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Homogeneous Catalytic Synthesis of Alkyl Formates from the Reaction of Alkyl Halides, CO_2, and H_2 in the Presence of Anionic Group 6 Carbonyl Catalysts and Sodium Salts

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Abstract: Group 6 metal pentacarbonyl chlorides and bridging hydrides, $(CO)_5MCl^-$ and $(\mu\text{-H})[M_2(CO)_{10}]^-$ (M = Cr, Mo, or W), have been found to be effective homogeneous catalyst precursors for the production of long chain formate esters (HCO_2R, R = *n*-butyl or *n*-octyl) from CO_2, H_2, and alkyl halides (RX; X = Cl, Br, or I) in the presence of alkali-metal salts ($NaHCO_3$, Na_2CO_3, or K_2CO_3). For all the catalytic reactions conversions were found to be between 26 and 40% with respect to RX. The selectivities toward the alkyl formates were found to be higher than 70%. The only other organic products detected (by GC and GC–IR) were the corresponding alcohols, which were produced by the hydrolysis of the formate esters. The proposed catalytic cycle involves the reaction of $(CO)_5MCl^-$ with dihydrogen in the presence of sodium salts to produce the terminal hydride $(CO)_5WH^-$. The latter complex dimerizes under the reaction conditions with subsequent formation of the bridging hydride $(\mu\text{-H})[M_2(CO)_{10}]^-$, which was detected in the reaction solution. The terminal hydride rapidly inserts CO_2 to produce the formate complex $(CO)_5MO_2CH^-$, which in turn reacts with the alkyl halide to yield the formate esters and regenerate the halide complex $(CO)_5MCl^-$. This latter process is shown to proceed via loss of a carbon monoxide ligand. Subsequent oxidative addition of the alkyl halide to the metal center followed by reductive elimination of alkyl formate, or direct alkylation of the distal oxygen of the carboxylate ligand to afford alkyl formate and the metal halide complex, completes the reaction cycle. The overall process has been found very useful for the synthesis of long-chain alkyl formates starting from inexpensive starting materials such as CO_2 and alkyl halides.

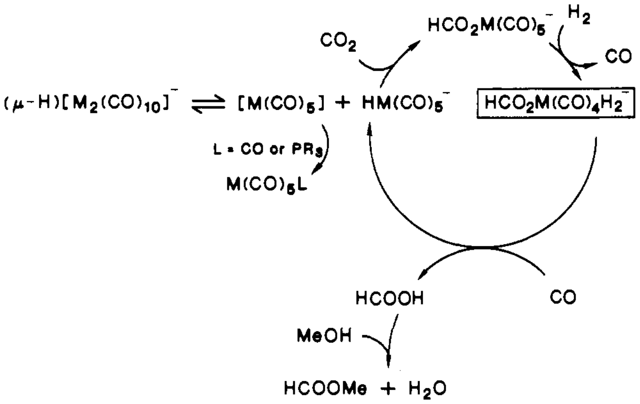
In the past few years, formate esters have become an important class of organic compounds mainly because of their versatility as chemical feedstocks[1-5] and as raw materials for the perfume and fragrance industry.[6] Specifically, formate esters (methyl, ethyl, pentyl, etc.) have been used as starting material for the production of aldehydes,[2] ketones,[2] carboxylic acids,[3] and amides.[5] For example, methyl formate can be hydrolyzed to formic acid[3c,d] or catalytically isomerized to acetic acid.[3b] On the other hand, alkyl formates have been employed in the perfume and fragrance industry in amounts of approximately 1000- to 3000 lb/year.[6] Among the formates that have been commonly used for these purposes are octyl,[6a] heptyl,[6b] ethyl,[6c] and amyl formates.[6d]

Our recent interest in the chemistry of carbon dioxide,[7] the cheapest and most abundant of the carbon oxides, has included investigations of the synthesis of alkyl formates utilizing CO_2 as a source of chemical carbon (eq 1).[8,9] The catalysts or catalyst

$$CO_2 + H_2 + ROH \xrightarrow{[cat.]} HCO_2R + H_2O \qquad (1)$$

precursors employed in these studies were anionic group 6 carbonyl complexes[8] or group 8 metal carbonyl clusters,[9] where reaction conditions were 500 psi (CO_2/H_2) and 125 °C. For the group 6 metal catalysts, the turnover numbers obtained for the methyl formate production were ca. 15 by using methanol as solvent for a 24-h reaction period. The anionic metal carbonyls examined as catalyst precursors included: $(\mu\text{-H})M_2(CO)_{10}^-$, $HCO_2M(CO)_5^-$, and $CH_3CO_2M(CO)_5^-$ as their PPN salts (PPN = bis(triphenylphosphine)nitrogen(1+) and M = Cr or W). The proposed reaction pathway is depicted in Scheme I.

Scheme I



Carbonylation of methanol (eq 2), where carbon monoxide originates from the reverse water-gas shift reaction (eq 3), was

$$CO + MeOH \xrightarrow{[cat.]} HCO_2Me \qquad (2)$$

$$CO_2 + H_2 \overset{[cat.]}{\rightleftharpoons} CO + H_2O \qquad (3)$$

ruled out as a possible route to methyl formate in this instance. This conclusion is based on the observation that when $(^{13}CO)_5\text{-}WO_2CH^-$ was utilized as catalysts in the presence of $^{12}CO_2$, only $H^{12}CO_2Me$ was detected initially via GC–MS.[8] Additionally, when $CH_3CO_2W(CO)_5^-$ was employed as the catalyst, the first formed product in quantitative yield was CH_3CO_2H, with subsequent esterification affording $CH_3CO_2CH_3$.

Mechanistic aspects of carbon dioxide hydrogenation processes carried out in solvents other than methanol, e.g., ethanol or propanol, were completely consistent with those noted in methanol solvent.[10] However, the catalytic activities were considerably lower in these alcohols as compared with methanol, by a factor of about 3. This effect was attributed to a solvent inhibition of the addition of dihydrogen to the unsaturated metal species. For this reason, we have turned our attention toward the reaction of alkyl halides with CO_2 and H_2 in order to provide a more effective pathway

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(3) (a) Pruett, R. L. Eur Pat. Appt. EP 45637A1, 1982; *Chem. Abstr.* **1982**, *96*, 180799f. (b) Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693. (c) Czaikowski, M. P.; Bayne, A. R. *Hydrocarbon Process.* **1980**, *59*, 103. (d) Leonard, J. D. U.S. Patent 4299981, 1981.

