A CO-bridged $Mn_2(CO)_9$ formed photochemically in alkane matrices at 77 K is reasonable in view of the fact that the first row $Fe_2(CO)_9$ and $Co_2(CO)_8$ are CO-bridged species.[10] The lack of $Mn(CO)_5$ formation could be due to the fact that geminate recombination is efficient in the rigid medium compared to 298 K fluid solutions. Earlier[1] results are consistent with a "cage" effect on the efficiency of formation of solvent-separated $Mn(CO)_5$.[11]

The finding of clean dissociative loss of CO at 77 K in a rigid medium prompts a consideration of the relative efficiency of Mn–Mn scission vs. Mn–C scission at 298 K in fluid solution. We thus irradiated $Mn_2(CO)_{10}$ in solutions containing a two-electron donor, L, PPh_3, or CH_3CN, and a $Mn(CO)_5$ scavenger, CCl_4. The objective of such experiments is to establish whether the presence of CCl_4 would suppress the formation of $Mn_2(CO)_{10-x}L_x$ to determine whether $Mn_2(CO)_{10-x}L_x$ is formed via substitution of $Mn(CO)_5$ followed by radical coupling (eq 3–5)[1,4] or via direct

$$Mn(CO)_5 \xrightarrow{L} Mn(CO)_4L + CO \qquad (3)$$

$$2Mn(CO)_4L \rightarrow Mn_2(CO)_8L_2 \qquad (4)$$

$$Mn(CO)_4L + Mn(CO)_5 \rightarrow Mn_2(CO)_9L \qquad (5)$$

capture of the photogenerated $Mn_2(CO)_9$ (eq 6). If the prompt

$$Mn_2(CO)_9 + L \rightarrow Mn_2(CO)_9L \qquad (6)$$

formation of $Mn_2(CO)_9$ is the exclusive route to the substitution, the expectation is that $Mn_2(CO)_9L$ would be the *only* initial product. However, the $Mn_2(CO)_9L$ could also be very photosensitive in the presence of L and yield $Mn_2(CO)_8L_2$. We thus used a Fourier transform infrared spectrometer to determine the product distributions at very low-extent conversion (<5%) where secondary irradiation is negligible. In an alkalne solvent, near-UV irradiation of $Mn_2(CO)_{10}$ in the presence of 10 mM PPh_3 yields both $Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$ as primary products. In the presence of 10 mM PPh_3 and 10 mM CCl_4 the $Mn_2(CO)_9PPh_3$ is formed with the same chemical efficiency based on $Mn_2(CO)_{10}$ consumed, but no $Mn_2(CO)_8(PPh_3)_2$ is observed. Rather, $ClMn(CO)_4PPh_3$ is formed. The CCl_4 thus suppresses formation of $Mn_2(CO)_8(PPh_3)_2$, but not $Mn_2(CO)_9PPh_3$. The amount of $Mn_2(CO)_9PPh_3$ formed is 30 ± 5% of $Mn_2(CO)_{10}$ consumed in the presence of CCl_4. These data are consistent with formation of PPh_3 substitution products via both Mn–Mn bond cleavage and via prompt loss of CO.

Irradiation of $Mn_2(CO)_{10}$ in CH_3CN solvent initially yields only $Mn_2(CO)_9(CH_3CN)$.[12] Irradiation in CH_3CN containing CCl_4 initially yields both $Mn_2(CO)_9(CH_3CN)$ and $Mn(CO)_5Cl$ in a ratio of 1/5 that is the same for CCl_4 concentrations in the range 0.001–3.0 M. The point is that CCl_4 does not suppress the quantum yield for $Mn_2(CO)_9(CH_3CN)$ formation. Irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ in CH_3CN initially yields only $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$; no $Mn_2(CO)_9(CH_3CN)$ is detected. Under the same conditions but in the presence of 100 mM CCl_4, irradiation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ yields $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ and $Mn(CO)_5Cl$. The $Mn(CO)_5$ radicals do not undergo substitution by CH_3CN.

