Table I. The Antimicrobial Spectra of Negamycin and Its Antipode on 0.5% Peptone Agar

Test organisms	Minimum inhibitory concentration, μg/ml: Negamycin	Antipode of negamycin
Staphylococcus aureus FDA 209P	12.5	50
Escherichia coli K-12	3.1	100
Escherichia coli K-12 ML1629	1.6	100
Shigella sonnei 191-66	6.3	200
Salmonella typhi T-63	3.1	100
Klebsiella pneumoniae PCI 602	3.1	100
Pseudomonas aeruginosa A3	6.3	100
Pseudomonas aeruginosa No. 12	6.3	100

trideoxy-D-*arabino*-hex-1-enopyranose (**12**) was obtained in excellent yields from **3** by the usual methods. Methanol was added to **12** in the presence of HCl to afford **13**. The primary alcohol was tosylated and replaced by azide with NaN_3 in DMF to give **15**. The secondary alcohol at C-4 was subjected to mesylation and then treated with potassium thiolacetate, affording **16**: mp 160–163°; $[\alpha]^{20}D$ +167° (*c* 0.9, $CHCl_3$); $J_{3,4} = 4$ and $J_{4,5} = 2.5$ Hz, in a fair yield. The azide and *S*-acetyl groups were reduced with Raney Ni in methanol at the same time. After acetylation of the primary amino group, methyl 3,6-diacetamido-2,3,4,6-tetradeoxy-α-D-*threo*-hexopyranoside (**17**), mp 192–193°, $[\alpha]^{20}D$ +137° (*c* 0.8, H_2O), was obtained in a good yield. Hydrolysis of **17** followed by oxidation with bromine–water afforded a crystalline lactone of (3*S*,5*S*)-3,6-diacetamido-5-hydroxyhexanoic acid (**18**), mp 183–185°, $[\alpha]^{25}D$ +8.7° (*c* 2.3, H_2O).

The total syntheses of negamycin and the antipode have been completed using the δ-hydroxy-β-lysines[8] obtained from **11** and **18**, respectively.[1,9]

The antimicrobial spectra of negamycin and its antipode are shown in Table I, showing that the latter has generally far weaker activity against a variety of organisms than that of the former, but it is noteworthy that the antipode still has a definite biological activity.

Acknowledgment. We wish to express our deep gratitude to Professor S. Umezawa, Keio University, for his encouragement through the course of this work.

(8) These hydroxy amino acids were obtained by acid hydrolysis of the lactones **11** and **18** followed by purification with resin chromatography of Amberlite CG-50, respectively.

(9) Satisfactory elemental analyses were obtained for all the compounds for which melting point or [α]D values were given. All the compounds cited showed reasonable spectral data.

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Cationic Metal–Carbene Complexes in Cycloaddition Reactions. Synthesis and Reactions of Iron–Cyclopropyl Complexes

Sir:

Although numerous cyclopropyl derivatives of the main group elements are known,[1] no transition metal complexes having a σ-bonded cyclopropane ring have been reported.[2] Our interest in the nucleophilic properties of transition metal–allyl complexes[4] in metal-assisted cycloaddition reactions prompted us to re-examine the synthesis of the isomeric cyclopropyl derivatives with a view toward comparing their chemistry.

We wish now to report the preparation of two such complexes (**1** and **2**) and their reactions with electro-

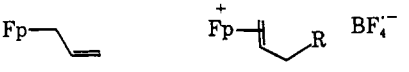
1 **2**

Fp ≡ $(h^5\text{-}C_5H_5)Fe(CO)_2$

philic reagents. Each may be prepared in moderate yield by treatment of the requisite cyclopropyl bromide[5] with $(h^5\text{-}C_5H_5)Fe(CO)_2Na$, while the first may also be obtained by alkylation of $(h^5\text{-}C_5H_5)Fe(CO)_2Br$ with cyclopropyllithium.[6]

The parent complex **1** is an air-stable amber oil, which may be distilled at room temperature under high vacuum without decomposition.[7] The comparative electronegativity of the cyclopropyl group is manifest in the carbonyl stretching frequencies of **1** (2014 and 1961 cm^{-1}) and of a typical secondary alkyl derivative $(h^5\text{-}C_5H_5)Fe(CO)_2(i\text{-}C_3H_7)$ (2006, 1952 cm^{-1}). Its nmr spectrum, taken in CS_2, exhibits two high-field multiplet absorptions at τ 9.48 (three protons) and 10.12 (two protons) assignable to protons trans and cis, respectively, to the carbon–metal bond.

