J. Am. Chem. Soc. 1984, 106, 4041-4043

Table I. Calculated Splitting Values for the Cyclobutadiene Automerization

compd		$\hbar\omega_F$, cm^{-1}	$\hbar\omega_i$, cm^{-1}	ΔE, cm^{-1}	$10^{11}\omega_T$, s^{-1}
GS	TS				
1	**2**	1764	1929*i*	9.03	5.39
1[a]	**2**[a]	1588	1736*i*	3.80	2.28
3	**5**	1700	1929*i*	7.87	4.71
3[a]	**5**[a]	1530	1736*i*	3.28	1.96
4	**6**	1698	1853*i*	6.63	3.96
4[a]	**6**[a]	1528	1668*i*	2.71	1.62

[a] 10% correction of the calculated vibrational frequency (see ref 8).

structures, **2**, **5**, and **6**, would be expected to be biradicals. Our results differ little from those given earlier by straightforward MINDO/3 calculations, implying that **3** is not a real biradical.[1]

The geometries and heats of formations (kcal/mol) calculated for **1** and **3** are shown on and below the formulas with values for high-level ab initio calculations in parenthesis. The barrier height calculated by MINDO/3/HE/CI (8.1 kcal/mol) is less than that from the ab initio calculation (12.0 kcal/mol), as expected (see below).

Since the vibrational frequencies differed only a little from the earlier MINDO/3 values[1] they are supplied as supplementary material, together with comparisons with experiment[9] and ab initio[10] calculations.

Since MINDO/3 contains an implicit allowance of vibrational/rotational energy via its parametrization,[11] it should give a good estimate of the barrier height for automerization of **1**, whereas the ab initio one corresponds to a reaction where neither **1** nor **2** has any vibrational energy. The ab initio value therefore has to be corrected for the loss of zero point energy corresponding to the transition coordinate. From the calculated vibrational frequencies this is estimated to be 3.6 kcal/mol, almost exactly the difference between the MINDO/3 (8.1 kcal/mol) and ab initio (12.0 kcal/mol) barriers.

The reaction dynamics of the automerization were then studied by using the procedures of Bicerano et al.,[12] based on the method of periodic orbits described by Miller.[13] This treats the system in terms of a double-minimum model, analogous to that used in discussing inversion of ammonia. Tunneling leads to a splitting of the energy levels, the ground states splitting being given by

$$\Delta E = (h\omega_F/(2\pi^2))e^{-\theta} \tag{1}$$

where ω_F is the frequency of the normal mode of vibration (F) leading to reaction and for the Eckart[14] barrier θ is given[13] by

$$\theta = [V_{\text{eff}} - (E_0 V_{\text{eff}})^{1/2}]4\pi^2/(h\omega_i) \tag{2}$$

where V_{eff} is the effective barrier height, ω_i is the value of the (imaginary) frequency corresponding to the transition coordinate in the TS, and $E_0 = h\omega_{\text{F}}/(4\pi)$. In the present treatment,[12,13] all vibrations except that (F) leading to reaction are assumed to contribute adiabatically, so V_{eff} is given in terms of V_0, the barrier on the potential surface, by

$$V_{\text{eff}} = V_0 + \sum_{k=1}^{3n-6} (h\omega_k{}^{\ddagger} - h\omega_k)/4\pi \tag{3}$$

where the $\omega_i{}^{\ddagger}$ are the vibration frequencies of the TS. In MINDO/3, however, the zero point energy is taken into account via the parameterization so the second term in eq 3 should be neglected. The MINDO/3 values for the relevant quantities in eq 1–3 are (for **1**)

$$V_{\text{eff}} = V_0 = 8.14\ \text{kcal/mol}\ (2856\ \text{cm}^{-1}) \tag{4}$$

$$E_0 = h\omega_F/(4\pi) = 882\ \text{cm}^{-1} \tag{5}$$

$$h\omega_i = 1929i(\text{cm}^{-1})2\pi \tag{6}$$

The ground-state splittings estimated for **1** and its isotopically substituted isomers, **3** and **4**, are shown in Table I, together with tunneling rates (ω_T) calculated from the following expression:[14,13]

$$\omega_T = 2\Delta E/h \tag{7}$$

Table II. Calculated Classical Rate Constants

temp, K	ΔS, cal/(mol K)	A, s^{-1}	k, s^{-1}
100	−1.33	2.89×10^{12}	4.58×10^{6}
350	−0.28	1.72×10^{13}	1.41×10^{8}

