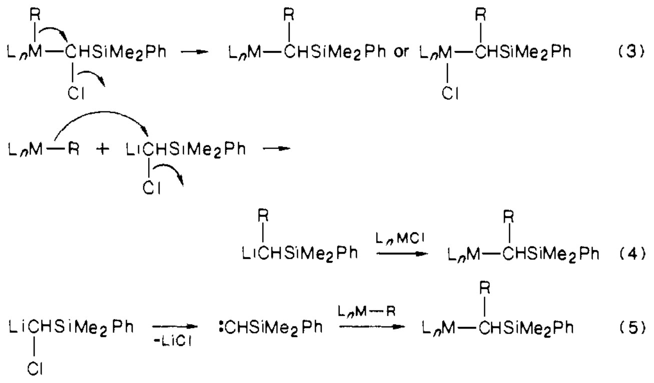
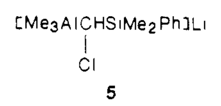
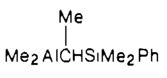


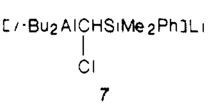
The currently available data on the reaction of organoalanes with **1** clearly favor the 1,2-migration path over the other two. First, the reaction of either i-Bu_3Al or Me_3Al with **1** monitored at 23 ± 0.1 °C by GLC follows first-order kinetics ($k = 2.0 \times 10^{-2}$ min^{-1}, $r = 0.998$ or $k = 3.4 \times 10^{-3}$ min^{-1}, $r = 0.998$) in a 4:1 mixture of THF and cyclohexane, but it does not obey second-order kinetics, disfavoring the direct displacement path (eq 4). Mixing i-Bu_3Al with $ClCH_2SiMe_2Ph$ does not induce any reaction under comparable conditions. Second, examination of the mixture of the reaction of Me_3Al with **1** by ^1H NMR indicates that, upon mixing the two reagents, the Me signal for Me_3Al at −1.03 ppm initially shifts to −1.24 ppm, although the signal at −1.03 ppm is quite insensitive to various solvents such as cyclohexane, THF, and even TMEDA, staying well within the −1.01 to −1.03 ppm range. The Me signal for $LiAlMe_4$ appears at −1.33 ppm. As the reaction proceeds, the signal at −1.24 ppm shifts back to −1.02 ppm over several hours. The signals at −1.24 and −1.02 ppm, we believe, are attributable to the formation of **5** and **6**. Although we have not monitored the reaction of i-Bu_3Al with **1** by ^1H NMR, quenching an aliquot of this reaction mixture shortly after raising the reaction temperature to 23 °C gave 0.79 equiv of $ClCH_2SiMe_2Ph$ and 0.16 equiv of i-$BuCH_2SiMe_2P$ along with 0.45 equiv of Me_3SiCH_2Ph out of 1.5 equiv of $ClCH_2SiMe_2Ph$. Under comparable conditions, quenching a solution which initially contained only **1** without i-Bu_3Al gave a considerable amount of an unidentified but apparently dimeric product but little or none of $ClCH_2SiMe_2Ph$. These results again indicate the formation of an aluminate complex **7** which slows down decomposition of the $ClCHSiMe_2Ph$ anion and releases $ClCH_2SiMe_2Ph$ upon quenching.


$[Me_3Al\underset{|}{\underset{Cl}{C}}HSiMe_2Ph]Li$

5


$Me_2Al\overset{Me}{\overset{|}{C}}HSiMe_2Ph$

6


$[i\text{-}Bu_2Al\underset{|}{\underset{Cl}{C}}HSiMe_2Ph]Li$

7

The reaction of organoalanes with $LiCHCl_2$[8] leads to formation of two new carbon–carbon bonds within one molecule. Thus, the reaction of i-Bu_2AlPh, generated in situ from i-Bu_2AlCl and PhLi, with $LiCHCl_2$ (1.3 equiv) at −100 to 40 °C in a mixture of THF–ether–hexane–cyclohexane (5:3:3:1) produced, after hydrolysis, i-$BuCH_2Ph$ in 53% yield. Under similar conditions the reaction of i-$Bu_2AlCh{=}CHHex$-n-(E) with $LiCHCl_2$ produced a 75% combined yield of a nearly 1:1 mixture of i-$BuCH_2CH{=}CHHex$-n and i-$BuCH{=}CHHept$-n, each of which was an E and Z mixture. Although this reaction needs to be further developed, it appears to represent the first example of double-transfer reactions in which two carbon groups of an organoalane get transferred to one molecule, i.e., $LiCHCl_2$.

