There is little parallel between the HMO and HCS analysis of aromatic character.[19,20] Perhaps in restrospect this is to be expected but an intriguing question remains: why does HMO theory reflect so accurately the realities of conjugation in organic π-electron systems?

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(19) The possibility remains that this type of analysis would succeed with other elements such as lithium where the bond strength between pairs of atoms is weaker than it is in hydrogen. The overwhelming stability of diatomic hydrogen in comparison to extended structures is a primary problem in the HCS analysis. The ability of lithium to form a metal contrasts with the molecular solid formed in the solid state by hydrogen (at atmospheric pressure).

(20) The results also throw some doubt on the practice of modeling conjugated organic polymers with HCS.

Carbene Insertion into Methanol: A Case of Reversible Ylide Formation

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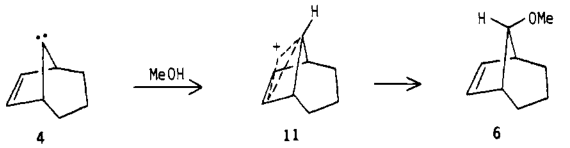
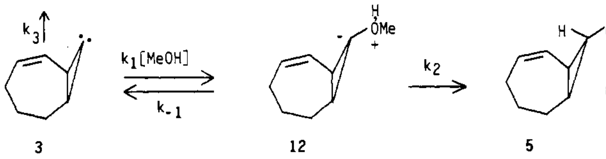
We[1] recently demonstrated that the Skattebol rearrangement[2] of **3** (to **4**)[3] proceeds via free carbenes. To gain insight into the mechanism(s) by which these carbenes insert into MeOH, we investigated the solvent deuterium isotope effects for the reaction shown in Scheme I.

Three general mechanisms for the insertion of **3** and **4** into MeOH may be considered: (1) initial protonation to give a carbocation[4] (e.g., eq 1), (2) possibly reversible[4a,5] ylide formation (e.g., eq 2), and (3) direct, three-center, O–H bond insertion. Table I summarizes the isotope effect data we have obtained at room temperature. The percent deuterium incorporations were obtained by GC-Ms at low-ionizing voltages.[6] Despite some scatter, the isotope effects are not a function of the [MeOH].[7] Table II displays the temperature-dependent isotope effects, measured in 20% methanolic benzene (or toluene). Rearranged product **6** shows a consistently secondary isotope effect, with small differential activation parameters ($\Delta\Delta H^{\ddagger} \approx 50$ cal/mol, $\Delta\Delta S^{\ddagger} \approx 0$). This is consistent with a constant mechanism over the temperature range studied. Although a secondary isotope effect might be unexpected for either the protonation (eq 1) or direct insertion mechanisms, it is appropriate for eq 1 if the reaction is close to diffusion controlled.



(1)



(2)

Scheme I

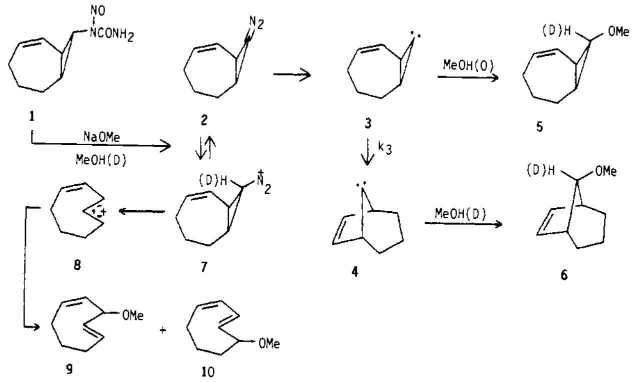
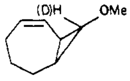
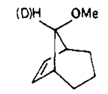


Table I. Room Temperature Solvent Isotope Effect Data[a,b]

conditions	k_H/k_D[e]  **5**	 **6**
30% methanol[c]	1.15	1.17
50% methanol[c]	1.41	1.10
80% methanol[c]	1.15	1.08
100% methanol[c]	1.33	1.23
MeOH:MeOD = 1:2 (v/v)[d]	1.13	1.19
MeOH:MeOD = 1:1 (v/v)[d]	1.15	1.08
MeOH:MeOD = 2:1 (v/v)[d]	1.06	0.93

[a] All reactions were carried out at [**1**] = 0.051 M, [NaOMe] = 0.185 M, and with benzene as the cosolvent. [b] Deuterium incorporations in 80% MeOD/20% PhH were **5**, 98.3%; **6**, 99.9%. [c] MeOH:MeOD = 1:1 (v/v). [d] Total methanol = 80%. [e] The error is difficult to estimate, but from duplicate runs, ± 0.05 to ± 0.15 seems reasonable.

