1993**, 115, 9283−9284. (b) Lipshutz, B. H.; Sengupta, S. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1992; Vol. 41, Chapter 2, pp 135−631.

(19) Keto ester **24** was prepared in a manner akin to that described for **18** by: Schanchez, I. H; Ortega, A.; Garcia, G.; Larraza, N. I.; Flores, H. J. *Synth. Commun.* **1985,** 15, 141−149 (see Experimental Section).

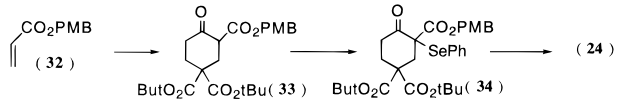
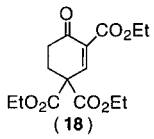
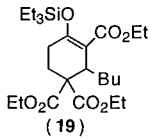
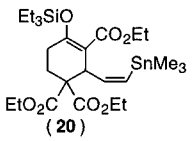
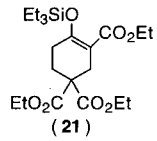
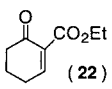
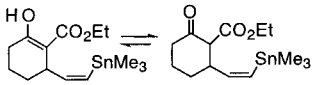
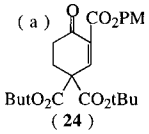
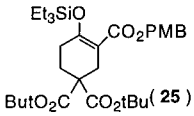
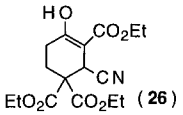
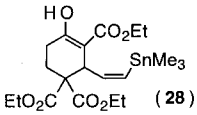
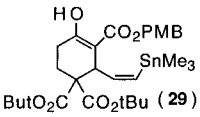
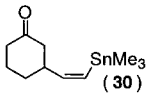
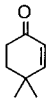
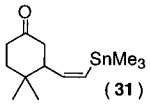


Table 2. Addition of Cuprates to α,β-Unsaturated Enones and Keto Esters

Entry	Cuprate	Compound	Activator	Results	Yield
1	(4d)	 (18)	Et_3SiCl	 (19)  (20)  (21)	**19:20:21** 42 : 31 : 7
2	(4e)	(18)	Et_3SiCl	(20) (21)	**20 : 21** 46 : 5
3	(4e)	(18)	Et_3SiCl	(20) (21)[b]	20 : 35
4	(22a)	(18)	Et_3SiCl	(19)	93
5	(9)	(18)	Et_3SiCl	(20) (21)	32 : 31
6	(9)	 (22)	Et_3SiCl	 (23) ca 1 : 1 mixture	52
7	(9)	(a)  (24)	Et_3SiCl	 (25)	65
8	(9)	(18)	TMSCN	 (26)	65
9	(9)	(18)	BSA	 (28)	92
10	(9)	(24)	BSA	 (29)	79
11	(9)	Cyclohexenone	BSA	 (30)	87
12	(9)		BSA	 (31)	72

PMB = *p*-methoxybenzyl. [a] See ref 19. [b] Large scale 700 mg run.

68, and 125 MHz in $CDCl_3$. Chemical shifts (δ values) are listed relative to $CHCl_3$ (δ 7.24) for ^1H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR. All tin coupling constants refer to Sn−H coupling constants (J_{Sn-H}) and, unless otherwise indicated, are given as an average of the ^{117}Sn and ^{119}Sn values. Where necessary, COSY and HETCOR were performed to allow complete peak assignment. Infrared spectra were obtained on an FTIR spectrophotometer. It should be noted that Me_3SnH is a highly volatile toxic liquid. The Lipshutz procedure for its preparation and handling is recommended (see refs 1 and 13c). In general, all trimethyltin compounds are potentially toxic and should be handled with care (ref 1).

Typical Experimental Procedure Using Triethylsilyl Chloride (Procedure A). To diisopropylamine (freshly distilled, 1.48 mL, 11.3 mmol, 1.2 equiv) in dry THF (5 mL), at −78 °C under argon, was added nBuLi (2.4 M) in hexanes (600 mg, 3.89 mL, 9.36 mmol). After 30 min the near-colorless solution was transferred via cannula to a cold (−78 °C) solution of CuCN (402 mg, 4.68 mmol) and lithium chloride (396 mg, 9.36 mmol) in dry THF (20 mL). The initial colorless solution immediately turned mauve and then royal blue. After 40 min the reaction was treated slowly, over 35 min, with Me_3SnH (1.51 g, 9.36 mmol). The color rapidly changed to black and then to black/green and thence to an intense yellow. The solution was kept at this temperature for 1 h and then treated at −78 °C, in a closed system, with gaseous acetylene (via inverted burette, acetone free) (262 mL, 12.0 mmol, 2.5 equiv with respect to CuCN), which was taken up in 17 min. After 10 min at −78 °C, the resulting bright yellow solution was placed in a bath at −50 °C. The reaction was left for 1 h under a positive acetylene atmosphere and then for 40 min in the absence of acetylene. The solution was recooled to −78 °C and treated rapidly with cyclohexenone (300 mg, 3.12 mmol) followed immediately by Et_3SiCl (940 mg, 6.24 mmol). After 15 min the reaction was complete by TLC. After a further 15 min the solution was poured into a mixture of ice-cold Et_2O: 1:4 NH_4OH/NH_4Cl. The mixture was stirred at rt for 15 min. The resulting deep blue mixture was extracted with ether and

purified either by Kugelrhor distillation (ca. 110 °C at 0.5 mm) or by flash column chromatography using (pentane + 1% Et_3N) to afford **6** (1.1 g, 89%) as a clear colorless oil.