(4) Dryvy, D. J.; Williams, P. S. Eur. Pat. Appt. EP106656A 1984; *Chem. Abstr.* **1984**, *101*, 90427a.

(5) Green, M. J. Eur. Pat. Appt. EP107441A1, 1984; 110378r.

(6) (a) Opdyke, D. L. J. *Food Cosmet. Toxicol* **1979**, *17*(suppl. 1), 883. (b) *Ibid.* **1978**, *16*(suppl. 1), 771. (c) *Ibid.* **1978**, *16*(suppl. 1), 737. (d) *Ibid.* **1980**, *18*(6), 649.

(7) (a) Darensbourg, D. J.; Kudaroski, R. *Adv. Organomet. Chem.* **1983**, *22*, 129 and references therein. (b) Darensbourg, D. J.; Ovalles, C. *ChemTech* **1985**, *15*, 636 and references therein.

(8) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750.

(9) Darensbourg, D. J.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc.* **1983**, *105*, 5937.

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Table I. Synthesis of Formate Esters from the Reaction of Alkyl Halides with CO_2 and H_2 in the Presence of $NaHCO_3$[a]

det	cat.[b]	alkyl halide[c]	% convn[d]	% sel ROH[e]	% sel HCO_2R[f]	$(CO)_5MX^-$[g]	$(\mu\text{-H})[M_2(CO)_{10}]^-$[g]	$M(CO)_6$[g]
1	$(CO)_5WCl^-$	*n*-BuCl	26	17.2	82.8	60	30	10
2	$(\mu\text{-H})[W_2(CO)_{10}]^-$	*n*-BuCl	31	37	63	45	45	10
3	$(CO)_5CrCl^-$	*n*-BuCl	34	14.4	85.6			
4	$(\mu\text{-H})[Cr_2(CO)_{10}]^-$	*n*-BuCl	47	9	91			
5	$(CO)_5WCl^-$	(*n*-octyl)Cl	40	13.2	86.8	40	40	20
6	$W(CO)_6$	*n*-BuCl		traces				
7	$(CO)_5WCl^-$	*n*-BuCl	26[h]		100	95		5
8	$(CO)_5WCl^-$	*n*-BuCl	32[i]	34.4	65.6	30	60	10
9	$(\mu\text{-H})[W_2(CO)_{10}]^-$	*n*-BuBr	19	28.2	71.8	90		10
10	$(\mu\text{-H})[W_2(CO)_{10}]^-$	*n*-BuI	19	2.4	97.6	100		

[a] Temp = 150 °C; 24-h reactions; 300 psi of CO_2 and 300 psi of H_2 at room temperature, final pressure = 1050 psi; THF as solvent, 20–30 M excess of $NaHCO_3$. [b] [Cat.] = 1×10^{-2} and PPN^+ as counterion. [c] 30–40 molar excess of alkyl halide. [d] Percent of conversion with respect to the initial amounts of *n*-BuCl (±10%); duplicate runs gave similar results. [e] Percent of selectivity toward alcohol production. [f] Percent of selectivity toward formate ester production. [g] Percent of metal complexes at the end of the 24-h period (determined via FTIR in the $\nu(CO)$ region). [h] 10 equiv of hydroquinone was added. [i] 1 equiv of benzoyl peroxide was added.

to higher molecular weight alkyl formates (butyl or octyl) using CO_2 as a source of carbon. Anionic group 6 metal complexes were used as catalysts, and the presence of a sodium salt ($NaHCO_3$ or $NaOCH_3$) was required in order to regenerate the catalytically active intermediates. Herein we describe the mechanism of this latter reaction as well as that for the overall process.

Results and Discussion

Catalytic Studies. Anionic group 6 carbonyl chlorides and bridging hydrides $(CO)_5MCl^-$ and $(\mu\text{-H})[M_2(CO)_{10}]^-$ (M = Cr or W) have been found (Table I) to be active catalysts or catalyst precursors for the reaction of alkyl halides with CO_2 and H_2 under moderate conditions (loading pressure of CO_2 and H_2, 300 psi each, and 150 °C) to produce alkyl formates (eq 4), where R = butyl or octyl and X = Cl, Br, or I.

$$RX + CO_2 + H_2 \xrightarrow[NaY]{[cat.]} HCO_2R + NaX + HY \qquad (4)$$

The metal carbonyls ($(CO)_5MX^-$, $(\mu\text{-H})M_2(CO)_{10}^-$, and $M(CO)_6$) present at the completion of a catalytic run account for greater than 95% of the initial metal content (calculated by FT-IR spectroscopy in the carbonyl region). In all of the reactions reported in this section, the percent of recovery of the organic products were higher than 90% (based on the initial amount of RX). The $M(CO)_6$ detected in these reactions was found to be catalytically inactive as is shown in Table I, entry 6.

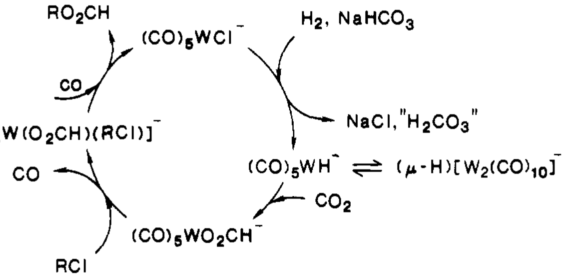
In the absence of either the transition-metal complex, the sodium salt, the carbon dioxide, or hydrogen, no alkyl formates were detected in the reaction solution. Although control reactions are not indicated in Table I, identical runs were carried out in the absence of one component at a time, and in all cases only trace quantities of alcohols were detected in the reaction solutions. Thus, all components are necessary for the successful completion of eq 4. In the catalytic runs, a large percentage of the sodium salt additive ($NaHCO_3$) remained undissolved in the reactor. Since the transition-metal species present in solution during catalysis and isolated at the end of a catalytic period quantitatively account for the initial metal loading, the possibility of heterogeneous catalytic reactions occurring at the surface of the solid is unlikely.