Using our calculated enthalpy and entropy of activation values, we arrive at the estimates of the classical rates of automerization shown in Table II. Comparison of Tables I and II shows that the rate of tunneling is greater by 3 powers of 10 even at 350 K.

The ground-state splitting we calculate for **1** (Table I) is large enough to be observed experimentally, in the form of an absorption in the microwave spectra of **1**. Since the relevant vibrational frequency is IR inactive this splitting will not appear in the IR spectrum of **1**.

We are currently studying the possibility of analogous tunneling in other automerization processes.

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Supplementary Material Available: Tables I–VII of de Broglie wavelengths, MINDO/3 and ab initio results, calculated and theoretical vibrational frequencies for D_{2h} and D_{4h} states, splitting values, and rate constants (4 pages). Ordering information is given on any current masthead page.

Photochemistry of $H_4Ru_4(CO)_{12}$ in Rigid Alkane Matrices at Low Temperature: Spectroscopic Detection and Characterization of Coordinatively Unsaturated $H_4Ru_4(CO)_{11}$

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We wish to report the spectroscopic detection and characterization of a reactive intermediate from the photoexcitation of $H_4Ru_4(CO)_{12}$ showing that loss of CO, eq 1, is the only net

$$H_4Ru_4(CO)_{12} \xrightarrow{h\nu} H_4Ru_4(CO)_{11} + CO \tag{1}$$

chemical result of near-UV irradiation of $H_4Ru_4(CO)_{12}$ in an alkane matrix at 77 K. While light-induced loss of CO from mononuclear and dinuclear complexes is known,[1-5] our new results constitute the first direct observation of the cluster product from light-induced loss of CO from a high nuclearity metal carbonyl complex with retention of the cluster core, providing a possible

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0002-7863/84/1506-4041$01.50/0

model for photodissociation of nonbridging CO from metal surfaces.[6] Interest in this system stems additionally from the fact that polynuclear organotransition-metal compounds containing empty "surface" coordination sites may be important in the activation of hydrocarbons.[7] A coordinatively unsaturated cluster has been proposed as an intermediate for both the thermal[8,9] and photochemical[10,11] catalytic reactions of alkenes where $H_4Ru_4(CO)_{12}$ is used as a catalyst. The direct reaction of $H_4Ru_4(CO)_{11}$ with two-electron donors accounts for the photosubstitution behavior[10] of $H_4Ru_4(CO)_{12}$ in fluid solution at 298 K and provides a low-temperature synthesis of a new class of $H_4Ru_4(CO)_{11}$(alkene) species thought to be important in catalytic reactions of alkenes.[8-11]

The $H_4Ru_4(CO)_{12}$ complex and its substituted derivatives were prepared according to literature procedures.[12] Figure 1a shows clean FTIR and UV–vis spectral changes accompanying near-UV irradiation of ~0.1 mM $H_4Ru_4(CO)_{12}$ in deoxygenated 3-methylpentane glass at 77 K.[13] All absorbance changes occur in constant ratio at up to 60% conversion. Within experimental error, the amount of CO (2132 cm^{-1})[14] detected is consistent with the appearance of one CO for every $H_4Ru_4(CO)_{12}$ molecule consumed.[15] The intense metal-centered electronic transition at 357 nm remains essentially unchanged, blue shifting slightly to 354 nm after large conversion of $H_4Ru_4(CO)_{12}$ has been detected by FTIR. This result indicates retention of the metal-cluster framework in the primary photoproduct. The additional growth of a weak, low-energy absorption centered at ~436 nm is consistent with the coordinative unsaturation associated with the primary photoproduct. IR spectral features in the CO stretching region of the primary photoproduct show similarities to those observed for well-characterized $H_4Ru_4(CO)_{11}L$ complexes,[16] including the case where L = PPh_3, Figure 1b. On the basis of this evidence, we propose that eq 1 represents the low-temperature photochemistry of matrix-isolated $H_4Ru_4(CO)_{12}$ in an alkane. Warm-up to 298 K of an alkane matrix containing the photogenerated $H_4Ru_4(CO)_{11}$ and CO leads to regeneration of $H_4Ru_4(CO)_{12}$.

