Hydrocondensation of Carbon Dioxide with Methanol Catalyzed by Anionic Ruthenium Complexes: Isolation, Structural Characterization, and Catalytic Implications of the Dinuclear Anion $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$

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The anionic ruthenium complex $[Ru(CO)_3Cl_3]^-$ (**1**) was found to catalyze the formation of methyl formate from CO_2, H_2, and CH_3OH in the presence of a strong base. From the basic methanol solution, the dinuclear anion $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$ (**2**) has been isolated as the bis(triphenylphosphoranylidene)ammonium salt and characterized by a single-crystal X-ray diffraction analysis. In anion **2**, two $Ru(CO)_2Cl$ units are held together by a μ_2-OCH_3 ligand and by two μ_2-η^2-$OCOCH_3$ bridges; apart from the three bridging ligands there is no direct Ru−Ru interaction (distance 3.380 Å). Complex **2** was found to react with 2 equiv of $[OCH_3]^-$ to give two reactive intermediates **3** and **4**, the latter one being considered as the catalytically active species in the hydrocondensation reaction. On the basis of the spectroscopic data and the isolation of aromatic analogues from the reaction of **2** with various phenolates, the constitution of $[Ru_2(CO)_6(OCH_3)_4(\mu_2\text{-}OCH_3)]^-$ is proposed for the active species **4**. The elimination of water as an inherent side product of the methyl formate formation from CO_2, H_2, and CH_3OH was found to be the limiting factor of this catalytic reaction: It hydrolyses the methoxide employed as cocatalyst and thus deactivates the catalytic system. In the presence of trimethyl orthoformate as a water trap, the catalytic turnover numbers observed are considerably higher.

Introduction

Methyl formate has been proposed as a versatile intermediate in the synthesis of oxygenated base chemicals.[1,2] It is presently used for the synthesis of formamides and formic acid. A potential future use includes the synthesis of dimethyl carbonate, acetic acid, methyl glycolate, diphosgene, and methyl propionate.[3] At present the most widely used method of producing methyl formate is the carbonylation of methanol catalyzed by sodium methoxide, first patented in 1925 by BASF.[4] Alternative methods are the dehydrogenation of methanol,[5] the hydrogenation of carbon monoxide,[6] and the dimerization of formaldehyde.[7]

One of the most interesting synthetic routes to methyl formate is based on carbon dioxide, a readily available environmentally friendly C_1 building block:[8] CO_2 reacts with methanol and molecular hydrogen to give methyl formate and water. This exothermic reaction has been referred to as hydrocondensation of carbon dioxide with methanol.[2] The first reports of this reaction being successfully catalyzed appeared in the Russian literature.[9] Not only phosphine complexes of transition metals[9,10] but also carbonyl metalates of transition metals[11] show catalytic activity; in many cases basic additives have a positive effect on the course of the reaction. Darensbourg *et al.* reported the anionic ruthenium clusters $[H_3Ru_4(CO)_{12}]^-$, $[HRu_3(CO)_{11}]^-$, and $[HRu_3(CO)_{10}(CO_2)]^-$ to catalyze the hydrocondensation of carbon dioxide and methanol, the catalytic turnover numbers ranging from 3.8 to 7.3.[12] Efficient catalysis was observed with $RuP(Me_3)_4Cl_2$ and NEt_3 in supercritical carbon dioxide: under these conditions, Noyori *et al.* described turnover numbers ranging from 31 to 3500.[13]

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Table 1. Catalytic Activity of Various Catalyst/Promoter Systems

catalyst	promoter	ratio	TON[a]
$[N(PPh_3)_2][Ru(CO)_3Cl_3]$	none		32
$[N(PPh_3)_2][Ru(CO)_3Cl_3]$	NEt_3	1:10	62
$[N(PPh_3)_2][Ru(CO)_3Cl_3]$	$Na[OCH_3]$	1:10	108
$[N(PPh_3)_2][Ru(CO)_3I_3]$	$Na[OCH_3]$	1:10	49
$[N(PPh_3)_2][Ru(CO)_3Cl_3]$	$K[OCH_3]$	1:10	170
$[N(PPh_3)_2][Ru(CO)_3Cl_3]$	$K[OCH_3]$	1:5	88

[a] mol of $HCOOCH_3$/mol of Ru. Experimental conditions: 0.01 mmol Ru, 10 mL of CH_3OH, 60 bar ($CO_2/H_2 = 20/40$), 160 °C, 14 h.

In this paper we report the use of the anionic complex $[Ru(CO)_3Cl_3]^-$ as a catalyst precursor for the hydrocondensation of carbon dioxide with methanol, its activation with potassium methoxide, the isolation and structure characterization of dinuclear intermediate $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$ (**2**) as the bis(triphenylphosphoranylidene)ammonium salt, and its implication in the catalytic process.

Results and Discussion

Hydrocondensation of Carbon Dioxide with Methanol. The reaction of carbon dioxide with molecular hydrogen and methanol to give methyl formate and water (eq 1) was studied. The reaction is exothermic, and the standard reaction enthalpy is −25.37 kJ·mol^{-1}.

$$CO_2 + H_2 + CH_3OH \longrightarrow HCOOCH_3 + H_2O \qquad (1)$$

The anionic ruthenium complex $[Ru(CO)_3Cl_3]^-$ (**1**) was found to catalyze this reaction in methanol solution in the presence of methoxide as a promoter (Table 1). Complex **1** is considerably more active than its iodide analogue, $[Ru(CO)_3I_3]^-$. Ay any rate, the influence of a base additive as a promoter is very important: Without base the catalytic effect is almost negligible; a nitrogen base has only little effect, whereas the $[OCH_3]^-$ anion dramatically increases the catalytic activity. Potassium methoxide has a stronger promoting effect than sodium methoxide, but a large excess (10 equiv) of the promoter with respect to the catalyst is required (Table 1).