The percent conversions (based on alkyl halide) were found to be between 20 and 60% (Table I). The ROH produced was generated from the hydrolysis of the formate esters (eq 5), where

$$HCO_2R + H_2O \rightarrow ROH + HCO_2H \qquad (5)$$

the water necessary for this reaction is produced by the decomposition of the carbonic acid which is afforded by the $NaHCO_3$ additive. The conversion and selectivity toward octyl formate production were found to be as high as those reported for the *n*-butyl analogue, indicating that this catalytic process can be successfully used in the synthesis of long-chain formate esters from hydrogen, carbon dioxide, and alkyl halides. Radical scavenger (hydroquinone) or radical initiator (benzoyl peroxide) exhibited only a small effect on the percent conversion, Table I (entries 7 and 8), although these reagents significantly altered the alcohol/formate and the metal product distribution.

Scheme II



The dependency of the conversion and selectivity on the nature of the halide is shown in Table I. As can be seen, the butyl formate production was lower for the bromide and iodine alkyl halides than that found with the chloride analogue. The metal carbonyl sepcies present at the end of the *n*-butyl bromide and *n*-butyl iodide reactions were exclusively the anions $(CO)_5MX^-$ (X = Br and I). The decrease in reactivity exhibited in the bromide and iodide cases is due to an enhanced stability of the $(CO)_5MX^-$ species which inhibits formation of the catalytically active metal hydride species (vide infra).

A general catalytic cycle for the production of formate esters starting from alkyl halides, CO_2, and H_2 is shown in Scheme II. The catalyst precursor $(CO)_5MX^-$ is shown to react with dihydrogen in the presence of a sodium salt to produce the terminal hydride $(CO)_5MH^-$. This reaction is similar to the one reported by Halpern, James, and co-workers for the generation of the metal hydride from ruthenium(III) halides.[11]

The presence of basic sodium salts serve to consume the protons afforded by the reaction of dihydrogen with $M(CO)_5X^-$, with concomitant formation of the catalytically active terminal metal hydride. This terminal hydride is expected to undergo a rapid conversion to a metalloformate intermediate, $(CO)_5MO_2CH^-$, via CO_2 insertion or to the bridging hydride $(\mu\text{-H})[M_2(CO)_{10}]^-$, which is detected at the end of the reaction period (see Table I). The CO_2 insertion reaction with the $(CO)_5MH^-$ anion to produce the formate complex is a well-documented reaction.[7] Similarly, formation of $(\mu\text{-H})[M_2(CO)_{10}]^-$ from $(CO)_5MX^-$ and H_2 has been independently investigated, and the results will be presented later on.

Congruent with Scheme II, reactions performed in the absence of alkyl halides show the formation of $(CO)_5MO_2CH^-$ species (detected by the IR band at 1622 cm^{-1} attributed to the formate ligand). The metalloformate complex has also been used as a catalyst precursor with higher conversion being obtained (Table II, entry 11) when compared with that found for $(CO)_5MX^-$ catalysts. In a similar manner, use of the $(CO)_5MO_2CCH_3^-$ as catalyst produced not only 48% conversion of the *n*-butyl formate

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[11] (a) Halpern, J.; James, B. R. *Can. J. Chem.* **1966**, *44*, 671. (b) James, B. R.; Rattray, A. D.; Wang, D. K. W. *J. Chem. Soc., Chem. Commun.* **1976**, 792.

Table II. Synthesis of Formate Esters from the Reaction of RX with CO_2 and H_2 in the Presence of $NaHCO_3$[a]

det	cat.[b]	alkyl halide[c]	% convn[d]	% sel ROH[e]	% sel RO_2CH[f]	$(CO)_5MX^-$[g]	$(\mu\text{-}H)[M_2(CO)_{10}]^-$[g]	$M(CO)_6$[g]
11	$(CO)_5WO_2CH^-$	*n*-BuCl	41	26	74	45	40	15
12	$(CO)_5WO_2CCH_3^-$	*n*-BuCl	48[h]	34	66	45	45	10
13	$(CO)_5WCl^-$	*n*-BuCl	25[i]		100		20	80
14	$(CO)_5WCl^-$	*t*-BuCl	8.6	26.7	73.3	40	50	10
15	$(CO)_5WCl^-$	*i*-BuCl	100[j]					

[a-g] Same as *a*–*g* Table I. [h] One equiv of $n\text{-}BuO_2CCH_3$. Reaction carried out under 100 psi of CO, 250 psi of CO_2, and 250 psi of H_2 at room temperature. Final pressure at reaction conditions = 1050 psi. [j] Isobutane was detected in the gas phase.

Table III. Synthesis of *n*-Butyl Formate from the Reaction of *n*-BuCl with CO_2 and H_2 Using $(CO)_5WCl^-$ as Catalyst[a]

det	additive[b]	% Convn[c]	% sel ROH[d]	% sel RO_2CH[e]	$(CO)_5MX^-$[f]	$(\mu\text{-}H)[M_2(CO)_{10}]^-$[f]	$M(CO)_6$[f]
16	$NaHCO_3$, H_2O	26	58	42	60	30	10
17	NaOH	2.2	47	53	100		
18	$NaHCO_3$, Et_3N	26	19.6	80.4	30	60	10
19	Na_2CO_3	11	73	27	100		
20	K_2CO_3	9	59	41	100		
21	Li_2CO_3	3.2	100		100		
22	$NaBF_4$	3.5	100				100
23	$NaNO_3$	1.0	100		100		
24	NaOMe	45	30.5	69.5	35	60	5
25	NaOMe	64[g]	36.4	63.6	40	40	20
26	NaOMe	49[h]	9	91	100		

[a] Same as *a* Table I. [b] 20–30 M excess. [c-f] Same as *c*–*f* Table I. [g] RX = (*n*-octyl)Cl. [h] No hydrogen was used.

(Table II, entry 12) but also 1 equiv of *n*-butyl acetate. These results strongly suggest that a metalloformate species is the most likely intermediate in the catalytic process depicted in Scheme II.

