Midland, MI. DMSO was dried over 4-Å molecular sieves. Exact FAB mass spectra were obtained on an Extrel 4000 instrument in the positive-ion detection mode. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The MALDI mass spectra were acquired using a PerSeptive Biosystems Voyager RP time-of-flight mass spectrometer. Positive-ion mass spectra were acquired in the linear mode, and the ions were generated by using a nitrogen laser (337 nm) pulsed at 3 Hz with a pulse width of 3 ns. Ions were accelerated at 30000 V and amplified using a multichannel plate. Spectra (70 to 180) were summed into a 500-MHz Techtronix digital storage oscilloscope and downloaded to a computer for data processing. All data processing was performed using GRAMS (Gallactic Industries, Salem, NH). Spectra of TEMPO-labeled dendrimers were obtained using a *trans*-3-indoleacrylic acid matrix with a matrix:-analyte ratio of 8000:1. Bovine serum albumin (BSA, MW = 66431 g mol^{-1}) was used as an external standard. An aliquot corresponding to 12 pmol of the analyte was deposited on the laser target.[9] The MALS analyses were performed by Wyatt Technology Corporation, Santa Barbara, CA, using a DAWN EOS detector with a solid-state laser operating at 690 nm. Nanopure water (G-6-TEMPO-80) or 17 mM acetic acid (G-6-TEMPO-198) were used as solvents. The EPR spectra were recorded on a Varian E9 X-band spectrometer with a field of 3368 G, a modulation frequency of 100 kHz, a modulation amplitude of 1 G, and a microwave power of 10 mW.

2: 4-Amino-TEMPO (**1**) was first purified by gradient elution flash chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 4/1). Succinic anhydride (1.6 g) was added to the purified 4-amino-TEMPO (2.8 g) in THF (150 mL), and the reaction mixture was stirred at ambient temperature for 18 h. The solvent was evaporated to near dryness, and the residue subjected to gradient elution flash chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 9/1). The hygroscopic solid was immediately used in the next step. Yield 2.1 g (47%). Exact FAB mass spectrum: 273.1797 [M^+], calcd: 273.1814.

3: Compound **2** (8.0 g) was dissolved in THF (300 mL), after which first NHS (3.45 g) and then EDAC (5.8 g) were added. The mixture was stirred at ambient temperature for 18 h. The solvent was evaporated, the residue redissolved in $CHCl_3$ (300 mL), and the mixture extracted with water (2 × 100 mL). The organic phase was then separated and dried over $MgSO_4$, and its volume reduced to about 10 mL. The product was isolated by gradient elution flash chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 9/1). Yield 8.5 g (78%). Exact FAB mass spectrum: 370.1972 [M^+], calcd: 370.1978.

General procedure for the preparation of G-6-TEMPO-198 and G-6-TEMPO-80: A 10% stock solution of G-6 PAMAM™ dendrimer (15 mL) was lyophilized and the resultant solid heated to 80 °C in DMSO (200 mL) to affect complete dissolution. A solution of active ester **3** (6.0 g or 0.98 g, respectively) in DMSO (100 mL) was then added, followed by triethylamine (100 mL). The reaction mixture was then stirred at 90 °C for 72 h. After cooling, the triethylamine was removed by evaporation and the solution diluted with 10% aqueous acetic acid (300 mL) and methanol (200 mL). Unchanged active ester and *N*-hydroxysuccinimide were removed by ultrafiltration with deionized water by using a stirred cell (Amicon, MA) fitted with a 30-K membrane (Filtron, MA). Occasional precipitation of a solid material in the cell occurred. In such cases, the precipitate was brought back into solution by the addition of small portions of methanol and 10% aqueous acetic acid, after which the diafiltration was continued until no low molecular weight species were detected inside the cell (size-exclusion HPLC). The resulting solute was lyophilized to obtain the products as light orange powders. G-6-TEMPO-198: C 53.72, H 8.56, N 16.10. MALDI-TOF mass spectra: number average MW 101000; weight average MW 102000. G-6-TEMPO-80: C 49.56, H 8.13, N 16.75. MALDI-TOF mass spectra: number average MW 71000; weight average MW 72000.

Reoxidation of TEMPOL-H by spin-labeled dendrimers: The oxidation of TEMPOL-H (1 mM) to TEMPOL by TEMPO-conjugated dendrimer in the presence of 50 μM dendrimer was performed in Ar-saturated water (G-6-TEMPO-198) or Ar-saturated PBS (G-6-TEMPO-80 and G-6), and measured as a function of time. The plotted signal intensity due to the reoxidized TEMPOL-H (divided by gain, see Figure 1) was adjusted by subtracting the signal intensities of blank solutions of G-6-TEMPO-198 or G-6-TEMPO-80.