Typical Experimental Procedure Using Bis(trimethylsilyl)acetamide BSA (Procedure B). The bright yellow solution of cuprate **9** (3.36 mmol), generated as described above, was recooled to −78 °C and treated rapidly with BSA (1.11 mL, 4.48 mmol), followed by a solution of keto ester **18** (700 mg, 2.24 mmol) in dry THF (3 mL). After 15 min, TLC (hexane: CH_2Cl_2:EtOAc = 10:2:1) indicated complete reaction. After a further 15 min the solution was poured into a mixture of ice-cold Et_2O:1:4 NH_4OH /NH_4Cl. The mixture was stirred at ambient temperature for 15 min. The resulting deep blue mixture was extracted with ether and purified by flash column chromatography using (hexane:CH_2Cl_2:EtOAc = 10:2:1 + 1% Et_3N) to afford **28** as a wax (1.03 g, 92%).

The following compounds described in Table 1 were isolated in the course of addition of mixed cuprates **4** to cyclohex-2-enones.

1-[(Triethylsilyl)oxy]-3-(trimethylstannyl)cyclohex-1-ene (5): IR (film) 1653 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.6 (s, 9H, $^2J_{Sn-H}$ = 51.0 Hz), 0.67 (q, J = 8.0 Hz, 6H), 0.95 (t, J = 8.0 Hz, 9H), 1.55−1.75 (m, 2H), 1.78−2.20 (m, 4H), 5.0 (d, J = 4.0 Hz, 1H, $^2J_{Sn-H}$ = 24.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) −9.56, 5.95, 7.60, 24.11, 24.35, 26.85, 30.39, 107.65, 146.38; MS (EI) (M^+ + 1, 0.4) 361 (M − CH_3, 2.3), 211(M − C_3H_9Sn, 100), 115 (M − $C_9H_{17}OSn$, 35); HRMS calcd for $C_{15}H_{32}OSiSn$ − C_3H_9Sn 211.1518, found 211.1521.

1-[(Triethylsilyl)oxy]-3-methylcyclohex-1-ene (7) (R = Me): IR (film) 2954, 2933, 1664 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.63 (q, J = 8.0 Hz, 6H), 0.92−1.40 (m, 15H), 1.42−1.85 (m, 4H), 1.95−2.06 (m, 2H), 2.15−2.32 (m, 1H), 4.75 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 5.95, 7.56, 22.48, 23.13, 30.08, 30.33, 31.70, 110.37, 148.80; MS (EI) 226 (M^+, 29), 211 (M − CH_3, 100), 197 (37), 115 (24), 103 (49); HRMS calcd for $C_{13}H_{26}$-OSi 226.1753, found 226.1756.

1-[(Triethylsilyl)oxy]-3-phenylcyclohex-1-ene (7) (R = Ph): IR (film) 1661, 1651, 849, 737 cm^{-1}; ^1H (200 MHz, $CDCl_3$) 0.58 (q, J = 8.0 Hz, 6H), 0.96 (t, J = 8.0 Hz, 9H), 2.52 (ddd, J = 5.0, 13.0, 19.8 Hz, 2H), 2.27 (bs, 1H), 2.40−2.55 (m, 2H), 2.70−2.78 (m, 2H), 6.39 (s, 1H), 7.32−7.38 (m, 3H), 7.45−7.53 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 6.59, 7.36, 23.35, 28.59, 37.60, 46.25, 124.69, 125.39, 128.03, 129.26, 137.93, 158.86; MS (EI) 172 (M − H − $C_6H_{15}Si$, 68) 144 (M − $C_{10}H_8O$, 100), 115 (49); HRMS calcd for $C_{18}H_{28}OSi$ − H − $C_6H_{15}Si$ 172.0888, found 172.0886.

1-[(Triethylsilyl)oxy]-3-(1,1-dimethylethyl)cyclohexene (7) (R = tBu): IR (film) 2957, 1669, 1653 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.58 (q, J = 8.0 Hz, 6H), 0.88 (t, J = 8.0 Hz, 9 H), 1.11 (s, 9H), 1.88 (m, 2H), 2.30−2.39 (m, 4H), 5.94 (bs, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 7.55, 8.33, 24.85, 27.43, 29.73, 38.16, 38.85, 123.35, 173.61; MS (CI) 153 (M − C_6H_{15}-Si, 100), 124 (M − H − $C_8H_{19}Si$, 32); HRMS calcd for $C_{16}H_{32}$-OSi − $C_6H_{15}Si$ 153.1279, found 153.1275.

The following compounds were prepared by addition of cuprate **4d** to cyclohex-2-enones and keto esters.

