The Stereochemistry of the Silyl-cupration of Allenes

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The silyl-cupration of the stereochemically defined allenes **6** and **7** is stereospecifically *syn*, giving the allylsilanes **8** and **9**, respectively

Metallo-metallations are a relatively new class of reaction, closely related to the better known hydrometallations and carbometallations. Although known for the addition of two different main-group metals to a triple bond,[1] stoichiometric metallo-metallations usually involve the addition of copper to one end of a triple bond, and of a silyl, germyl or stannyl group to the other.[2-5] Subsequently, the copper is replaced by a proton, or by a halogen or carbon electrophile, making these reactions useful for the synthesis of vinyl-silanes, -germanes, and -stannanes.[5] In transition metal-catalysed reactions, the transition metal, commonly copper, palladium or manganese, is replaced *in situ*, as part of the catalytic cycle, by a main group metal such as magnesium, boron, aluminium, zinc, or tin, before subsequent reaction.[6,7] The stereochemistry of the metallo-metallation of triple bonds has been abundantly proved to be *syn*,[3-7] but, occasionally, and especially when copper becomes attached to a carbon carrying an anion-stabilising group, the overall process is *anti* rather than *syn*,[1-3] probably because of equilibration following a kinetically *syn* process. Metallo-metallations of double bonds are much less common, but are known for the transition metal-catalysed addition of silicon–silicon bonds to 1,3-dienes,[8] for the transition metal-catalysed addition of silicon–magnesium, silicon–aluminium, and silicon–zinc bonds to allenes,[7,9] for the stoichiometric silyl-cupration and stannyl-cupration of allenes,[10,11] and, most recently, for the stoichiometric silyl-zirconation[12] and the platinum-catalysed silyl-silylation of isolated double bonds.[13] Only in the last of these cases has the stereochemistry been examined: the addition of two fluorodimethylsilyl groups to norbornene takes place on the *exo* face and is therefore *syn*[13] but, in the nature of this system, it is not possible to use it to prove that the reaction is stereospecific in the Zimmerman sense.[14] We now report a metallo-metallation of a single bond that is, not surprisingly, stereospecifically *syn*. The double bond in question is that of a trisubstituted allene, and the metallo-metallation is silyl-cupration.

Results and Discussion

We have already shown that 1,1,3-trimethylallene **1** reacts with our silyl-cuprate reagent to give, with high *regio*selectivity, the allylsilane–vinylcuprate **2**, and, hence, after aqueous work up, the allylsilane **3** (Scheme 1).[10] To prove that the stereochemistry of this process is *syn*, we needed a stereochemically defined allene, and we chose for this purpose the diastereoisomeric pair **6** and **7**. Of several methods by which these might have been prepared selectively, the best in our hands was the conjugate addition of methylmagnesium chloride to the prop-2-ynylic ethers **4** and **5**, catalysed by copper bromide, in a process that is known to be stereospecifically *syn*.[15]