Reaction of $[Ru(CO)_3Cl_3]^-$ (1) with $[OCH_3]^-$. In order to investigate the promoting effect of the methoxide on the catalyst precursor, we reacted the anion **1** with an excess of potassium methoxide in methanol solution. The reaction depends on the ratio of the methoxide added and can be followed by infrared spectroscopy: The two ν(CO) absorptions of complex **1**, the 1:2 ratio being characteristic for the $Ru(CO)_3$ unit, change after addition of 1.5 equiv of methoxide to two absorptions of equal intensity, indicating the formation of a species (**2**) containing an $Ru(CO)_2$ unit. With 2.0 equiv of methoxide, another species (**3**) is formed, also showing the typical pattern of an $Ru(CO)_2$ unit with two ν(CO) bands of equal intensity. With 2.5 equiv (or more) of methoxide, another species (**4**) is formed, revealing again the pattern of an $Ru(CO)_3$ unit with two ν(CO) absorptions of 1:2 intensity ratio (Table 2). No color change is associated with the reaction; all the species formed are colorless like the starting material **1**.

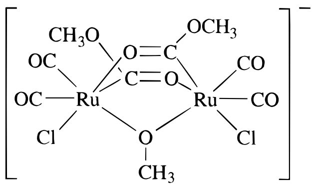
Table 2. IR Study of the Reaction of $[Ru(CO)_3Cl_3]^-$ (1) with $[OCH_3]^-$ [a]

	ratio $[OCH_3]^-$/**1**			
	0	1.5	2.0	2.5
ν(CO)/cm^{-1}	2129 (s) 2055 (vs)	2057 (s) 1993 (s)	2043 (s) 1979 (s)	2032 (s) 1965 (vs)
species formed	**1**	**2**	**3**	**4**

[a] Conditions: Solvent CH_3OH, 25 °C, $[N(PPh_3)_2][Ru(CO)_3Cl_3]$, $K[OCH_3]$.

Isolation of the Dinuclear Anions $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)X_2]^-$ (X = Cl, 2; X = I, 2a). If, in the reaction of $[Ru(CO)_3Cl_3]^-$ with $[OCH_3]^-$, 1.5 equiv of methoxide is added in methanol solution, the anionic species **2** formed can be isolated as the bis(triphenylphosphoranylidene)ammonium salt by crystallization from methanol. Anion **2** is found to be a dinuclear complex, $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$, containing two $Ru(CO)_2$ moieties (eq 2).

$$\underset{(\mathbf{1})}{2\,[Ru(CO)_3Cl_3]^-} + 3\,[OCH_3]^- \longrightarrow \underset{(\mathbf{2})}{[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-} + 4\,Cl^- \qquad (2)$$



(**2**)

The salt $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ ($[N(PPh_3)_2]$**2**) is an air-sensitive, colorless, crystalline material which is only soluble in polar organic solvents. It is obtained in a yield of 76% after recrystallization from methanol. In the infrared spectrum, the new anion **2** shows, apart from the two ν(CO) bands at 2057(s) and 1993(s) cm^{-1}, an absorption at 1528 (m) cm^{-1}, which is characteristic for the OCO moieties.

The reaction of the iodide analogue with 1.5 equiv of methoxide in methanol yields the analogous dinuclear anion $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)I_2]^-$ (**2a**), which crystallizes also as the bis(triphenylphosphoranylidene)ammonium salt. The solid $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)I_2]$ ($N(PPh_3)]$**2a**) is a yellow, air-sensitive material which also shows two ν(CO) bands at 2042(s) and 1977(s) cm^{-1}, characteristic for a $Ru(CO)_2$ moiety, and a ν(OCO) absorption at 1530 (m) cm^{-1} in the infrared spectrum. Anion **2a** is strictly analogous to the chloride derivative **2**.

X-ray Structure Analysis of $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ [$N(PPh_3)]$2). The structure of the dinuclear anion **2** was solved by X-ray diffraction analysis of a single crystal of the bis(triphenylphosphoranylidene)ammonium salt. Important bond lengths and angles are given in Table 3; the ZORTEP plot is shown in Figure 1. The molecule possesses crystallographic C_2 symmetry and contains two $Ru(CO)_2Cl$ moieties held together by a disordered μ_2-OCH_3 bridge lying on the 2-fold axis and two μ_2-η^2-$OCOCH_3$ bridges, each ruthenium atom being surrounded by six coordinating atoms. The Ru−Ru distance [3.3805(13) Å] is too long for a bonding interaction, in accordance with the electron count of 36 for **2**. A

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for 2, with Esd's in Parentheses

Interatomic Distances			
Ru(1)−Ru(1)[a]	3.3805(13)	C(1)−O(1)	1.138(10)
Ru(1)−C(1)	1.850(9)	C(2)−O(2)	1.097(9)
Ru(1)−C(2)	1.864(9)	C(3)−O(3)	1.334(8)
Ru(1)−C(3)	2.005(8)	C(4)−O(3)	1.462(9)
Ru(1)−O(4)	2.124(5)	C(5)−O(5)	1.338(14)
Ru(1)−O(5)	2.097(5)	C(3)a−O(4)	1.252(8)
Ru(1)−Cl(1)	2.470(2)		
Bond Angles			
C(1)−Ru(1)−C(2)	88.6(4)	C(2)−Ru(1)−Cl(1)	89.7(3)
C(1)−Ru(1)−C(3)	91.5(4)	C(3)−Ru(1)−Cl(1)	174.2(2)
C(2)−Ru(1)−C(3)	93.5(3)	O(5)−Ru(1)−Cl(1)	91.00(13)
C(1)−Ru(1)−O(5)	171.9(3)	O(4)−Ru(1)−Cl(1)	89.0(2)
C(2)−Ru(1)−O(5)	98.2(3)	C(1)−Ru(1)−Ru(1)[a]	135.7(3)
C(3)−Ru(1)−O(5)	83.7(3)	C(2)−Ru(1)−Ru(1)[a]	123.1(3)
C(1)−Ru(1)−O(4)	90.6(3)	C(3)−Ru(1)−Ru(1)[a]	59.6(2)
C(2)−Ru(1)−O(4)	178.5(3)	O(5)−Ru(1)−Ru(1)[a]	36.3(2)
C(2)−Ru(1)−O(4)	87.9(2)	O(4)−Ru(1)−Ru(1)[a]	58.3(2)
O(5)−Ru(1)−O(4)	82.7(2)	Cl(1)−Ru(1)−Ru(1)[a]	114.57(6)
C(1)−Ru(1)−Cl(1)	93.5(3)		

[a] Symmetry transformations used to generate equivalent atoms. $-x + {}^{\prime}_{2}, -y + {}^{1}/_{2}, z$.

