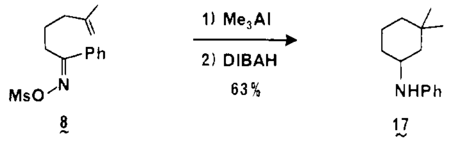
grating the group anti to the departing sulfonate group in either an endocyclic or an exocyclic mode to the so-formed ring, we refer to them as endo(B) and exo(B) rearrangements, respectively. Further, when the breaking double bond is endocyclic to the so-formed ring, we refer to them as suffix endo and exo correspondingly. Thus, four possible cyclization modes are endo(B)-endo, endo(B)-exo, exo(B)-endo, and exo(B)-exo as depicted in Scheme I–IV each of which also illustrates the representative examples. Another example of the endo(B)-exo cyclization by use of an oxime–P_2O_5 system was previously reported by Gawley.[4]

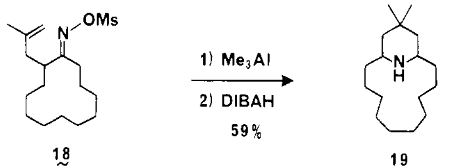
The following features of our new process are noteworthy: (1) The reaction proceeds at low temperature in aprotic solvent (CH_2Cl_2) with only 1 equiv of Lewis acid. (2) Aliphatic and aromatic ketones with acyclic and cyclic structures are equally employable. (3) The products are easily predictable, since our mild reaction conditions are free from the complicated syn/anti equilibrium of oximes. (4) Both carbocyclic and heterocyclic structures are prepared efficiently via exo(B) and endo(B) cyclizations, respectively.

Two unusually short syntheses illustrated in Scheme V heavily depend on our new process. Thus, solenopsin B was prepared in two steps from a simple acyclic precursor.[13] The similar endo(B) cyclizations provided a direct entry to a variety of heterophanes from macrocyclic ketones as illustrated in the facile synthesis of muscopyridine. The requisite oxime **16** was readily available from 2-allylcyclododecanone in four steps.[14] Reaction of **16** with MsCl (1.1 equiv)–NEt_3 (1.5 equiv) in CH_2Cl_2 at −20 °C for 30 min produced the corresponding oxime mesylate quantitatively, which was converted cleanly to muscopyridine (80% yield) as the sole product by treatment with Me_3SiOTf (1.1 equiv)[15] in $CHCl_3$ at 25 °C for 1.5 h followed by exposure with active MnO_2 (20 equiv)[16] in the presence of NEt_3 (5 equiv) at 50 °C for 1.5 h.[17]

Up to this point the cyclization was terminated by the deprotonation, yielding α,β-unsaturated imines. The intermediary cations, however, may also be captured by carbon nucleophiles to afford saturated imines. Initial efforts are given in eq 1 and 2. Treatment of a solution of the oxime mesylate **8** (n = 2) in CH_2Cl_2 with Me_3Al (4 equiv) at 25 °C for 1 h followed by reduction with DIBAH (3 equiv) produced the methylated product **17** in 63% yield.[18] Similarly, the amine **19** was obtained in 59% yield from the oxime mesylate **18**.[19] It should be noted that neither **17** or **19** may be synthesized in a single operation by an alternative method.[2]



(1)



(2)

Acknowledgment. This work was supported by the Ministry of Education, Japanese Government (Grant-In-Aids 57102008 and 57118006).

Registry No. (E)-**1**, 84099-04-7; **2**, 84099-05-8; **3**, 84099-06-9; (E)-**4** (R = R′ = H), 84099-07-0; (E,X)-**4** (R = H; R′ = prenyl), 84099-08-1; (E)-**4** (R = Me; R′ = H), 84099-09-2; **5**, 5194-85-4; **6**, 84099-10-5; **7**, 84099-11-6; (E)-**8** (n = 1), 84099-12-7; (E)-**8** (n = 2), 84099-13-8; **9**, 84099-14-9; **10**, 84099-15-0; (E)-**11**, 84099-16-1; **12**, 84099-17-2; **12** (4a,10-didehydro), 84099-18-3; (E)-**13**, 84099-19-4; **14**, 84099-20-7; **14** (1,2-didehydro), 84099-21-8; (±)-**15**, 84099-22-9; **16**, 84099-23-0; **16** (mesylate), 84099-24-1; **17**, 84099-25-2; **18**, 84099-26-3; **19**, 84099-27-4; **19** (1,16-didehydro), 84099-28-5; (Z)-3-(phenylimino)-1-methylcyclopentene, 84099-29-6; (Z)-3-(phenylimino)-1-methylcyclohexene, 84099-30-9; (±)-2-allylcyclododecanone, 84099-31-0; 2-allyl-12-(phenylselenyl)cyclododecanone, 84099-32-1; 2-allyl-11-methylcyclododecanone, 84099-33-2; 1,16-dihydromuscopyridine, 84099-34-3; (±)-muscopyridine, 56912-83-5; solenopsin B, 32778-77-1; cis-2-methyl-6-tridecylpiperidine, 35285-26-8; (Z)-1-isopropylidene-4-methyl-2-(phenylimino)cyclohexane, 84099-35-4.

