resents a rare example[15] of clean chirality induction to an sp^2 carbon which is not part of a ring, during a carbon-centered free-radical cyclization. Furthermore, the highly efficient insertion of the oxygen atom at C-22 into the C–Si bond[16] of the heterocyclic units **4** and **9** has provided a novel entry to the synthesis of the 22-hydroxylated natural and 20-iso-steroid side chains.

The results described herein have considerable implications beyond the synthesis of the steroid side chains. We believe that this type of chirality transmission approach employing the α-silyl radical-mediated cyclization should have the potential to be effectively applied in the synthesis of various acyclic molecules or their equivalents.

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Photoreduction of CO_2 to CH_4 in Aqueous Solutions Using Visible Light

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Reduction of CO_2 to combustible organic products by means of solar light is of substantial interest as a means for solar energy conversion and storage.[1-3] Serious attempts have recently been directed toward the development of light-induced CO_2-fixation processes.[4-7] Reduction of CO_2 to carbon monoxide,[4] formate,[5,6] and other organic acids[7] has been reported, using homogeneous catalysts,[4,5] semiconductor particles,[6] or artificially enzyme catalyzed coupled systems.[7] Reduction of CO_2 to methane, the methanation process (eq 1), is of substantial industrial importance.[8,9]

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (1)$$

This reaction proceeds at high temperatures and pressures and is catalyzed by metal catalysts such as Ru, Mo, and Ni. Electrocatalyzed reduction of CO_2 using Ru electrodes has been reported.[10] Here we wish to report on the photocatalyzed reduction of CO_2 to methane using tris(bipyrazine)ruthenium(II), $Ru(bpz)_3^{2+}$, as sensitizer[11] and a Ru metal colloid as catalyst for the process.

The system is composed of an aqueous solution, pH 9.5, that includes $NaHCO_3$, 0.05 M, $Ru(bpz)_3^{2+}$, 1×10^{-4} M, triethanolamine, TEOA, 0.17 M, as electron donor, and a Ru colloid, 20 $mg \cdot L^{-1}$, prepared by the citrate reduction method.[12] Illumination of this system under a gaseous atmosphere of CO_2, $\lambda > 420$ nm, results in the formation of methane. Methane analysis was performed by gas chromatography (Porapak T column) by comparison to an authentic sample as well as by mass spectrometry. The rate of CH_4 formation at time intervals of illumination[12] is displayed in Figure 1a and corresponds to a quantum yield of $\phi = 0.0025\%$. Exclusion from the system of the sensitizer, $Ru(bpz)_3^{2+}$, or the Ru colloid prevents the formation of CH_4. Similarly, exclusion of $NaHCO_3$ and CO_2 eliminates any production of methane. These results imply that all of the components are essential for the reduction of CO_2 to CH_4. The turnover number of $Ru(bpz)_3^{2+}$ is 15, implying a cyclic activity of the system.

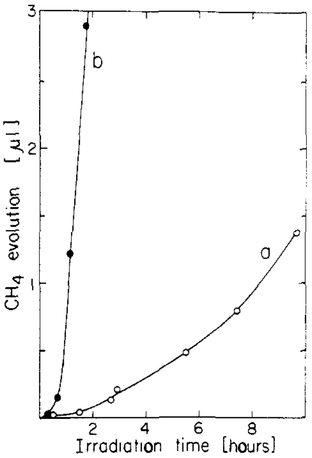

Figure 1. Rate of CH_4 formation as a function of illumination time: (a) in H_2O; (b) in water–ethanol 2:1 solution.

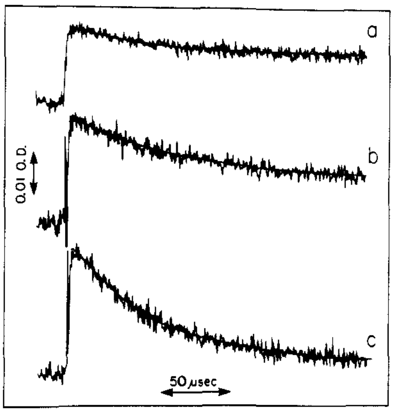

Figure 2. Transient spectra formed upon illumination of $Ru(bpz)_3^{2+}$, 2.2×10^{-5} M and TEOA, 0.17 M solution pH 9.5. Systems are flashed at $\lambda = 440$ nm and product is followed at $\lambda = 500$ nm: (a) under CO_2 or argon; (b) in the presence of Ru colloid (20 $mg \cdot L^{-1}$) under argon; (c) in the presence of Ru colloid (20 $mg \cdot L^{-1}$) under CO_2.

The photophysical properties of $Ru(bpz)_3^{2+}$ have been studied in detail.[11,13] It exhibits a long-lived excited state ($\tau = 1.04$ μs) that is reductively quenched by triethanolamine, TEOA (eq 2),

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (2)$$

$k_q = 2 \times 10^8$ M^{-1} s^{-1}. The photoproduct, $Ru(bpz)_3^+$, formed by the electron-transfer process is a powerful reductant, $E°[Ru(bpz)_3^+/Ru(bpz)_3^{2+}] = -0.86$ V vs. SCE.