We believe that the results presented here have just opened up a major new area of 1,2-migration reactions of organo main group metals other than organoboranes. Unlike the latter, organometals containing Al, Mg, Zn, Cd are readily hydrolyzed to produce organic products. This would make the synthetic significance of their 1,2-migration reactions quite distinct from those of organoboranes.

Acknowledgment. We thank the National Science Foundation (CHE 8503075) and the Petroleum Research Fund administered by the American Chemical Society (18710-AC1) for support of this research. We also thank Dr. Brian O'Connor for carrying out the reaction of n-Pr_3Al with $LiCH(Cl)SiMe_2Ph$.

Supplementary Material Available: IR, ^1H NMR, and ^{13}C NMR data for **2–4** and other unnumbered compounds in this paper. (2 pages). Ordering information is given on any current masthead page.

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[8] (a) Kobrich, G.; Flory, K.; Drischel, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 513. (b) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 1529.

Synthesis and Characterization of a Silver(I) Triflate Sandwich Complex of 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triyne. The First Example of a 12-Membered Macrocycle Sandwich Complex

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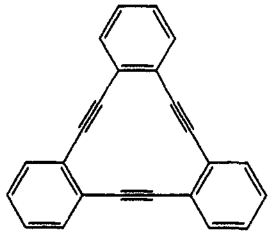
The ligand 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne[1] (TBC) has shown much versatility in its reaction chemistry with various transition-metal compounds via binding of the transition-metal center to the carbon–carbon triple bond.



TBC

Complexes of TBC already synthesized and structurally characterized include mononuclear nickel(0) and copper(I) complexes,[2,3] a trinuclear copper(I) complex,[4] and a tetranuclear cobalt(0) cluster.[5] This communication reports the synthesis of a novel silver(I) sandwich complex **1** from the reaction of $AgSO_3CF_3$ with TBC. Numerous examples of 3–8-membered hydrocarbon ring transition-metal sandwich complexes[6] have been previously reported, but complex **1** is the first example of a 12-membered macrocycle sandwich complex.

All manipulations were performed by using standard inert atmosphere techniques. In a typical reaction, $AgSO_3CF_3$[7] (0.171 g, 0.666 mmol) and TBC[8] (0.100 g, 0.333 mmol) were allowed

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[1] Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751–757.

[2] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719–6721.

[3] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Organometallics* **1987**, *6*, 676–678.

[4] Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *Inorg. Chem.*, submitted for publication.

[5] Djebli, A.; Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.*, submitted for publication.

[6] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980; pp 1161–1173.

[7] $AgSO_3CF_3$ was purchased from Alfa Products and recrystallized from diethyl ether/hexane.

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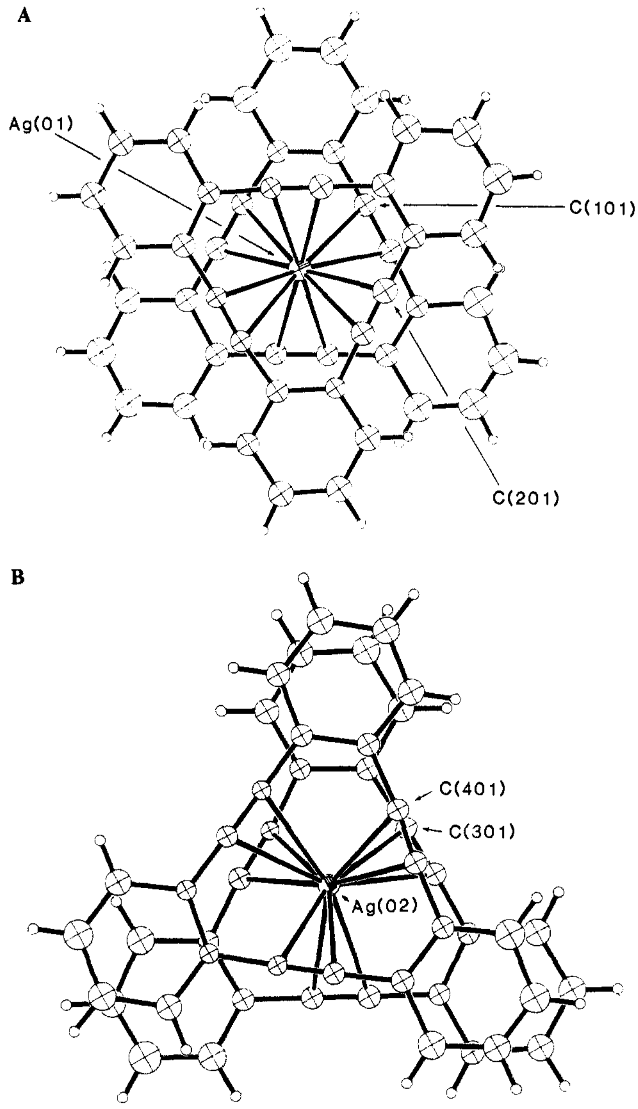