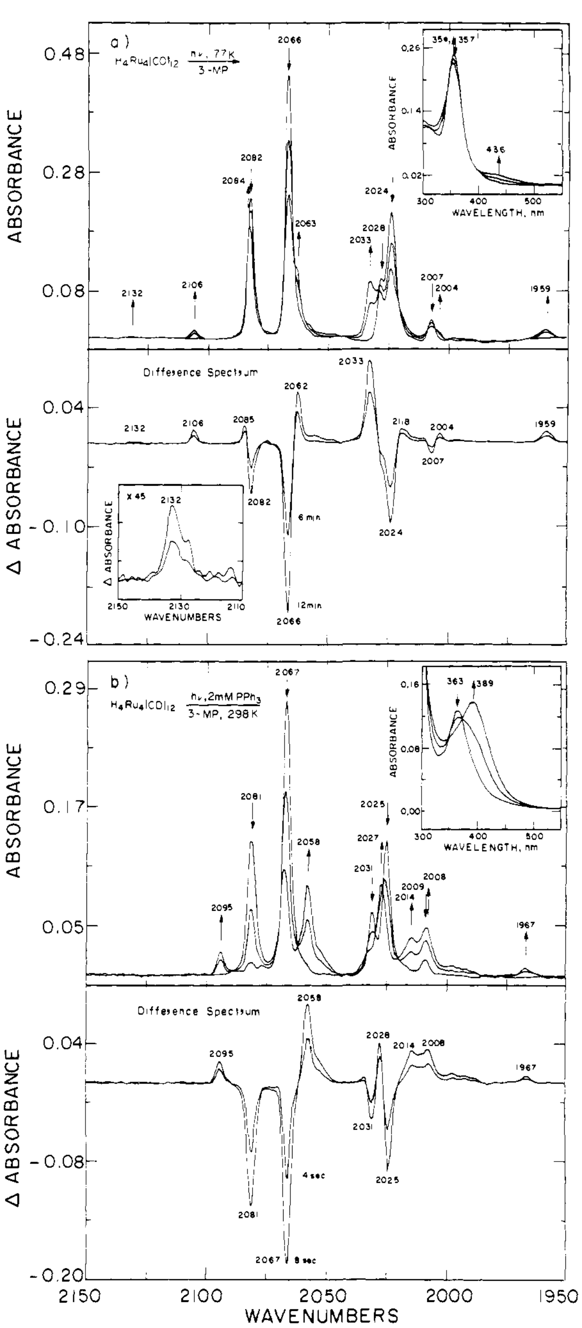

Figure 1. (a) Infrared and UV–vis (top insert) spectral changes (top) and difference spectra (bottom) accompanying near-UV irradiation of $H_4Ru_4(CO)_{12}$ in a 3-methylpentane matrix at 77 K. The band growing in at 2132 cm^{-1} (lower inset) is attributed to free CO in the matrix. The molar absorptivity of the IR band at 2066 cm^{-1} is 53 000 ± 10% M^{-1} cm^{-1} and that of the UV band at 357 nm is 29 000 ± 10% M^{-1} cm^{-1} for $H_4Ru_4(CO)_{12}$ at 77 K. (b) Infrared and UV–vis (insert) spectral changes (top) and difference spectra (bottom) accompanying near-UV irradiation at 298 K of a 3-methylpentane solution initially containing 0.1 mM $H_4Ru_4(CO)_{12}$ and 2 mM PPh_3. The molar absorptivity of the IR band at 2067 cm^{-1} is 37 000 ± 10% M^{-1} cm^{-1} and that of the UV band at 363 nm is 18 000 ± 10% M^{-1} cm^{-1} for $H_4Ru_4(CO)_{12}$ at 298 K. The photoproduct bands and their intensities are the same as for an authentic sample of $H_4Ru_4(CO)_{11}PPh_3$.