The reduction potential for half-cell reaction of CO_2 reduction to CH_4 (eq 2) at pH 7 corresponds to $E°' = -0.24$ V vs. NHE.[14] Electrochemical studies[10] have indicated that CO_2 is reduced to CH_4 at a Ru electrode at an applied potential that corresponds to -0.5 V vs. SCE. Thus, photogenerated $Ru(bpz)_3^+$ is thermo-

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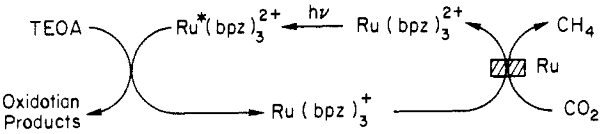

Figure 3. Schematic cycle for the photosensitized reduction of CO_2 to CH_4.

dynamically capable of reducing CO_2 to CH_4. To account for the functions of the different components included in the system that leads to the reduction of CO_2, a laser flash photolysis study was performed (Figure 2). Flashing a system that includes $Ru(bpz)_3^{2+}$ and TEOA under an inert Ar atmosphere results in the trace displayed in Figure 2a. Namely, flashing of the system results in the formation of $Ru(bpz)_3^{+}$. This photoproduct decays for ca. 80 μs, as a result of back reaction with $TEOA^{•+}$, and later is accumulated as a result of irreversible decomposition of the latter photoproduct. A similar trace is observed under a CO_2 atmosphere, implying that $Ru(bpz)_3^{+}$ is unaffected by CO_2 in the absence of the catalyst. Introduction of the Ru colloid to the $Ru(bpz)_3^{2+}$–TEOA system under Ar atmosphere results upon flashing in the trace displayed in Figure 2b. It is evident that in the presence of the Ru colloid, the photoproduct $Ru(bpz)_3^{+}$ decays ($\tau = 170\ \mu s$), implying that electron transfer to the colloid occurs. We attribute this decay process to a charging process of the Ru colloid[15] by $Ru(bpz)_3^{+}$. Even more interesting is the behavior of flash-photogenerated $Ru(bpz)_3^{+}$ in the presence of the Ru colloid and CO_2 (Figure 2c). It can be seen that in the presence of these two components $Ru(bpz)_3^{+}$ rapidly decays and its lifetime is considerably shortened ($\tau = 50\ \mu s$), as compared to the system in the absence of CO_2 or the system where the Ru colloid is excluded. These results clearly indicate that electron transfer from $Ru(bpz)_3^{+}$ is very rapid in the presence of the Ru colloid and CO_2 together. This effect might be attributed to either improvement of the charging capability of the Ru colloid (via, for example, electron transfer from the colloid to adsorbed CO_2), or to direct reduction of CO_2 adsorbed to the metal colloid. Nevertheless, the decay curve of $Ru(bpz)_3^{+}$ in the presence of the Ru metal and CO_2 shows a single exponential decay, and thus the first possibility is preferred. In view of these results, we suggest the schematic cycle presented in Figure 3 as a possible route for the photoreduction of CO_2 to CH_4.

Previous studies have shown that $Ru(bpz)_3^{2+}$ can be effectively reduced by TEOA in ethanol.[10] Thus, we have studied the reduction of CO_2 to methane using $Ru(bpz)_3^{2+}$ as sensitizer, TEOA as electron donor, and the Ru colloid in a mixture of H_2O–ethanol (2:1). The rate of CH_4 formation is displayed in Figure 1b and corresponds to a quantum yield of $\phi = 0.04\%$. The higher quantum yield obtained under these conditions is mainly attributed to the effectiveness of $Ru(bpz)_3^{+}$ formation in this medium. Introduction of the Ru colloid to the photogenerated $Ru(bpz)_3^{+}$ in the water–ethanol mixture results in the evolution of CH_4 and recovery of $Ru(bpz)_3^{2+}$. These results are consistent with the previously described mechanistic cycle outlined in Figure 3. It should be noted that in the absence of CO_2, no H_2 evolution is detected. Thus, the conversion to methane is not considered to proceed via hydrogenation of CO_2 but rather via electron transfer to metal-activated CO_2 followed by protonation. In the electrochemical reduction of CO_2 to CH_4, it has been observed[10] that the Ru electrode undergoes partial oxidation by CO_2 to form CO. In our system no CO formation is detected, yet such partial oxidative corrosion of the Ru colloid is not excluded.

In conclusion, we have demonstrated that the photosensitized reduction of CO_2 to CH_4 can be accomplished with photogenerated $Ru(bpz)_3^{+}$ in the presence of colloidal Ru. The functions of the metal colloid in this process clearly indicate that in the presence of CO_2, electron transfer from $Ru(bpz)_3^{+}$ to the colloid-associated CO_2 is effective. Further experiments utilizing other catalysts and attempts to further characterize mechanistic aspects of the process are now under way in our laboratory.

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Neutral Gas-Phase Analogs of Condensed-Phase Post-Transition-Metal Cluster Ions: Laser Vaporization and Photoionization of Sn/Bi and Pb/Sb Alloys

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The recent development of laser vaporization/molecular beam technology[1] has resulted in numerous studies of gas-phase metal cluster molecules.[2] Various experiments have examined the structures of diatomic[3] and triatomic[4] species, as well as size-dependent properties such as ionization potentials,[5] chemical reactivity,[6] and fragmentation.[7] Semiconductors[8] and other materials[9] have also been included in this growing area of research. Prior to the development of these rather exotic techniques, however, cluster systems had already been studied for many years in condensed phases. For example, borane,[10,11] carborane,[10–12] transition-metal carbonyl,[13] and post-transition-metal ion[14–17] cluster systems are well characterized. In general, condensed-phase clusters have limited volatility and are coordinatively saturated with external ligands so that detailed comparisons with bare-metal gas-phase species are not possible. However, ionic clusters of the post-transition elements (Sn_5^{2-}, Pb_9^{4-}, Bi_9^{5+}, etc.)[15] are ligand-free, consisting of charged metal polyhedral networks accompanied by counterions. These systems have been investigated extensively through NMR and X-ray diffraction experiments[15] and theoretical treatments using molecular orbital methods as well as less rigorous electron counting techniques.[13,14] In this report we describe the observation of neutral gas-phase counterparts to these condensed-phase ionic clusters. These results establish one of the few existing links between cluster research in these different environments.

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