The final step of the mechanism is the reaction of $(CO)_5MO_2CH^-$ with alkyl halides to regenerate the active species $(CO)_5MCl^-$ and 1 mol of alkyl formate. This type of reaction has been reported[12,13] to be quite general for other metalloformate or metallocarboxylate complexes. However, little is known about the mechanistic details of this process; hence a kinetic study has been undertaken and is reported upon in a later section.

The percent conversion to alkyl formates was not affected by the presence of 100 psi of carbon monoxide (Table II, entry 13). This observation is in contrast to that reported for methyl formate production from carbon dioxide and hydrogen in methanol catalyzed by anionic metal hydrides.[8] In this case there was a marked decrease in methyl formate formation in the presence of 100 psi of added carbon monoxide. The retardation by carbon monoxide was ascribed to the requirement of a vacant coordination site at the metal center during the rate-determining hydrogenation step of the metal-bound formate ligand to afford formic acid and the anionic metal hydride intermediate. The rate-limiting step in the process reported upon herein does not involve the removal of the carboxylate ligand from the metal center (vide infra).

The use of alkyl halides with different steric requirements is shown in Table II, entries 14 and 15. In the reaction with *tert*-butyl chloride, the conversion was found to be reduced by 4–6-fold which suggests that sterically demanding alkyl halides react to a lesser extent. Indeed, isobutyl chloride produced no HCO_2R. However, isobutane was detected in the gas phase indicative of a reduction reaction involving the terminal hydride similar to that previously reported by Darensbourg and coworkers[14] (eq 6). This was further demonstrated by careful

$$(CO)_5MH^- + RX \rightarrow (CO)_5MX^- + RH \qquad (6)$$

analysis of the GC traces of the reactions with *n*-butyl and *tert*-butyl chloride that revealed small amounts of *n*-butane and isobutane respectively, dissolved in the reaction solution. The small amount of alkanes (present in the gas phase as well) may be responsible for the ca. 10% of the original amount of alkyl halide that was unrecovered at the end of the catalytic runs (vide infra).

The possible involvement of water-gas shift chemistry (eq 7) in these catalytic processes has also been investigated. Reactions carried out in the presence of an excess of water and bases show little effect on the percent of conversion toward the desired products (Table III, entries 16–18). However, the selectivities toward alcohol and formate were dramatically changed by the presence of water due to the hydrolysis of the formate ester (eq 5).

$$M(CO)_6 + 2OH^- \rightarrow (CO)_5MH^- + HCO_3^- \qquad (7)$$

The solubility and basicity of the sodium salts used as additive were found to be important requirements for the successful synthesis of formate esters. For less soluble additives such as NaOH and M_2CO_3 (M = Li, Na, K) the percent conversions were found (Table III, entries 17 and 19–21) to be much lower than those found with the more soluble $NaHCO_3$. On the other hand, the use of a very soluble $NaBF_4$ produced total decomposition of the catalyst (Table III, entry 22) by the abstraction of Cl^- (eq 8). The product of decomposition of the adduct $(CO)_5M(THF)$ is the catalytically inert $M(CO)_6$. A similar reaction has been reported in the literature involving the carboxylate analogue $(CO)_5WO_2CCH_3^-$ in the presence of Na^+ to produce sodium acetate.[13]

$$(CO)_5WCl^- + Na^+ \rightarrow (CO)_5M(THF) + NaCl \qquad (8)$$

A property that could not be completely separated from the solubility of the salt additive is the basicity of the additive. The more basic salts gave the best conversion toward formate esters because of their necessity for the activation of dihydrogen. The use of less basic salts, such as $NaNO_3$, produced no conversion toward the desired products (Table III, entry 23). However, the basic salt (NaOH) is too insoluble in THF leading to low conversion. In conclusion, the most appropriate additives are the ones that show the highest solubility and basicity (for example, $NaHCO_3$).

When NaOMe was used as the additive, higher conversions to alkyl formates were found (Table III, entries 24 and 25) than those reported with $NaHCO_3$ (Table I). Congruent with eq 5, methyl formate was detected in the reaction mixture when NaOMe was used as additive. The formation of the former can be rationalized by using eq 9.

$$HCO_2R + CH_3OH \rightarrow ROH + HCO_2CH_3 \qquad (9)$$

Control reactions carried out in the absence of hydrogen (Table III, entry 26) showed higher conversion to formate ester than that

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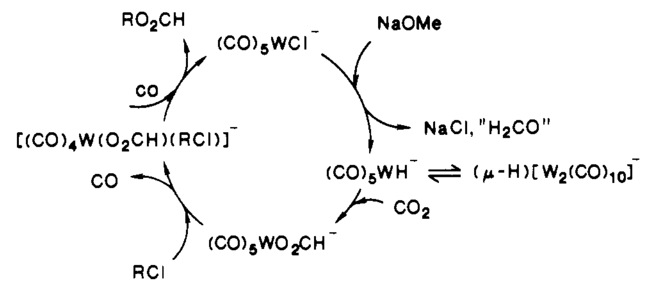
(12) Misonso, A.; Uchida, Y.; Hidai, M.; Kuse, T. *J. Chem. Soc., Chem. Commun.* **1986**, 981.

(13) Darensbourg, D. J.; Kudaroski, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 3672.

(14) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.

Scheme III



found in the presence of H_2 (Table III, entry 24), suggesting an alternative pathway for the formation of alkyl formate from alkyl halides for the reactions in which NaOMe was used as additive. Furthermore, $(CO)_5WCl^-$ and sodium methoxide were found to react, in refluxing THF under a nitrogen atmosphere, to produce $(\mu\text{-H})[W_2(CO)_{10}]^-$ in quantitive yield. A reasonable pathway to account for the latter reaction involves a methoxy containing intermediate afforded by reaction 10.

