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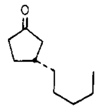
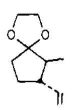
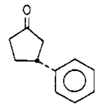
[13] The absolute configuration of **9a** was confirmed by decarbalkoxylation to iv, $[\alpha]_D$ +86.7°. A sample of iv prepared by our published procedure[14]



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.

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[16] Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

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[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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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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Table I. Formation of Methyl Formate from the Oxides of Carbon Using Anionic Ruthenium Carbonyl Clusters[a]

run	catalyst[b]	P_{CO_2}[c]	P_{H_2}[c]	P_{CO}[c]	turnovers[d]
1	$HRu_3(CO)_{11}^-$	250	250		4.1
2	$HRu_3(CO)_{11}^-$	250	250		3.8
3	$HCO_2Ru_3(CO)_{10}^-$	250	250		5.7
4	$H_3Ru_4(CO)_{12}^-$	250	250		7.3
5	$Ru_3(CO)_{12}$	250	250		<0.3
6	$HCO_2Ru_3(CO)_{10}^-$	250	250	100	4.1
7	$HCO_2Ru_3(CO)_{10}^-$	250	250	250	3.9
8	$HCO_2Ru_3(CO)_{10}^-$		250	250	6.3
9	$HRu_3(CO)_{11}^-$			250	106[e]
10	$HRu_3(CO)_{11}^-$		250	250	40
11	$H_3Ru_4(CO)_{12}^-$			250	88

[a] Temperature 125 °C and reaction time 24 h. Methanol used as solvent. [b] Catalyst concentrations were all 9.2×10^{-3} M, and the counterion was PPN = *bis*(triphenylphosphine)imminium. [c] Loading pressures at ambient temperature in psi. [d] Turnover = mol of HCO_2Me/mol of catalyst. [e] A control reaction carried out employing $HRu_3(CO)_{11}^-$ as catalyst under 250 psi of pure nitrogen (at ambient temperature) and 125 °C resulted in *no* formation of methyl formate.

temperature of 125 °C (see Table I).[13] A catalyst turnover rate of 3.8–4.1 per 24 h was observed under these circumstances with an equivalent quantity of water being detected. The $HCO_2Ru_3(CO)_{10}^-$ species, which constitutes a suspect intermediate in reaction 3 catalyzed by $HRu_3(CO)_{11}^-$, displayed a slightly greater catalytic activity for alkyl formate production with a turnover rate of 5.7 per 24 h. This metalloformate species has been synthesized independently from either $Ru_3(CO)_{12}$ and $[PPN][O_2CH]$ or CO_2 insertion into $HRu_3(CO)_{11}^-$, and it has been fully characterized.[10]

In both instances, i.e., utilizing either $HRu_3(CO)_{11}^-$ or $HCO_2Ru_3(CO)_{10}^-$ as catalyst precursor, the metal carbonyl species recovered in near quantitative yield at the end of a 24-h reaction period was the tetraruthenium derivative, $H_3Ru_4(CO)_{12}^-$. Subsequent catalytic runs employing $H_3Ru_4(CO)_{12}^-$ as catalyst reveal this anionic carbonyl hydride to be slightly more effective at catalyzing the production of methyl formate with a turnover rate of 7.3 being observed. $H_3Ru_4(CO)_{12}^-$ was recovered unchanged at the end of a 24-h catalytic run. Hence, it is *suggested* that a tetranuclear species is the catalytically active species during all the experiments described above.

Formation of $H_3Ru_4(CO)_{12}^-$ from the Ru_3 units is indicative of some degree of cluster fragmentation. This reaction was observed to be reversible under a carbon monoxide atmosphere, where $H_3Ru_4(CO)_{12}^-$ yields $HRu_3(CO)_{11}^-$. Indeed the stoichiometry of this reaction has been established by Shore and co-workers[14] to be as described in eq 4, where an equilibrium constant of 0.02

$$3[H_3Ru_4(CO)_{12}]^- + 9CO \rightleftarrows 3HRu_3(CO)_{11}^- + Ru_3(CO)_{12} + 3H_2 \quad (4)$$

at 60 °C and a total gas pressure of 1 atm in glyme was determined. In addition, the well-characterized analogous reaction of the neutral tetraruthenium species with CO also affords the Ru_3 core according to the stoichiometry described in eq 5.[15,16]

$$H_4Ru_4(CO)_{12} + 5CO \rightleftarrows Ru_3(CO)_{12} + Ru(CO)_5 + 2H_2 \quad (5)$$