$H_4Ru_4(CO)_{12}$ exhibits an intense low-energy absorption band at 363 nm, which sharpens and blue shifts to 357 nm on cooling to 77 K. Such behavior is characteristic of absorptions associated with metal-centered $\sigma \rightarrow \sigma^*$ transitions.[17] The delocalized σ and

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σ^* orbitals ultimately derive from the octahedral e_g set of the metal d orbitals, with some admixture of s and p character.[18] Surprisingly, the $\sigma \rightarrow \sigma^*$ transition energy for the $H_4Ru_4(CO)_{11}$ is nearly unchanged or even slightly blue-shifted compared to $H_4Ru_4(CO)_{12}$. However, the first absorption feature of $H_4Ru_4(CO)_{11}$ is much lower in energy and intensity than that for $H_4Ru_4(CO)_{12}$. The lower energy, weak absorption is consistent with a significant stabilization of a localized σ^* level that becomes the LUMO,[19] in much the same way that coordinatively unsaturated mononuclear compounds are viewed, e.g., $Cr(CO)_5$ compared to $Cr(CO)_6$.[1,2b]

The finding of clean loss of CO from $H_4Ru_4(CO)_{12}$ at 77 K prompts a consideration of the relative importance of metal–metal vs. metal–ligand bond cleavage in the photosubstitution of two-electron donor ligands, L, for CO at 298 K. If metal–metal bond homolysis is important to photosubstitution in fluid solution, associative substitution at two radical centers is expected to give some $H_4Ru_4(CO)_{10}(L)_2$ as a primary photoproduct, whereas none is expected in the thermal reaction of matrix-isolated $H_4Ru_4(CO)_{11}$ with excess L.[20] We thus used FTIR spectroscopy to determine product distributions at low-extent conversion (<20%) where secondary irradiation is negligible. Room temperature irradiation of 0.1 mM $H_4Ru_4(CO)_{12}$ in a deoxygenated alkane solution containing 2 mM PPh_3 results in clean FTIR and UV–vis spectral changes, Figure 1b, consistent with essentially quantitative formation of $H_4Ru_4(CO)_{11}(PPh_3)$[16] ($\sim$2095 cm^{-1}) at up to 95% conversion of $H_4Ru_4(CO)_{12}$ ($\sim$2081 cm^{-1}). A portion of this same solution was photolyzed at 77 K to generate matrix-isolated $H_4Ru_4(CO)_{11}$. Warming of this glass results in net spectral changes at 298 K which are consistent with conversion of all $H_4Ru_4(CO)_{11}$ to $H_4Ru_4(CO)_{11}(PPh_3)$. These spectral changes are indistinguishable from spectral changes obtained in the 298 K photolysis at a similar extent conversion, Figure 1b. The absence of any $H_2Ru_4(CO)_{12}PPh_3$[21] in the photolyzed mixture rules out loss of H_2 from $H_4Ru_4(CO)_{12}$ at 77 or 298 K. Thus, photosubstitution of $H_4Ru_4(CO)_{12}$ in fluid solution at 298 K is completely accounted for by the intermediacy of photogenerated $H_4Ru_4(CO)_{11}$. In support of loss of CO at 298 K as the dominant photoreaction, we note the absence of $H_4Ru_4(CO)_{10}(PPh_3)_2$ as a primary photoproduct, even at PPh_3 concentrations exceeding 0.1 M. An associative mechanism for photosubstitution is apparently ruled out by the fact that the quantum yield for substitution is independent of entering-group concentration.[10]