1-[(Triethylsilyl)oxy]-3-butylcyclohexene (7) (R = nBu): IR (film) 1664, 1189, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 0.65 (q, J = 8.0 Hz, 6H), 0.88 (m, 3H), 0.96, 0.91 (2 × t, J = 8.0 Hz, 9H), 1.7 (bq, J = 7.0 Hz, 2H), 1.21−1.32 (bs, 5H), 1.48−1.50 (m, 1H), 1.65−1.79 (m, 2H), 1.92−2.20 (m, 2H), 2.06−2.12 (m, 1H), 4.81 (bd, J = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 4.90, 6.53, 13.94, 21.69, 22.77, 28.77, 29.09, 29.83, 34.42, 36.58, 109.2, 150.12; MS (EI) 268 (M^+, 6), 239 (M − C_2H_5, 4), 211 (M − C_4H_9, 100); HRMS calcd for $C_{16}H_{32}OSi$ 268.2222, found 268.2228

3-[(2(Z)-(Trimethylstannyl)ethenyl]cyclohexan-1-one (entry 5, Table 1; 30, Table 2): IR (film) 1725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.15 (s, 9H, $^2J_{Sn-H}$ = 58.0 Hz), 1.49−1.88 (m, 3H), 2.01−2.41 (m, 5H), 5.81 (d, J = 12.5 Hz, $^2J_{Sn^{119}}$ = 75.2 Hz, $^2J_{Sn^{117}}$ = 71.6 Hz), 6.3 (dd, J = 8.4, 12.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) −7.51, 25.82, 32.29, 41.45, 46.95, 48.14, 128.81, 150.09, 208.92; MS (EI) 288 (M^+, 1), 273 (M − CH_3, 100), 165 (M − $C_8H_{11}O$, 29), 151 (37); HRMS calcd for $C_{11}H_{20}OSn$ 288.0536, found 288.0538.

1-[(Triethylsilyl)oxy]-3-butyl-4, 4-dimethylcyclohex-1-ene (entry 7, Table 1): IR (film) 1688, 1198 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.4−0.8 (m, 9H), 0.8−1.1 (m, 21H), 1.2−1.5 (m, 4H), 1.9−2.1 (m, 1H), 4.8 (bs, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 5.90, 7.56, 14.87, 22.17, 23.61, 27.97, 29.02, 30.72, 31.02, 32.11, 37.03, 44.63, 106.83, 148.32; MS (EI) 296 (M^+, 10), 239 (M − C_4H_9, 69), 183 (100), 155 (30), 111 (17); HRMS (EI) calcd for $C_{18}H_{36}OSi$ 296.2535, found 296.2530.

Triethyl 4-[(triethylsilyl)oxy]-2-butylcyclohex-3-ene-1,1,3-tricarboxylate (19): IR (film) 2937−1736, 1716, 1640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), 0.62 (q, J = 8.0 Hz, 2H), 0.81 (m, 3H), 0.91 (t, J = 8.0 Hz, 3H), 1.15−1.32 (m, 15H), 2.12−2.40 (m, 4H), 3.52 (collapsed t, 1H), 4.05−4.38 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 7.16, 8.38, 15.63, 16.06, 24.35, 24.62, 30.09, 31.22, 35.14, 39.46, 58.48, 60.97, 62.47, 113.97, 155.95, 167.09, 167.80, 170.38; MS (CI, NH_3) 485 (M^+, 0.3), 455 (M − C_2H_5, 0.5), 397 (M − C_6H_{15}, 1), 371 (28), 325 (61), 313 (M + H − $C_8H_{12}O_4$, 100); MS (EI) 455 (M^+ − C_2H_5, 0.5), 397 (1), 370 (7), 313 (100); HRMS (EI) calcd for $C_{19}H_{30}O_7Si$ − C_2H_5 455.2483, found 455.2465.

The following compounds were prepared using procedure A.

1-[(Triethylsilyl)oxy]-3-[2(Z)-(trimethylstannyl)ethenyl]cyclohex-1-ene (6): IR (film) 1659, 1197, 765 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.04 (s, 9H, $^2J_{Sn^{119}}$ = 54.0 Hz, $^2J_{Sn^{117}}$ = 51.3 Hz), 0.63 (q, J = 12.0 Hz, 6H),) 0.95 (t, J = 12.0 Hz, 9H), 1.18−1.32 (m, 1H), 1.48−1.82 (m, 3H), 1.95−2.05 (m, 2H), 2.59−2.62 (m, 1H), 4.65 (dd, J = 2.0, 4.0 Hz, 1H), 5.73 (d, J = 12 Hz, 1H, $^2J_{Sn^{119}}$ = 83.7 Hz, $^2J_{Sn^{117}}$ = 78.3 Hz), 6.23 (dd, J = 10.0, 12.0 Hz, 1H, $^3J_{Sn^{119}trans}$ = 153.9 Hz, $^3J_{Sn^{117}trans}$ = 147.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) −8.34, 5.06, 6.70, 21.60, 29.40, 29.56, 42.89, 101.17, 127.49, 151.29, 153.58; MS (EI) 401 (M − 1, 3), 387 (M − CH_3, 19), 237 (M − C_3H_9Sn, 100), 211 (56), 165 (33), 115 (49); HRMS calcd for $C_{17}H_{34}OSnSi$ − CH_3 387.1166, found 387.1169.