Silyl-cupration of these allenes gave the known[16] allylsilanes **8** and **9**, respectively, the reaction requiring, however, a temperature between −40 °C and room temperature, rather warmer than the corresponding reaction of trimethylallene
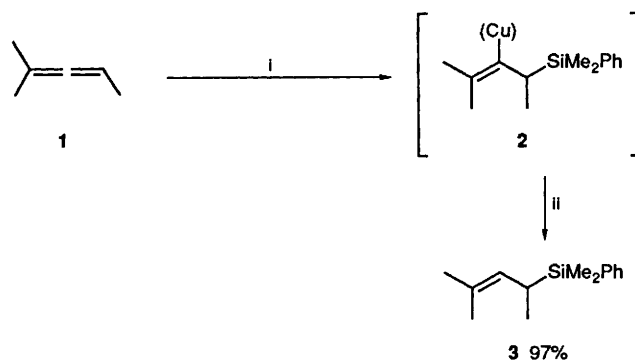
Scheme 1 *Reagents and Conditions:* i, $(PhMe_2Si)_2CuLi\cdot LiCN$, tetrahydrofuran, −78 °C, 1 h; ii, NH_4Cl, MeOH
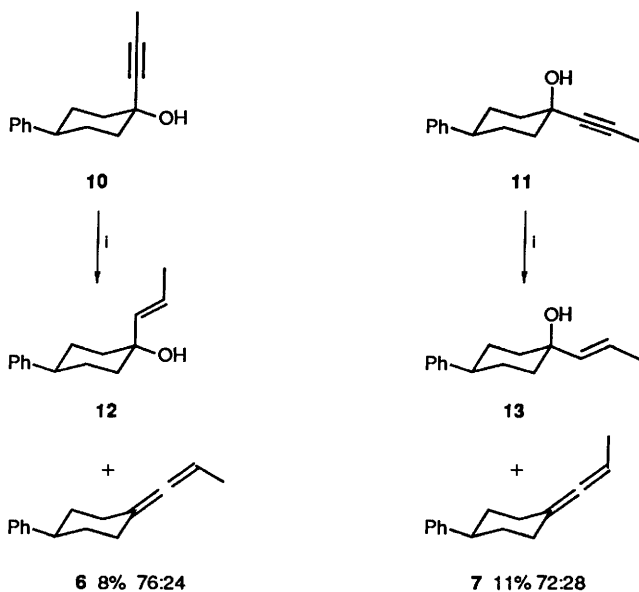
(Scheme 2). The structures of the allylsilanes were unambiguously identifiable from their ^{13}C NMR spectra, which were closely similar, but still recognisably different from each other, and identical with the spectra of authentic samples. Within the limits of the ^{13}C NMR spectroscopic analysis, and assuming that the vinylcuprate is protonated with retention of configuration, the reaction was completely stereospecific in the *syn* sense. The high degree of stereospecificity is only found if the lowest possible temperature and the shortest possible time are used—when the reaction mixture from the reaction of the allene
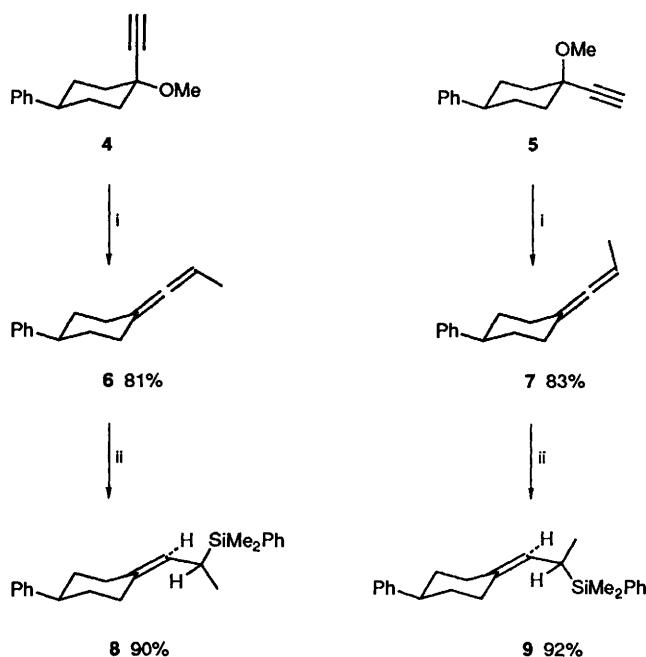
Scheme 2 *Reagents and conditions:* i, $MeMgClCuBr$, Me_3SiCl, Et_2O–hexane; ii, $(PhMe_2Si)_2CuLi\cdot LiCN$, tetrahydrofuran, −40–25 °C

Table 1 Bond lengths Å

Bond	Length (Å)	Bond	Length (Å)
C(1)–C(2)	1.503(7)	C(1)–C(6)	1.511(7)
C(1)–C(7)	1.297(6)	C(2)–C(3)	1.524(10)
C(3)–C(4)	1.525(8)	C(4)–C(5)	1.524(7)
C(4)–C(10)	1.498(8)	C(5)–C(6)	1.522(10)
C(7)–C(8)	1.304(7)	C(8)–C(9)	1.492(9)
C(10)–C(11)	1.412(8)	C(10)–C(15)	1.379(7)
C(11)–C(12)	1.370(8)	C(12)–C(13)	1.371(8)
C(13)–C(14)	1.399(9)	C(14)–C(15)	1.362(8)

