surfaces by a wide variety of spectroscopic techniques.[13] Figure 1B shows the Raman spectrum after the evacuated cell is backfilled to 100 torr with carbon monoxide. The lines due to adsorbed benzene are replaced by two new peaks at 1476 and 1098 cm⁻¹ which are congruent with those found in the spectrum of pure acetylene on alumina-supported rhodium, Figure 1C,[6] indicating that benzene has undergone a decyclotrimerization to acetylene. On rhodium, acetylene is irreversibly chemisorbed and it is not released and detected by mass spectroscopic analysis of the gas phase in our experiments. Thus, its formation from benzene is stoichiometric, not catalytic.

Detailed mechanistic interpretation of these results is difficult but a first-order analysis is possible using concepts previously developed to rationalize bridge to terminal CO rearrangement on supported palladium.[14] In the C_6H_6–Rh–Al_2O_3 system, coadsorption of CO, a strong π acceptor ligand, withdraws electron density from the metal.[15] Raman studies of acetylene on Rh–Al_2O_3[6] indicate that the hydrocarbon forms a $\sigma_2\pi$ surface compound which formally donates two electrons to the metal via the two metal–carbon σ bonds and accepts approximately 0.5 electron by back-bonding into the π^* orbitals. Benzene, in contrast, behaves essentially as a net π acceptor.[17] Therefore, generation of three $\sigma_2\pi$-C_2H_2(ads) molecules from one η_6-C_6H_6(ads) serves to restore electron density to the metal and also leads to increased hydrocarbon–metal bonding.

In agreement with our empirical results, Somorjai and co-workers[13,16] have analyzed LEED data for the c(2√3 × 4) rect phase of benzene on Rh(111), formed in the presence of CO, and found evidence for an in-plane distortion such that the C-C bonds alternate between 1.25 ± 0.1 and 1.6 ± 0.1 Å. Such a distorted, unsymmetrical structure *may* represent an intermediate in benzene decyclization.

The above analysis explicitly predicts that the benzene to acetylene conversion is associated with strong π acceptor coadsorbates and that σ donors should have no effect. Experimental support is derived from experiments in which NO and benzene were coadsorbed on Rh–Al_2O_3. Here, Raman spectroscopy again shows that $\sigma_2\pi$-C_2H_2 is formed as predicted although the surface chemistry is more complex in that other, yet unidentified, products are also produced. Ammonia, which is expected to act only as a σ donor, produces no detectable acetylene under comparable conditions.

The significance of these findings goes beyond transformations of hydrocarbons on metals. Two important implications are that structural rearrangements may be anticipated in the presence on metal surfaces of additional ligands which strongly perturb the metal electron density and that strong adsorbate–metal bonding may provide a thermodynamic driving force for reactions that seem improbable based solely on gas- or solution-phase energetics where such bonding is absent.

Registry No. CO, 630-08-0; NO, 10102-43-9; Rh, 7440-16-6; benzene, 71-43-2; acetylene, 74-86-2.

(13) Koel, B. E.; Crowell, J. E.; Mate, C. M.; Somorjai, G. A. *J. Phys. Chem.* **1984,** *88,* 1988.

(14) Gelin, P.; Siedle, A. R.; Yates, J. T., Jr. *J. Phys. Chem.* **1984,** *88,* 2978.

(15) This crude description has been placed on a firm theoretical basis by S. Sung and R. Hoffmann who have carried out molecular orbital calculations on CO adsorbed on different transition metals: Sung, S.-S.; Hoffmann, R. *J. Am. Chem. Soc.* **1985,** *107,* 578. We are grateful to Prof. Hoffmann for communicating to us these results prior to publication.

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(17) Cf.: Mingos, D. M. P. *Compr. Organomet. Chem.* **1982,** *3,* 1. Net acceptor behavior is also evidenced by an intense d → π^* charge-transfer absorption in the UPS spectrum of C_6H_6 Pd(111): Netzer, F. P.; Mack, J. U. *J. Phys. Chem.* **1983,** *79,* 1017.

Kinetic Molecular Design of Uranophile. Linear Tris(dithiocarbamate) as a Strong and Rapid Extracting Reagent for Uranyl Ion from Dilute Carbonate Solution

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The molecular design of strong ligands specific for a given metal ion has been generally achieved by considering (1) the size fitting, (2) the nature of the ligand–metal interaction, and (3) the orientation in the ligation. We have recently designed and synthesized several *uranophiles*, macrocyclic ligands **1–3**, specific

cyclic $\{(CH_2)_5\text{-}COCH_2CO\}_3^-$ **1**

cyclic $\{(CH_2)_8\text{-}C(CO_2H)_2\}_3$ **2**
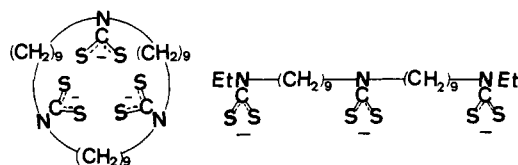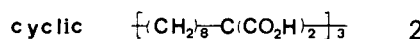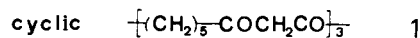
3   **4**