Figure 1. ORTEP labeling diagrams of the staggered (1A) and eclipsed conformations (1B) of $[Ag(TBC)_2]^+$. The thermal ellipsoids are drawn at the 20% probability level except for the hydrogens which are drawn arbitrarily small for clarity. A general labeling diagram for all non-hydrogen atoms in the TBC rings is available in the Supplemetary Material.

to react to THF (20 mL) for several days. The reaction was monitored via IR spectroscopy and allowed to continue until there was no further change. Slow addition of hexane (5 mL) at the end of the reaction period yields crystals of a silver complex of TBC. Polymerized THF is also produced in this reaction. The reactants and products are light sensitive, consequently the reaction vessel was covered with aluminum foil. Various ratios of $AgSO_3CF_3$ to TBC (1:2, 2:1, and 1:3) gave $[Ag(TBC)_2(SO_3CF_3)]\cdot TBC\cdot 1/2C_6H_{14}$ and recovered starting materials. The yields for the crystalline materials were between 5% and 10%. Combination of a 3:1 ratio of $AgSO_3CF_3$ to TBC yields no crystalline material and considerable poly-THF.

The IR spectrum[9] shows two bands at 2208 and 2180 cm^{-1} (br) corresponding to the $C\equiv C$ stretch of free and complexed TBC, respectively. Both ^1H NMR (variable temperature −90 °C to 25 °C) and $^{13}C\{^1H\}$ NMR spectra[10] of the sample in toluene-d_8 show

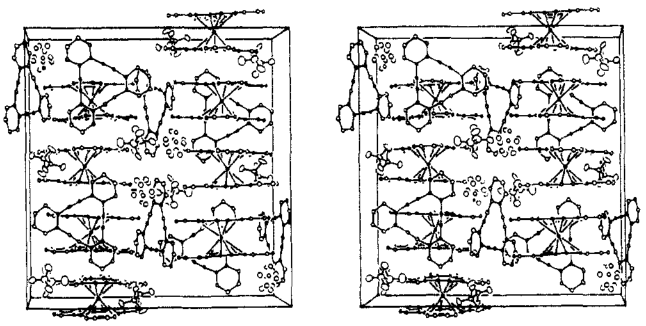

Figure 2. Stereoview packing diagram of $2[Ag(TBC)_2(SO_3CF_3)]\cdot 2TBC\cdot C_6H_{14}$. The thermal ellipsoids are drawn at the 5% probability level, and the hydrogen atoms are omitted for clarity. The b-axis points upward, and the c-axis points to the right.

only free TBC[1,3,8b] and hexane. Toluene has been shown to complex $AgSO_3CF_3$,[11] and the silver complex **1** is probably dissociated in solution. Elemental analysis is consistent with the formula $[Ag(C_{24}H_{12})_2(SO_3CF_3)]\cdot C_{24}H_{12}\cdot 1/2C_6H_{14}$.[12]

Compound **1** was characterized by single-crystal X-ray analysis.[13,14] The asymmetric unit was found to contain the following: one bis(TBC)silver(I) staggered sandwich (Figure 1A), one bis(TBC)silver(I) eclipsed sandwich (Figure 1B), two free TBC molecules, two noncoordinated triflate anions, and a disordered hexane solvent molecule. Figure 2 is a stereoview packing diagram looking down the a-axis.

Group theoretical analysis[15] shows all 24 electrons of the two TBC ligands are available for bonding independent of symmetry. The staggered molecule is C_3, whereas the eclipsed molecule is clearly C_s. The molecular geometries for the complexed and free TBC ligands are identical within experimental error. Even though there is a significant change in the $C\equiv C$ stretching frequency of TBC upon complexation, the bond lengths, as determined in the crystallographic experiment, are not changed significantly.