Gaseous hydrogen chloride reacts with **1** to give $(h^5\text{-}C_5H_5)Fe(CO)_2Cl$ and a mixture of cyclopropane and propene. The compound reacts rapidly with fluoroboric acid and with trityl fluoroborate, as does the isomeric h^1-allyl complex **3**, to give the propene complexes **4**[8] and **5**,[7] respectively.



3 **4**, R = H; **5**, R = CPh_3

The formation of **4** with fluoroboric acid does not proceed as might be anticipated, through cleavage of C_2–C_3 with metal migration. Thus, treatment of the 1-deuterio derivative **1**-*d* with fluoroboric acid gave the

(1) For a list of references to these, see A. H. Cowley, J. L. Mills, T. H. Loehr, and T. V. Long, *J. Amer. Chem. Soc.*, **93**, 2151 (1971).

(2) Several attempts to prepare such derivatives of manganese, rhenium, iron, and iridium by decarbonylation of the related acyl–metal complexes were unsuccessful.[3]

(3) M. I. Bruce, M. Z. Igbal, and F. G. A. Stone, *J. Organometal. Chem.*, 20, 161 (1969).

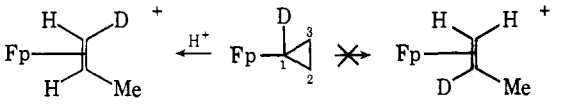
(4) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971).

(5) D. Seyferth, *et al.*, *ibid.*, 87, 4259 (1965); D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, 28, 703 (1963). The norcarane complex **2** was obtained from the mixture of stereoisomeric halides formed in the reduction of the corresponding dibromide. The Fp group is assigned as exo since models show that the alternative endo form would be prohibitively crowded.

(6) In view of the low reactivity of cyclopropyl halides in SN2 reactions, it seems likely that the former synthesis involves an initial metal–halogen exchange reaction.

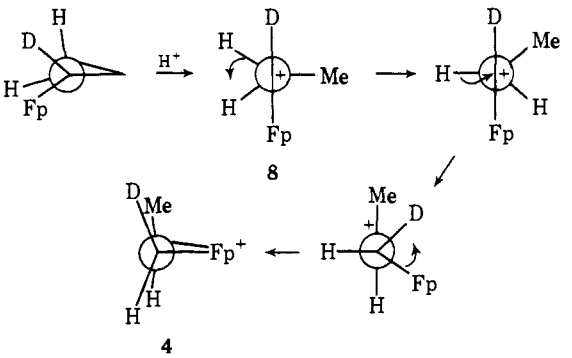
(7) An acceptable C and H analysis was obtained for this compound.

(8) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).



6 1-*d* 7

cation **6** exclusively[9] and not **7**. This product may be accounted for by a mechanism involving initial formation of cationic metal–carbene complex **8**[10] through cleavage of C_1–C_2, and the rapid rearrangement of this ion through minimum energy conformational changes as depicted below The alternative cleavage of C_2–C_3



8

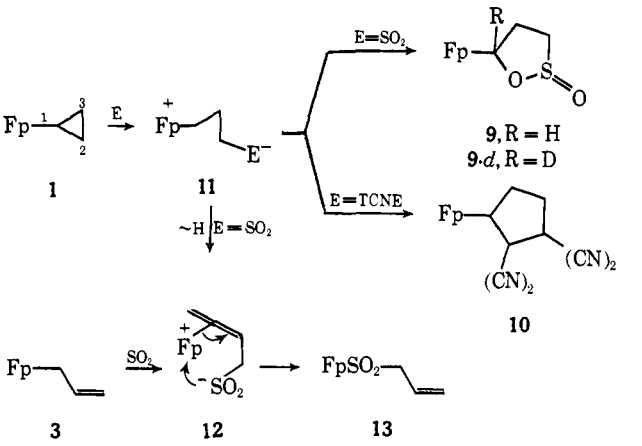
4

cannot be assisted by the metal atom owing to the orthogonality of C–C and Fp–C bonds which precludes a concerted process.