Our results are consistent with previous reports that added CO suppresses both the thermal[8c,d,9a,e] and photochemical[10,11] isomerization and hydrogenation of olefins when $H_4Ru_4(CO)_{12}$ is used as a catalyst. Preliminary studies show that photogenerated $H_4Ru_4(CO)_{11}$ reacts thermally with ethylene ($\sim$0.1 M) in an alkane matrix at 77 K. The product has infrared spectral features in the carbonyl region characteristic of $H_4Ru_4(CO)_{11}L$-type compounds[16] different from those observed for $H_3Os_4(CO)_{11}(HC_2HR)$ products isolated[22] from photolysis of solutions containing $H_4Os_4(CO)_{12}$ and $RCH{=}CH_2$. On the basis of these IR spectral features, we tentatively formulate this species as $H_4Ru_4(CO)_{11}(C_2H_4)$. Similar spectral features are observed when $H_4Ru_4(CO)_{12}$ is photolyzed in a neat 1-pentene matrix at 77 K. We are currently working to more fully characterize these "$H_4Ru_4(CO)_{11}$(olefin)" species and to investigate their significance in catalysis.

Note Added in Proof. Recent results show that near-UV irradiation of $H_4Ru_4(CO)_{12}$ in a methylcyclohexane matrix at 77 K yields CO loss but the $H_4Ru_4(CO)_{11}$ has a different structure than for the $H_4Ru_4(CO)_{11}$ in the 3-methylpentane matrix. Warmup of the $H_4Ru_4(CO)_{11}$ in methylcyclohexane yields the structure generated in 3-methylpentane. These findings will be elaborated in the full paper.

Acknowledgment. This research was supported in part by the Office of Naval Research and the National Science Foundation. We appreciate helpful discussions with Professor R. Hoffmann and the private communication of calculations relating to $H_4Ru_4(CO)_{11}$.

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Molecular Design for Hosts in Crystalline Host–Guest Complexes

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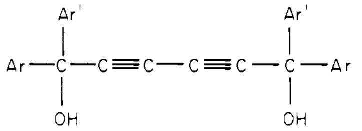
In 1968 F. Toda reported[1] that diacetylenic diol **1** forms crystalline stoichiometric host–guest complexes[2] with a variety of small molecules. Thirty-five different guests, both polar (ketones, aldehydes, esters, ethers, amides, amines, nitriles, sulfoxides, sulfides) and relatively nonpolar (arenes, alkenes, alkynes, haloalkanes), were mentioned. Recently Toda showed that chiral hosts **2** can discriminate between enantiomeric guests.[3]



$$Ar-\overset{Ar'}{\underset{OH}{C}}-C\equiv C-C\equiv C-\overset{Ar'}{\underset{OH}{C}}-Ar$$

1, Ar = Ar′ = Ph
2, Ar ≠ Ar′

Some X-ray structures of Toda's complexes have been determined.[3,4] Features that contribute to complex formation are hydrogen bonding with the OH groups, the linear nature of the acetylenic bond, and π interactions with the aryl rings.

We thought that the overall molecular shape of **1** might also be important in its complex-forming capability. Toda's hosts contain a long molecular axis with sp^3 carbons at each end that bear large, relatively rigid groups. Such host molecules are likely to pack well only when aligned (roughly) along the long axis. The large end groups, however, act as "spacers" which prevent the hosts from packing closely, hence creating substantial voids in the crystal. These voids can then be occupied by guest molecules. In general, the voids might be expected to follow the long molecular axis, leading to channel-type complexes.[4,5] If this structural feature[6] of Toda's compounds is significant, it should be possible

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(6) In our first X-ray paper,[4] we described this shape as "wheel-and-axle". Because wheel may imply rotation, we think the term spacer may be more precise.