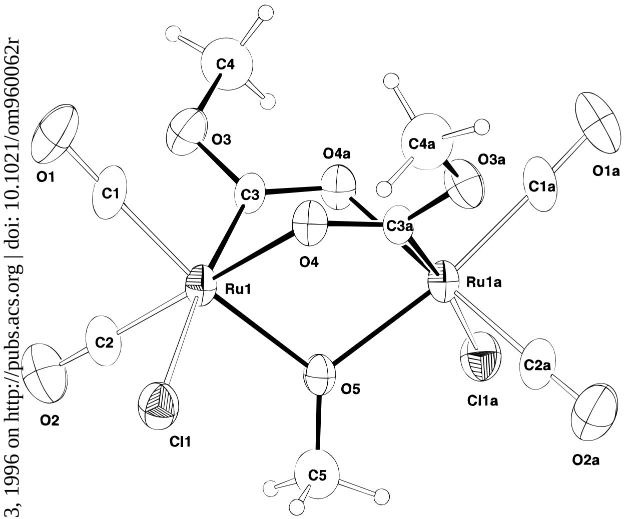


Figure 1. Zortep drawing of $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$ (**2**).

similar complex, $Ru_2\{\mu_2\text{-}OCCCH_3CCH_3(\eta^2\text{-}CCH_3CHCH_3)\}\{\mu_2\text{-}OCN(CH_3)_2\}(CO)_5$, reported by Kaesz *et al.*,[14] was found to contain a metal−metal bond with a Ru−Ru distance of 2.681 Å, as required by the electron count of 34. The bridging Ru(1)−O(4) distance is 2.124(5) Å, while the Ru(1)−C(3) and C(3)−O(4) distances are 2.005(8) and 1.462(9) Å, respectively. The lengthening of the C(3)−O(4) bond with respect to an organic carbonyl bond is due to the coordination of both carbon and oxygen to ruthenium atoms.

NMR Study of the Dinuclear Anions 2 and 2a in Solution. The proton NMR spectra of the anions $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)X_2]^-$ (X = Cl, **2**; X = I, **2a**) present a surprising phenomenon concerning the methyl protons (Figure 2): In both cases the μ_2-OCH_3 group and the two μ_2-η^2-$OCOCH_3$ groups give rise to six singlet signals instead of two, as expected from the molecular structure established for **2** by X-ray diffraction (**2**, δ = 3.57, 3.73, 3.77, 3.81, 3.86, and 3.91 ppm; **2a**, δ = 3.78, 3.85, 3.92, 3.95, 4.08, and 4.10 ppm). The total intensity of the six signals (as expected) 9 with respect to the signal of the $[N(PPh_3)_2]^+$ cation (30). Accordingly, the ^{13}C NMR spectra show also six methyl signals (**2**, δ = 49.0, 49.1, 51.0, 53.2, 63.2, and 63.9 ppm; **2a**, δ = 48.9, 51.2, 53.5, 66.0, 69.6, and 70.6 ppm). This phenomenon is even observed at −60 °C.

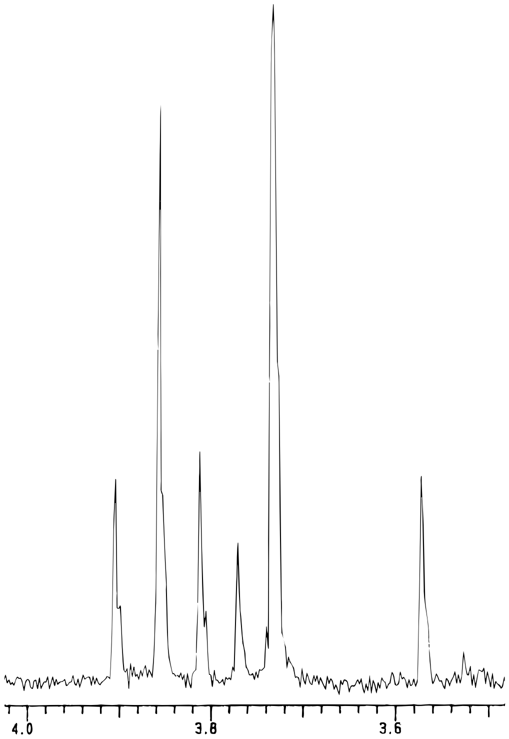


Figure 2. ^1H NMR spectrum of the methyl protons of complex $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$ ($[N(PPh_3)_2]$**2**) in d_6-acetone-d_6.

These findings cannot be explained by the existence of two isomers of **2**, one of which has the two μ_2-η^2-$OCOCH_3$ bridges in the same orientations and the other having the two μ_2-η^2-$OCOCH_3$ bridges in opposite orientation, because both isomers would give rise to only two methyl signals with 1:2 ratio. Furthermore, assuming that only one of these isomers crystallizes (**2**), whereas the other one remains in solution, the NMR spectrum of the isolated crystals should then show only the two signals of the isomer. However, when pure crystalline $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ $[N(PPh_3)_2]$**2**) is dissolved in acetone-d_6, six different methyl signals are always observed. The only explanation to account for this is to assume isomerization in solution, presumably involving the fragmentation of the μ_2-η^2-$OCOCH_3$ ligands into μ_1-OCH_3 and μ_1-CO ligands (Scheme 1). Each of the three species assumed to be present in solution would give rise to two methyl signals, as observed in the NMR spectra.

