

of 2^+ with O_2 to form the peroxy cation radical 3^+ (Scheme II) and back electron transfer from the Lewis acid, or **1**, will lead to **4** and **5**. The intriguing aspect of the reaction is, however, the preference for formation of the trans-anti-cis and trans-syn-cis epidioxides.¹³ It is likely that formation of 2^+ proceeds when **1** and 1^+ lie above one another in approximately parallel planes, as would be required by an FMO-controlled process.^{3,14} Thus, two such orientations of the reactants which are approximately equivalent in terms of FMO overlap will give the diastereomeric cation radicals (S^*,S^*)- 2^+ and (S^*,R^*)- 2^+ in each of which the bridging C4-C4' bond is pseudoaxial to both rings (Scheme III). Addition of O_2 to the allyl radical in each dimer cation radical is constrained for steric reasons to the lower, or *si*, face. In the reaction leading to **4**, ring closure can only proceed through the lower, or *re*, face of the second ring to deliver the trans-anti-cis epidioxide. In that reaction leading to **5**, ring closure can only proceed through the *si* face to give the trans-syn-cis epidioxide.

These reactions afford a type of product not encountered in singlet oxygen reactions,¹⁵ and which, as carbon-carbon bond formation is associated with the oxygenation process, offer considerable mechanistic and synthetic appeal. As far as we can ascertain, compounds related to **4** and **5** have not previously been described.

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Supplementary Material Available: Frontier orbital coefficients in 1-methylcyclohexa-1,3-diene and its cation radical and spin densities and charge distributions in the cation radical, 1H NMR and HRMS data for **4**, **5**, **11**, and **12**, and ORTEP diagram, angles, bond lengths, least-squares coordinates, and thermal parameters for **11** (8 pages). Ordering information is given on any current masthead page.

(13) The four other epidioxides that can be formed will possess respectively cis-syn-cis, trans-syn-trans, cis-anti-cis, and trans-anti-trans configurations.

(14) Association of the benzene cation radical with benzene takes place in such a manner: Milosevich, S. A.; Saichek, K.; Hinchey, L.; England, W. B.; Kovacic, P. *J. Am. Chem. Soc.* **1983**, *105*, 1088 and references therein.

(15) Reaction of **1** with 1O_2 generated by means of methylene blue on alumina in CH_2Cl_2 at $-78^\circ C$ gave quantitatively the endoperoxide **6**.

Surface Conversion of Benzene to Acetylene

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Benzene is well-known to be a quite stable molecule and its chemistry is dominated by C-H substitution processes in which the C_6 aromatic ring is preserved. Cyclization of acetylenes to arenes is catalyzed by numerous molecular organometallic compounds¹ and also proceeds on metal surfaces, notably Pd(111).²⁻⁴ These observations suggest that these two hydrocarbons may be in equilibrium and the reverse process, decyclotrimerization of

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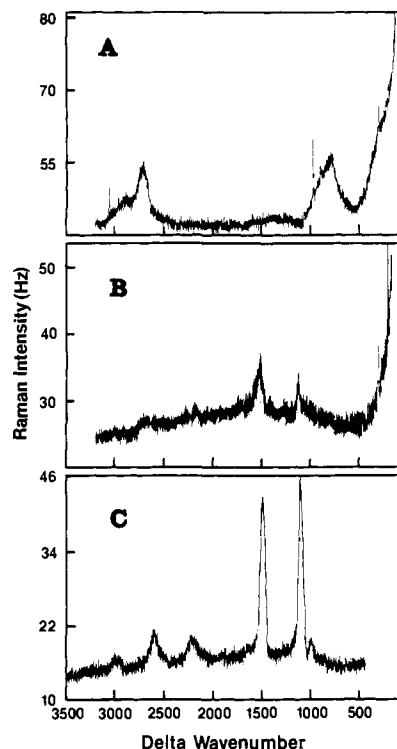


Figure 1. Raman spectrum of (A) benzene, (B) benzene plus CO, and (C) acetylene on 10% Rh on alumina obtained with 4880-Å laser excitation, 100-mW power input.

benzene to acetylene, may be possible. We wish to report results which demonstrate that, in the presence of certain coadsorbates, conversion of benzene to acetylene occurs on metallic rhodium catalysts, a reaction that appears to be without precedent.

