carboxyl groups converging at their active sites. However, the intrinsic value of the new structures derives from their rigidly maintained shape, a feature that permits examination of stereoelectronic effects of *carboxyl oxygen*[13] for the first time. We shall report on these experiments in due course. In the meantime, we note that peracid derivatives of such structures have shown unprecedented selectivity in olefin epoxidation reactions.[14]

Acknowledgment. We are indebted to the National Science Foundation for support and to Professor K. N. Houk and D. Spellmeyer for structural computations.

(13) Gandour, R. *Bioorg. Chem.* **1981**, *10*, 169-176.
(14) Rebek, J.; Marshall, L.; Wolak, R.; McManis, J. *J. Am. Chem. Soc.* **1984**, *106*, 1170-1171.

Molecular Recognition: Three-Point Binding Leads to a Selective Receptor for Aromatic Amino Acids

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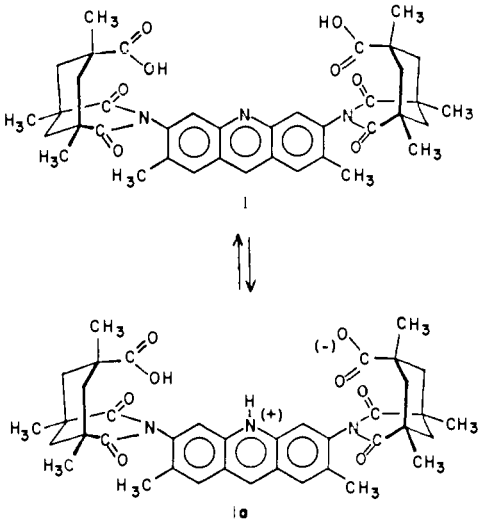
In a recent disclosure we introduced the acridine derivative **1** and described its binding behavior.[1] It features a rapidly assembled and rigidly maintained molecular cleft into which molecules of complementary size, shape, and hydrogen-bonding capacity are bound. Because NMR spectra of **1** indicate the presence of its zwitterionic form, **1a**, eq 1, it appeared probable



(1)

that molecules of complementary charge could also be bound within its cleft. In fact, phenylalanine, tryptophan, and tyrosine O-methyl ether[2] were extracted from their aqueous solutions with high efficiency by **1** into $CDCl_3$; NMR spectroscopy indicated that these amino acids occupied nearly 50% of the available receptor molecules **1**.

The sheer lipophilicity of these amino acids can only be partially responsible for their recognition by **1** since leucine, isoleucine, and valine, which show even less affinity for water,[3] were not extracted

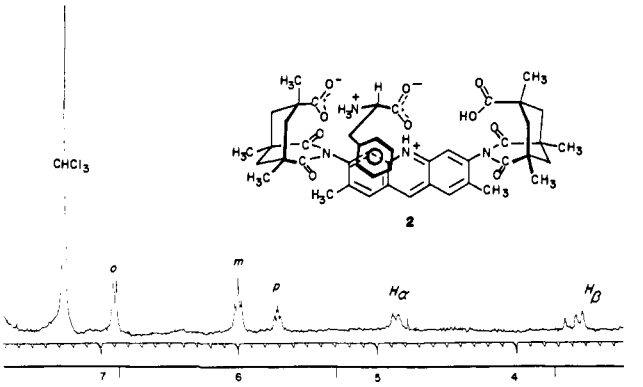
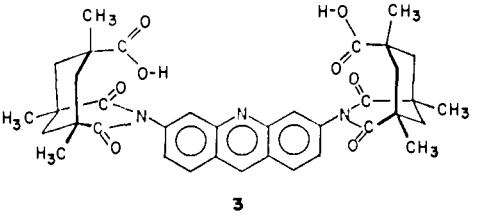
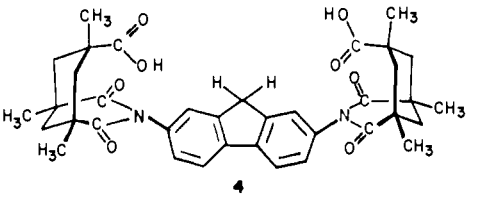


Figure 1. Portion of the 300-MHz NMR spectra of phenylalanine in contact with **1** in $CDCl_3$. Structure **2** is proposed.

to any appreciable extent. Rather, more specific interactions of the aromatic residues with the acridine nucleus must provide the selectivity. The NMR spectrum of the phenylalanine complex is reproduced below; the dramatic upfield shifts of the phenyl protons are most easily rationalized by the stacking interactions, perhaps of a charge-transfer nature, in the structure **2** proposed in Figure 1. Similar spectra were observed with tryptophan and the tyrosine derivative, but no evidence for extraction of phenylglycine was obtained. Inspection of CPK models reveals that this last amino acid is unable to achieve the stacking interaction while maintaining the charge-charge interactions and their attendant hydrogen bonds within the cleft.