Reaction of $[Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]^-$ (2) with Various Phenolates OR^- [R = p-$C_6H_4NO_2$, R = p-$C_6H_4CH_3$, R = p-$C_6H_4C(CH_3)_3$]. The dinuclear anion **2**, obtained from the reaction of the catalyst precursor **1** with 1.5 equiv of methoxide, is an intermediate in the formation of the catalytically active species, since it has a much higher catalytic activity as the anion **1** (without additional base). However, it certainly is not the catalytically active species itself, because its activity is further increased by addition of methoxide (Table 5).

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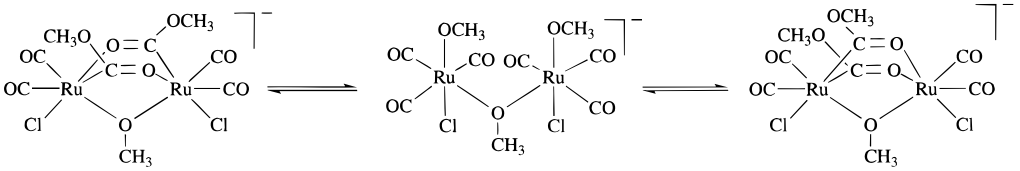
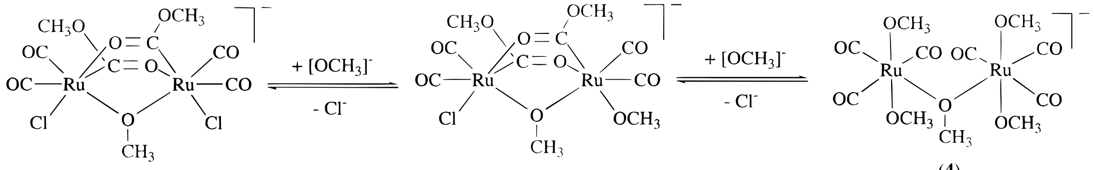
Scheme 1. Proposed Isomerization Mechanism of Anion 2 in Solution



Scheme 2. Proposed Structures for 3 and 4 in the Reaction of 2 with Methoxide



(**2**) (**3**) (**4**)

Table 4. IR[a] and ^{1}H NMR[b] Data for the Anions 3a and 4a,b

		^{1}H NMR (ppm)			
complex[c]	IR (cm^{-1})	OCH$_3$	C$_6$H$_4$	CH$_3$	[N(PPh$_3$)$_2$]$^+$
[Ru$_2$(CO)$_4$(CO$_2$CH$_3$)$_2$(OCH$_3$)(OC$_6$H$_4$NO$_2$)Cl]$^-$ (**3a**)	2043 (s), 1980 (s), 1530 (m)[d]	3.56−3.96 (m)	6.81 (d), 8.04 (d)		7.53−7.78 (m)
[Ru$_2$(CO)$_6$(OCH$_3$)$_3$(OC$_6$H$_4$CH$_3$)$_2$]$^-$ (**4a**)	2039 (s), 1973 (vs)	3.52−4.01 (m)	6.73−6.94 (m)	2.20 (s)	7.53−7.79 (m)
[Ru$_2$(CO)$_6$(OCH$_3$)$_3${OC$_6$H$_4$C(CH$_3$)$_3$}$_2$]$^-$ (**4b**)	2038 (s), 1973 (vs)	3.47−4.01 (m)	6.79−7.22 (m)	1.26 (s)	7.53−7.71 (m)

[a] In methanol, cm^{-1}. [b] In acetone-d_6 (25 °C), ppm. [c] Cation [N(PPh$_3$)$_2$]$^+$. [d] ν(OCO).

A careful study of the effect of the methoxide promoter on the anion [Ru$_2$(CO)$_4$(μ_2-η^2-CO$_2$CH$_3$)$_2$(μ_2-OCH$_3$)Cl$_2$]$^-$ (**2**) shows that **2** reacts with 1 equiv of K[OCH$_3$] to give species **3**, and with 2 equiv (or more) to give species **4**, already observed in the reaction of anion **1** with an excess of potassium methoxide. Since the dinuclear anion **2** contains two chloro ligands, it can be assumed that they are successively replaced by methoxo ligands. However, since only **3** shows a ν(CO) pattern of an Ru(CO)$_2$ moiety, it must be assumed that, after a straightforward substitution of the first chloride to give **3**, the substitution of the second chloride is accompanied by the fragmentation of the two η_2-η^2-OCOCH$_3$ bridges into μ_1-OCH$_3$ and μ_1-CO ligands to give **4** (Scheme 2). This is in line with the isomerization of the anion **2** in solution (see above), observed by NMR spectroscopy.

Since anion **4** is always present in methanol solutions containing a large excess of methoxide, and since under these conditions the maximum catalytic activity is observed, we believe anion **4** to be the catalytically active species in hydrocondensation of carbon dioxide with methanol. As the infrared spectrum shows the typical pattern of an Ru(CO)$_3$ unity and no ν(OCO) absorption, indicative of the OCOCH$_3$ bridges, we propose a dinuclear structure for **4** in which two Ru(CO)$_3$(OCH$_3$)$_2$ moieties are held together by a μ_2-OCH$_3$ bridge; this formulation would be in accordance with the 18 electron rule.