To confirm the lack of substitution of $Mn(CO)_5$ by CH_3CN we have oxidized $Mn(CO)_5^-$ by the outer-sphere, one-electron oxidant $Fe(\eta^5\text{-}C_5H_5)_2^+$ in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ with and without 10 mM PPh_3. In the absence of PPh_3, $Mn_2(CO)_{10}$ is formed as the only product when the $Fe(\eta^5\text{-}C_5H_5)_2^+$ is slowly added to the $Mn(CO)_5^-$.[13] Under the same conditions with 10 mM PPh_3 the products are dominated by $Mn_2(CO)_8(PPh_3)_2$. Thus, PPh_3, but not CH_3CN, will replace a CO of $Mn(CO)_5$ in competition with coupling of the radicals. This result leads to the conclusion that substitution of $Mn(CO)_5$ can occur via an associative mechanism involving a 19-e$^-$ species.[14]

To conclude, dissociative loss of CO from photoexcited $Mn_2(CO)_{10}$ in a rigid matrix yields a CO-bridged $Mn_2(CO)_9$ species that will react with 2-electron donors to yield $Mn_2(CO)_9L$. The rigid matrix apparently precludes the formation of $Mn(CO)_5$ that is invoked in the photochemistry at 298 K in fluid solution.[1] In fluid solution the prompt loss of CO accounts for 30 ± 5% of the excited states that react, and Mn–Mn bond cleavage accounts for the remainder.

Acknowledgment. We thank the National Science Foundation for support of this research. We appreciate the gift of $Mn_2(CO)_{10-x}(^{13}CO)_x$ from Professor Donald J. Darensbourg of Texas A&M University.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_9$, 86633-01-4; $Mn_2(CO)_9$(2-MeTHF), 86633-02-5; $Mn_2(CO)_9PPh_3$, 14592-26-8; $ClMn(CO)_4PPh_3$, 14841-08-8; CO, 630-08-0; CCl_4, 56-23-5; 2-MeTHF, 96-47-9; PPh_3, 603-35-0; CH_3CN, 75-05-8; methylcyclohexane, 108-87-2; 3-methylpentane, 96-14-0.

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[9] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

[10] Wender, I.; Pino, P. "Organic Synthesis via Metal Carbonyls"; Interscience Publishers: New York, 1968. There are several derivatives of Mn carbonyl having a CO bridge: (a) Triplett, K.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 5747–5751 and references therein. (b) Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607–1613.

[11] We note related work on other M–M-bonded complexes where photoreactions other than homolysis of the M–M bond have been invoked: (a) Hughey, J. L., IV; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440–4441. (b) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421–424. (c) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753–2755. (d) Caspar, J. V.; Meyer, T. J. *Ibid.* **1980**, *102*, 7795–7797. (e) Stiegman, A. E.; Tyler, D. R. *Ibid.* **1982**, *104*, 2944–2945.

[12] (a) Koelle, U. *J. Organometal. Chem.* **1978**, *155*, 53–62. (b) Ziegler, M. S.; Haas, H.; Sheline, R. K. *Chem. Ber.* **1965**, *98*, 2454–2459.

[13] If $Fe(\eta^5\text{-}C_5H_5)_2^+$ is present in excess, the $Mn(CO)_5$ radicals are oxidized: Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1261.

[14] It is noteworthy that the $Mn(CO)_5$ radicals are oxidized more rapidly in CH_3CN solvent than in a nondonor solvent[12] consistent with interaction of $Mn(CO)_5$ with CH_3CN. However, in the case of the 19e$^-$ $Mn(CO)_5(CH_3CN)$ the loss of CO does not occur in competition with loss of the CH_3CN. In the oxidation of $Mn(CO)_5$ by TCNE the product is $Mn(CO)_5$(TCNE) and ligation of TCNE to $Mn(CO)_5$ was invoked[12] to account for the fast rate of oxidizing $Mn(CO)_5$.