1-[(Triethylsilyl)oxy]-3-[2(Z)-(trimethylstannyl)ethenyl]-4,4-dimethyl cyclohex-1-ene (entry 10, Table 1): IR ($CDCl_3$) 1238, 1366, 1661 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.14 (s, 9H, $^2J_{Sn^{119}}$ = 54.0 Hz, $^2J_{Sn^{117}}$ = 51.0 Hz),), 0.64 (q, J = 7.0 Hz, 6H), 0.82 (s, 3H), 0.93, 0.96 (2 × t, J = 7.0 Hz, 9H), 1.31−1.38 and 1.47−1.54 (m, 2H), 1.9−2.04 (m, 2H), 2.25−2.30 (m, 1H), 4.53 (bs, 1H), 5.75 (d, J = 12.1 Hz, 1H, $^2J_{Sn^{119}}$ = 83.7 Hz, $^2J_{Sn^{117}}$ = 79.7 Hz), 6.23 (dd, J = 9.9, 12.0 Hz, 1H, $^2J_{Sn^{119}trans}$ = 156.7 Hz, $^2J_{Sn^{117}trans}$ = 149.2 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) −8.26, 5.06, 6.71, 24.47, 27.45, 28.07, 31.22, 34.92, 106.7, 128.49, 149.79, 150.3; MS (CI, NH_3) 429 (M^+, 12), 415 (M − CH_3, 60), 265 (M − C_3H_9Sn, 73), 239 (M − $C_5H_{11}Sn$, 100), 209 (78); HRMS (EI) calcd for $C_{19}H_{38}OSiSn$ − CH_3 415.1479, found 415.1493.

Diethyl 4-[(triethylsilyl)oxy]-2-[2(Z)-(trimethylstannyl)-ethenyl]cyclohexen-3-ene-1,1- dicarboxylate (entry 11, Table 1): IR (film) 1738, 1668 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.18 (s, 9H), 0.59 (q, J = 10.8 Hz, 6H), 0.92 (t, J = 10.0 Hz, 9H), 1.14, 1.21 (2 × t, J = 9 Hz, 6H), 1.9−2.32 (m, 4H), 3.50 (dd, J = 4.6, 10.0 Hz, 1H), 3.9−4.2 (m, 1H), 4.08−4.21 (m, 3H), 4.64 (d, J = 4.6 Hz, 1H), 5.78 (d, J = 11.9 Hz, 1H, $^2J_{Sn-H}$ 73.5 Hz), 6.19 (dd, J = 10.0, 11.9 Hz, 1H, $^3J_{Sn^{119}trans}$ = 148.5 Hz, $^3J_{Sn^{117}trans}$ = 139.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) −8.48, 4.93, 6.63, 14.06, 24.41, 26.68, 45.07, 56.22, 61.2, 61.33, 105.75, 130.70, 146.26, 149.33, 170.06, 170.45; MS (EI) 546 (M^+, 1), 531 (M − CH_3, 18), 381 (M − C_3H_9Sn, 100), 355 (M − $C_5H_{11}Sn$, 22), 165 (M − $C_{20}H_{33}O_5Si$, 19); HRMS calcd for $C_{23}H_{42}O_5SiSn$ − CH_3 531.1588, found 531.1568.

Methyl (*E*)-3-(Trimethylstannyl)but-2-enoate (13) (Contains ca. 10% Impurity). To a solution of the cuprate **9** (2.38 mmol) prepared as outlined above was added methyl 2-butynoate (**12**) (200 mg, 2.04 mmol). The resulting pale red solution was stirred for 0.5 h and then worked up as above. Chromatographic purification over silica gel using (hexane: CH_2Cl_2:EtOAc = 20:2:1) as eluent provided the title compound (497 mg, 92%) as a pale yellow oil: IR (film) 2918, 1733, 1706 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.17 (s, 3H, $^2J_{Sn-H}$ = 56.5 Hz), 2.15 (s, 3H), 3.71 (s, 3H), 6.40 (bs, 1H, $^3J_{Sn-H\ cis}$ = 115.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) 6.83, 27.50, 51.67, 51.97, 129.98, 170.63; MS (EI) 263 (M^+ − 1, 28), 165 (M − $C_5H_7O_2$, 100), 135 (44); HRMS calcd for $C_8H_{16}O_2Sn$ − H 263.0094 found, 263.0088.

1-[(Triethylsilyl)oxy]cyclohexa-1,3-diene (14). To a solution of diisopropylamine (DIPA) (1.02 mL, 789 mg, 7.8 mmol) in dry THF (8 mL) at −78 °C, under argon, was added nBuLi (7.8 mmol). After 30 min, the solution was added to a cold (−78 °C) solution of CuCN (349 mg, 3.9 mmol, 1.5 equiv) and LiCl (330 mg, 7.8 mmol) in dry THF (18 mL). The resulting mauve/blue solution was stirred for 30 min and then treated with Et_3SiCl (540 μL, 391 mg, 2.6 mmol, 2 equiv) followed immediately by cyclohex-2-enone (0.252 mL, 250 mg, 2.6 mmol). After 1 h the reaction was almost complete by TLC analysis. The reaction was left for a further 15 min and then worked up as described above to afford an opaque pale green oil (1.14 g). The oil was applied to column of silica (50 g) and flash-eluted with pentane:1% Et_3N as solvent to give a clear oil (468 mg) that was repurified (using the same eluent) over silica to give the diene **14** (328 mg, 60%) as a clear colorless oil: IR (film) 1664, 1646, 1586 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.71 (q, J = 10.0 Hz, 6H), 0.98 (t, J = 10.0 Hz, 9H), 2.21−2.31 (m, 4H), 5.12 (d, J = 6.0 Hz, 1H), 5.42 (m, 1H), 5.81 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 6.75, 8.37, 25.51, 30.09, 102.40, 118.54, 124.90, 153.84; MS (EI) 210 (M^+, 100), 179 (42), 151 (M − 1 − C_4H_{10}, 47), 115 (M − C_6H_7O, 28), 87 (58); HRMS calcd for $C_{12}H_{22}OSi$ 210.1440 found, 210.1442.