Both anions **3** and **4** cannot be isolated as the bis(triphenylphosphoranylidene)ammonium salts because they decompose rapidly when the methanol is evaporated. The color of solutions containing **3** and **4** turns brownish upon concentration. In order to place our interpretation of the anions **3** and **4** for which we have only infrared evidence on more solid grounds, we synthesized the analogous anions containing aromatic substituents instead of methyl groups. For these reasons, we reacted the anion [Ru$_2$(CO)$_4$(μ_2-η^2-CO$_2$CH$_3$)$_2$(μ_2-OCH$_3$)Cl$_2$]$^-$ (**2**) with various phenolates in the place of methoxide: with 2 equiv of *p*-methylphenolate or *p-tert*-butylphenolate, the anions [Ru$_2$(CO)$_6$(OCH$_3$)$_3$(OR)$_2$]$^-$ (R = *p*-C$_6$H$_4$CH$_3$, **4a**; R = *p*-C$_6$H$_4$C(CH$_3$)$_3$, **4b**) analogous to **4** are formed (eq 3). In contrast to **4**, **4a**,**b** are more stable and can be isolated as the bis(triphenylphosphoranylidene)ammonium salts. The intermediates found with 1 equiv of the phenolate can be detected by IR spectroscopy but not isolated. However, with *p*-nitrophenolate, the reaction with anion **2** stops at the first reaction step (eq 4) to give the anion [Ru$_2$(CO)$_4$(μ_2-η^2-CO$_2$CH$_3$)$_2$(μ_2-OCH$_3$)(OR)Cl]$^-$ (R = *p*-C$_6$H$_4$-NO$_2$, **3a**), analogous to **3**, which is obtained as the bis(triphenylphosphoranylidene)ammonium salt upon concentration of the methanol solution.

$$\underset{(\mathbf{2})}{[\mathrm{Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2}]^-} + 2\mathrm{OR^-} \longrightarrow [\mathrm{Ru_2(CO)_6(OCH_3)_3(OR)_2}]^- + 2\mathrm{Cl^-} \quad (3)$$

$$\mathrm{R} = p\text{-}\mathrm{C_6H_4CH_3}\text{: } \mathbf{4a}$$

$$\mathrm{R} = p\text{-}\mathrm{C_6H_4C(CH_3)_3}\text{: } \mathbf{4b}$$

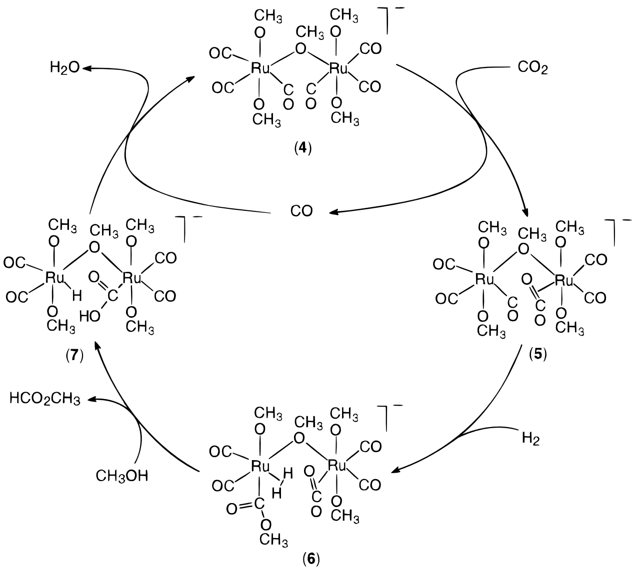
$$\underset{(\mathbf{2})}{[\mathrm{Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2}]^-} + \mathrm{OR^-} \longrightarrow [\mathrm{Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)(OR)Cl}]^- + \mathrm{Cl^-} \quad (4)$$

$$\mathrm{R} = p\text{-}\mathrm{C_6H_4NO_2}\text{: } \mathbf{3a}$$

None of these bis(triphenylphosphoranylidene)ammonium salts is crystalline enough for X-ray structure determination, so that the characterization of the anions **3a** and **4a,b** is based on the spectroscopic (Table 4) and microanalytical data. A mass spectroscopic study using FAB negative with a MNBA matrix confirms the composition of the anions.

The anions **3a** and **4a**,**b** contain, by contrast to their analogues **3** and **4**, two differents oxygen ligands; however, the exact positions of the OCH$_3$ and the *p*-OC$_6$H$_4$R (R = CH$_3$, C(CH$_3$)$_3$, NO$_2$) ligands (with

Scheme 3. Possible Catalytic Cycle for the Hydrocondensation of Carbon Dioxide with Methanol



respect to each other) are unknown. All attempts to crystallize these anions with various cations haved failed so far.

Proposed Catalytic Cycle for the Hydrocondensation of Carbon Dioxide with Methanol. We have been able to show that the activation of the mononuclear anion $[Ru(CO)_3Cl_3]^-$ (**1**), employed as the catalyst precursor, by the methoxide promoter occurs in three steps, leading successively to the anions **2**, **3**, and **4**, the latter one being considered as the catalytically active species. The isolation and structure determination of the intermediary anion **2** confirms the formation of dinuclear anions without Ru−Ru bonds, in which the two ruthenium moieties are held together by at least one μ_2-OCH_3 bridge. On the basis of this evidence, a catalytic cycle is proposed for the reaction of CO_2, H_2, and CH_3OH to give $HCOOCH_3$ and H_2O, involving **4** as the active species (Scheme 3).

We assume anion **4** to react under the catalytic conditions with carbon dioxide to give a species **5** in which a CO ligand at one ruthenium center has been replaced by a CO_2 ligand. Molecular hydrogen could now enter the coordination sphere of the second ruthenium center with insertion of a carbonyl ligand into a Ru−OCH_3 bond (**6**). From **6**, methyl formate could be eliminated by combination of $OCOCH_3$ and H fragments, with oxydative addition of methanol to give **7**. In the last step, water is eliminated from OH and H fragments with coordination of the carbon monoxide eliminated in the first step, thus closing the cycle to reproduce **4**. This cycle is hypothetical and still contains some speculative elements, but it is in accordance with all the experimental observations and serves to rationalize the catalytic process.

