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 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]

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

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

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

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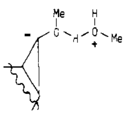
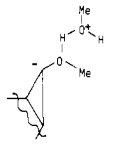
(8) Structure **12** is a simplistic representation of the ylide. Were it present, the 1,2-H shift would be a 4-electron process, disallowed in the suprafacial mode. A better representation might be i or ii or something more complex.



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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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.

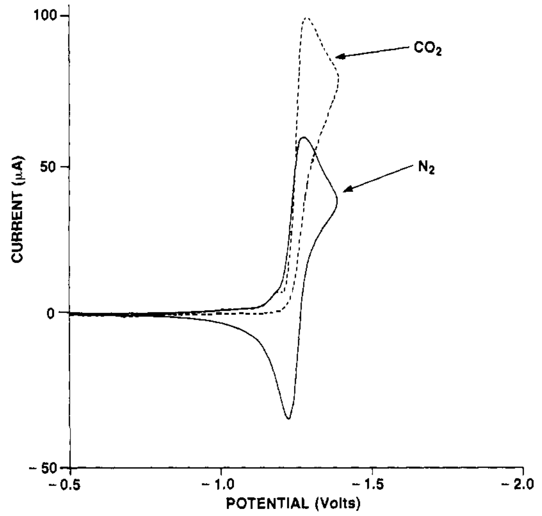

Figure 1. Cyclic voltammogram of 2 mM $Rh(diphos)_2Cl$ in 0.1 M Et_4NClO_4 in CH_3CN at a scan rate of 200 mV/s on a HMDE vs. a silver wire reference electrode.

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

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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.

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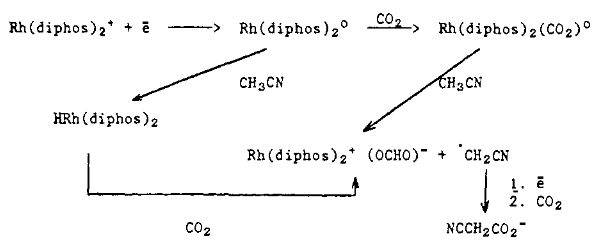
Scheme I



A glass cell was employed in which the anode and cathode compartments were separated by a medium glass frit. The working electrode was a 12-cm^2 mercury pool and the counter electrode was a 10-cm^2 platinum foil. The electrolysis solution was 60 mL of a 0.1 M solution of tetraethylammonium perchlorate in dry acetonitrile. To the catholyte was added 1.0 g of the rhodium complex. Before the electrolysis was started, the catholyte was saturated with CO_2. CO_2 was continually bubbled through the catholyte during the electrolysis. A current of 100 mA was passed through the cell. In the presence of the rhodium complex, the potential of the mercury pool (referenced to a silver wire electrode) varied from an initial value of approximately −1.55 V to a final potential of −1.45 V. In the absence of the rhodium complex, direct electroreduction of CO_2 was observed at −2.23 V. Hence, the presence of the rhodium complex caused a lowering in the reduction potential of CO_2 by approximately 700 mV (not as much lowering as in ref 1 but still significant).

The results of these constant-current electrolyses are shown in Table I. As can be seen, the CO_2 reduction product observed is the formate anion.[7] A small yield of cyanoacetate is also formed (characterized as the methyl ester by GC-mass spectral analysis) suggesting the presence of $(-)CH_2CN$ which was trapped by CO_2. No succinonitrile was detected. It should also be noted that in experiments in which more than 4*F*/mol of rhodium complex were passed, the quantities of formate obtained are greater than the initial molar quantities of $Rh(diphos)_2^+$, hence the reaction is electrocatalytic. The current efficiencies for the production of the formate anion varied between 42% for shorter electrolysis times and 22% for longer electrolytic experiments. The organometallic compounds isolated from the catholyte by sequential extractions with toluene and tetrahydrofuran were $HRh(diphos)_2$ and $Rh(diphos)_2^+$, respectively (60% combined yield). There is no evidence of reaction of CO_2 and $Rh(diphos)_2Cl$ prior to electrolysis.

While no mechanistic studies have been carried out, Scheme I contains our proposals for the mechanistic pathways involved. The electrogenerated species is able to react via two pathways, with CO_2 to generate a $Rh-CO_2$ species or with acetonitrile to produce the hydride (eq 2b). On the basis of the voltammetric results shown in Figure 1, we propose that while hydride formation does take place (as evinced by the isolation of the hydride from the catholyte), the predominant reaction pathway of the electrogenerated species is with CO_2. The rhodium-CO_2 species may then abstract a hydrogen atom from acetonitrile to give the ionic metalloformate derivative thereby regenerating the starting rhodium cation. The proposed metalloformate has been prepared by the interaction of $HRh(diphos)_2$[3] with CO_2 and been shown[8] to be ionized in acetonitrile by ^{31}P NMR spectroscopy and voltammetry. The reaction of $HRh(diphos)_2$ with CO_2 in acetonitrile is a slow reaction and would account for the isolation of the hydride from the catholyte. This last fact could also be a contributing factor to our declining current efficiencies on longer reaction times. This mechanism is supported by the fact that repeating the electrolysis in benzonitrile provides current efficiencies for formate production that are 50% of those obtained in acetonitrile, therefore implicating acetonitrile as the source of the hydrogen atom in the product formate.