Usually carbon–carbon triple bonds are considered to be two to four electron donors. The silver ion in the eclipsed sandwich is offset from the centroid of the two TBC ligands but equidistant to the two TBC ligands. The eclipsed conformation has a range of Ag–C distances of 2.47 (2)–2.94 (2) Å, whereas the staggered conformation has a range of Ag–C distances of 2.67 (2)–2.81 (2) Å (Ag–C_{mean} = 2.74 (4) Å). All Ag–C interactions are considerably greater than the sum of the radii for silver(I) and carbon.[16] The Ag–C bond lengths are consistent with the previously determined silver π-alkyne structures[17] which range from 2.27 (1)

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(8) (a) Hommes, H.; Verkruijjse, H. D.; Brandsma, L. *Tetrahedron Lett.* **1981**, *22*, 2495–2496. (b) Campbell, I. D.; Eglington, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87–98. (c) The above procedures have been modified in our laboratory to yield multigram quantities of TBC.

(9) Infrared spectra were recorded on a Mattson Cygnus 25 FT-IR spectrometer in Nujol mulls on KBr plates.

(10) NMR spectra were recorded on a Varian XL-200 spectrometer in toluene-d_8 (internal secondary reference ^1H $\delta = 2.09$ ppm; ^{13}C $\delta = 29.5$ ppm).

(11) Dines, M. B. *J. Organomet. Chem.* **1974**, *67*, C55–C58.

(12) Scwarzkopf Microanalytical Laboratory; Anal. Calcd for C and H. Calcd C, 76.00; H, 3.61. Found: C, 77.80; H, 3.32.

(13) The UCLA Crystallographic Computing Package, Dec. 1985.

(14) Crystallographic data: space group $P2_1/n$, $a = 15.369$ (3) Å, $b = 28.177$ (5) Å, $c = 26.751$ (4) Å, $\beta = 90.61$ (1)°, $V = 11584$ (3) Å^3, $Z = 4$, $\rho_{obsd} = 1.37$ (1) g·cm^{-3}, $\rho_{calcd} = 1.377$ (1) g·cm^{-3}. The data were collected from $3.0° \leq 2\theta \leq 40.0°$ at 23 °C (Mo Kα = 0.71073 Å) by using the wandering ω technique. The structure was solved by MULTAN and refined by Fourier and difference Fourier techniques and least-squares refinement. The structure contains 168 non-hydrogen atoms. Refinement on the 6856 data I g $\sigma(I)$ gives $R(F) = 0.137$ and $R_w(F) = 0.099$ with $R(F) = 0.080$ and $R_w(F) = 0.083$ for data $I \geq 3\sigma(I)$ (3958 data). All refined and derived quantities were obtained by refinement with the 6856 data $I \geq \sigma(I)$. The occupancies of the 12 atoms comprising the hexane were fixed at 0.5 giving one molecule of hexane per asymmetric unit. The triflates were refined as semirigid bodies by using the **A** matrix approach in ref 22a. The five totally symmetric vibrations were used as the basis for the distortion coordinates. The TLS treatment is described in ref 22b. All unique elements of the matrices **T** (six parameters), **L** (six parameters) and **S** (eight parameters) were refined for both triflates. Both refinement procedures are part of the UCLA Crystallographic Computing Package.

(15) Cotton, F. A. *Chemical Applications of Group Theory*, 2nd ed.; Wiley-Interscience: New York, 1971.

(16) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984; pp 289, 313.

(17) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1975**, *14*, 2630–2639. (b) Salah, O. M. A.; Bruce, M. I.; Churchill, M. R.; DeBoer, B. G. *J. Chem. Soc., Chem. Commun.* **1974**, 688–689. (c) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502–508. (d) Salah, O. M. A.; Knobler, C. B. *J. Organomet. Chem.* **1986**, *302*, C10–C12.

to 3.10 (3) Å. The Ag–C bond lengths for silver(I) alkene and arene complexes[18] range from 2.31 to 2.84 Å. The following bonding scheme is proposed for the eclipsed silver bis(TBC) unit. Four of the alkynes behave as two electron donors, while two alkynes are noninteracting giving an 18-electron count. The asymmetric nature of the metal-to-ligand interaction in the eclipsed conformtion is reminiscent of the bonding in ruthenium and rhodium bis-arene complexes.[19] In contrast, the staggered sandwich has a much smaller range of Ag–C distances for all silver–acetylene interactions leading to the conclusion that the six alkynes are donating 1.333 electrons each or that this is an electrostatic interaction. The hard–soft acid–base theory[20] provides an explanation for the preference of the soft silver cation for the soft alkyne carbons instead of the hard triflate oxygen.