for the uranyl ion. These molecules were based on design concepts **1–3**. In particular, we introduced O⁻ or S⁻ on the ligands[1] since the formation of U–O⁻ or U–S⁻ bonds is generally favored. Interestingly, we found that **3** showed a unique macrocyclic effect which unexpectedly led to slow rate–determining U–S⁻ bond formation. This finding prompted us to design uranophiles capable of showing rapid U–ligand bond formation rates (k) while maintaining satisfactorily large association constants (K). We now wish to report the successful "kinetic design" of a new class of uranophiles **4** having both a large K and a large k. It was observed that the macrocyclic uranophile **3** showed a much *slower* exchange rate than the monomeric uranophile $Et_2NCS_2^-$, in spite of the fact that in the former the equilibrium constant (K) for uranyl complexation is much larger. This unexpectedly slow carbonate–ligand exchange by **3** is due to the S_N2-type mechanism where the specific "topological requirement" for macrocyclic ligation is important,[2] while the fast S_N1-type mechanism was observed for CO_3^{2-} exchange by $Et_2NCS_2^-$.

On this basis, we predicted that fast uranyl binding might be achieved by avoiding such an overly restricted transition state, while maintaining the desired large association constants by using intramolecular tridentates. A linear tris(dithiocarbamate) should satisfy both requirements. We therefore prepared the linear tri(dithiocarbamic acid) **4** from $EtNH(CH_2)_9NH(CH_2)_9NHEt$ and CS_2/NaOH in a quantitative yield. The triamine was prepared from $Br(CH_2)_9NH(CH_2)_9Br$ and NaNTsEt. The structure of **4** was determined by elemental analysis and by 400-MHz ¹H and 100-MHz ¹³C NMR, IR, UV, and mass spectra: ¹H NMR δ (from 3-(trimethylsilyl)propionic-d_4 acid in D_2O) 4.04 (q, 4 H), 3.95–4.00 (m, 8 H) ($CH_2NCS_2^-$) with disappearance of 2.6 (CH_2N), 1.68–1.78 (8 H), 1.30–1.40 (20 H), 1.23 (6 H); ¹³C NMR δ (from dioxane) 140.8, 140.1 (NCS_2), -12.1, -12.5 and -17.3 (NCH_2) with disappearance at -16.9, -17.1, and -22.9 (amine NCH_2), -37.5 to -40.1 (CH_2), -54.9 (CH_3); IR 940 cm⁻¹

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(2) Tabushi, I.; Yoshizawa, A., manuscript in preparation.

Table I. Effective Formation of Ligand–Uranyl Complex[a]

ligand	product	eff formation, %
3	3·UO$_2^-$	ca. 100
4	4·UO$_2^-$	75
Et$_2$NCS$_2$	(Et$_2$NCS$_2$)$_3$·UO$_2^-$	6 × 10^{-7}

[a] [UO$_2^{2+}$] = 0.1 mM, [CO$_3^{2-}$] = 2.4 mM, [ligand] = 1.0 mM, T = 20 °C, pH 9.5.
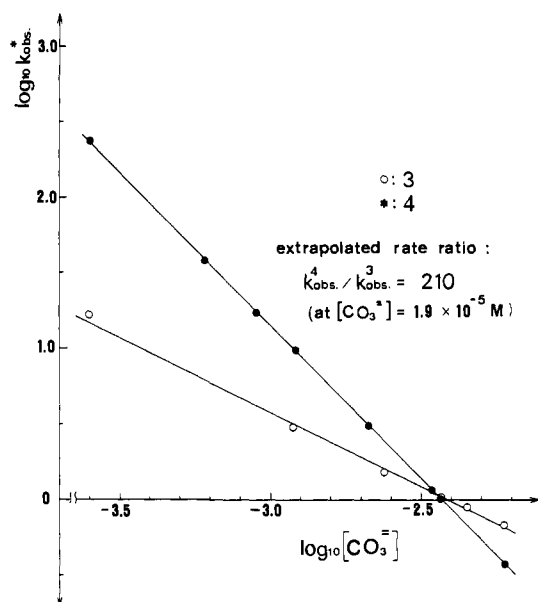
Figure 1. Dependence of log$_{10}$ k_{obsd} upon log$_{10}$ [CO$_3^{2-}$]: T = 20 ± 0.1 °C; [UO$_2$(CO$_3$)$_3^{4-}$] = 1.3 × 10^{-4} M; [CO$_3^{2-}$] = (2.5–63) × 10^{-4} M. k_{obsd}: for **3** from eq 3, k_{obsd} = k_3/[CO$_3^{2-}$]; for **4** from eq 2, k_{obsd} = k_4/[CO$_3^{2-}$]^2.