$$(CO)_5WCl^- + NaOMe \rightarrow (CO)_5WOMe^- + NaCl \quad (10)$$

An analogous methoxide complex, $MeOCr(CO)_5^-$, has been identified as an intermediate in the stoichiometric hydrogenation of formaldehyde to methanol in the presence of $HCr(CO)_5^-$ and CH_3COOH.[15] The methoxy complex, which is very CO labile, is expected to undergo β-hydrogen abstraction to yield the terminal hydride (eq 11) which in turn decomposes under the reaction conditions to provide the bridging hydride $(\mu\text{-H})[W_2(CO)_{10}]^-$ via eq 12.[16-18] No reaction between $NaHCO_3$ and $W(CO)_5Cl^-$ was observed under the same reaction conditions as those noted with NaOMe. The reversible nature of eq 11 has been noted for the reaction of $DW(CO)_5^-$ and benzaldehyde where substantial PhCDO was observed.[15]

$$(CO)_5WOMe^- \rightarrow (CO)_5WH^- + H_2CO \quad (11)$$

$$2(CO)_5WH^- + H^+ \rightarrow (\mu\text{-H})[W_2(CO)_{10}]^- + H_2 \quad (12)$$

Scheme III depicts the proposed catalytic cycle for the formation of alkyl formates from alkyl halides and CO_2 in the presence of sodium methoxide. As can be seen, no hydrogen is needed to carry out the process and the proposed process is very similar to that depicted in Scheme II. It is important to point out that for entries 24 and 26 in Table III, the conversion toward alkyl formate was quantitative with respect to the amount of NaOMe used (which was half of the amount of alkyl halide used).

Kinetic Studies. The two most important steps comprised in the catalytic cycle outlined in Scheme II, i.e., the reaction of $(CO)_5MX^-$ with H_2 to produce anionic metal hydrides and the reaction of $(CO)_5MO_2CH^-$ with alkyl halides to yield the formate ester and corresponding metal halide complex, have been subjected to mechanistic investigations. The results of independent kinetic measurements of these two processes are reported upon below.

Reaction of $(CO)_5WCl$ with H_2 To Produce $(\mu\text{-H})W_2(CO)_{10}^-$. The first step in the catalytic cycle, for the production of HCO_2R using anionic group 6 metal catalysts (Scheme II), is proposed to be the reaction between the anionic metal halide derivative with hydrogen in the presence of a sodium salt to yield the corresponding metal anion. Because of the high reactivity of the terminal hydride $(CO)_5MH^-$, the product observed in the reaction solution is the bridging hydride $(\mu\text{-H})[M_2(CO)_{10}]^-$. Hence, the reaction to be studied (eq 13) involves heterolytic cleavage of dihydrogen to form a metal hydride. This reaction is of importance because it involves the activation of dihydrogen by a transition-metal complex facilitated by a general base, a subject which has received much attention in recent years.[19,20]

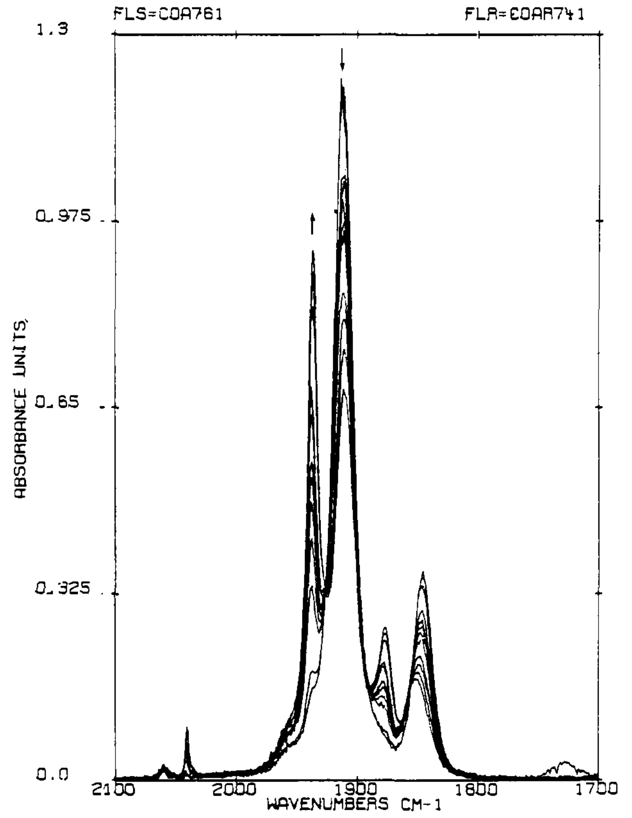


Figure 1. FTIR trace of the reaction of $(CO)_5WCl^-$ with H_2 to produce $(\mu\text{-H})[W_2(CO)_{10}]^-$.

Table IV. Effects of Additives on the Reaction of $PPN(CO)_5MCl$ with H_2 To Produce $[PPN][(\mu\text{-H})M_2(CO)_{10}]$ (Where M = Cr or W)

complex[a]	additive[b]	10^3k_{obsd},[c] 1/min	$t_{1/2}$, min
$[PPN][(CO)_5WCl]$	$NaHCO_3$	9.0	77.6
$[PPN][(CO)_5WCl]$	$NaHCO_3$[d]	8.8	78.8
$[PPN][(CO)_5WCl]$	$NaHCO_3 + (Bz)_2O_2$[e]	8.1	82.0
$[PPN][(CO)_5WCl]$	$NaHCO_3$ + AIBN[e]	7.4	85.0
$[PPN][(CO)_5WCl]$	$NaHCO_3 + NEt_3$	12.0	52.4
$[PPN][(CO)_5WCl]$	NaOMe	>20.0	
$[PPN][(CO)_5CrCl]$	$NaHCO_3$	3.7	140.0

[a] Concentration = 1×10^{-2} M. [b] 20–30 Molar excess. [c] Pseudo-first-order rate constant ($\pm 0.1 \times 10^{-3}$). [d] P_{H_2} = 400 psi and $P_{CO} = P_{Ar}$ = 100 psi at room temperature. Rate was calculated by the disappearance of $(CO)_5WCl^-$. The primary reaction product was $W(CO)_6$. [e] Radical initiator:$[PPN][(CO)_5MCl]$ = 1.1 M.

$$(CO)_5WCl^- + H_2 + NaHCO_3 \rightarrow (\mu\text{-H})[W_2(CO)_{10}]^- + NaCl + H_2CO_3 \quad (13)$$

The kinetic reactions were carried out in a Parr stainless-steel reactor heated to 150 °C and under a total pressure of 600 psi at room temperature (900 psi at 150 °C). The samples were withdrawn into Teflon-capped vials and analyzed by FTIR in the ν(CO) region. The rate of the reaction was followed by measuring the appearance of the product $(\mu\text{-H})[W_2(CO)_{10}]^-$ at 1938 or at 1940 cm⁻¹ for $(\mu\text{-H})[Cr_2(CO)_{10}]^-$. A typical example of a kinetic measurement is shown in Figure 1, with the rate data being summarized in Table IV.