Supplementary Material Available: Spectroscopic data for new compounds described in this paper (1 page). Ordering information is given on any current masthead page.

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[13] Solenopsin B possesses the trans structure. The ratio of cis/trans isomers was determined by GC assay (silicone OV-101, 185 °C) to be 46:54: t_r of the cis isomer = 14.55 min; t_r of the trans isomer = 16.55 min. See: Matsumura, Y.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1982**, *23*, 1929.

[14] The syn oxime was produced in 33% yield. The stereochemical assignments for **16** and its syn isomer are tentative and based in part on ^1H NMR analysis according to ref 7c.

[15] A number of Lewis acids were screened for a new pyridine synthesis by using 2-allylcyclododecanone oxime mesylate as a substrate and active MnO_2 as an oxidant. The yields of [10](2,6)pyridinophane thus obtained follow: Et_2AlCl (39%); $SnCl_4$ (65%); Me_3SiI (68%); Me_3SiOTf (80%).

[16] It should be worthy of note that active MnO_2 was the reagent of choice and other oxidizing agents (DDQ, O_2, H_2O_2–$FeCl_3$, Br_2, etc.) gave less satisfactory results.

[17] The spectra of the synthetic muscopyridine were identical in all respects with those of the authentic specimen, which are kindly provided from Dr. K. Utimoto.

[18] In addition to the methylated amine **17**, the deprotonated amine **10** was produced in 8% yield.

[19] The yield of the deprotonated product was 19%.

A New Approach to Construction of Artificial Monolayer Assemblies

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Preparation of artificial supermolecular organizates represents an important new goal of modern chemistry. Within this framework, the study of monolayer assemblies and their applications has expanded tremendously in recent years, encompassing now a wide variety of subjects ranging from biological membranes to solid-state electronic devices.[1] Modern film-building techniques have evolved; however, the basic approach common to all of them is still that devised by Langmuir and Blodgett (LB) some 50 years ago.[2] Although the LB procedure is powerful as a tool for handling molecular entitites, it suffers from some inherent drawbacks, mainly due to the extensive use of mechanical manipulation in the formation and transfer of the monolayer films.[3]

We are hereby describing a different approach to assembling of artificial layered structures based on self-association and self-organization of molecules occurring spontaneously at solid–fluid interfaces. Our approach takes advantage of the possibility of obtaining oriented compact monolayers by adsorption of amphiphiles from a fluid (solution, melt, or vapor) onto a polar solid surface contacting the fluid phase.[4] We have recently shown that under suitable conditions adsorption may be used to prepare organized mixed monolayers of several components (including dyes

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[1] See for example: Kuhn, H.; Möbius, D.; Bücher, H. In "Techniques of Chemistry"; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Part IIIB, pp 577–702. Vincett, P. S.; Roberts, G. G. *Thin Solid Films* **1980**, *68*, 135.

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[3] Gaines, G. L., Jr. *Thin Solid Films* **1980**, *68*, 1. Honig, E. P. *J. Colloid Interface Sci.* **1973**, *43*, 66. Kopp, F.; Fringeli, U. P.; Mühlethaler, K.; Günthard, Hs. H. *Biophys. Struct. Mech.* **1975**, *1*, 75.

[4] Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513. Levine, O.; Zisman, W. A. *J. Phys. Chem.* **1957**, *61*, 1068. Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* **1956**, *11*, 60. Bartell, L. S.; Ruch, R. J. *J. Phys. Chem.* **1956**, *60*, 1231; **1959**, *63*, 1045.