Table 2 Bond angles (°)

Angle	
C(2)–C(1)–C(6)	114.2(3)
C(6)–C(1)–C(7)	122.0(4)
C(2)–C(3)–C(4)	112.0(4)
C(3)–C(4)–C(10)	113.0(4)
C(4)–C(5)–C(6)	111.5(5)
C(1)–C(7)–C(8)	178.7(7)
C(4)–C(10)–C(11)	121.8(4)
C(11)–C(10)–C(15)	116.5(5)
C(11)–C(12)–C(13)	121.0(6)
C(13)–C(14)–C(15)	119.6(5)
C(2)–C(1)–C(7)	123.8(3)
C(1)–C(2)–C(3)	111.4(5)
C(3)–C(4)–C(5)	109.3(4)
C(5)–C(4)–C(10)	114.0(5)
C(1)–C(6)–C(5)	112.2(4)
C(7)–C(8)–C(9)	125.5(6)
C(4)–C(10)–C(15)	121.7(5)
C(10)–C(11)–C(12)	121.0(4)
C(12)–C(13)–C(14)	118.9(6)
C(10)–C(15)–C(14)	123.0(6)

10

11

12

13

6 8% 76:24

7 11% 72:28

Scheme 3 *Reagents:* i, LiAlH₄, Et₂O

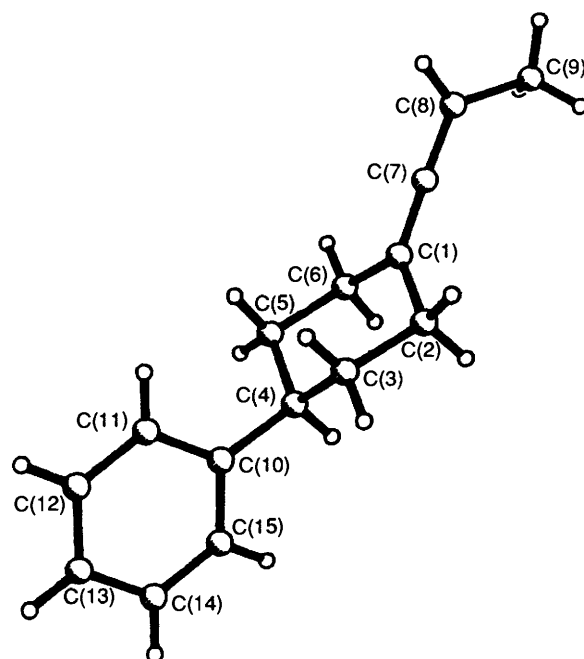**Fig. 1** The molecular structure of the allene **6**

6 and the silyl-cuprate was left at room temperature for 12 h, the yield dropped to 30% and the allylsilanes **8** and **9** were now present in equal amounts.

In our efforts to prepare the allenes **6** and **7** stereochemically pure, we tried several other methods. Methyl-cupration of the acetate corresponding to the ether **4** gave the allenes **6** and **7** in a ratio of 22:78. This is, as expected,[17] kinetically a stereospecifically *anti* process, but the methyl cuprate is evidently epimerising the allenes, just as cuprates are known to racemise homochiral allenes.[18] With longer reaction times, the allenes were completely equilibrated to a 50:50 mixture. Lithium aluminium hydride reduction of the prop-2-ynyl alcohols **10** and **11** was also selective, giving the allenes **6** and **7**, respectively. However these reactions were incompletely *anti* stereospecific, and yields were, in any case, low because the *trans* allylic alcohols **12** and **13** were the major products (Scheme 3). This type of allene-forming reaction was thought at first to be stereospecifically *syn*,[19] but later work showed it to be *anti*,[20] with which we concur. Nevertheless, the doubt about the sense of the stereospecificity of this reaction and the low level of that stereospecificity, coupled with the importance in the present context that we assign stereochemistries to the allenes **6** and **7** correctly, led us to carry out an X-ray crystallographic structure determination of one of them. The allene **6** was thus proved to have the structure shown in Fig. 1. Bond lengths and angles are listed in Tables 1 and 2, respectively.