Table II. Variable-Temperature Solvent Isotope Effects

temp, °C	k_H/k_D **5**	**6**
40[a]	1.06	0.96
24[a]	1.15	1.01
10[a]	1.20	1.02
−78[b,d]	2.21	1.10
−78[c,d]	2.85	1.25

[a] Reactions in 40% MeOH/40% MeOD/20% benzene (by volume), with [**1**] = 0.051 M and [NaOMe] = 0.185 M. [b] Reaction in 40% MeOH/40% MeOD/20% toluene with same [**1**] and [NaOMe] as at high temperatures. [c] Same as *b*, but with MeOH:MeOD = 1:2. [d] Deuterium incorporations in 80% MeOD/20% toluene were **5**, 94.5%; **6**, 99.2%. This may indicate a small amount of **5** arises from unexchanged **7** at −78 °C.

Table III. Activation Parameters Based on **6**/**5** Ratios[a]

$R[\text{slope(high } T)] = \Delta H_1^{\ddagger} - \Delta H_3^{\ddagger} = -4.9 \pm 0.3$ kcal/mol
$-R[\text{intercept(high } T)] = \Delta S_1^{\ddagger} - \Delta S_3^{\ddagger} = -26 \pm 1$ eu
$R[\text{slope(low } T) - \text{slope(high } T)] = \Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} = 3.7\text{–}4.9$ kcal/mol
$-R[\text{intercept(low } T) - \text{intercept(high } T)] = \Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger} = 13\text{–}19$ eu

[a] Data is corrected for k_H/k_D differences.

The dramatically different isotope effect seen for **5** at −78 °C is explicable by a change in the rate-determining step with temperature. Thus the first step in eq 2 is rate limiting at the higher temperatures (secondary isotope effect), while the proton-shift step[8] becomes the slow one at low temperature (primary isotope

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(1) Warner, P.; Chu, I-S. *J. Org. Chem.*, accepted for publication.

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(3) Kirmse, W.; Richarz, U. *Chem. Ber.* **1978**, *111*, 1883.

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(6) Isotope effects for **9** and **10** were difficult to determine accurately due to (a) incorporation of only ca. 82% *d* in **9** and 86% *d* in **10** in 80% MeOD/20% PhH and (b) large P-1 and P-2 peaks in the mass spectra. The values obtained at room temperature were k_H/k_D(**9**) = 1.9, k_H/k_D(**10**) = 2.9; at −78 °C they were k_H/k_D(**9**) = 2.5, k_H/k_D(**10**) = 3.4. We do not yet know if these values are really different.

(7) (a) MeOH is aggregated over the entire (high) concentration range we examined. Thus one would not expect the nonlinear behavior seen by Griller[7b] at quite low [MeOH] due to different methanol oligomers. (b) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

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effect).

A completely separate indication of the changing nature of the insertion of **3** into methanol comes from the temperature dependence of the **6**/**5** ratio. Equation 3 was derived from Scheme

$$\frac{[\mathbf{6}]}{[\mathbf{5}]} = \frac{k_3}{k_1[\mathrm{MeOH}]/(1 + (k_{-1}/k_2))} \qquad (3)$$

$$[\mathrm{MeOH}][\mathbf{6}]/[\mathbf{5}] = k_3/k_1 \qquad (4)$$

$$[\mathrm{MeOH}][\mathbf{6}]/[\mathbf{5}] = (k_3/k_1)(k_{-1}/k_2) \qquad (5)$$

I and eq 2. A high (eq 4) and low (eq 5) temperature limit can be recognized. From a plot of ln ([MeOH]([**6**]/[**5**])) vs. $1/T$, the quantitites in Table III were obtained. We note that were ylide formation not reversible at low temperature, the expected **6**/**5** value would be 0.14, rather than the 2.6 observed.[9]

In summary, separate lines of evidence, involving temperature-dependent (a) isotope effects and (b) product ratios, indicate that carbene **3** inserts into methanol via (reversible) ylide (**12**) formation, while carbene **4** inserts via another mechanism (probably protonation). The activation enthalpy for reaction of **3** with methanol is lower than that for rearrangement to **4**, but the latter reaction is kinetically preferred due to entropy. Similarly, ylide **12** is enthalpically favored for kinetic return to **3**.[8] That it does not do so at high temperatures is due to the $\Delta S^{\ddagger}$ term.

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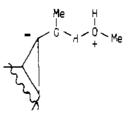
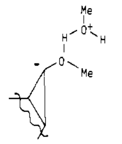
[8] Structure **12** is a simplistic representation of the ylide. Were it present, the 1,2-H shift would be a 4-electron process, disallowed in the suprafacial mode. A better representation might be i or ii or something more complex.



i



ii

The proton transfer may thus gain an appreciable barrier. It is not clear whether the proton transfer is intra- or intermolecular or whether those possibilities are adequately distinguishable in an aggregated solvent medium.