The silver sandwiches form infinite chains parallel to the 2_1 axis stacked metal over metal alternating eclipsed and staggered sandwiches. The cocrystallization of staggered and eclipsed conformations of sandwich complexes is unusual but not unprecedented. The cocrystallization of eclipsed and staggered conformations of bis(1,3,5,7-tetramethylcyclooctatetraene)uranium has been reported.[21] The shortest unique silver–silver vectors in the unit cell are 7.102 (3) and 7.115 (3) Å and are approximately parallel to the *b*-axis. The five unique interplanar spacings for the least-squares plane defined by each TBC bound to silver range between 3.45 (1) and 3.58 (1) Å (Tables XVI–XXI in the Supplementary Material). All dihedral angles between coordinated TBC planes are less than 5°. The chains of $[Ag(TBC)_2]^+$ are surrounded by a tube of free TBC molecules whose planes are nearly perpendicular to the planes of the sandwiches and to each other (Figure 2). The triflate anions do not directly interact with the silver ions. The closest silver–(triflate atom) distance is greater than 6.8 Å. The triflate anions show considerable thermal motion and have been refined as semirigid bodies with TLS motion.[22] The hexane solvent molecule is disordered and modeled as two molecules of six carbons each at half occupancy.

Studies of the reaction chemistry of **1** including the interconversion of the staggered and eclipsed conformations and the synthesis of other transition-metal sandwich complexes of TBC are currently under investigation in our laboratory.

Acknowledgment. J.D.F. thanks the BF Goodrich Company for financial support through the BF Goodrich Fellowship at CWRU. A.D. thanks the Algerian Government for support. Acknowledgment is made to the donors of The Petroleum Research Fund administered by the American Chemical Society for support of this work.

Supplementary Material Available: Tables of crystal data, data collection reduction, and refinement details, positional and thermal parameters, semirigid body TLS refinement details, bond distances and angles, and least-squares planes analysis for the crystal structure of $2[Ag(TBC)_2(OTF)]\cdot 2TBC\cdot C_6H_{14}$ and a general labeling diagram for all six TBC molecules (25 pages); table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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(18) (a) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979–1985. (b) Mak, T. C. W.; Ho, W. C.; Huang, N. Z. *J. Organomet. Chem.* **1983**, *251*, 413–421. (c) Albinati, A.; Meille, S. V.; Carturan, G. *J. Organomet. Chem.* **1979**, *182*, 269–274. (d) Lewandos, G. S.; Gregston, D. K.; Nelson, F. R. *J. Organomet. Chem.* **1976**, *118*, 363–374. (e) Ermer, O.; Eser, H.; Dunitz, J. D. *Helv. Chim. Acta* **1971**, *54*, 2469–2475. (f) Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1972**, *11*, 388–395. (g) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3167–3172. (h) Taylor, I. F.; Hall, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 5745–5749. (i) Jackson, R. B.; Streib, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 2539–2543. (j) McKechnie, J. S.; Newton, M. G.; Paul, I. C. *J. Am. Chem. Soc.* **1967**, *89*, 4819–4825. (k) Baenziger, N. C.; Haight, H. L.; Alexander, R.; Doyle, J. R. *Inorg. Chem.* **1966**, *5*, 1399–1401. (l) Nyburg, S. C.; Hilton, J. *Acta. Crystallogr.* **1959**, *12*, 116–121. (m) Mathews, F. S.; Lipscomb, W. N. *J. Phys. Chem.* **1959**, *63*, 845–850.

(19) (a) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2049. (b) Huttner, G.; Lange, D.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 556. (c) Churchill, M. R.; Mason, R. *Proc. R. Soc. London, A* **1966**, *292*, 61.

(20) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976; Chapter 3.

(21) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1973**, *12*, 458.

(22) (a) Strouse, C. E. *Acta. Crystallogr., Sect. A.: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1970**, *26*, 604–608. (b) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 63–76.