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Scheme I. Multilayer Formation by Adsorption, Using Bifunctional Silane Surfactants as Monolayer Building Units

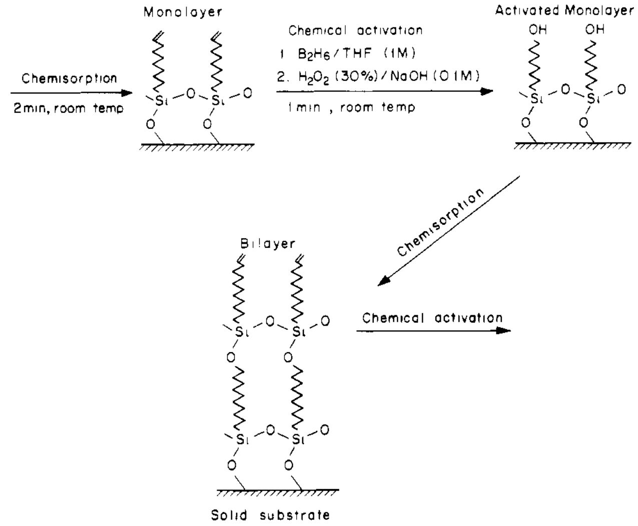

Table I. Advancing Contact Angles (deg) on Films Built on a Silicon ATR Prism

film	*n*-hexadecane	water	figure
HTS/Si	40	105	
HTS/Si activated	0	50	
HTS/HTS/Si	34	98	1a
HTS/HTS/Si activated	0	50	1b
OTS/HTS/HTS/Si	44	105	1d
HTS/Si	45	107	1f

or other nonamphipathic components) on a variety of solid surfaces.[5] Moreover, covalent monolayer-surface binding (chemisorption) and intralayer cross-linking were used to obtain monolayers of unusual mechanical, chemical, and electrical stability.[5,6]

So far, only one-monolayer films could be obtained by adsorption. Surfaces covered by monolayers exposing nonpolar moieties (like methyl groups, for instance) become inert to further binding of molecules from the fluid phase, which provides the means for controlling the adsorption process and preventing deposition of material as a poorly defined thick film.[7] However, this prevents formation of ordered multilayers as well. It is the purpose of the present communication to propose a multilayer assembling procedure aimed at circumventing this difficulty. Our strategy is based on a two-step sequence involving monolayer adsorption followed by chemical activation of the exposed surface, in order to provide polar adsorption sites for the anchoring of the next monolayer. This is accomplished by means of a bifunctional surfactant possessing in addition to the usual polar "head" also an apolar terminal function convertible into a suitable polar group after completion of the adsorption step.[8] To demonstrate the feasibility of this new monolayer deposition method, we synthesized a surfactant having the molecular structure $CH_2{=}CH(CH_2)_{14}SiCl_3$ (HTS, 15-hexadecenyltrichlorosilane).[9] The $SiCl_3$ function enables covalent attachment of the molecules to surfaces rich in hydroxyl groups,[5,6] while the terminal ethylenic double bond provides a convenient path for the activation of the monolayer outer surface via hydroboration and H_2O_2 oxidation to terminal hydroxyls[10] (see Scheme I).

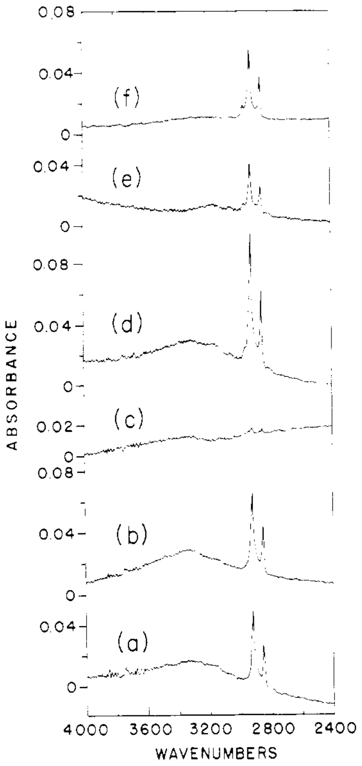

Figure 1. Infrared ATR spectra on Si prism (45°, 17 reflections) measured with a Nicolet MX 1 Fourier transform spectrophotometer: (a) HTS/HTS/Si bilayer; (b) HTS/HTS/Si activated bilayer; (c) Subtraction b–a; (d) OTS/HTS/HTS/Si trilayer; (e) OTS third monolayer, subtraction d–b; (f) OTS/Si monolayer.