Enantioselective Carbocyclization: A Facile Route to Chiral Cyclopentanes

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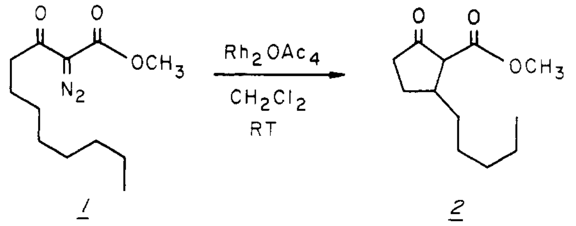
Newark, Delaware 19711

Received March 28, 1983

An aspect of enzyme reactivity that synthetic organic chemists have long envied is the ability to regio- and enantioselectively functionalize an unactivated hydrocarbon chain. To duplicate such a process in the laboratory, it would be necessary to first develop a method for efficient bond formation at an unactivated center ("remote functionalization").[2] It would then be necessary to control the folding of the rapidly coiling hydrocarbon chain in such a way that the desired site was particularly available for reaction. We recently reported a method for remote functionalization that showed excellent regioselectivity (**1** → **2**).[3] We



1 2

now report that substantial chiral induction can in fact be achieved in the course of such cyclizations. This opens a general route to functionalized cyclopentanes of high optical purity, reasonable

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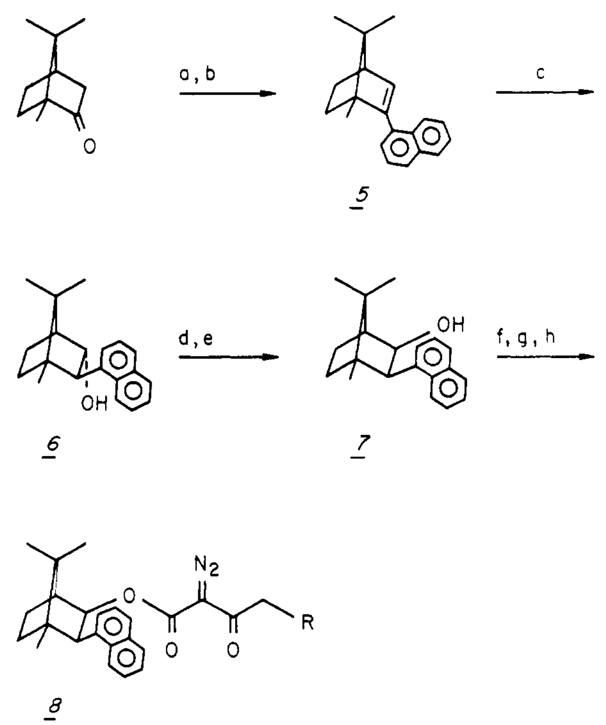
[1] Fellow of the Alfred P. Sloan Foundation, 1983–1985.

[2] Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

[3] Taber, D. F.; Petty, E. H. *J. Org. Chem.* **1982**, *47*, 4808.

0002-7863/83/1505-5935$01.50/0

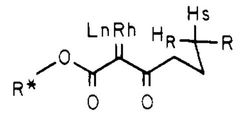
Scheme I



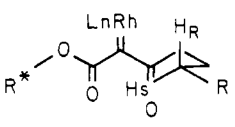
[a] α-Naphthylmagnesium bromide, THF, reflux, 18 h. [b] SOCl$_2$. [c] BH$_3$·DMS, PhCH$_3$, reflux, 18 h; NaOH, H$_2$O$_2$. [d] PCC. [e] LiAlH$_4$. [f] Diketene, Et$_3$N. [g] NaH, THF; *n*-BuLi; RBr. [h] TsN$_3$, CH$_3$CN.

precursors to the wide variety of cyclopentane-containing natural products.