The cationic metal–carbene complex may be trapped through the reaction of **1** with uncharged electrophiles. Thus, treatment of **1** with SO_2 in benzene gives a mixture of stereoisomeric sultines (**9**):[7] mp 74–76°; ir (KBr) 1945, 2000 (C≡O), 1120 cm^{-1} (OSO);[11] nmr (CD_3NO_2) τ 3.90 (d, 0.4, CHOSO) 4.49 (t, 0.6, CHOSO), 4.99, 5.02 (2 s, 5, Cp), 6.5–7.6 (m, 4, CH_2). Reaction of SO_2 with **1-*d*** gave **9-*d***. Analogously, treatment of **1** with tetracyanoethylene (TCNE) gave the cycloaddition product **10**:[7,12] mp 119–121°; ir (KBr) 1965, 2021 (C≡O), 2250 cm^{-1} (C≡N); nmr (CD_3NO_2) τ 4.66 (s, 5, Cp), 6.8–8.0 (m, 5, CH, CH_2).

These products evidently arise through collapse of the dipolar intermediate **11** whose formation, like that of **8**, proceeds through metal-assisted electrophilic cleavage of C_1–C_2. Rearrangement of **11** (E = SO_2) through hydrogen migration to **12** proceeds competitive with its collapse to **9**, as is evidenced by the formation of a small amount of the metal allyl sulfone (**13**),[7] identical with the product obtained from **3** and SO_2.

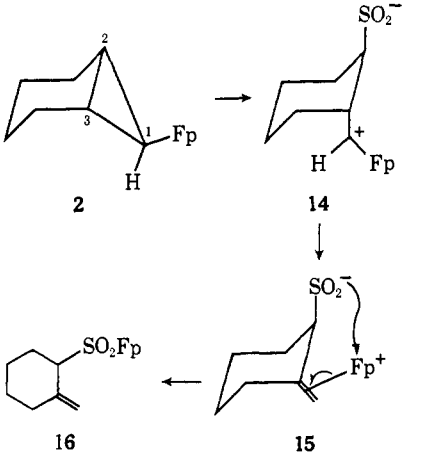
The reaction of SO_2 with the norcarane metal complex **2**[7] illustrates the delicate balance between these competing reaction paths. This reaction yields only the metal allyl sulfone (**16**):[7] mp 149° dec; ir(KBr)



1 **11** **9**, R = H; **9-*d***, R = D **10**

3 **12** **13**

2026, 2060 (C≡O), 1042, 1175 cm^{-1} (SO_2); nmr (C_2D_6SO) τ 4.67 (s, 5, Cp), 4.87 (m, 2, =CH_2), 6.45 (m, 1, CH), 7.7–8.9 (m, 8, CH_2). The stereochemistry of **2** is such that edge attack by the electrophile from either side of the cyclopropane ring on C_1–C_2 is blocked. The alternative reaction path involving corner attack[13] of the electrophile at C_2 results in inversion at this center and formation of the trans ion **14** which, owing to its stereochemistry, preferently rearranges to **15** and thence to the observed product.



2 **14** **16** **15**

Acknowledgment. This work was supported by grants from the National Science Foundation (GP-27991X), National Institutes of Health (GM-16395), and the Army Research Office (70-G88).

(9) The stereochemistry at the methylene group of the product is evident from its nmr spectrum (CD_3NO_2), which exhibits doublet absorption at τ 6.03 (J = 8 Hz), but fails to show doublet absorption at 6.43 (J = 15 Hz) present in the undeuterated complex.

(10) This is ample precedent for such an ion: H. J. Beck, E. O. Fischer, and C. G. Kreiter, *J. Organometal. Chem.*, **26**, C41 (1971); L. Knauss and E. O. Fischer, *ibid.*, **31**, C68 (1971), and references cited therein; F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971); K. Ofele, *Angew. Chem., Int. Ed. Engl.*, **7**, 900 (1968); P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971); M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971); P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 5044 (1966).

(11) The parent 1,2-oxathiolane 2-oxide and 1,2-oxathiane 2-oxide exhibit ir absorption at 1105 and 1125 cm^{-1}, respectively: D. N. Harp, T. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

(12) This product is isomeric with the product mp 193–196° dec obtained from the cycloaddition reaction of the allyl complex **3** and TCNE.

(13) R. T. Lalonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967). For leading references to the question of edge and corner electrophilic attack on cyclopropane rings, see J. B. Hendrickson and R. K. Boeckman, *ibid.*, **93**, 4491 (1971).

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Direct Evidence for the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene[1]

Sir:

Silicon difluoride, the best characterized structural analog to carbenes, is also the least prone to undergo

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