The stereospecificities in the reactions described in this paper may have consequences in applications in organic synthesis. One of our allylsilane syntheses involves the stereospecifically *anti* reaction of our silyl-cuprate with *trans* allylic acetates.[16]

Thus the acetate of the alcohol **12** gave the allylsilane **8**, and the acetate of the alcohol **13** gave the allylsilane **9**. Occasionally, however, this route has suffered, because the reduction of a prop-2-ynyl alcohol with lithium aluminium hydride, by which we prepared the *trans* allylic alcohols, sometimes gave the allene as the major, not the minor, product.[21] Since the allene-forming reaction is stereospecifically *anti*, and the silyl-cupration of the allene is now known to be *syn*, the allylsilane obtained will be largely the same diastereoisomer that is obtained by the stereospecifically *anti* reaction of our silyl-cuprate on the acetate of the *trans* allylic alcohol. Thus the extent to which allene or *trans* allylic alcohol is formed by lithium aluminium hydride reduction of a prop-2-ynyl alcohol is less important, since both will give largely the same allylsilane stereoisomer: both **6** and **12** will give **8**, and both **7** and **13** will give **9**.

Experimental

1-*Ethynyl*-1-*methoxy*-4-*phenylcyclohexanes* **4** and **5**.—The

Table 3 Atomic coordinates/10⁻⁴

	x	y	z
C(1)	1312	1935(2)	925
C(2)	1595(7)	2703(2)	529(9)
C(3)	1073(7)	3213(2)	1837(8)
C(4)	1713(5)	3026(2)	4017(7)
C(5)	1308(7)	2258(2)	4350(8)
C(6)	1824(7)	1731(3)	3081(9)
C(7)	698(6)	1476(2)	−444(9)
C(8)	107(7)	1015(3)	−1836(8)
C(9)	909(7)	548(3)	−2843(9)
C(10)	1340(6)	3563(2)	5345(8)
C(11)	−107(6)	3683(2)	5308(9)
C(12)	−433(6)	4189(2)	6498(9)
C(13)	639(7)	4589(2)	7776(9)
C(14)	2082(6)	4474(3)	7849(9)
C(15)	2392(6)	3973(2)	6649(8)

alcohol[16] (0.4 g, 2 mmol) in dry tetrahydrofuran (THF) (2 cm³) was added dropwise at 40 °C to a mixture of methyl iodide (0.14 cm³, 2.2 mmol) and a suspension of sodium hydride (60% dispersion in oil; 0.16 g, 4 mmol) in dry THF (6 cm³). The mixture was refluxed under argon for 2 h, then quenched with saturated aqueous ammonium chloride and extracted with ether. The extracts were washed with brine, dried (MgSO₄) and evaporated under reduced pressure to give, after chromatography (SiO₂, 12 g, eluting with hexane–EtOAc, 9:1 v/v), the trans-*ether* **4** (372 mg, 87%), from the *trans*-alcohol, as needles, m.p. 90–92 °C (from hexane–Et₂O) (Found: C, 83.8; H, 8.5. $C_{15}H_{18}O$ requires C, 84.0; H, 8.5%), $v_{max}(CHCl_3)/cm^{-1}$ 3250 and 1600 (C=C), δ(CDCl₃) 7.33–7.19 (5 H, m, Ph), 3.44 (3 H, s, OMe), 2.57 (1 H, s, acetylenic H), 2.50 (1 H, m, PhC*H*) and 2.24–1.55 (8 H, m, aliphatic H) (Found: M^+, 214.1352. $C_{15}H_{18}O$ requires M, 214.1357), m/z 214 (2%, M^+), 182 (100, M − MeOH), 181 (37), 167 (47), 104 (70), 95 (60) and 91 (66), and the cis-*ether* **5** (355 mg, 83%), from the *cis*-alcohol, as needles, m.p. 75–77 °C (from hexane) (Found: C, 84.3; H, 8.5. $C_{15}H_{18}O$ requires C, 84.0; H, 8.5%), $v_{max}(CHCl_3)/cm^{-1}$ 3280 and 1595 (C=C), δ(CDCl₃) 7.32–7.15 (5 H, m, Ph), 3.37 (3 H, s, OMe). 2.52–2.45 (1 H, m, PhC*H*), 2.44 (1 H, s, C≡CH) and 2.24–1.56 (8 H, m, aliphatic H) (Found: M^+, 214.1356. $C_{15}H_{18}O$ requires M, 214.1357), m/z 214 (10%, M^+), 199 (6, M − Me), 186 (26), 119 (23), 104 (74), 95 (100) and 91 (88).