Triethyl 4-[(triethylsilyl)oxy]-2-[2(*Z*)-(trimethylstannyl)ethenyl]cyclohex-3-ene-1,1,3-tricarboxylate (20): IR (film) 1738, 1722, 1693 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.22 (s, 9H, $^2J_{Sn-H}$ = 54.0 Hz), 0.58 (q, J = 7.5 Hz, 6H), 0.94 and 0.92 (2 × q, J = 7.5 Hz), 1.19−1.25 (2 × t, J = 7.3 Hz, 9H), 2.0−2.4 (m, 4H), 3.9−4.3 (m, 6H), 5.83 (d, J = 12.5 Hz, $^2J_{Sn^{119}}$ = 67.0, $^2J_{Sn^{117}}$ = 64.8 Hz), 6.20 (dd, J = 10.3, 12.5 Hz, $^3J_{Sn^{119}trans}$ = 148.5 Hz, $^3J_{Sn^{117}trans}$ = 141.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) −7.87, 5.76, 6.70, 13.95, 13.99, 14.63, 21.92, 26.09, 41.99, 57.99, 60.6, 61.45, 61.61, 99.44, 132.80, 145,03, 169.54, 169.65, 170.61, 171.92; MS (EI) 603 (M^+ − CH_3,19), 453 (M − C_3H_5-Sn, 9), 250 (8), 208 (14), 193 (100); HRMS (EI) calcd for $C_{26}H_{46}O_7SiSn$ − CH_3 603.1796, found 603.1825.

Triethyl 4-[(triethylsilyl)oxy)]cyclohex-3-ene-1,1,3-tricarboxylate (21): IR (film) 1735, 1654, 1648 cm^{-1}; ^1H (200 MHz, $CDCl_3$) 0.6 (q, J = 10.0 Hz, 6H), 0.98 (t, J = 8.4 Hz, 9H), 1.25, 1.28 (2 × t, J = 6.0 Hz, 9H), 2.15−2.25 (m, 2H), 2.35−2.41 (m, 2H), 2.79 (bs, 2H), 4.20 (q, J = 6.0 Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$) 5.76 6.53, 13.96, 14.22, 26.03, 26.60, 27.83, 52.93, 60.52, 61.58, 95.21, 170.12, 170.79, 171.92; MS (EI) 315 (M + 2, 100), 314 (M + H − $C_6H_{15}Si$, 36), 313 (M − $C_6H_{15}Si$, 3), 269 (31), 241 (M − $C_9H_{20}O_2Si$, 19), 196 (61), 195 (59), 167 (M − $C_{12}H_{25}O_4Si$, 100); HRMS calcd for $C_{21}H_{36}O_7Si$ + H − $C_6H_{15}Si$ 314.1365, found 314.1361.

Ethyl 2-oxo-6-[2(*Z*)-(trimethylstannyl)ethenyl]cyclohexanecarboxylate (23): IR (film) 1749, 1720, 1651 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 0.18, 0.19 (2 × s, 18H, $^2J_{Sn-H}$ = 52.5 Hz), 1.24 (t, J = 7.0 Hz, 6H), 1.54−1.86 (m, 7H), 2.12−2.58 (m, 1H), 2.25 (collapsed dd, 4H), 2.42 (d, J = 15.0 Hz, 2H), 2.76 (td, J = 5.0, 9.2 Hz, J = 15.0 Hz, 1H), 3.05 (td, J = 2.5, 9.2, 10.0 Hz, 1H), 3.28 (d, J = 11.0 Hz, 1H), 4.16, 4.2 (2 × t, J = 7.0 Hz, 6H), 5.76 (d, J = 12.5 Hz, 1H, $^2J_{Sn-H}$ = 72.0 Hz), 5.88 (d, J = 12.2 Hz, 1H, $^2J_{Sn-H}$ = 70.0 Hz), 6.26 (dd, J = 9.3, 12.2 Hz, 1H), 6.26 (dd, J = 9.3 Hz, J = 12.2 Hz, 1H, $^3J_{Sn^{119}\ trans}$ = 141.0 Hz, $^3J_{Sn^{117}}$ = 136.0 Hz), 6.40 (dd, J = 9.3, 12.3 Hz, 1H, $^3J_{Sn^{119}\ trans}$ = 157.5 Hz, $^3J_{Sn^{117}\ trans}$ = 150.0 Hz), 12.57 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) −8.40, −8.43, 14.23, 14.53, 18.13, 24.86, 29.29, 31.33, 31.61, 38.94, 40.81, 48.29, 60.18, 60.85, 62.73, 100.77, 127.70, 131.72, 148.42, 153.65, 168.86, 172.81, 173.09, 205.10; MS (EI) 345 (M^+ − CH_3, 100), 299 (M − 1 − C_3H_8O, 50), 269 (45), 165 (M + H − $C_{12}H_{18}O_3$, 45); HRMS calcd for $C_{14}H_{24}O_3Sn$ − CH_3 345.0513, found 345.0526.