Since cluster fragmentation is obviously occurring under the conditions of catalysis, the ubiquitous issue of the involvement of mononuclear catalytically active species presents itself. A likely mononuclear candidate, $HRu(CO)_4^-$, would not be expected to survive the situation present during catalysis, for this species has been shown to be very short-lived in hot methanol, providing $HRu_3(CO)_{12}^-$.[17] A control experiment employing $Ru_3(CO)_{12}$ as catalyst afforded a good yield of $H_4Ru_4(CO)_{12}$ but displayed little activity for methyl formate production. This observation is consistent with the known much greater reactivity toward carboxylation exhibited by anionic metal hydride derivatives.[2d] In addition, methanolic solutions of $H_3Ru_4(CO)_{12}^-$ pressurized under carbon dioxide *in the absence of hydrogen* were ineffective at producing methyl formate. However, the ν(CO) infrared pattern of the reaction solution becomes more complex indicating the presence of other species in addition to $H_3Ru_4(CO)_{12}^-$. Experiments are underway to isolate and characterize these species.

When a catalytic run analogous to run 3, where $HCO_2Ru_3(CO)_{10}^-$ is the catalyst precursor, was carried out in the presence of 100- and 250-psi loading pressure of carbon monoxide there was some loss in catalytic activity for methyl formate production (runs 6 and 7). We have in subsequent experiments demonstrated that $HCO_2Ru_3(CO)_{10}^-$ undergoes facile ligand exchange with ^{13}C-labeled carbon monoxide.[10] Concomitantly, the metal carbonyl species at the end of the run was $HRu_3(CO)_{11}^-$, in contrast to $H_3Ru_4(CO)_{12}^-$ that was obtained in the absence of added carbon monoxide. On the other hand, further increase in P_{CO} (run 8) carried out in the absence of carbon dioxide led to an increase in activity for methyl formate formation.[18] A further run (no. 9) performed in the absence of both H_2 and CO_2 resulted in a greatly enhanced rate of methyl formate production, with a turnover rate of 106 being observed. In both runs 8 and 9, where carbon monoxide is present, the only metal-containing product at the end of a run was $HRu_3(CO)_{11}^-$. Evidently $HCO_2Ru_3(CO)_{10}^-$ first must undergo decarboxylation to $HRu_3(CO)_{11}^-$, a rather high-energy process, in the CO-derived methyl formate reaction since $HRu_3(CO)_{11}^-$ is a more effective catalyst than $HCO_2Ru_3(CO)_{10}^-$ (compare runs 8 and 10). Similarly, $H_3Ru_4(CO)_{12}^-$ in the presence of CO is first converted to $HRu_3(CO)_{11}^-$ to effect catalysis of the CO-derived methyl formate reaction.

Because of the much greater catalytic activity for methyl formate formation via CO/MeOH, there is the concern that reactions of CO_2/H_2 are proceeding via CO produced by the reverse of the water–gas shift reaction.[19] We feel that our findings for these processes are not consistent with such a proposal. For example, only trace quantities of CO (less than 0.05% of total gas composition) are detected during the CO_2/H_2 reaction, which is substantially smaller than the equilibrium distribution of CO from the water–gas shift reaction.[20] Furthermore, the hydrocondensation reaction of CO_2 is suppressed in the presence of CO, while the CO/MeOH route to methyl formate is retarded by hydrogen.