3-*Methyl-4-phenylcyclohexylidenebuta*-1,2-*dienes* **6** and **7**.— Copper(i) bromide (7 mg, 0.047 mmol) and trimethylsilyl chloride (0.12 cm³, 0.93 mmol) were added to a solution of the prop-2-ynylic ether (0.2 g, 0.93 mmol) in dry ether (5 cm³) and pentane (5 cm³), and methylmagnesium chloride (0.2 mol dm⁻³ solution in ether; 20 cm³) added dropwise at −78 °C. The white suspension was allowed to warm to room temperature and stirred under argon for 3 h, quenched with saturated aqueous ammonium chloride, and extracted with ether. The extract was washed with brine, dried (MgSO₄), and evaporated under reduced pressure to give, after chromatography (SiO₂, 7 g, eluting with hexane–EtOAc, 96:4 v/v), the trans-*allene* **6** (150 mg, 81%), from the ether **4**, as prisms, m.p. 72–74 °C (from MeOH) (Found: C, 91.1; H, 9.3. $C_{15}H_{18}$ requires C, 90.9; H, 9.1%), $v_{max}(CHCl_3)/cm^{-1}$ 1960 (C=C=C) and 1600 (C=C), δ_H(CDCl₃) 7.32–7.15 (5 H, m, Ph), 5.0 (1 H, m, C=C=CH), 2.57 (1 H, m, PhC*H*), 1.64 (3 H, d, *J* 6.8* Me) and 2.41–1.51 (8 H, m, aliphatic H); δ_C(CDCl₃) 199.3, 147.0, 128.4, 126.9, 126.0, 100.4, 83.6, 44.1, 34.7, 31.7 and 15.0 (Found: M^+, 198.1404.$C_{15}H_{18}$

* Throughout *J* values are given in Hz.
† For details of the crystallographic deposition scheme see Instructions for Authors (1991), *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

requires M, 198.1408), m/z 198 (100%, M^+), 183 (18, M − Me), 104 (22), 91 (26) and 79 (58); and the cis-*allene* **7** (154 mg, 83%) as an oil, from the ether **5** (Found: C, 91.1; H, 9.15. $C_{15}H_{18}$ requires C, 90.9; H, 9.1%); $v_{max}(CHCl_3)/cm^{-1}$ 1960 (C=C=C) and 1600 (C=C), δ_H(CDCl₃) 7.33–7.15 (5 H, m, Ph), 4.94 (1 H, m, C=C=CH), 2.58 (1 H, m, PhC*H*), 1.67 (3 H, d, *J* 6.9 Me) and 2.40–1.52 (8 H, m, aliphatic H) (Found: M^+, 198.1398. $C_{15}H_{18}$ requires M, 198.1408), m/z 198 (95%, M^+), 169 (32), 104 (71), 91 (70), and 79 (100, C_6H_7).

X-ray Crystal Structure Determination of the Allene **6**.— Suitable crystals of **6** were grown from methanol and mounted on glass fibres with epoxy resin.

CrystalData.—$C_{15}H_{18}$,M = 198.3,monoclinic,a = 9.685(2), b = 18.662(6), c = 7.133(2) Å, β = 108.01(2)°, U = 1225.9(6) Å³ (by least squares refinement on diffractometer angles for 25 automatically centred reflections in the range 50 < 2θ < 60°, λ = 1.5418 Å), space group Cc(No. 9), Z = 4, D_c = 1.074 g cm⁻³, $F(000)$ = 432. Transparent needles, crystal dimensions: 0.05 × 0.07 × 0.41 mm, μ(Cu-Kα) = 4.16 cm⁻¹.