In accordance with these assumptions, the catalytic reaction is retarded by carbon monoxide; CO pressure obviously blocks the step **4** → **5**. On the other hand, **5** can only be present in low concentration, because no product could be obtained from the reaction of **4** with CO_2 (in the absence of H_2). With molecular hydrogen (in the absence of CO_2), however, anion **4** is transformed into the tetranuclear anion $[H_3Ru_4(CO)_{12}]^-$.

An alternative explanation of the catalytic process would involve the reduction of CO_2 by H_2 to give CO and H_2O (water-gas shift reaction), catalyzed by the anionic ruthenium species, and then reaction of CO and CH_3OH to give $HCOOCH_3$, catalyzed by methoxide. However, no carbon monoxide could be detected in the gas phase of the reaction of carbon dioxide, hydrogen, and methanol in the presence of anion **1** or **2** (without methoxide). Therefore it is unlikely that the hydrocondensation of carbon dioxide and methanol involves carbon monoxide as an intermediate. This interpretation is in line with the findings of Darensbourg *et al.*[11a] using the anion $[HRu_3(CO)_{11}]^-$ as a catalyst precursor.

Autodeactivation of the Catalytic System by Water. The hydrocondensation of carbon dioxide and methanol (eq 1) produces not only methyl formate but also water. The catalytic system employed, anion $[Ru(CO)_3Cl_3]^-$ (**1**) (catalyst precursor) and $[OCH_3]^-$ (promoter), however, is very sensitive to water: Water hydrolyzes the methoxide anion to give methanol and hydroxide. Therefore the water formed in the catalytic process deactivates the catalyst promoter, so that the active species **4**, only stable in methanol with high methoxide concentration, is converted back into the catalyst precursor **1**. This means the catalytic reaction itself limits the catalytic process: The more product is formed, the more water is produced, and the more the catalytic system is deactivated.

The limiting effect of water can be demonstrated by two observations: First, if water (100 equiv) is added to a catalytic run, no catalytic reaction is observed. Second, if instead trimethyl orthoformate (100 equiv) is added as a water trap, the catalytic activity considerably increases (Table 5). Trimethyl orthoformate reacts rapidly with water according to eq 5 to give methyl formate and methanol.

$$HC(OCH_3)_3 + H_2O \longrightarrow HCOOCH_3 + 2\,CH_3OH \tag{5}$$

The methyl formate produced from the hydrolysis of trimethyl orthoformate has been deduced from the total amount of methyl formate formed to determine the methyl formate formed by the catalytic process. The TON values in Table 5 are corrected for the indirect methyl formate formation.

Conclusions

It has been shown that the anionic complex $[Ru(CO)_3Cl_3]^-$ (**1**) is activated by methoxide to give dinuclear anions containing methoxo ligands. These species catalyze the hydrocondensation of carbon dioxide and methanol to give methyl formate and water. The water formed is the limiting factor of the catalytic process, since it deactivates the methoxide promoter of the catalytic system.

Experimental Section

General Considerations. All preparations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Methanol was distilled under nitrogen over Mg. Bis(triphenylphosphoranylidene)ammonium chloride, potassium methylate, and trimethyl orthoformate were obtained from Fluka. ^1H and ^{13}C NMR spectra were measured on Varian Gemini 200 BB and Bruker AMX 400 FT-NMR spectrometers. Infrared spectra were recorded on a Perkin-

Table 5. Catalytic Activity of the Anions 1 and 2 with Promoter and Additive

catalyst[a]	promoter	additive	ratio	TON
$[Ru(CO)_3Cl_3]^-$	none	none	1	32
$[Ru(CO)_3Cl_3]^-$	$K[OCH_3]$	none	1:10	170
$[Ru(CO)_3Cl_3]^-$	$K[OCH_3]$	$HC(OCH_3)_3$	1:10:100	246
$[Ru_2(CO)_4(CO_2CH_3)_2(OCH_3)Cl_2]^-$	none	none	1	71
$[Ru_2(CO)_4(CO_2CH_3)_2(OCH_3)Cl_2]^-$	$K[OCH_3]$	none	1:10	459
$[Ru_2(CO)_4(CO_2CH_3)_2(OCH_3)Cl_2]^-$	$K[OCH_3]$	H_2O	1:10:100	80
$[Ru_2(CO)_4(CO_2CH_3)_2(OCH_3)Cl_2]^-$	$K[OCH_3]$	$HC(OCH_3)_3$	1:10:100	746

[a] Cation $[N(PPh_3)_2]^+$. Experimental conditions: 0.01 mmol of Ru, 10 mL of CH_3OH, 60 bar ($CO_2/H_2 = 20/40$), 160 °C, 14 h.

Elmer FT-IR 1720X spectrophotometer with 0.1 mm cells equipped with CaF_2 windows and are reported in cm^{-1}. Mass spectra were obtained on a Ribermag 10-10 mass spectrometer. Elemental analyses were performed by the Mikroelementaranalytische Laboratorien at Zurich. The following starting materials were prepared according to published procedures: $Ru_3(CO)_{12}$,[15] $[N(PPh_3)_2]I$,[16] and $[N(PPh_3)_2][Ru(CO)_3I_3]$.[17]

Synthesis of $[N(PPh_3)_2][Ru(CO)_3Cl_3]$ ($[N(PPh_3)_2]$1). The complex $[N(PPh_3)_2][Ru(CO)_3Cl_3]$ was prepared by a "one-pot" synthesis from $RuCl_3{\cdot}3H_2O$ and $[N(PPh_3)_2]Cl$. In a 100 mL stainless steel autoclave, $RuCl_3{\cdot}3H_2O$ (500 mg, 1.91 mmol) and $[N(PPh_3)_2]Cl$ (1096 mg, 1.91 mmol) were dissolved in 30 mL of distilled methanol. The autoclave was pressurized with CO (60 bar) and heated at 90 °C for 3 h. After cooling and venting, the pale yellow solution was filtered under a nitrogen atmosphere through a 2 cm layer of filter pulp and concentrated to about 10 mL. The product was crystallized at −35 °C. After 24 h, the crystalline precipitate was filtered out and dried under vacuum (990 mg, 62%). The filtrate was concentrated and cooled to −35 °C to give a second crop of 290 mg of product (total yield 81%). Anal. Calcd for $C_{39}H_{30}NO_3P_2Cl_3Ru$: C, 56.43; H, 3.64; N, 1.69. Found: C, 56.04; H, 3.85; N, 1.55. IR (ν(CO), CH_3OH): 2129 (s) and 2055 (vs) cm^{-1}.