The nature of the Ru_4 species that is suggested as the catalytically active intermediate in the CO_2 reduction process may be a formate species analogous to the $ClRu_4(CO)_{13}^-$ "butterfly" complex described by Geoffroy and co-workers.[21] Attempts to prepare such a derivative from the reaction of $ClRu_4(CO)_{13}^-$ and TlO_2CH has resulted in exclusive production of the very stable $HCO_2Ru_3(CO)_{10}^-$ species, further demonstrating the facile Ru_4

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[13] These experiments were carried out in a 300-mL Parr reactor equipped with liquid sampling facilities. In a typical run the catalyst solution was pressurized into the autoclave and brought quickly to the desired temperature. At the end of a 24-h run the autoclave was cooled and depressurized and the catalyst solution recovered in an inert (argon) atmosphere glovebox. Infrared analysis of these solutions were performed on either a Perkin-Elmer 283B equipped with Data Station or an IBM FTIR/85 spectrometer, and gas-liquid chromatography was performed on a Perkin-Elmer Sigma 2 chromatograph using a 10% Carbowax 20m over chromosorb column. Water was detected by GC on a Porapak Q column.

[14] Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444. The $Ru_4 \rightarrow Ru_3$ interconversion was shown by these researchers to proceed via the intermediacy of $HRu_4(CO)_{13}^-$.

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[16] Rosetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1983**, *70*, 121.

[17] Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

[18] Bradley has noted a similar effect during investigations of the homogeneous hydrogenation of CO by soluble ruthenium carbonyls, where an increase in P_{CO} resulted in an increase in the yield of formate. Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

[19] Indeed, when triruthenium clusters are used as catalyst precursors, CO may be a *partial* source of the methyl formate. Experiments are underway employing [^{13}C]carbon monoxide enriched clusters and short reaction times to definitively assess the role of CO in the CO_2/H_2 reaction.

[20] At 125 °C the equilibrium composition of CO is calculated to be 1.22 mol % assuming gaseous water. On the other hand if H_2O is in the condensed phase the CO content would be expected to be much greater at ~14 mol %.

[21] Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985.

→ Ru_3 or vice versa conversion. Hopefully a better understanding of the details of the rather complicated sequence of reactions can be arrived at by means of in situ high-pressure FTIR studies, which are presently underway in our laboratories.[22]

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 80-09233 and the Robert A. Welch Foundation is greatly appreciated.

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(22) Our investigations employing mononuclear group 6B pentacarbonyl hydride and formate derivatives as catalysts for HCO_2Me production from CO_2/H_2 in MeOH strongly support a mechanism involving reductive elimination of formic acid from the metal center. Subsequent reactions of formic acid with methanol provide methyl formate.

A Mononuclear, Low-Valent, Electron-Rich Osmium Methylene Complex

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Molecules with transition-metal–carbon multiple bonds are being increasingly recognized as the active species in many catalytic reactions.[1] It is important, therefore, to define the factors that affect the reactivity of these multiple linkages. For the metal–carbon double bond the prototype ligand is methylene, and a mononuclear example of this ligand was first structurally characterized in $Ta(=CH_2)(CH_3)Cp_2$.[2] Methylene complexes of metals from groups 6,[3] 7,[4] and 8[5] also have now been observed, but in many cases their characterization was by spectroscopic methods at low temperatures. Studies of the reactivity of these complexes indicate two distinct patterns of behavior. $Ta(=CH_2)(CH_3)Cp_2$ and many related molecules[6] contain nucleophilic methylene centers, a property that has been attributed to extremely effective Ta–C orbital overlap.[7] On the other hand, cationic methylene complexes from groups 6, 7, and 8 have been shown to contain electrophilic carbene centers.[3-5]

We report here (i) the synthesis and X-ray crystal structure of a low-valent methylene complex of osmium, $Os(=CH_2)Cl(NO)(PPh_3)_2$ (I), in which the methylene ligand is *not* electrophilic, (ii) reactions of I with various electrophilic reagents, (iii) a demonstration that the electron-rich osmium–carbon double bond in I can interact with an electrophilic metal-center $[Au(PPh_3)]^+$ forming an osmium–gold μ-methylene complex, and (iv) the crystal structure of $\overline{Os(CH_2AuI})Cl(NO)(PPh_3)_2$.