The growing process of multilayer films of the type described in Scheme I was followed by wettability and infrared multiple internal reflection (ATR) measurements.[11] Contact angles for *n*-hexadecane and water measured on films of HTS and OTS (octadecyltrichlorosilane, $CH_3(CH_2)_{17}SiCl_3$) grown on a silicon ATR crystal are given in Table I. The IR spectra corresponding to the films in Table I are depicted in Figure 1.[12]

The expected periodicity in the wetting properties of the growing multilayer film alternating between a hydroxyl-rich (polar) or vinyl/methyl-rich (nonpolar) outer surface could indeed be observed. As the HTS films are perfectly stable under the conditions of the activation reaction (Figure 1, curves a–c), the observed alternation in the contact angles cannot be attributed to a trivial film deposition–film removal cycle, thus furnishing evidence for the two-step film growing process proposed in Scheme I.[12]

Under the conditions of present ATR measurements it is a good approximation to consider the absorbance intensities of the methylene bands around 2900 cm^{-1} as proportional to the amount of material in the film.[9,13,14] The IR curves in Figure 1 provide, therefore, direct evidence of the step by step growing in thickness of the film.[12,15] Adsorption of a third layer of OTS on top of the activated HTS bilayer is confirmed by both the increase in the absorbance of the $-CH_2-$ bands as well as the appearance of the weak $-CH_3$ band at 2958 cm^{-1}, which is obviously absent in the HTS spectrum (Figure 1, compare curves e, f, and a). However, the HTS bilayer and the third OTS monolayer are less compact than the first OTS monolayer, as indicated by their lower contact angles and lower intensities of their $-CH_2-$ IR bands, by ca. 30% and 20%, respectively. This reflects the inability of HTS

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(5) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92. Sagiv, J. *Is. J. Chem.* **1979**, *18*, 339, 346.

(6) Polymeropoulos, E. E.; Sagiv, J. *J. Chem. Phys.* **1978**, *69*, 1836.

(7) Such surfaces are usually hydrophobic, oleophobic, and autophobic.

(8) A bifunctional surfactant containing two polar end groups would not adopt the required perpendicular orientation, thus preventing formation of an ordered molecular array.

(9) The synthesis as well as other experimental details of the method will be described in a forthcoming publication.

(10) Brown, A. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975.

(11) Additional confirming evidence was obtained from external reflection IR measurements and ellipsometry on metal mirrors.[9]

(12) The weak C=C stretching band at 1641.5 cm^{-1} was not detectable in the ATR mode.[11]

(13) Harrick, N. J. "Internal Reflection Spectroscopy"; Interscience: New York, 1967.

(14) Takenaka, T.; Nogami, K.; Gotoh, H.; Gotoh, R. *J. Colloid Interface Sci.* **1971**, *35*, 395.

(15) The broad OH bands around 3300 cm^{-1} will be discussed in ref 9.

to form perfect monolayer structures, most probably because of insufficient length of its hydrocarbon chain.[11]

In conclusion, experimental evidence has been provided demonstrating the feasibility of the multilayer assembling procedure outlined in Scheme I. Though not perfect, the present multilayer films are first examples of artificial planned structures of this type realized exclusively by chemical means. Besides its theoretical significance, this "chemical approach" might offer, if optimized, important practical advantages over the classical LB method.

Bridging Ligand Effects in Quadruply Bonded Dichromium(II) Compounds

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Most quadruply bonded dichromium(II) compounds can be divided into two different groups.[1] The first group is characterized by the presence of four carboxylato ligands, some interaction in the axial position, and a Cr–Cr bond length ranging from 2.283 to 2.541 Å, while the second group is characterized by ligands derived from weaker acids, infrequent axial interactions, and Cr–Cr bond lengths of less than 1.90 Å. The wide range of Cr–Cr bond lengths has been attributed to two factors.[2] Of these two factors, the effect of the axial interaction has been investigated experimentally.[1-8] The inductive effect of the bridging ligand, however, has not been investigated as thoroughly, although experiments are presently underway.[9] We have used generalized molecular orbital (GMO) and configuration interaction (CI) calculations on tetrakis(formato)dichromium and tetrakis(formamidato)dichromium to investigate this problem. Our calculations predict that the latter has a much stronger Cr–Cr bond.