Bis(1,1-dimethylethyl) *p*-Methoxybenzyl 4-Oxocyclohex-2-ene-1,1,3-tricarboxylate (24) (See Ref 19). A vigorously stirred solution of the selenide **34** (300 mg, 0.485 mmol) in CH_2Cl_2 (2 mL) and water (0.2 mL) at 0 °C was treated with 30% hydrogen peroxide (0.163 mL, 1.45 mmol, 3 equiv) in water (0.5 mL). The reaction was complete in 15 min. The solution was diluted and then washed sequentially with $NaHCO_3$, water, and brine. Drying and removal of solvent gave a colorless gum (114 mg, 51%): IR (film) 1732, 1669 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 1.56 (s, 18H), 2.5−2.58 (m, 2H), 2.68−2.74 (m, 2H), 3.90 (s, 3H), 5.30 (s, 2H), 6.98 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.70 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) 27.90, 28.90, 35.20, 55.5, 57.1, 66.90, 83.90, 114.10, 128.0, 130.10, 150.10, 160.0, 164.10, 166.90, 193.0; MS (EI) 460 (M^+, 0.4), 404 (M + H − C_4H_9, 0.1), 348 (2), 212 (14), 137 (M − $C_{17}H_{23}O_6$, 47), 121 (M − $C_{17}H_{23}O_7$, 100); HRMS calcd for $C_{25}H_{32}O_8$ 460.2097, found 460.2101.

Bis(1,1-dimethylethyl) *p*-methoxybenzyl 4-[(triethylsilyl)oxy]cyclohex-3-ene-1,1,3-tricarboxylate (25): IR (film) 1727, 1717, 1683 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 0.60 (q, J = 8.0 Hz, 6H), 0.91 (t, J = 8.0 Hz, 9H), 1.42 (s, 18H), 2.04 (collapsed dd, J = 5.4 Hz, 2H), 2.22 (collapsed dd, J = 5.4 Hz, 2H), 2.76 (bs, 2H), 3.78 (s, 3H), 5.09 (s, 2H), 6.84 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) 5.45, 6.69, 27.42, 27.87, 29.39, 30.53, 53.86, 55.34, 65.38, 81.34, 106.15, 113.78, 129.03, 130.11, 158.72, 159.43, 166.63, 170.19; MS (CI, NH_3) 577 (M + 1, 0.1), 503 (M − C_4H_9O, 1) 455 (M − C_8H_9O, 4), 299 (10) 121 (M − $C_{23}H_{38}O_7Si$, 100); HRMS (CI) calcd for $C_{31}H_{48}O_8Si$ − C_4H_9O 503.2465, found 503.2437

Triethyl 4-Oxo-2-cyanocyclohexane-1,1,3-tricarboxylate (26). A solution of the cuprate **9** (0.38 mmol) generated as described in procedure A was recooled to −78 °C and treated with TMSCN (69 μL, 52 mg, 0.52 mmol, 2 equiv with respect to enone ester) followed by a solution of keto ester **18** (80 mg, 0.26 mmol) in dry THF (0.2 mL) added rapidly. The bright yellow color was retained, and after 15 min TLC indicated complete reaction. The reaction was left a further 0.5 h and then worked up in the usual way to give an orange oil (180 mg). Flash chromatographic purification of the oil on silica (10 g) using (hexane:CH_2Cl_2:EtOAc = 10:2:1) as eluent provided the title compound **26** (57 mg, 65%) as a pale brown wax: IR (film) 2222, 1741, 1686 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 1.21, 1.36, 1.39 (3 × t, J = 8.1 Hz, 9H), 2.2−2.7 (m, 4H), 4.15 (m, 6H), 4.49 (s, 1H), 12.42 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) 13.91, 13.96, 14.14, 23.39, 25.96, 30.67, 55.59, 62.70, 62.91, 93.67, 118.36, 166.96, 167.40, 170.07, 173.07; MS (EI) 339 (M^+, 43), 294 (M − C_2H_5O, 32) 265 (M − H − $C_3H_5O_2$, 100); HRMS calcd for $C_{16}H_{21}O_7N$ 339.1318, found 339.1315.

The following compounds were prepared using procedure B.