Total Synthesis of (±)-Ginkgolide B

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Extracts of the ginkgo tree, *Ginkgo biloba*, now widely recommended in Asian and European medicine (annual sales ca. $500 000 000 per annum), have been found to antagonize platelet activating factor (PAF),[1] a very fundamental mammalian regulator.[2] Ginkgo extracts increasingly find therapeutic use in the treatment of cerebrovascular and peripheral circulatory problems of the elderly and asthma. The most active anti-PAF agent in the ginkgo extract is the hexacyclic C_{20} trilactone ginkgolide B (**1**)[3] (IC_{50} 10^{-7}–10^{-8} M in various tests),[1] which appears to antagonize all known PAF-induced membrane events. The first total synthesis of ginkgolide B (racemic form) is described herein. A recent paper from these laboratories[4] has reported the total synthesis of the related C_{15} ginkgolide, (±)-bilobalide,[5] by a totally different approach.

Reaction of 1-morpholinocyclopentene with dimethoxyacetaldehyde in benzene at 23 °C for 18 h, stirring of the resulting solution with 6 N hydrochloric acid at 0 °C for 30 min, extractive isolation and distillation (145–146 °C at 15 Torr) provided enone **2** in 70% yield.[6-8] Enone **2** was converted into the enol silyl ether **3** (93% yield) by reaction in ether with the cuprate reagent t-$Bu_2CuCNLi_2$ (1.5 equiv relative to **2**; prepared from reaction of cuprous cyanide and *tert*-butyllithium in a 1:2 ratio at −78 °C for 50 min and then at −45 °C for 30 min) at −78 °C for 10 min and then at −45 °C for 30 min, followed by silylation of the resulting enolate with 5 equiv each of trimethylchlorosilane and triethylamine (−45 °C for 45 min, then −10 °C for 5 min) and extractive isolation. Addition of **3** in methylene chloride to a solution of 1,3,5-trioxane (1.2 mol equiv) and titanium tetrachloride (3.6 equiv) in methylene chloride at −78 °C (over 20 min), further reaction (−78 °C for 2 h and −45 °C for 1 h), and finally treatment with one-half volume of methanol (0 °C initially then 23 °C for 12 h) produced stereoselectively[9] cyclopentanone **4**, mp 25–27 °C, as a 2:1 mixture of two C(11) anomeric methyl acetals (ginkgolide numbering) in 65% yield. Deprotonation of **4** with 1.25 equiv of lithium diisopropylamide (LDA) in dimethoxyethane (−78 °C for 1 h, 0 °C for 20 min) and subsequent reaction with *N*-phenyltriflimide[10] (0 °C for 1.5 h, 23 °C for 1 h) afforded after

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(1) (a) Braquet, P. *Drugs of the Future* **1987**, *12*, 643–699. (b) Braquet, P.; Godfroid, J. J. *Trends Pharmacol. Sci.* **1986**, *7*, 397–403. (c) Barnes, P. J.; Chung, K. F. *Ibid.* **1987**, *8*, 285–286. (d) Max, B. *Ibid.* **1987**, *8*, 290–292.

(2) Hanahan, D. J. *Ann. Rev. Biochem.* **1986**, *55*, 483–509.

(3) (a) Sakabe, N.; Takada, S.; Okabe, K. *J. Chem. Soc. Chem. Commun.* **1967**, 259–261. (b) Okabe, K.; Yamada, K.; Yamamura, S.; Takada, S. *J. Chem. Soc. C* **1967**, 2201–2206. (c) Nakanishi, K. *Pure Appl. Chem.* **1967**, *14*, 89–113.

(4) Corey, E. J.; Su, W.-g. *J. Am. Chem. Soc.* **1987**, *109*, 7534.

(5) Nakanishi, K.; Habaguchi, K.; Nakadaira, Y.; Woods, M. C.; Maruyama, M.; Major, R. T.; Alauddin, M.; Patel, A. R.; Weinges, K.; Bähr, W. *J. Am. Chem. Soc.* **1971**, *93*, 3544–3546, and references contained therein.

(6) See: Barco, A.; Benetti, S. *Synthesis* **1981**, 199–200.

(7) All reaction products were liquids unless otherwise noted. Satisfactory high resolution mass spectra were obtained for all stable products.

(8) Dimethoxyacetaldehyde was prepared in 72% yield by ozonolysis of acrolein dimethyl acetal (CH_2Cl_2 at −78 °C). See: Bestmann, H.; Ermann, P. *Chem. Ber.* **1983**, *116*, 3264–3266.

(9) The trans arrangement of the vicinal β-*tert*-butyl and α-oxymethyl substituents in **4** was demonstrated by ^{1}H NOE experiments involving irradiation of the *tert*-butyl group of **4** and the isomer of **4** with the cis arrangment of these substituents (available to us by an alternative synthetic route but not produced under the conditions indicated for **4**).

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