[9] We note that the [**9** + **10**]/[**5** + **6**] ratio, which is dependent upon the equilibrium between **2** and **7** and the rates at which **2** and **7** lose N_2, is linear between −78 and 40 °C, indicating no gross mechanistic changes for those elementary steps.

Electrochemical Reduction of CO_2 Catalyzed by $Rh(diphos)_2Cl$

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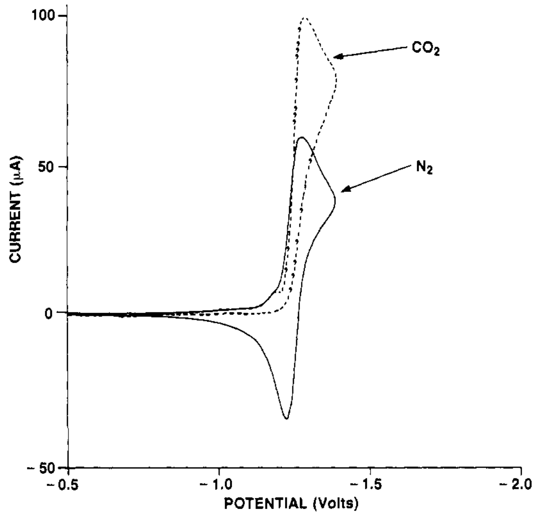

Figure 1. Cyclic voltammogram of 2 mM $Rh(diphos)_2Cl$ in 0.1 M Et_4NClO_4 in CH_3CN at a scan rate of 200 mV/s on a HMDE vs. a silver wire reference electrode.

Table I

mol of $Rh(diphos)_2{}^+Cl^-$	mol of formate	F/mol of cplx	current efficiency, %
1.07	0.85	4.0	42.5
1.07	1.23	6.0	41.0
1.07	1.41	7.0	40.3
1.07	1.70	8.16	41.6
1.07	1.06	9.0	23.6
1.07	1.22	10.6	23.0

The electrochemical reduction of CO_2 may prove to be an important reaction in the development of alternate sources of fuels and chemicals. A major problem associated with this purpose is the high negative potential needed to effect this reduction directly. A number of publications have sought to address this issue by utilizing in situ electrogenerated organometallic catalysts. These catalysts all have in common the ability to lower the effective reduction potential of CO_2, in some cases by up to 1.3 V. To date, the catalysts used have been tetraazamacrocylic transition-metal complexes[1] and the iron–sulfur clusters[2] $Fe_4S_4(SR)_4{}^{2-}$. We now report that the complex $Rh(diphos)_2Cl$[3] (diphos = 1,2-bis(diphenylphosphino)ethane) catalyzes the electroreduction of CO_2 in acetonitrile solution. This rhodium complex was first studied electrochemically by Pilloni and co-workers[4] who reported its electrochemical reduction to the corresponding rhodium hydride proceeded via the anion $Rh(diphos)_2{}^-$, as shown in eq 1. Subsequent investigations of this rhodium[5] system and the analagous iridium[6] system led to the proposal that the mechanism did not involve the anion shown in eq 1 but involved a neutral species $M(diphos)_2{}^0$ produced by the initial step of a three-step mechanism (eq 2a–c). We have investigated the interaction of this neutral electrogenerated species with CO_2 by cyclic voltammetry, and the results are shown in Figure 1.

$$Rh(diphos)_2{}^+ + 2e^- \rightarrow Rh(diphos)_2{}^- \xrightarrow{+H^+} HRh(diphos)_2 \qquad (1)$$

$$Rh(diphos)_2 + e^- \rightarrow Rh(diphos)_2{}^0 \qquad (2a)$$

$$Rh(diphos)_2{}^0 + CH_3CN \rightarrow HRh(diphos)_2 + \cdot CH_2CN \qquad (2b)$$

$$\cdot CH_2CN + e^- \rightarrow {}^-CH_2CN \qquad (2c)$$

As reported earlier,[5] the cyclic voltammogram under a nitrogen or argon atmosphere exhibits a reversible one-electron couple, signifying the formation of the neutral species followed by its reoxidation to the starting rhodium cation (eq 2a). Introduction of CO_2 to the voltammetric system causes the oxidation wave previously observed to disappear, while the current associated with the reduction wave increases substantially. This increase in current is attributed to an electrocatalytic reaction between the electrogenerated species and CO_2. Based on these voltammetric results, constant-current preparative electrolyses were undertaken.

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[1] (a) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. J. *J. Chem. Soc., Chem. Commun.* **1974**, 158. (b) Hiratsuka, K.; Takahashi, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1977**, 1137. (c) Takahashi, K.; Hiratsuka, K.; Sasaki, H.; Toshima, S. *Ibid.* **1979**, 305. (d) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (e) Bradley, M. G.; Tysak, T.; Graves, D. J.; Vlachapoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349.

[2] Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, J. *J. Am. Chem. Soc.* **1982**, *104*, 6834.

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