The convergence of the functional groups of the receptor also appears to be an important factor in complex formation. Extraction studies with **3**, in which rotation about the c_{aryl}-N_{imide}





bond is possible,[4] show complexation with these aromatic amino acids is much reduced (10-20% as efficient as with **1**) but still of the same stacking nature. The fluorene derivative **4**, lacking both zwitterionic character and a well-placed aromatic ring, showed no evidence of binding to these amino acids at all. Thus structure **2** is supported by all of the available evidence, but a 2:1 complex (diacid/amino acid) is also possible.

The binding specificity of **1** and its ability to extract amino acids with such efficacy is unique. Such species have frequently been transported across liquid membranes as ammonium salts by crown ethers and detergents[5] or as carboxylates by other phase-transfer agents. Binding and transport of the actual zwitterionic forms has been disappointing. For example, Pederson[6] noted complex

(1) Rebek, J.; Askew, B.; Islam, N.; Killoran, M.; Nemeth, D.; Wolak, R. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) The low solubility of tyrosine in H_2O precluded its study directly. Typically, saturated solutions of the amino acids in water (2 mL) were stirred at 0 °C for 2 min with 1 mL of $CDCl_3$ containing ca. 0.5 mg of **1**. The organic phase was dried (Na_2SO_4) and concentrated to record the NMR spectrum. The amino acids were readily washed out of such samples by mere shaking with water.
(3) For a recent discussion, concerning the hydrophilicities of amino acid side chains, see: Wolfenden, R.; Anderson, L.; Cullis, P. M.; Southgate, C. C. *Biochemistry* **1981**, *20*, 849-855.
(4) Rebek, J.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.*, in press.
(5) Lehn, J. m. *J. Chem. Soc.* **1973**, *95*, 6108-6110. Newcomb, M.; Toner, J. L.; Helgeson, C.; Cram, D. J. *Ibid.* **1979**, *101*, 4941-4947.
(6) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036. For a more recent study, see: Behr, J.-P.; Lehn, J.-M.; Vierling, P. *Helv. Chim. Acta* **1982**, *65*, 1853-1866.

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formation with dibenzo-18-crown-6 annd glycine hydrochloride but not glycine itself in MeOH. The only successful case involves phenylalanine transport in a photoactivated system.[7] The present cases suggest that suitable derivatives of **1** should permit recognition of other side chains and our current research is directed at this prospect.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

(7) Sunamoto, J.; Iwamoto, K.; Mohri, Y. *J. Am. Chem. Soc.* **1982**, *104*, 5502–5504.

Photoassisted Polymerization of Terminal Alkynes by $W(CO)_6$ Involving Catalyst Generation by an Alkyne to Vinylidene Ligand Rearrangement

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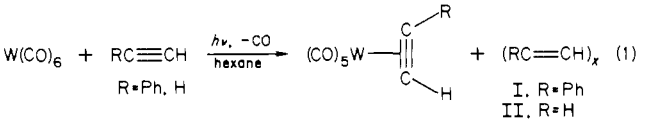
Katz and co-workers[1] have demonstrated that $(CO)_5W\{C(OMe)Ph\}$ (**1**) catalyzes the polymerization of alkynes, and the mechanism of Scheme I which involves carbene–alkyne and metallacyclobutene intermediates has been implicated. We independently prepared the important alkyne–carbene intermediate **2** by low-temperature photolysis of **1** in the presence of alkynes and showed that it leads to alkyne polymerization upon warm-up.[2] Herein we demonstrate that use of a *preformed* carbene complex is not necessary since *active alkyne polymerization catalysts can be formed by photolysis of $W(CO)_6$ with terminal alkynes in hydrocarbon solutions.* A key step in the catalyst generation is rearrangement of a coordinated alkyne to a vinylidene ligand.

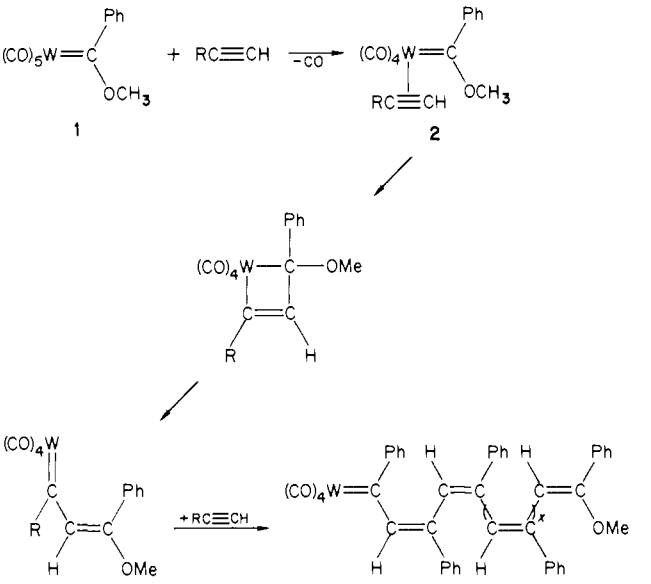
Irradiation of $W(CO)_6$ in the presence of alkynes has been reported to give unstable $(CO)_5W(\eta^2\text{-alkyne})$ complexes.[3] We verified these earlier results with $CH_3C{\equiv}CCH_3$, $PhC{\equiv}CPh$, $t\text{-BuC}{\equiv}CH$, $PhC{\equiv}CH$, and $HC{\equiv}CH$ but also observed formation of large amounts of red poly(phenylacetylene) (I) and black *trans*-poly(acetylene) (II) in the latter two cases, eq 1.[4] The