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Photochemical Carbonylation of Ethane under Supercritical Conditions**

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The photochemical carbonylation of hydrocarbons and aromatic compounds [Eq. (1)] by rhodium catalysts of the general formula [Rh(CO)L_2Cl] (where L = PMe_3, PPh_3) is

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well known,[1] and the mechanism of these reactions has been examined by several groups.[2] This reaction has been extended to liquid propane[3] and recently the carbonylation of benzene to benzaldehyde and benzyl alcohol in supercritical CO_2 ($scCO_2$), has been reported in the patent literature.[4]

Methane and ethane are the major constituents of natural gas and are attractive C_1 and C_2 synthons for organic synthesis. Direct conversion to their alcohols would be particularly attractive, but carbonylation to the $n+1$ aldehydes would also open up a significant hydrocarbon reservoir to nonfuel applications. A wide range of catalytic reactions have been examined in supercritical media[5, 6] although to the best of our knowledge only the patent noted above has utilized the $[Rh(CO)(PMe_3)_2Cl]$ photochemical catalyst. The research presented herein was undertaken to establish whether photocatalytic carbonylation could be extended to methane and ethane, and to provide a preliminary understanding of the behavior of the catalyst under supercritical conditions.

Supercritical ethane, sc-ethane, ($T_c = 32.1\,^\circ C$, $P_c = 48.8$ atm) is an excellent solvent for organometallic catalysts. As the introduction of solutes and gases such as CO alters the phase behavior of supercritical fluids, photochemical studies in these single-phase mixtures were carried out at ethane pressures and temperatures well above the critical point.

Single-phase mixtures of ethane (100 atm), CO (13.6 atm), and $[Rh(CO)(PMe_3)_2Cl]$ (5.0 mg) were photolyzed at 60 °C with a high-pressure mercury lamp for 12 h. A quartz-windowed water filter was used to remove IR radiation from the source beam, but otherwise the light was unfiltered. During this time bands of the catalyst (1969 cm^{-1}) were found to decrease slightly, while a new band grew in at 1734 cm^{-1}. After photolysis the reaction mixture was vented into a cooled Schlenk flask and the recovered product was analyzed by mass spectrometry, which confirmed the presence of propionaldehyde. No effort has been made to optimize the yields from these photolyses.

Poliakoff and co-workers have photolyzed $[Cp^*Ir(CO)_2]$ ($Cp^* = C_5Me_5$) in single-phase mixtures of methane (270 atm, 295 K) and observed the oxidative addition product, $[Cp^*Ir(CO)(H)(CH_3)]$ by IR spectroscopy.[6h] Under similar conditions (300 atm methane, 10 atm CO, 308 K) we detected no bands attributable to $[Rh(CO)(PMe_3)_2Cl]$ in the supercritical phase. The lack of solubility of the catalyst under these conditions made it impossible to proceed with the photochemical studies.

Our inability to carry out the photolyses in sc-methane prompted us to examine the possibility of using a mixed-solvent system with $scCO_2$ ($T_c = 31.1\,^\circ C$, $P_c = 73$ atm) as the primary medium. The solubility of the rhodium compound in single-phase mixtures of CO_2 (40 °C, 75 – 90 atm) was established by using the Chrastil relationship.[7] Under the conditions used in our studies the solubility of the rhodium catalyst was found to be on the order of 8×10^{-5} M, and the rhodium catalyst displayed strong bands in the metal carbonyl region of the IR spectrum. Full details of this methodology for determining the solubilities in $scCO_2$ will be published separately.[8]

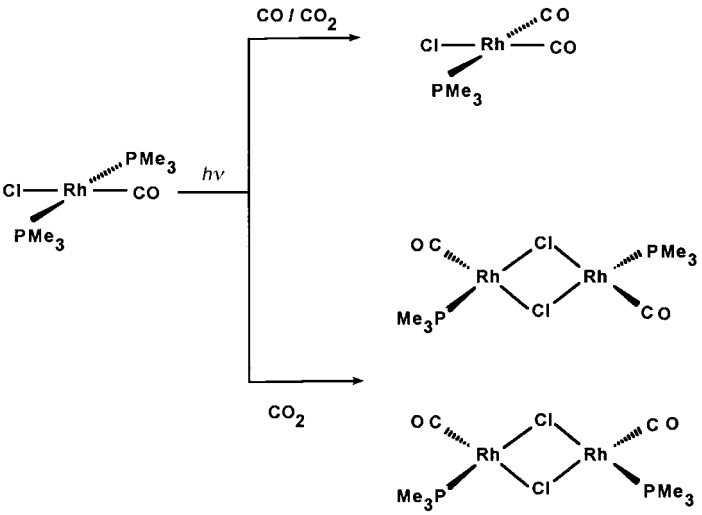
Photolysis of a mixture of single-phase mixtures of CO_2 (110 atm), CO (10 atm), and ethane (34 atm) with 3.4 mg of catalyst at 40 °C for 12 h resulted in the decrease in the band for the catalyst (1966 cm^{-1}) and the appearance of a new band at 1743 cm^{-1}. After photolysis the reaction mixture was vented into $CDCl_3$, and an NMR spectrum confirmed the presence of propionaldehyde. Yields are less than 5% based on initial loading of ethane under these conditions.