Triethyl 4-oxo-2-[(2(*Z*)-(trimethylstannyl)ethenyl]cyclohexane-1,1,3-tricarboxylate (28): IR (film) 1749, 1738, 1651, 1646 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.22 (s, 9H, $^2J_{Sn-H}$ = 51.3 Hz), 1.19, 1.28 (2 × t, J = 6.0 Hz, 9H), 2.2−2.42 (m, 4H), 3.90−4.04 (m, 2H), 4.02 (d, J = 10 Hz, 1H), 4.13−4.29 (m, 4H), 5.83 (d, J = 12.5 Hz, 1H, $^2J_{Sn^{119}}$ = 71.5 Hz, $^2J_{Sn^{117}}$ = 67.8 Hz), 6.1 (dd, J = 10.0, 12.5 Hz, 1H, $^3J_{Sn^{119}trans}$ = 151.2 Hz, $^3J_{Sn^{117}trans}$ = 145.8 Hz), 12.5 (s, 1H); ^{13}C NMR (68MHz, $CDCl_3$) −7.85, 13.98, 14.66, 21.94, 26.12, 41.73, 58.01, 60.60, 61.6, 99.46, 132.82, 145.07, 169.54, 170.62, 171.94; MS (EI) 489 (M^+ − CH_3, 19), 443 (9), 205 (M − 2 − $C_{11}H_{18}O_3Sn$, 100), 165 (M − $C_{17}H_{23}O_7$, 55), 149 (45), 103 (73); HRMS (EI) calcd for $C_{20}H_{32}O_7Sn$ − CH_3 489.0935, found 489.0942.

Bis(1,1-dimethylethyl) *p*-methoxybenzyl) 4-oxo-2-[2(*Z*)-(trimethylstannyl)ethenyl] cyclohexane-1,1,3-tricarboxylate (29): IR (smear) 3750−3000, 1741, 1732, 1717, 1653, 1645 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.38 (s, 9H, $^2J_{Sn-H}$ = 54.0 Hz)), 1.47 (s, 9H), 1.97−2.39 (m, 4H), 3.77 (s, 3H), 3.99 (d, J = 10.0 Hz, 1H), 5.01 (d, J = 12.1 Hz, 1H), 5.33 (d, J = 12.0 Hz, 2H), 5.88 (d, J = 12.5 Hz, 1H, $^2J_{Sn-H}$ = 55.0 Hz), 6.13 (dd, J = 12.0 Hz, 1H, $^3J_{Sn^{119}trans}$ = 153.9 Hz, $^3J_{Sn^{117}trans}$ = 145.8 Hz), 6.85 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 12.29 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) −7.49, 22.57, 26.39, 27.68, 27.81, 41.58, 55.25, 58.66, 65.81, 81.53, 81.75, 99.62, 113.86, 128.33, 129.72, 132.77, 145.05, 159.48, 168.86, 171.24, 171.57; MS (EI) 637 (M^+ − CH_3, 1), 185 (11), 165 (M − $C_{27}H_{35}O_8$, 10), 121 (M − $C_{22}H_{35}O_7Sn$, 100), 84 (99); HRMS calcd for $C_{30}H_{44}O_8Sn$ − CH_3 637.1823, found 637.1847.

3-[2(*Z*)-(Trimethylstannyl)ethenyl]cyclohexan-1-one (30): IR (film) 2970, 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.15 (s, 9H, $^2J_{Sn-H}$ = 58.0 Hz), 1.49−1.88 (m, 3H), 2.01−2.41 (m, 5H), 5.81 (d, J = 12.5 Hz, $^2J_{Sn^{119}}$ = 75.4 Hz, $^2J_{Sn^{117}}$ = 71.4 Hz), 6.3 (dd, J = 8.4, 12.5 Hz, 1H, $^3J_{Sn^{119}\ trans}$ = 146.0 Hz, $^3J_{Sn^{117}\ trans}$ = 138.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) −7.51, 25.82, 32.29, 41.45, 46.95, 48.14, 128.81, 150.09, 208.92; MS (EI) 288 (M^+, 1), 273 (M − CH_3, 100), 165 (M − $C_8H_{11}O$, 29), 151 (37); HRMS calcd for $C_{11}H_{20}OSn$ 288.0536, found 288.0538.

3-[2(*Z*)-(Trimethylstannyl)ethenyl]-4,4-dimethylcyclohexan-1-one (31): IR (film) 2940, 1717 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.12 (s, 9H, $^2J_{Sn-H}$ = 64.8 Hz), 0.98 (s, 3H), 1.08 (s, 3H), 1.50−1.80 (m, 2H), 2.02−2.48 (m, 4H), 5.86 (d, J = 12.5 Hz, 1H, $^2J_{Sn^{119}}$ = 78.3 Hz, $^2J_{Sn^{117}}$ = 74.2 Hz), 6.3 (dd, J = 10.0, 12.5 Hz, $^3J_{Sn^{119}trans}$ = 125.6 Hz, $^3J_{Sn^{117}trans}$ = 119.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) −8.31, 20.48, 29.02, 38.18, 39.90, 44.36, 54.44, 131.40, 147.83, 210.5; MS (EI) 316 (M^+, 0.8), 301 (M − CH_3, 100), 165 (M − $C_{10}H_{14}O$, 54), 151 (M − C_3H_9Sn, 31); HRMS calcd for $C_{13}H_{24}OSn$ − CH_3 301.0614, found 301.0616.