Synthesis of $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ ($[N(PPh_3)_2]$2). The complex $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ was prepared by dropwise addition of 1.5 equiv of $K[OCH_3]$ (25% methanolic solution, 266 μL, 0.903 mmol) to a methanol solution (40 mL) of $[N(PPh_3)_2][Ru(CO)_3Cl_3]$ (500 mg, 0.602 mmol) at 25 °C. The solution remained colorless. The solution was filtered under the same conditions as in the synthesis of **1** and concentrated to about 10 mL. The complex was crystallized at −35 °C and gave (after two crystallizations) colorless crystals of **2** (245 mg, 76% yield). Anal. Calcd for $C_{45}H_{39}NO_9P_2Cl_2Ru_2$: C, 50.38; H, 3.66; N, 1.31. Found: C, 50.06; H, 3.92; N, 1.43. IR (CH_3OH): ν(CO), 2057 (s), 1993 (s), cm^{-1}; ν(OCO), 1528 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.53−7.80 ppm (m, phenyls, $[N(PPh_3)_2]^+$); δ 3.57, 3.73, 3.77, 3.81, 3.86, 3.91 ppm (6 s, 3 OCH_3). ^{13}C NMR (acetone-d_6): δ 49.0, 49.1, 51.0, 53.2, 63.2, 63.9 ppm (6 s, 3 OCH_3). MS: m/z (**2**) = 534.

Synthesis of $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)I_2]$ ($[N(PPh_3)_2]$2a). The complex $[N(PPh_3)_2][Ru(CO)_3I_3]$[17] (200 mg, 0.181 mmol) was dissolved in 20 mL of methanol. Then 1.5 equiv of $K[OCH_3]$ (25% methanolic solution, 80 μL, 0.272 mmol) was added drop by drop at 25 °C. The orange solution was filtered and concentrated to about 5 mL. The complex of **2a** was crystallized at −35 °C giving orange crystals (75 mg, 0.060 mmol, 66% yield). Anal. Calcd for $C_{45}H_{39}NO_9P_2I_2Ru_2$: C, 43.09; H, 3.13; N, 1.12; I, 20.21. Found: C, 43.24; H, 3.20; N, 1.08; I, 20.09. IR (CH_3OH): ν(CO), 2042 (s), 1977 (s) cm^{-1}; ν(OCO), 1530 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.53−7.80 ppm (m, phenyls, PPN^+); δ 3.78, 3.85, 3.92, 3.95, 4.08, 4.10 ppm (6 s, 3 OCH_3). ^{13}C NMR (acetone-d_6): δ 48.9, 51.2, 53.5, 66.0, 69.6, 70.6 ppm (6 s, 3 OCH_3).

Reaction of Complexes 2 and 2a with $K[OCH_3]$. To a solution of the $[N(PPh_3)_2]$ salt of **2** (100 mg, 0.093 mmol) in 10 mL of methanol was added 1 equiv of $K[OCH_3]$ (25% methanolic solution, 28 μL, 0.093) drop by drop. Infrared monitoring in the ν(CO) region indicated the formation of a new compound **3** [2043 (s) and 1979 (s) cm^{-1}]. This complex reacted with a second 1 equiv of $K[OCH_3]$ to form a complex **4** [2032 (s) and 1965 (vs) cm^{-1}] characteristic of an $Ru(CO)_3$ unit. Complexes **3** and **4** decomposed to give a black oil on evaporation of the methanol. By reaction of the iodo analogue **2a** with methoxide (2 equiv), the solution showed the same infrared spectrum [2032 (s) and 1965 (vs) cm^{-1}] of **4**, being indicative of the absence of halide ligands in **4**.

Synthesis of $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)(O\text{-}p\text{-}C_6H_4NO_2)Cl]$ ($[N(PPh_3)_2]$3a). The $[N(PPh_3)_2]$ salt of **2** (100 mg, 0.093 mmol) was dissolved in 10 mL of methanol. Addition at 25 °C of 1 equiv of phenolate $K[O\text{-}p\text{-}C_6H_4NO_2]$ (16.5 mg, 0.093 mmol), prepared from the corresponding phenol and KH in the THF, resulted in the formation of complex **3a**. The solution was filtered through filter pulp. After evaporation of the solvent, we obtained 100 mg of the $[N(PPh_3)_2]$ salt of **3a** (61% yield). Anal. Calcd for $C_{51}H_{43}N_2O_{12}P_2ClRu_2$: C, 52.11; H, 3.69; N, 2.38; Cl, 3.01. Found: C, 51.67; H, 3.59; N, 2.54; Cl, 2.96. IR (CH_3OH): ν(CO), 2043 (s), 1980 (s) cm^{-1}; ν(OCO), 1530 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.53−7.78 ppm (m, phenyls, PPN^+); δ 6.81, 8.04 ppm (2d, C_6H_4); δ 3.56−3.96 ppm (m, 3 OCH_3).