The substantial preference for five-membered ring formation that we observed[3] suggested a highly ordered transition state. After consideration of molecular models, a transition state such as **3** seemed plausible: the first three methylenes of the chain have



3



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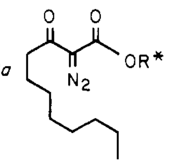
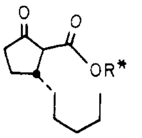
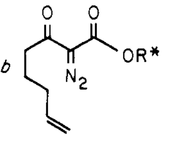
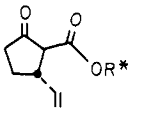
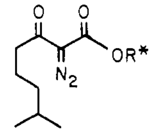
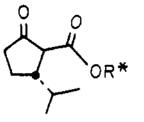
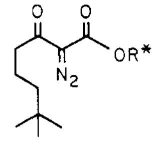
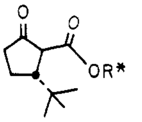
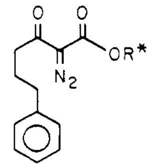
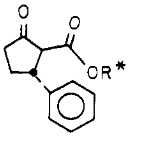
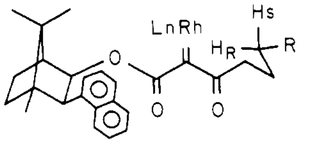
adopted a staggered conformation, leading to a chair-like six-membered ring, with the hydrogen atom that is to be transferred (H$_R$)[4] being included in the ring. The assumption was that the pendant alkyl group should be equatorial, as shown.

It should be noted that the transition-state enantiomeric to **3** is **4**, in which the hydrocarbon chain is swung across the front face of the β-keto ester, rather than the back face. In making this change, the methylene into which insertion will take place has rotated so that now H$_S$ is directed toward the reactive carbenoid center. To achieve enantioselectivity, it is necessary to selectively destabilize one of these two transition states. We sought to achieve such destabilization by judicious choice of a chiral ester R*. After some preliminary experimentation,[5] we have found that esters **8**, derived[6,7,8] from alcohol **7**,[9] readily prepared from camphor (Scheme I),[10,11] cyclize with excellent diastereoselectivity.

Table I

starting diazo ester	product[a]	chemical yield, %[b]	diastereoselectivity[c]
8a 	 9a	60	87:13
8b 	 9b	62	92:8
8c 	 9c	60	83:17
8d 	 9d	55	83:17
8e 	 9e	62	85:15[d]

[a] The absolute configurations of **9a**, **9b**, and **9e** were assigned by correlation with known absolute rotations (ref 13). The major diastereomer is shown. [b] Yield of pure chromatographed material. [c] Diastereoselectivity calculated on the basis of HPLC analysis. [d] Diastereoselectivity calculated by conversion to α,β-unsaturated ester **10** followed by HPLC analysis.



8

We assume that in the intermediate carbenoid the ester is in an extended conformation[12] and that the two carbonyls lie in a plane, as shown. The alternative extended ester conformation is destabilized by a nonbonding interaction with the methyl group at C-7 on the bornane. The naphthalene ring then covers the front

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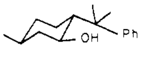
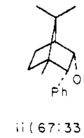
(4) The tacit assumption underlying this analysis is that insertion proceeds with retention of absolute configuration: Ledon, H.; Linstrumelle, G.; Julia, S. *Tetrahedron Lett.* **1973**, 25.

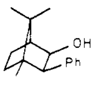
(5) In the course of preliminary studies, we prepared and cyclized the analogues of 8a from chiral alcohols i–iii. The diastereoselectivity observed is given in parentheses.



i (63:37)



ii (67:33)



iii (81:19)

(6) Mauz, O. *Liebigs Ann. Chem.* **1974**, 345.

(7) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

(8) Regitz, M.; Hocker, J.; Liedhegener, A. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V., p 197.

(9) The preparation of 7 (see supplementary material) is derived from the literature procedure for the corresponding phenyl derivative: Coxon, J. M.; Hartshorn, M. P.; Lewis, A. J. *Aust. J. Chem.* **1971**, *24*, 1017.

(10) (+)-Camphor is inexpensive. (−)-Camphor is readily prepared from the inexpensive (−)-borneol: Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2031.

(11) Professor W. Oppolzer has also explored bornane-derived chiral directing groups: Oppolzer, W.; Chapuis, C.; Dao, G. M.; Reichlin, D.; Godel, T. *Tetrahedron Lett.* **1982**, *23*, 4781.