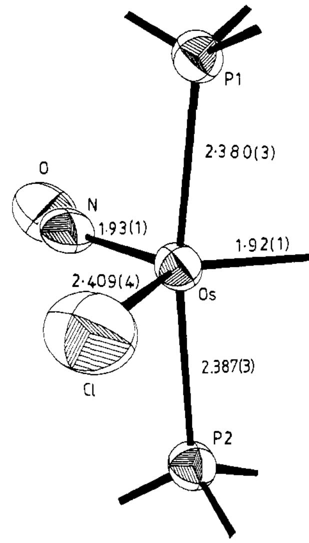
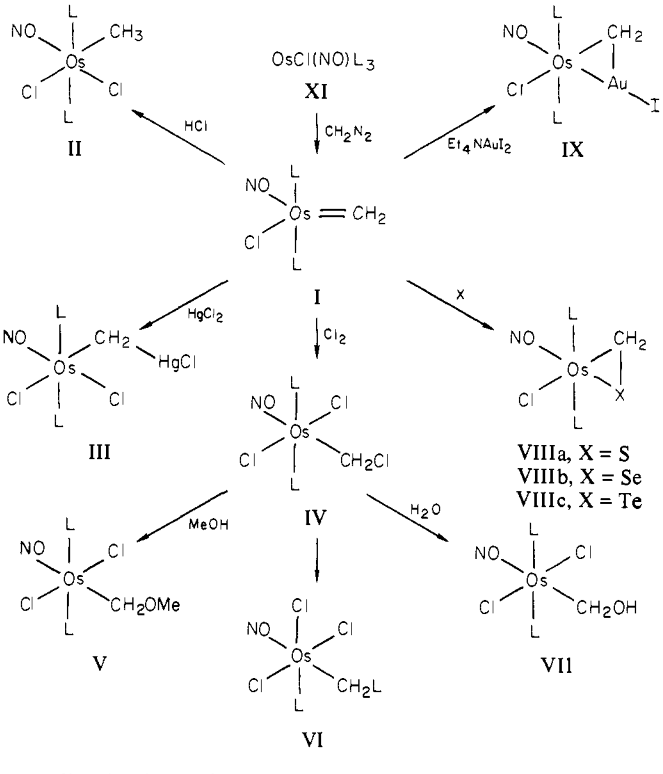


Figure 1. Inner coordination sphere of $Os(=CH_2)Cl(NO)(PPh_3)_2$ (thermal parameters for the methylene hydrogens have been set artificially small). Interatomic angles: C–Os–Cl, 126.6 (4)°; P1–Os–P2, 170.4 (1)°; C–Os–N, 118.8 (5)°; Cl–Os–N, 114.6 (4)°; Os–N–O, 155.4 (1.6)°.

Scheme I. Synthesis and Some Reactions of an Osmium Methylene Complex ($L = PPh_3$)[11]



Diazoalkanes have been extensively studied as transition-metal–carbene precursors but the ultimate products are usually bridging-carbene complexes.[8] Reaction between diazomethane and $IrCl(CO)(PPh_3)_2$ led to $Ir(CH_2Cl)(CO)(PPh_3)_2$.[9] Four coordination is much less common for osmium(0) than for iridium(I), and we find that diazomethane with $OsCl(NO)(PPh_3)_3$[10]

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(10) $OsCl(NO)(CO)(PPh_3)_2$[12] (1 g) is dissolved in CH_2Cl_2 (100 mL) and EtOH (10 mL). The solution is stirred for 10 min under O_2 (1 atm) while the color changes from brown to yellow. Removal of the solvent under reduced pressure yields a complex of stoichiometry $OsCl(CO_3)(NO)(PPh_3)_2$ (yield 810 mg, 78%). $OsCl(CO_3)(NO)(PPh_3)_2$ (810 mg) is dissolved in rigorously degassed benzene (50 mL) with PPh_3 (800 mg). The solution is heated under reflux for 5 min. Dark green crystals of $OsCl(NO)(PPh_3)_3$ form as the solution cools, and further material is obtained by addition of degassed *n*-hexane (yield 940 mg, 94%). $OsCl(NO)(PPh_3)_3$ (940 mg) is suspended in benzene (20 mL), and an ethereal solution of CH_2N_2 (20 mL)[13] is added dropwise. Tan-colored crystals of $Os(=CH_2)Cl(NO)(PPh_3)_2$ separate as the reaction proceeds. Recrystallization from CH_2Cl_2/EtOH yields orange crystals, 590 mg, 82%.

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