Attempts to carry out analogous reactions with methane in single-phase CO_2 mixtures were unsuccessful in that no new bands were observed in the region where one might expect the carbonyl stretching band of acetaldehyde, nor was any aldehyde detected by NMR spectroscopy of the vented reaction mixtures. Neither increasing the photolysis times nor the pressure of methane altered these results.

To our surprise we have found that the rhodium catalyst reacts slowly thermally and more rapidly photochemically with CO (10 atm) in single-phase CO_2 mixtures to give a product with IR bands at 2102 and 2006 cm^{-1}. In contrast, high-pressure IR studies established that $[Rh(CO)(PMe_3)_2Cl]$ did not thermally react with CO (34 atm) in petroleum ether over two days. $[Rh(CO)_2(PMe_3)Cl]$ has been found to display IR bands at 2093 and 2001 cm^{-1} in petroleum ether,[9] and we tentatively assign the new bands in the CO_2 mixtures to this species.

When the rhodium catalyst was photolyzed in single-phase CO_2 mixtures without other reactants a band at 1984 cm^{-1} was found to grow in as the catalyst band diminished. This mixture was vented into a Schlenk flask in a dry box, and the nonvolatile products were taken up into air-free $CDCl_3$. ^{13}P NMR spectroscopy established the presence of $OPMe_3$ in the photolyzed sample, as well at a new doublet at $\delta = 27.0$ ($J_{Rh,P} = 116$ Hz). Bands at 1983 cm^{-1} have been observed in petroleum ether solutions of $[Rh_2(CO)_4(\mu\text{-}Cl)]$ and PMe_3 (1:2) and are attributed to the formation of *cis*- and *trans*-$[Rh_2(CO)_2(PMe_3)_2(\mu\text{-}Cl)_2]$. The reactions of the rhodium catalyst in CO_2 with and without excess CO are presented in Scheme 1.

It is known that $[Rh(CO_2)(PBu_3)_2Cl]$ undergoes slow thermal decomposition at room temperature to $[Rh(CO)(OPBu_3)(PBu_3)Cl]$,[10] and that $[Rh(PR_3)_3Cl]$ and excess



Scheme 1. Photochemical reaction of $[Rh(CO)(PMe_3)_2Cl]$ in $scCO_2$ with and without excess CO.

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phosphane react catalytically with CO_2 in refluxing decalin (ca. 185 °C) to give OPR_3 in the rate order $PPh_3 < PBuPh_2 < PEt_3$.[11] The rate for the PPh_3 derivative is about 20 turnovers per day. In the current studies, it appears that CO_2 undergoes reaction with the catalyst to give $OPMe_3$. In the presence of an excess of CO $[Rh(CO)_2(PMe_3)Cl]$ is formed, while in the absence of CO $[Rh_2(CO)_2(PMe_3)_2(\mu\text{-}Cl)_2]$ is formed. We are presently investigating the mechanism of this reaction.

These studies have established the feasibility of carrying out photocatalysis of ethane to propionaldehyde in either single-phase ethane or CO_2 mixtures. A competing side reaction probably involving CO_2 cleavage and phosphine oxide formation may preclude the use of CO_2 as a medium for these rhodium catalysts.

Experimental Section

A thermostated, stainless steel, high-pressure photolysis cell fitted with CaF_2 IR windows and a sapphire photolysis window was used in all high-pressure studies. The cell volume is about 12 mL and the IR pathlength is 0.1 mm. A small spin bar inside the cell was used for mixing. The cell was designed with a maximum pressure rating of 700 atm. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT IR Spectrometer. $[Rh(CO)(PMe_3)_2Cl]$ was prepared by standard literature methods.[12]

In a typical reaction, the rhodium catalyst was added to the cell as a solid, then the sealed cell was charged with reactant gases using a high-pressure line equipped with a syringe pump. Gases such as CO_2 and ethane were condensed into the syringe pump by chilling the pump with ice packs and then charged into the heated cell.

Reaction mixtures were photolyzed by using a 350-W high-pressure Hg lamp. A 30-mm quartz-windowed, water filter was used to remove IR wavelengths from the incident beam. Photolysis times of 6 – 12 h were used, and IR spectra were recorded at the beginning of each photolysis reaction and at regular intervals during the photolysis. Samples for mass spectrometric and NMR analysis were recovered by venting the sample through a restrictor tube directly into $DCCl_3$ in a N_2-flushed Schlenk flask immersed in an ice water bath.

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Rearrangement of a Tricyclic 2,5-Cyclohexadienone: Towards a General Synthetic Route to the Daphnanes and (+)-Resiniferatoxin**

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The daphnane resiniferatoxin[1] (RTX) and structurally related tiglianes possess complex, densely functionalized architectures, along with important biological activity, that have inspired much innovative research in chemistry and biology. The recent isolation and cloning of the principal receptor targeted by resiniferatoxin holds great promise for the development of RTX-related therapeutics.[2, 3] In this regard, parallel advances in the design and synthesis of analogues is imperative because these may serve as cellular probes and useful pharmacologically important compounds.

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