The GMO method[10] consists of a multiconfiguration self-consistent field calculation followed by a CI calculation. All of the orbitals are kept doubly occupied except for those involved in the quadruple bond. For the eight electrons in the quadruple bond, the GMO wave function consists of the dominant single determinant (σ^2, π_x^2, π_y^2, δ^2) plus all paired double excitations, from these bonding orbitals to their antibonding counterparts (σ^*, π_x^*, π_y^*, δ^*), weighted equally.[10] Application of the variation principle yields a set of primary orbitals (σ, π_x, π_y, δ, σ^*, π_x^*, π_y^*, δ^*) in which the weakly occupied ones (σ^*, π_x^*, π_y^*, δ^*) are optimized to correlate the strongly occupied ones (σ, π_x, π_y, δ). The determination of the GMO orbitals is then followed by a full CI calculation in this restricted orbital space.

Because of the size of the dichromium systems, some additional approximations have been made. We have limited the study to two simple ligand systems, the tetrakis(formato)dichromium and the tetrakis(formamidato)dichromium. The bond distances and angles for the two systems are shown in Figure 1 and are based on average values compiled from a number of known carboxylato and carboxyamidato species.[2-4,11,12] The symmetry of the tetrakis(formato) species is D_{4h} while the symmetry of the tetrakis(formamidato) species is D_{2d} since the nitrogens are trans to each other. Even with this reduction in the size of the system, we have not been able to employ a very large basis set. The basis set consists of fully contracted functions on the ligands and the chromium core. The outer d function on the chromium has been split to give a double ζ representation in order that we might have a better description of the chromiums. Additional s and p functions have been added to represent the 4s and 4p orbitals with exponents of 0.10 and 0.15, respectively.

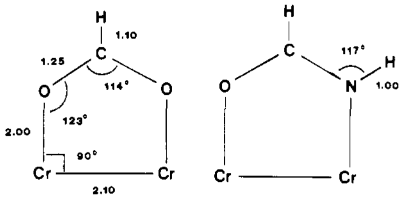

Figure 1. Structure of dichromium model compounds. The bond distances and angles given for the tetrakis(formato) species apply for the tetrakis(formamidato) species, as well.

Table I

	$Cr_2(O_2CH)_4$	$Cr_2(NH(O)CH)_4$
	Orbital Occupations	
σ	1.6	1.7
π	2.8	3.5
δ	1.3	1.5
δ^*	0.7	0.5
π^*	1.2	0.5
σ^*	0.4	0.3
	Important Configurations[a]	
$\sigma^2\pi^4\delta^2$	0.22	0.37
$\sigma^2\pi^4\delta^{*2}$	0.08	0.08
$\sigma^2\pi^2\delta^2\pi^{*2}$	0.16	0.13
$\pi^4\delta^2\sigma^{*2}$	0.02	0.02
	GVB Orbital Overlap Values	
σ	0.32	0.42
π	0.20	0.45
δ	0.13	0.26
	Ratio of d Orbital Coefficients	
σ	0.184	0.227
π	0.196	0.313
δ	0.211	0.272

[a] The values represent the sum of the square of the coefficients corresponding to different spin components of the same configuration.

The results are shown in Table I. In the first part, we have listed the orbital occupation numbers for the two systems. As can be seen, the number of electrons in the bonding orbitals increases upon going from the formato species to the formamidato species, especially in the π orbital. In the second part, we have listed the coefficients of the configurations that make up the ground-state wave function. As shown, the coefficient for the quadruple bond is much larger for the formamidato species than for the formato species. In the third part, we have listed the general valence bond (GVB) orbital overlap values.[13] These values were calculated from our natural orbital occupation numbers.[14] Again, the formamidato species has higher overlap values than the formato species for each orbital.

All three methods of analyzing the CI wave function indicate that the formamidato species has a stronger quadruple bond. One explanation for this effect can be found by examining the radial extent of the d functions on the Cr atoms. At the bottom of Table

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(1) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3464 and references therein.

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