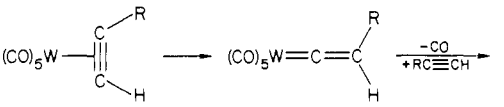
(1)

polymers were identified by their characteristic IR spectra and by a molecular weight measurement for $(PhC{=}CH)_x$, but the C, H analyses for both were persistently low, due to contamination by tungsten residues.[5] These products were repeatedly observed when either rigorously purified solvents, alkynes, and $W(CO)_6$ or as-received materials were used. With $HC{\equiv}CH$, irradiation was only necessary to *initiate* the polymerization since it continued 90 h after cessation of photolysis with no sign of abatement. However, polymerization of $PhC{\equiv}CH$ ceased when irradiation was stopped. IR monitoring of the active catalyst solutions showed only the presence of $W(CO)_6$ and $(CO)_5W(\eta^2\text{-alkyne})$, and thus the active polymerization agent must be present in trace amounts and must be extremely active.

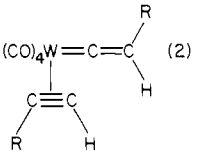
Scheme I



In related work, Masuda et al.[6] reported that polymerization occurred when $W(CO)_6$ was irradiated with alkynes in *halocarbon solvents*. This polymerization may proceed by the generation of halocarbene complexes which catalyze the polymerization by the mechanism of Scheme I or by the route suggested below for $W(CO)_6$ in hydrocarbon solutions. We suggest that irradiation of $W(CO)_6$ with terminal alkynes in *hydrocarbon solvents* leads to the formation of catalytically active vinylidene complexes by rearrangement of the initially formed η^2-alkyne complexes, eq 2.



3a, R=Ph
3b, R=H



(2)

Thermal or photochemical loss of CO from **3** and coordination of alkyne then allow entry into a catalytic cycle similar to that of Scheme I. The metal-assisted rearrangement of terminal alkynes to vinylidene ligands is now quite well established,[7] although the reaction has never been used for the present purpose. The proposed vinylidene intermediates **3a,b** have not been reported although related vinylidene complexes $(CO)_5M{=}C{=}CRR'$ (M = Cr, W) have been mentioned.[8] In one instance a vinylidene

(1) (a) Katz, T. J.; Ho, T. H.; Shih, N. Y.; Ying, Y. C.; Stuart, V. I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2659. (b) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (c) See also: Thoi, H. H.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2227.

(2) Foley, H.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(3) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 1264.

(4) A typical experiment involved photolysis ($\lambda > 300$ nm) of a hexane solution (60 mL) of $W(CO)_6$ (0.135 g, 0.32 mmol) and phenylacetylene (1.0 mL, 1.05 mmol) in a Schlenk flask at 25 °C for 24 h. Similar reaction conditions were employed for $HC{\equiv}CH$ which was passed through a saturated $NaHSO_3$ solution to remove the acetone stabilizer.

(5) **(PhC=CH)$_x$**: Anal. Calcd for $(C_8H_6)_x$: C, 94.12; H, 5.88. Found: C, 86.57; H, 5.81. ^1H NMR ($CDCl_3$) 7.74 ppm (br, m); mol wt (osmometry, THF) 1815, 1757 (two samples); IR (KBr) 697 s, 755 s, 1028 w, 1074 w, 1443 m, 1491 m, 3025 w, 3054 w cm^{-1}. For a discussion of the IR spectra of $(PhC{=}CH)_x$, see, for example: Tsonis, C. P.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1779. Kern, R. J. *Ibid.* **1969**, *7*, 621. Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717. ***trans*-(HC=CH)$_x$**: IR (KBr) 2965 m, 1076 m br cm^{-1}. For a discussion of the IR spectra of $(HC{=}CH)_x$, see: Kleist, F. D.; Byrd, N. R. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 3419. Watson, W. H.; McMordie, W. D.; Lands, L. G. *J. Polym. Sci.* **1961**, *55*, 137.

(6) (a) Masuda, T.; Kuwane, Y.; Yamamoto, K.; Higashimura, T. *Polym. Bull.* **1980**, *2*, 823. (b) Masuda, T.; Yamamoto, K.; Higashimura, K. *Polymer* **1982**, *23*, 1663. (c) Masuda, T.; Higashimura, T. *Acc. Chem. Res.* **1984**, *17*, 51.

(7) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789.

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