Work is continuing in an effort to improve the observed current efficiencies and to extend the lifetime of our electrocatalytic system. We also plan to expand our experiments to include the analogous iridium system.

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(7) The formate anion was characterized by esterifying it to its methyl ester followed by gas chromatographic analysis using the internal standard method for quantitative analysis.

(8) The ^{31}P NMR spectrum[9] and cyclic voltammetric behavior of the rhodium formate is identical with that of $Rh(diphos)_2Cl$, which is known to be a 1:1 electrolyte in acetonitrile.

(9) $^{31}P\{^1H\}$ spectrum: δ -56.86 (relative to H_3PO_4), J_{Rh-P} = 134 Hz.

Photochemical Cycloaddition of *N*-Methyltriazolinedione to Naphthalene

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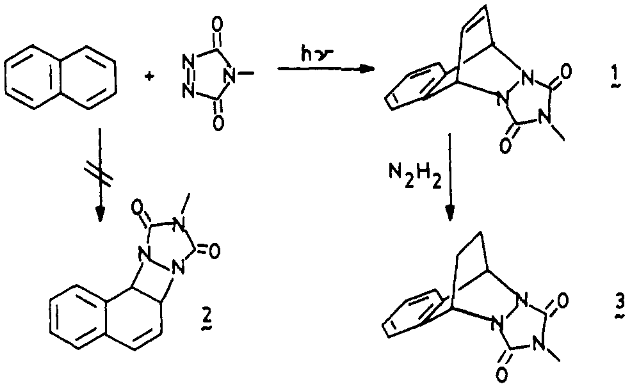
Received April 16, 1984

Additions of triazolinediones to organic molecules have led, inter alia, to a wide variety of 1,2-diazenes.[2] The derived azo compounds are of interest as potential biradical precursors and as routes to novel molecules. In contrast to an abundance of information on the thermal chemistry of triazolinediones, little attention has been paid to the photoadditions of these compounds.[3,4] We now wish to describe the novel photochemical addition of 4-methyltriazoline-3,5-dione (MTAD) to naphthalenes.

Visible irradiation of deaerated solutions of MTAD and naphthalene (15 mM each in CCl_4 or CH_2Cl_2; 1000-W incandescent bulb) for ca. 6 h gives, after solvent removal, a crystalline product. Although the product is thermally and acid labile, flash chromatography on silica gel gives reasonably pure material in ca. 40% yield. Spectroscopic[5] and chemical evidence are consistent with the [4 + 2] structure **1**. In particular, the ^1H NMR spectrum (200 MHz) shows characteristic aa′bb′ multiplets in the aromatic and olefinic/bridgehead regions, similar to other benzobicyclo[2.2.2]octenes.[6] Moreover, only seven signals appear in the ^{13}C NMR spectrum,[5] ruling out less symmetric structures such as **2**. Low-temperature irradiation and subsequent ^1H NMR (both at −78 °C) showed no evidence for the intermediacy of **2**. Adduct **1** can be reduced to **3**, which also exhibits appropriate spectra.[7]



To probe the generality of this reaction, the photoaddition of MTAD to a number of other aromatic compounds was attempted. We find no evidence for photochemical addition of MTAD to

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(1) Recipient of a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry.

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(5) Compound **1** ^1H NMR (200 MHz, $CDCl_3$) Ar AA′BB′ δ_A 7.34, δ_B 7.23 (J_{AB} = 5.4, $J_{AB'}$ = 1.2, $J_{BB'}$ = 6.0 Hz), olefin/bridgehead AA′BB′ δ_A 5.82, δ_B 6.82 (J_{AB} = 4.2, $J_{AB'}$ = 1.6, $J_{BB'}$ = 5.3 Hz), δ 2.9 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.0, 136.8, 134.5, 127.6, 123.5, 56.8, 25.3; IR (KBr) 1760, 1710, 1700 cm^{-1}; MS (30 eV), *m/e* calcd 241.0852, measured 241.0852, base peak 128.

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(7) Compound **3** ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 4 H), 5.25 (br s, 2 H), 2.90 (s, 3 H), 2.35 (m, 2 H), 1.65 (m, 2 H); MS (30 eV), *m/e* calcd 243.1009, measured 243.1008.

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