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(15) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428.

(16) The chemistry of the well-characterized $W(CO)_5OPh^-$ derivative has recently been described in detail.[17] In the absence of a β-hydrogen, CO loss, a prequiste in β-hydrogen abstraction in these systems,[18] results in formation of the tetrameric $[W(CO)_3(\mu_3\text{-OR})]_4^{4-}$ species.

(17) (a) Slater, S.; Lusk, R.; Schumann, B. F.; Darensbourg, M. Y. *Organometallics* **1982**, *1*, 1662. (b) Darensbourg, D. J.; Sanchez, K. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 290.

(18) (a) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 766. (b) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463.

(19) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319.

(20) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 22 and references therein.

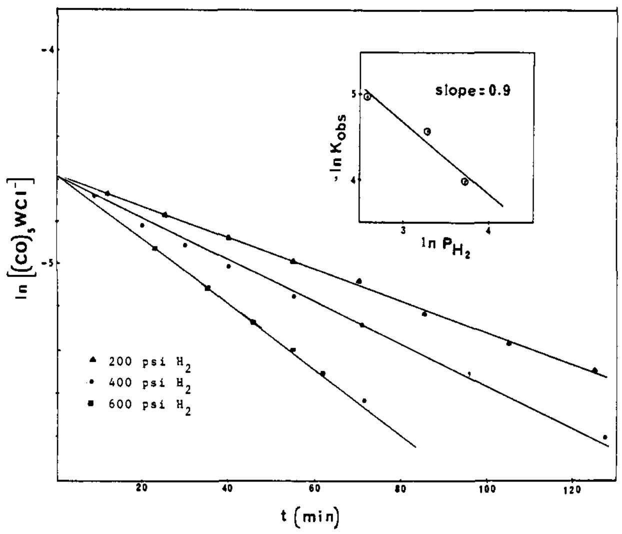
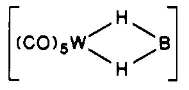


Figure 2. Plot of ln [$(CO)_5WCl^-$] vs. time as a function of hydrogen pressure.

The results of this kinetic study illustrated that the rate of the reaction was first-order with respect to the concentration of $(CO)_5WCl^-$ and also first-order in the partial pressure of hydrogen (see Figure 2). In the presence of 100 psi of carbon monoxide the reaction rate was not retarded (Table IV, entry 2). Radical initiators had no effect on the rate of the reaction as shown in Table IV, entries 3 and 4. Furthermore, a sample taken from the reactor during a kinetic run and rapidly cooled failed to give an ESR signal. These observations support the noninvolvement of an electron-transfer mechanism.

As expected for these type processes, the presence of an additional strong base, such as triethylamine, was found to increase the rate of reaction 13 (Table IV, entry 5). The rate determined for the Cr analogue was less than that found for its W counterpart (entry 7). The enhanced rate of reaction 13 exhibited by the larger tungsten metal complex is consistent with a sterically crowded transition-state comprised of the metal center, dihydrogen, and added base. Such a transition-state might resemble that previously proposed for H/D exchange studies involving $(CO)_5WH^-$ in alcoholic solvents, i.e., species **1**,[14] where B represents a general base,



1

The terminal anionic hydride $HM(CO)_5^-$ is the proposed catalytically active intermediate in the catalytic process described in the previous section (Scheme II). Dimerization of the terminal hydride (eq 14) is expected to occur very rapidly under the reaction conditions employed.[21]

$$2(CO)_5WH^- + Na^+ \rightarrow (\mu\text{-}H)[W_2(CO)_{10}]^- + NaH \quad (14)$$

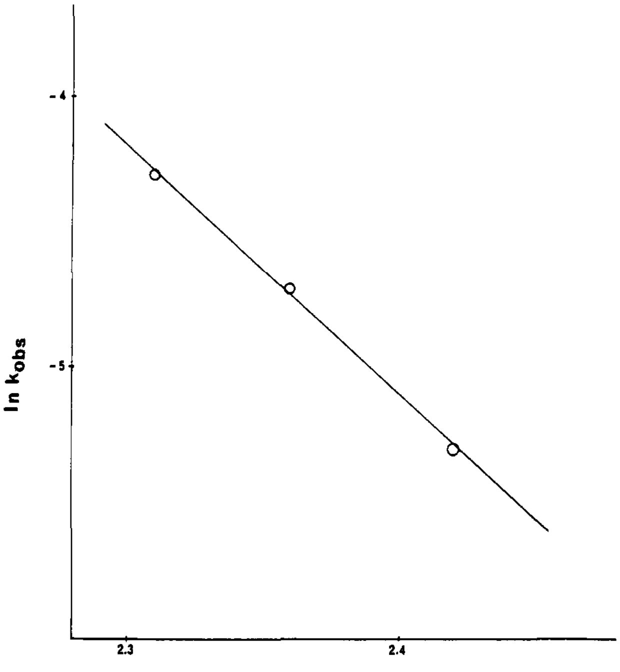


Figure 3. Arrhenius plot for the reaction of $(CO)_5WCl^-$ with H_2 in the presence of $NaHCO_3$.

Table V. Effects of Additives on the Reaction of $(CO)_5WO_2CH^-$ with n-BuCl To Produce $(CO)_5WCl^-$ and Butyl Formate

solv	additive	$10^3k_{obsd}{}^a$ 1/min	$t_{1/2}$, min
THF		24.7	27.2
THF	P_{CO} = 80 psi	11.6	59.6
THF	P_{CO} = 160 psi	4.3	161.0
THF	AIBN[b]	21.1	32.9
THF	$PPNO_2CH^c$	12.3	56.4
CH_3CN		1.0	682.1

[a] Psuedo-first-order constant ($\pm 0.1 \times 10^{-3}$); [n-BuCl] = 0.20 M. [b] 1.2 mol of AIBN/mol of $(CO)_5WO_2CH^-$. [c] No $(CO)_5WO_2CH^-$ was used.