(VC=S); mp 54–56 °C; MS, *m/e* 355 for triamine, 649 for dithiocarbamate 4·Na$_3$. Anal. Satisfactory for triamine 3·HBr. Dithiocarbamate **4** forms 1:1 complexes with uranyl ion in aqueous solution. This results in the appearance of new electronic absorption at 265 nm with corresponding disappearance of the free **4** absorptions at 260 and 283 nm.[1d] The molar ratio of **4** to UO$_2^{2+}$ in the complexes, the association equilibrium constants, and the stoichiometry of equilibria (eq 1) were determined by the electronic

$$UO_2(CO_3)_3^{4-} + 4^{3-} \rightleftarrows UO_2 \cdot 4^- + 3CO_3^{2-} \quad (1)$$

spectroscopy. Equilibrium constant thus obtained is (1.8 ± 0.2) × 10^{17} M^{-1} at 20 °C, pH 9.5 ± 0.1, for a concentration range of (4.5–430) × 10^{-4} M **4**. Compound **4** binds UO$_2^{2+}$ strongly and is more than 10^8 times as effective in uranyl–uranophile complex formation as Et$_2$NCS$_2^-$ (see Table I).

Rates of carbonate displacement of UO$_2$(CO$_3$)$_3^{4-}$ by **4** were measured in an aqueous solution at pH 9.5 ± 0.1 at 20 ± 0.1 °C by the use of stopped-flow-electronic spectroscopy by following the change in absorption at 450 nm.[1d] Observed rates are dependent on concentrations of **4** (or **3**) and carbonate:

$$\frac{d[4 \cdot UO_2^-]}{dt} = k_4 \frac{[4][UO_2(CO_3)_3^{4-}]}{[CO_3^{2-}]^2} \quad (2)$$

$$\frac{d[3 \cdot UO_2^-]}{dt} = k_3 \frac{[3][UO_2(CO_3)_3^{4-}]}{[CO_3^{2-}]} \quad (3)$$

The relative rate (eq 4) is expected to be a function of carbonate

$$\frac{d[4 \cdot UO_2^-]}{d[3 \cdot UO_2^-]} = \frac{k_4[4]}{k_3[3][CO_3^{2-}]} \quad (4)$$

concentration (eq 4). Observed rate constants are plotted against CO$_3^{2-}$ concentration (Figure 1). Clearly, the rate equations are not the same for **3** and **4**. In fact, inverse first- and second-order dependence on CO$_3^{2-}$ was observed for **3** and **4**, respectively. Thus, at lower CO$_3^{2-}$ concentrations, **4** displays a much faster rate of

exchange than does **3**. Compound **4** might be more useful for extracting UO$_2^{2+}$ from natural sea water in a rapid ocean current,[3] since the extrapolated rate ratio is estimated to be ca. 210, in favor of the new linear ligand **4** to macrocycle **3**.

(3) The flow rate of the Black Current near Mikurajima Island, Izu area, reaches to 2 m/s (0.001 s/mm contact time) and any practical adsorbent must show very rapid uranyl uptake rate under the condition of [CO$_3^{2-}$] = 1.9 × 10^{-5} M. Tabushi, I.; Kobuke, Y.; Nakayama, N.; Aoki, T.; Yoshizawa, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 445.

An Unusual Substituent Effect on a Palladium-Mediated Cyclization: A Total Synthesis of (±)-Sterepolide

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Recently, a new class of sesquiterpenoids, the isolactaranes, have emerged.[1,2] Sterepolide (**1**), a metabolite of the fungus *Stereum*
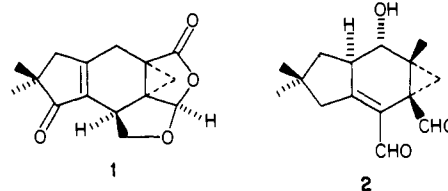
purpureum which is a cause of the silver leaf disease common to a number of fruit trees,[2b] and merulidial (**2**), a highly active antibiotic,[2c] are two representatives. Scheme I summarizes a retrosynthetic analysis of sterepolide. The key to this analysis is the availability of the reactive diene **6** in permitting the use of a Diels–Alder-based strategy.[3] Our recent discovery of a Pd-based isomerization of acyclic 1,6-enynes[4] suggested the possibility that **7** be considered as a suitable precursor except for the fact that all of the previous examples strongly indicated that the 1,4-diene **11** rather than the 1,3-diene **6** should be the observed product.
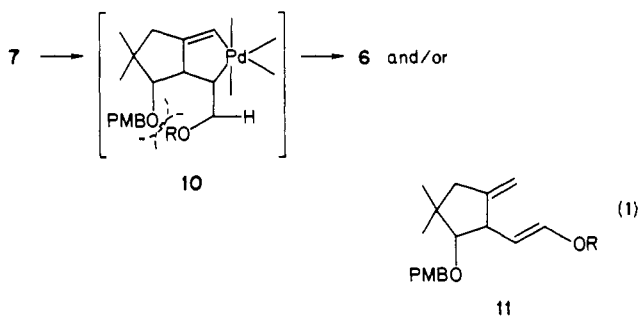
Furthermore, previous work on the Heck reaction[5] demonstrated

(1) For a review, see: Ayer, W. A.; Browne, L. M. *Tetrahedron* **1981**, *37*, 2199.

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(4) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781.

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