Synthesis of $[N(PPh_3)_2][Ru_2(CO)_6(OCH_3)_3(OR)_2]$ (anions: R = $p\text{-}C_6H_4CH_3$, 4a; R = $p\text{-}C_6H_4C(CH_3)_3$, 4b). The $[N(PPh_3)_2]$ salt of **2** (100 mg, 0.093 mmol) was dissolved in 10 mL of methanol, and 2 equiv of phenolate K[OR] (R = $p\text{-}C_6H_4CH_3$, 27 mg, 0.186 mmol; R = $p\text{-}C_6H_4C(CH_3)_3$, 35 mg, 0.186 mmol) prepared from to the corresponding phenol and KH in THF was added at 25 °C. The solution was filtered, and after evaporation of the solvent, we obtained the $[N(PPh_3)_2]$ salts of **4a** (100 mg, 88% yield) and **4b** (100 mg, 83% yield). Anal. Calcd for $C_{59}H_{53}NO_{11}P_2Ru_2$ (**4a**): C, 58.27; H, 4.39; N, 1.15. Found: C, 57.57; H, 4.46; N, 1.15. IR (CH_3OH, **4a**, ν(CO)): 2039 (s), 1973 (vs). ^1H NMR (**4a**, acetone-d_6): δ 7.53−7.79 ppm (m, phenyls, PPN^+); δ 6.73−6.94 ppm (m, 2 C_6H_4); δ 3.52−4.01 ppm (m, 3 OCH_3); δ 2.20 ppm (s, 2 CH_3). Anal. Calcd for $C_{65}H_{65}NO_{11}P_2Ru_2$ (**4b**): C, 60.04, H, 5.04. Found: C, 60.03; H, 5.18. IR (CH_3OH, **4b**, ν(CO)): 2038 (s), 1973 (vs). ^1H NMR (**4b**, acetone-d_6): δ 7.53−7.71 ppm (m, phenyls, PPN^+); δ 6.79−7.22 ppm (m, 2 C_6H_4); δ 3.47−4.01 ppm (m, 3 OCH_3); δ 1.26 ppm (s, 6 CH_3). MS: m/z (**4b**) = 763.

Reaction of $[Ru_2(CO)_6(OCH_3)_5]^-$ (4) with CO_2. The $[N(PPh_3)_2]$ salt of **2** (100 mg, 0.093 mmol) was dissolved in 10 mL of methanol, and 2 equiv of $K[OCH_3]$ (25% methanolic solution, 56 μL, 0.186 mmol) was added at 25 °C. After the infrared spectrum indicated the complete conversion into **4** (20 min), the solution was transferred into an autoclave, pressurized with CO_2 (20 bar), and stirred 14 h at 160 °C. After cooling and venting, the solution showed no change in the infrared spectrum and contained **4**.

Reaction of $[Ru_2(CO)_6(OCH_3)_5]^-$ (4) with H_2. The $[N(PPh_3)_2]$ salt of **2** (100 mg, 0.093 mmol) was dissolved in 10

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Table 6. Crystal and Intensity Data for the Complex $[N(PPh_3)_2][Ru_2(CO)_4(\mu_2\text{-}\eta^2\text{-}CO_2CH_3)_2(\mu_2\text{-}OCH_3)Cl_2]$ ($[N(PPh_3)]2$)

formula	$C_{45}H_{39}NO_9P_2Cl_2Ru_2$
fw	1072.76
cryst shape	rectangular block
cryst color	white
cryst system	orthorhombic
cryst size	0.46 × 0.30 × 0.30 mm
space group	*Pccn*
a, Å	17.921(3)
b, Å	17.145(3)
c, Å	14.899(2)
α, deg	90.00
β, deg	90.00
γ, deg	90.00
V, $Å^3$	4577.8(13)
Z	4
D(calcd), $g\cdot cm^{-3}$	1.557
T, °C	20
radiation; wavelength, Å	Mo Kα; λ(Mo Kα) = 0.710 73 (monochromator)
linear abs coeff, mm^{-1}	0.901
scan method	ω/θ
θ limit, deg	164−27.50
no. of unique data	5260
no. of obsd data	2622
criterion for recognizing	$>2\sigma(I)$
intensity variation	<1%
R(obsd data)[a]	0.0818
R_w(obsd data)[a]	0.1000

[a] $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$.

mL of methanol, and 2 equiv of $K[OCH_3]$ (25% methanolic solution, 56 μL, 0.186 mmol) was added at 25 °C. After the infrared spectrum indicated the complete conversion into **4** (20 min), the solution was transferred into an autoclave, pressurized with H_2 (40 bar), and stirred 14 h at 160 °C. After cooling and venting, the infrared spectrum of the solution showed complete conversion to the anion $[H_3Ru_4(CO)_{12}]^-$.[18]

X-ray Structure Analysis. Table 6 summarizes crystal and intensity data for the complex **2**. Final atomic coordinates for **2** are given in the Supporting Information. Intensity data were collected at ambient temperature on a Stoe-Siemens AED2 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.717 03 Å) and with the $\omega-\theta$ scan mode. The structure was solved by using the SHELXS-86 program[19] and was refined on F^2 using SHELXL-93.[20] Only 50% of the data can be considered to be observed. A table of anisotropic thermal parameters for **2** is available as Supporting Information. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Catalytic Runs. Catalytic runs were carried out in a 100 mL glass-lined stainless steel autoclave equipped with a manometer and a magnetic stirrer. The catalyst precursor was placed into the autoclave and dissolved with 10 mL of methanol. The promoter $K[OCH_3]$ (and eventually trimethyl orthoformate) was added to the solution. Then, the reactor was closed and flushed three times with CO_2 (20 bar). Finally, the gases CO_2 (20 bar) and H_2 (40 bar) were introduced. The autoclave was heated to the appropriate temperature and stirred magnetically. After 14 h, the reactor was cooled to room temperature and depressurized. The gases were trapped in a "gas mouse" and analyzed by gas chromatography on a DANI 86.10 equipped with a Carboxen-1000 column and a thermoconductivity detector. Samples were analyzed by GC on a DANI 86.10 by using a 60 m × 0.25 mm capillary column SPB-1 and a FID detector. Toluene was used as an internal standard. The catalytic turnover number (TON) correspond to the number of moles of methyl formate produced/mole of catalyst.

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Supporting Information Available: Tables of data collection parameters, positional and thermal parameters, and bond distances and angles (14 pages). Ordering information is given on any current masthead page.

OM960062R

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