***p*-Methoxybenzyl Acrylate (32) (See Ref 19).** To a solution of *p*-methoxybenzyl alcohol (2.0 g, 0.014 mol) in dry THF (30 mL, 0.5 M) at 40 °C, under argon, was added sodium hydride (60% dispersion, 590 mg, 0.015 mol, 1.05 equiv). Vigorous effervescence ensued as the temperature climbed to *ca.* 48 °C. After 15 min the opaque mixture was cooled to −78 °C and treated with a solution of acryloyl chloride (1.9 g, .021 mol, 1.5 equiv) in dry THF (10 mL). After 2 h at −78 °C TLC showed complete reaction. The mixture was diluted with ethyl acetate (60 mL) and washed with 2 N HCl, saturated $NaHCO_3$, water, and brine. The organic layer was dried and evaporated to an oil (2.79 g), which was applied to a column of silica gel (100g) and flash chromatographed using hexanes: CH_2Cl_2: EtOAc 20:2:1 as eluent to provide the title compound as a colorless oil (1.68 g, 93%): IR (film) 1728 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 3.81 (s, 3H), 5.81 (s, 2H), 5.84 (dd, J = 2.4, 10.3 Hz, 1H), 6.15 (dd, J = 10.2, 17.3 Hz, 1H), 6.4 (d, J = 17.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) 55.27, 66.13, 113.94, 127.97, 128.43, 130.1, 159.66, 166.08; MS (EI) 192 (M^+, 65), 121 (M − $C_3H_3O_2$, 100); HRMS calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0787.

Bis(1,1-dimethylethyl) *p*-Methoxybenzyl 4-Oxocyclohexane-1,1,3-tricarboxylate (33). To a warm (40−45 °C) suspension of NaH (30 mg, 1.25 mmol, 2.5 equiv) in dry THF (200 μL) under argon was added di-*tert*-butyl malonate (106 μL, 0.478 mmol). Following complete evolution of hydrogen, a solution of *p*-methoxybenzyl acrylate **32** (100 mg, 0.502 mmol) in dry THF (100 μL) was added dropwise, over 20 min. Reaction was complete in 40 min. The dirty yellow solution was diluted with CH_2Cl_2 (10 mL) and washed with 2 N HCl, water, and brine. The extract was dried and evaporated to a wax (298 mg). Flash chromatography over silica gel (30 g) using hexanes:CH_2Cl_2:EtOAc 10:2:1 as eluent afforded the title compound as a colorless solid (167 mg, 81%): IR (smear) 2940, 1717 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 2.42−2.50 (m, 2H), 2.78 (s, 2H), 3.91 (s, 3H), 5.26 (s, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.4 (d, J = 9.0 Hz, 2H), 12.3 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) 26.17, 16.66, 27.72, 27.80, 53.99, 55.27, 65.79, 81.49, 95.34, 113.88, 128.09, 129.85, 130.23, 170.04, 170.74, 171.84; MS (EI) 462 (M^+, 0.4), 406 (M − C_4H_{10}, 0.8), 137 (M − $C_{17}H_{25}O_6$, 13), 121 (M − $C_{17}H_{25}O_7$, 100); HRMS calcd for $C_{25}H_{34}O_8$ 462.2253, found 462.2249.

Bis(1,1-dimethylethyl) *p*-Methoxybenzyl 4-Oxo-3-(phenylselenyl)cyclohexane-1,1,3-tricarboxylate (34). A solution of PhSeCl (683 mg, 3.56 mmol, 1.05 equiv) in dry CH_2Cl_2 (28 mL) at 0 °C under argon was treated with dry pyridine (287 μL, 281 mg, 3.56 mmol, 1.1 equiv). After 15 min a solution of the triester **33** (1.5 g, 3.24 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min. The initial brown solution gradually lightened to a bright yellow. Reaction was 90% complete in 1 h at 0 °C with no further change after 4 h. The solution was allowed to warm to ambient temperature over 15 min and then washed with 2 N HCl (10 mL), saturated $NaHCO_3$ (10 mL), and brine. Drying and evaporation of the organic phase afforded an oil (1.7 g). Flash chromatography using hexanes:CH_2Cl_2:EtOAc 20:2:1 as eluent provided the title selenide as a low-melting solid (1.22 g, 61%): IR (smear) 1726, 1661, 1614 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$), 1.40 (s, 9H), 1.46 (s, 9H), 1.95 to 2.09 (m, 1H), 2.30 to 2.60 (m, 2H), 2.71 (d, J = 16.2 Hz, 2.80−2.95 (m, 1H), 2.92 (d, J = 16.4 Hz, 1H), 3.8 (s, 3H), 4.8 (d, J = 12.0 Hz, 1H), 5.20 (d, J = 12.0 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 7.2−7.4 (m, 5H), 7.5 (d, J = 9.0 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) 27.7, 27.76, 30.11, 36.26, 39.47, 53.69, 55.28, 59.21, 67.35, 82.06, 82.16, 113.81, 126.01, 127.21, 128.62, 129.45, 130.18, 138.38, 168.30, 169.42, 169.59, 203.01; MS (EI) 618 (M^+, 0.4), 462 (M + H − C_6H_5Se, 0.2), 406 (M + 2 − $C_{10}H_{14}Se$, 0.4), 137 (M − $C_{23}H_{29}O_6Se$, 9.5), 121 (M − $C_{23}H_{29}O_7Se$, 100); HRMS calcd for $C_{31}H_{38}O_8Se$ 618.1731, found 618.1727.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of **5**, **6**, **7** (R = nBu), **14**, **19**−**21**, **23**−**26**, **28**−**31**, and the products of Table 1, entries 7, 10, and 11 (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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