Additional support for rationalizing reaction 13 in terms of a base-assisted heterolytic activation of dihydrogen can be found upon comparing the values of the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, of this process with those reported in the literature for other metal systems.[22] It has been reported that $\Delta H^{\ddagger}$ values close to 60 kJ mol^{-1} and $\Delta S^{\ddagger}$ values of −155 to −60 J mol^{-1} K^{-1} offer indirect support for a two-stage hydrogen activation process similar to that proposed for reaction 13. An Arrhenius plot was determined for the reaction of $(CO)_5WCl^-$ with H_2 in the presence of 20–30 M excess of $NaHCO_3$ in the 140–160 °C temperature range. The results are illustrated in Figure 3, where activation parameters were calculated ($\Delta H^{\ddagger}$ = 76.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −107 J mol^{-1} K^{-1}). These parameters are well within the range of those reported in the literature for base-assisted heterolytic cleavage of dihydrogen. The possible reaction of $(CO)_5WH^-$ with $(CO)_5WCl^-$ to produce the bridging hydride $(\mu\text{-}H)[W_2(CO)_{10}]^-$ was found not to occur in refluxing THF (eq 15). Indeed, the

$$(CO)_5WH^- + (CO)_5WCl^- + Na^+ \nrightarrow (\mu\text{-}H)[W_2(CO)_{10}]^- + NaCl \quad (15)$$

amount of bridging hydride detected in the reaction mixture corresponded to half of the moles of $(CO)_5WH^-$ reacted (calculated by FTIR in the ν(CO) region). The absorbance of the peaks attributed to $(CO)_5WCl^-$ did not change during the 4-h reaction period.

Reaction of $(CO)_5WO_2CH^-$ with n-Butyl Chloride. Currently, no mechanistic details are evident for reaction 16; hence we have

$$(CO)_5WO_2CH^- + n\text{-}BuCl \rightarrow (CO)_5WCl^- + n\text{-}BuO_2CH \quad (16)$$

undertaken a kinetic investigation of this process. The rate of this reaction was monitored by the appearance of a band at 1626 cm^{-1} in the infrared spectrum attributed to the product n-BuO_2CH. The reactions were carried out in a Fisher-Porter tube at 50 °C and under a pressure of argon of 80 psi using THF as solvent. Samples were withdrawn into Teflon-capped vials and were rapidly transferred to the FTIR spectrometer. The results of these kinetic measurements are provided in Figure 4 and Table V. It can be concluded from Figure 4 that the reaction is first order with respect to the concentration of n-BuCl, hence the rate constants reported in Table V are pseudo-first-order values. The effects of additives on the rate of reaction 16 are depicted in Table V. The rate constants were found to decrease with an increase in the CO

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(21) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871.

(22) James, B. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Eds.; Pergamon: Oxford, England, 1982; Vol. 8, p 281.

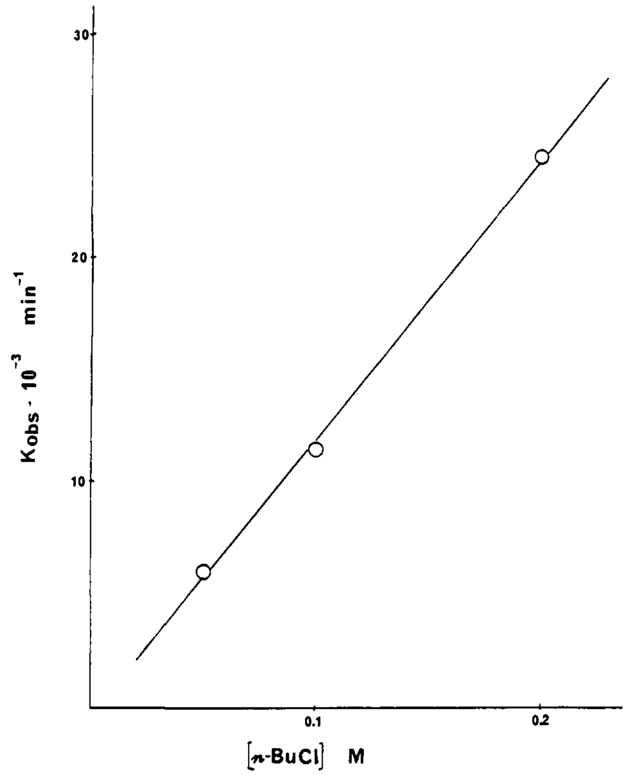


Figure 4. Effect of changing the concentration of n-BuCl on the rate of the reaction of $(CO)_5WO_2CH^-$ with n-BuCl.

pressure (Table V, entries 2 and 3) suggesting a reaction pathway which involves CO dissociation prior to the formation of products. The presence of a radical initiator, AIBN, showed little effect on the rate of reaction (Table V) suggesting that electron-transfer mechanisms are, most probably, not involved in this process. This result is to be contrasted with the reported[23] mechanism of the reaction of *cis*-$[M(CO)_2(dmpe)_2]$ (M = Cr or Mo; dmpe = $Me_2PCH_2CH_2PMe_2$) with alkyl halides (RX = CCl_4, CBr_4, or C_4Cl_6) to form *trans*-$[M(CO)_2(dmpe)_2]X$ and subsequently *cis*-$[M(CO)_2(dmpe)_2X]X$ which involves paramagnetic (free radical) species as shown by ESR measurements.

On the other hand, it has been reported that for the reactions of alkyl halides with $Ir(Cl)(CO)(PMe_3)_2$ there was no effect on the reaction rate by radical initiators at temperatures below 60 °C.[24] Between 60 and 80 °C the presence of benzoyl peroxide, or AIBN, caused a pronounced increase on the rate of alkyl halide addition to the iridium complex.