The analytical probe in our experiments is Raman spectroscopy which we have previously shown to be useful for surface chemical characterization on supported catalysts and metal particles.^{5,6} The catalyst is 10% rhodium supported on α -alumina, reactions on which were carried out in an ultrahigh vacuum combination reactor and Raman cell.⁷

Benzene was admitted to the cell to ca. 60 torr. The Raman spectrum at this stage, Figure 1A, shows broad lines near 2960 and 1000 cm^{-1} due to chemisorbed benzene and sharp peaks at 3063 and 992 cm^{-1} which correspond to the most intense lines in the spectrum of liquid benzene. The latter are assigned to a physisorbed multilayer phase as inferred from earlier infrared data,¹² they are not apparent when the laser beam is focused on the sample holder instead of the catalyst sample. The lines due to physisorbed benzene disappear upon evacuation of the cell. The Raman spectrum of chemisorbed benzene on Rh/Al_2O_3 is consistent with a η_6 bonding mode found on single crystal metal

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(7) The supported catalyst was prepared by the method of Yang and Garland⁸ according to which alumina impregnated with $RhCl_3$ is reduced with 100 torr of hydrogen at 150 $^\circ C$. The reduction is performed in a combination ultrahigh vacuum reactor-spectrometer cell after which the cell is evacuated to 5×10^{-7} torr and baked at 150 $^\circ C$ for 8 h and then cooled prior to introduction of adsorbates. It is known⁹ that, at 10% loading, the average metal particle size is ca. 2.6 nm and has a raftlike morphology. Infrared spectroscopy of CO on such particles indicates that the group frequencies and bridge:terminal CO ratio are similar to those on $Rh(111)$.¹⁰ Pure alumina exhibits an intense luminescence¹¹ which frustrates collection of background spectra and which is effectively quenched in the presence of metallic rhodium.

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surfaces by a wide variety of spectroscopic techniques.¹³ Figure 1B shows the Raman spectrum after the evacuated cell is back-filled 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 $\text{C}_6\text{H}_6\text{-Rh-Al}_2\text{O}_3$ system, coadsorption of CO, a strong π acceptor ligand, withdraws electron density from the metal.¹⁵ Raman studies of acetylene on $\text{Rh-Al}_2\text{O}_3$ 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 $\sigma_2\pi\text{-C}_2\text{H}_2(\text{ads})$ molecules from one $\eta_6\text{-C}_6\text{H}_6(\text{ads})$ 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 $c(2\sqrt{3} \times 4)$ rect phase of benzene on $\text{Rh}(111)$, 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 $\text{Rh-Al}_2\text{O}_3$. Here, Raman spectroscopy again shows that $\sigma_2\pi\text{-C}_2\text{H}_2$ 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.

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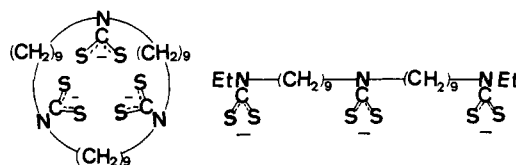
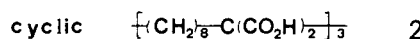
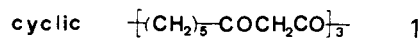
Kinetic Molecular Design of Uranophile. Linear Tris(dithiocarbamate) as a Strong and Rapid Extracting Reagent for Uranyl Ion from Dilute Carbonate Solution

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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



3

4

for the uranyl ion. These molecules were based on design concepts 1-3. In particular, we introduced O^- or S^- on the ligands¹ 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* $\text{Et}_2\text{NCS}_2^-$, 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 $\text{S}_{\text{N}}2$ -type mechanism where the specific "topological requirement" for macrocyclic ligation is important,² while the fast $\text{S}_{\text{N}}1$ -type mechanism was observed for CO_3^{2-} exchange by $\text{Et}_2\text{NCS}_2^-$.

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 $\text{EtNH}(\text{CH}_2)_9\text{NH}(\text{CH}_2)_9\text{NH}\text{Et}$ and CS_2/NaOH in a quantitative yield. The triamine was prepared from $\text{Br}(\text{CH}_2)_9\text{NH}(\text{CH}_2)_9\text{Br}$ and NaNTEt . The structure of 4 was determined by elemental analysis and by 400-MHz ^1H and 100-MHz ^{13}C 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) ($\text{CH}_2\text{NCS}_2^-$) with disappearance of 2.6 (CH_2N), 1.68-1.78 (8 H), 1.30-1.40 (20 H), 1.23 (6 H); ^{13}C 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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