(12) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757 and references cited therein.

face of the β-keto ester, destabilizing transition-state **4** and directing cyclization toward H_R.

We have briefly surveyed the cyclization of a range of representative β-keto esters (Table I). In three of the five cases (**9a**, **9b**, and **9e**), the absolute stereochemistry of the major diastereomer was confirmed by optical rotation.[13] The other two (**9c** and **9d**) are assumed to have the same absolute configuration. While diastereoselectivity is good in all cases, it is better in some cases than in others. We are actively investigating the variables in this reaction, especially the influence of different ligands on rhodium, in an effort to improve diastereoselectivity. In the meantime, it should be noted that the diastereomeric esters are separable chromatographically,[16] opening a practical route to cyclopentane derivatives of high optical purity.

The development of new methods for carbocyclic ring formation is basic to the development of synthetic organic chemistry. As synthetic targets become more sophisticated, the development of strategies for the enantioselective construction of carbocycles will be increasingly important.[17] We propose that the approach outlined above, detailed transition-state analysis leading to design of a substrate for which one of two enantiomeric (diastereomeric)[18] transition states is selectively destabilized, should be applicable to a wide variety of ring-forming reactions.[19]

Acknowledgment. This investigation was supported by CA 22757 and CA 34383, awarded by the National Cancer Institute, DHHS, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Vanderbilt University Research Council.

Supplementary Material Available: Complete experimental details for the preparation of **5–10** (12 pages). Ordering information is given on any current masthead page.

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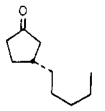
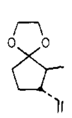
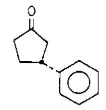
(13) The absolute configuration of **9a** was confirmed by decarbalkoxylation to iv, $[\alpha]_D$ +86.7°. A sample of iv prepared by our published procedure[14]



iv



v



vi

showed $[\alpha]_D$ +107°. Similarly, **9b** was converted (ethylene glycol, H^+; Dibal; *N,N*-dimethylsulfamoyl chloride; Na, lNH_3) to v, $[\alpha]_D$ −23.6° (lit.[15] $[\alpha]_D$ −24.1°). Finally, decarbalkoxylation (Me_2SO, H_2O, NaCl, 170°) of **9e** proceeded, with substantial racemization, to give vi, $[\alpha]_D$ +45.9°. Professor G. Posner (personal communication) reports $[\alpha]_D$ −87.6° for the enantiomer.

(14) Taber, D. F.; Saleh, S. A.; Korsmeyer, R. W. *J. Org. Chem.* **1980**, *45*, 4699.

(15) Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W.-D.; Baier, H.; Adam, F.; Durner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1029.

(16) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

(17) Several strategies for the enantioselective preparation of carbocycles have been reported. For leading references, see: (a) Intermolecular Diels–Alder reaction: Ensley, H. E.; Parnell, C. A.; Corey, E. J. *J. Org. Chem.* **1978**, *43*, 1610. Horton, D.; Machinami, T. *J. Chem. Soc., Chem. Commun.* **1981**, 88. (b) Intramoleculer Diels–Alder reaction: Nicolaou, K. C.; Papahatjis, D. P.; Claremon, D. A.; Dolle, R. E., III *J. Am. Chem. Soc.* **1981**, *103*, 6967. (c) Intermolecular alkylation: Meyers, A. I.; Williams, D. R.; Erickson, G. W.; White, S.; Durelinger, M. *J. Am. Chem. Soc.* **1981**, *103*, 3081. (d) Intramolecular alkylation: Quinkert, G.; Schwartz, U.; Stark, H.; Weber, W.-D.; Baier, H.; Adam, F.; Durner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1029. Yamamoto, K.; Tsuji, J. *Tetrahedron Lett.* **1982**, *23*, 3089. (e) Conjugate addition: Kogen, H.; Tomioka, K.; Hashimoto, S.-I.; Koga, K. *Tetrahedron* **1981**, *37*, 3951. Posner, G. H.; Hulce, M.; Mallamo, J. P.; Drexler, S. A.; Clardy, J. *J. Org. Chem.* **1981**, *46*, 5246. (f) Intramolecular aldol condensation: Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615. Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699. (g) Cyclopropanation: Mukaiyama, T.; Fujimoto, K.; Takeda *Chem. Lett.* **1979**, 1207. Monpert, A.; Martelli, J.; Gree, R.; Carrier, R. *Tetrahedron Lett.* **1981**, *22*, 1961. (h) Biomimetic polyolefin cyclization: Demailly, G.; Solladie, G. *Tetrahedron Lett.* **1980**, *21*, 3355. (i) [2 + 2] cycloaddition: Houge, C.; Frisque-Hesbain, A. M.; Mockel, A.; Declerq, J. P.; Germain, G.; Van Meerssche, M. *J. Am. Chem. Soc.* **1982**, *102*, 2920.