Data Collection and Processing.—Nicolet R3mμ diffracto-meter,ω/2θ scan mode, scan speed 2.50–29.3° min⁻¹,ω scan range 1.8° plus Kα-separation, graphite monochromated Cu-Kα radiation; 2869 reflections measured (5.0 ≤ 2θ ≤ 116.0°, ±*h*, −*k*, ±*l*), 1678 unique (merging R = 0.082, no absorption correction applied), giving 1567 with $F > 6σ(F)$. Linear and approximately isotropic decay, *ca.* 22%, attempt to correct during data reduction.

Structure Analysis and Refinement.—Non-centrosymmetric direct methods are used for non-hydrogen atoms, H-atoms are located from Fourier difference synthesis. Full-matrix least squares refinement is used with all anisotropic carbons. H atoms constrained to ride on relevant carbon atoms, C–H 0.96 Å, and the aromatic and non-aromatic hydrogens were assigned common isotropic displacement parameters. The weighting scheme $w^{-1} = σ^2(F) + 0.0035F^2$, with σ(F) from counting statistics gave acceptable agreement analysis. The final con-verged R and R_w values were 0.089 and 0.084, respectively, and S = 1.45 for 137 refined parameters. The relatively high residuals were considered to be related to the significant decomposition during data collection. Attempts to establish the crystal polarity for the structure by refining Rogers' η-parameter[22] were inconclusive. A final Fourier map showed no significant regions of electron density in chemically sensible positions; largest peak 0.37 eÅ⁻³, largest hole −0.77 eÅ⁻³. Final atomic co-ordinates and equivalent isotropic displacement parameters are listed in Table 3. The structure was solved and refined using the SHELXTL-PLUS package on a Micro-Vax II computer.[23] Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.†

The Silyl-cupration of the Allenes.—The allene (50 mg, 0.25 mmol) in dry THF (tetrahydrofuran) (3 cm³) was added dropwise to the dimethyl(phenyl)silyl-cuprate reagent² (0.55 mmol) [prepared by addition of dimethyl(phenyl)silyl-lithium (0.086 mol dm⁻³ solution in THF; 1.3 cm³) to copper(i) cyanide (50 mg, 0.55 mmol) in dry THF (4 cm³)] at −50 °C. The red mixture was allowed to warm to room temperature and stirred under argon for 2 h, after which it was treated with saturated aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried (MgSO₄), and evaporated under reduced pressure to give a yellow oil, which was chromatographed (SiO₂, hexane) to give the allylsilane[16] **8** (75 mg, 90%) (from the allene **6**), $v_{max}(CHCl_3)/cm^{-1}$ 1245 (SiMe),

and 1110 (SiPh); δ_H(CDCl$_3$) 7.55–7.11 (10 H, m, 2 × Ph), 4.95 (1 H, d, J 11.1, C=CH), 1.02 (3 H, d, J 7.2, Me), 2.63–0.87 (8 H, m, aliphatic H), 0.30 (3 H, s, SiMe$_A$Me$_B$), and 0.29 (3 H, s, SiMe$_A$Me$_B$); δ_C(CDCl$_3$) 147.2, 138.3, 134.9, 134.1, 128.8, 128.2, 127.6, 126.9, 125.8, 124.9, 44.8, 37.3, 36.2, 34.3, 28.6, 21.0, 15.6, −5.0, and −5.1, and the allylsilane[16] **9** (77 mg, 92%) (from the allene **7**), v_{max}(CHCl$_3$)/cm^{-1} 1245 (SiMe), and 1110 (Si–Ph), δ_H(CDCl$_3$) 7.55–7.14 (10 H, m, 2 × Ph), 4.96 (1 H, d, J 10.9, C=CH), 2.63–1.26 (8 H, m, aliphatic H), 1.04 (3 H, d, J 7.1, Me), and 0.33 (6 H, s, SiMe$_2$); δ_C(CDCl$_3$) 147.2, 138.3, 135.1, 134.2, 128.8, 128.3, 127.5, 126.8, 125.9, 125.2, 44.8, 36.9, 35.9, 35.1, 28.9, 21.2, 15.8, −4.6, and −5.4. Both sets of spectra matched those of the authentic samples.

Acknowledgements

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