(18) The enantiomeric transition states (e.g., **3** and **4**) become diastereomeric when remote chiral centers (e.g., those of alcohol **7**) are included in the analysis.

(19) It should be noted that the rhodium-catalyzed cyclizations described here are probably mechanistically related to the iridium-mediated distal C–H activation recently reported: Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1982**, *103*, 2448.

Homogeneous Catalysts for Carbon Dioxide/Hydrogen Activation. Alkyl Formate Production Using Anionic Ruthenium Carbonyl Clusters as Catalysts

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College Station, Texas 77843

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The industrial uses of carbon dioxide as a source of chemical carbon are presently limited to the production of carboxylic acids, carbonates, carbon monoxide, and urea.[1] Nevertheless, there are several reports in the literature for the laboratory syntheses of organic substances derived from carbon dioxide.[2] Included in these are the catalytic formations of alkyl formates and formamides. For example, numerous mononuclear transition-metal phosphine complexes ($(Ph_3P)_3RhCl$, $(Ph_3P)_2Ir(CO)Cl$, $(Ph_3P)_2PtCO_3$, etc.) have been shown to be effective catalysts for dimethylformamide formation from the reduction of CO_2 and molecular hydrogen in the presence of dimethylamine.[3] Similarly, the synthesis of methyl formate by CO_2 reduction with H_2 in CH_3OH has been demonstrated to be catalyzed by transition-metal phosphine complexes.[4] More recently Evans and Newell have found the anionic iron carbonyl hydrides $HFe(CO)_4^-$ and $HFe_3(CO)_{11}^-$ to be modest catalysts for conversion of CO_2, H_2, and alcohols into formate esters.[5]

In all of these CO_2 reduction processes identification of reaction intermediates have been lacking, and little definitive understanding of the reaction pathways exists. If carbon dioxide is to become a viable feedstock for organic chemicals, it is paramount that better catalysts for these processes be uncovered and mechanistic aspects of their function be more clearly defined. We have initiated investigations aimed at fully characterizing potential intermediates in CO_2 reduction processes, both with regard to structure and reactivity.[6-10] In this communication we wish to report on the catalytic hydrocondensation of CO_2 and molecular hydrogen by anionic ruthenium clusters in the presence of methanol to provide methyl formate. Effective catalysts for the production of methyl formate utilizing C_1 chemistry is of practical significance since it is an intermediate in the production of formic acid (eq 1)[11] and can be catalytically isomerized to acetic acid (eq 2).[12]

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH \qquad (1)$$

$$HCOOCH_3 \rightarrow CH_3COOH \qquad (2)$$

We have found $HRu_3(CO)_{11}^-$ to be an effective catalyst or catalyst precursor for the production of methyl formate from carbon dioxide via reaction 3. The conditions for the reaction

$$CO_2 + H_2 + CH_3OH \xrightarrow{[\text{catalyst}]} HCOOCH_3 + H_2O \qquad (3)$$

were moderate pressures of carbon dioxide and hydrogen (250 psi of CO_2 and 250 psi of H_2 at ambient temperature) and a

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