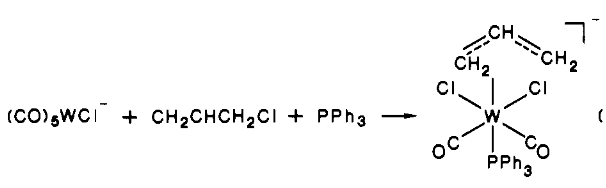
The $[PPN][O_2CH]$ salt was found to react with n-BuCl at a slower rate than that found for $(CO)_5WO_2CH^-$, ruling out a mechanism involving a reaction between free formate ion and n-butyl chloride. The most probable mechanism (eq 17–19), which

$$(CO)_5WO_2CH^- \rightleftharpoons \{(CO)_4WO_2CH^-\} + CO \qquad (17)$$

$$\{(CO)_4WO_2CH^-\} + n\text{-BuCl} \rightarrow [(CO)_4W(O_2CH)(n\text{-Bu})(Cl)]^- \qquad (18)$$

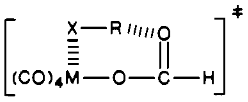
$$(CO)_4W(O_2CH)(n\text{-Bu})(Cl)]^- \xrightarrow{+CO} (CO)_5WCl^- + n\text{-BuO}_2CH \qquad (19)$$

is consistent with the results discussed herein, initially involves the dissociation of CO from $W(CO)_5O_2CH^-$, a process well-documented to readily occur at equatorial carbonyl ligand sites. This requisite CO loss accounts for the retardation of this process by added carbon monoxide. Although the oxidative addition of alkyl halides to $W(CO)_5X^-$ species is without precedence in the literature, oxidative addition of allyl chloride to $W(CO)_5Cl^-$ to afford $(CO)_2W(CH_2CHCH_2)(PPh_3)Cl_2^-$ (eq 20) has been reported by Boyer et al.[25] In the absence of added PPh_3 dimeric products are produced. Similarly, Doyle[26] has presented spectroscopic evidence for the addition of allyl halides to the carboxylate anion $(CO)_5WO_2CR^-$ to yield the oxidative addition product $(CO)_3W(O_2CR)(CH_2CHCH_2)Cl^-$ (R = H, CH_3). We have further investigated this reaction and have crystallographically characterized dimeric W(II) products from this process.[27]



(20)

An important caveat which must be noted is the fact that allyl halides may be quite unique among alkyl halides. In this regard a general reaction pathway which is consistent with our observations is a concerted process. This involves the interaction between the distal oxygen of the carboxylate ligand and the carbon atom of the alkyl halide with concomitant interaction of the halide with the metal as illustrated below (**2**). Indeed, the enhanced basicity of the distal oxygen atom of the formate ligand has been demonstrated by its strong interaction with kryptofix-221 encapsulated sodium ion.[28]



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Concluding Remarks

In this account we have described a catalytic process for the synthesis of long-chain alkyl formates from alkyl halides, carbon dioxide, and dihydrogen employing anionic group 6 metal carbonyl halides as catalyst precursors. This process is of enhanced importance in light of the usefulness of long-chain alkyl formates and of the reluctance of the alternative metal-based catalyzed alcohol carbonylation reactions to provide these compounds. Mechanistic aspects of this catalytic methodology have been forthcoming from kinetic investigations of the component reactions that comprise the proposed catalytic cycle. These have led to the following conclusions.

The rate-limiting process in the catalytic cycle is the reaction between the anionic halide complexes $M(CO)_5X^-$ and H_2 in the presence of a general base to provide anionic metal hydrides. This process was shown to be first-order in both metal complex and dihydrogen and was not inhibited by addition of carbon monoxide.

The well-established formation of metalloformate $M(CO)_5O_2CH^-$ from $M(CO)_5H^-$ and CO_2 is followed by a less facile process involving the reaction of the metalloformate with RX. This latter reaction is first-order in both metal complex and alkyl halide and is inhibited by carbon monoxide.

Consistent with the rate-determining step in catalysis being formation of the metal hydride intermediate, the metal-catalyzed reaction of $RX/CO_2/H_2$ to provide HCOOR is not inhibited by moderate pressures of CO.

Experimental Section

All manipulations were carried out either in an argon drybox or on a double manifold Schlenk vacuum line under an atmosphere of dry nitrogen. Routine infrared spectra were recorded in 0.10–1.0 mm NaCl

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(23) Connor, J. A.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1979**, 1318.

(24) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236.

(25) Boyer, M.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1980**, *190*, 177.

(26) Doyle, G. A. *J. Organomet. Chem.* **1975**, *84*, 323.

(27) The reaction of allyl X (X = Cl^- or $CH_3CO_2^-$) with $W(CO)Y^-$ (Y = Cl^- or $CH_3CO_2^-$) yields the W(II) dimer of the formula $[W_2(CO)_4(\pi\text{-allyl})_2(\mu\text{-}X)(\mu\text{-}Y)_2]^-$. The partial hydrolysis of these dimers leads to complexes where one of the Y ligands is replaced by a bridging OH^- group. The X-ray crystal structures of two complexes have been carried out, where X = $CH_3CO_2^-$ and Y = Cl^- and X = Y = $CH_3CO_2^-$.

(28) Darensbourg, D. J.; Pala, M. *J. Am. Chem. Soc.* **1985**, *107*, 5687.

sealed cells on an IBM FTIR Model 32 spectrophotometer. For recording high-pressure infrared spectra, an IBM FTIR 85 instrument was used. The GC analysis were carried out by using a Perkin-Elmer Sigma 2 chromatograph, equipped with a Perkin-Elmer recorder LCI-100. The apparatus used for GC–IR experiments consists of an IBM 85 FTIR spectrometer equipped with a low-volume light pipe and MCT detector which is coupled to a Perkin-Elmer Sigma 3 GC unit. Proton and ^{13}C NMR measurements were carried out on a Varian Model EM-390 and a Varian Model XL-200 spectrometer, respectively. ESR experiments were carried out on a Varian E-GS spectrometer.

Tetrahydrofuran was dried by refluxing over sodium benzophenone ketyl solution under a nitrogen atmosphere and distilling prior to use. Acetonitrile was dried over P_2O_5 followed by distillation.

Starting Materials. Chromium and tungsten hexacarbonyls were purchased from Strem Chemicals and sublimed under vacuum at 60 °C. Bis(triphenylphosphine)nitrogen(1+) chloride (PPNCl, Strem) was used as received. Potassium acetate (KO_2CCH_3), *tert*-butyl chloride, isobutyl chloride, and sodium methoxide were purchased from Aldrich Chemical and used without further purification. Alpha Chemicals was the source of sodium formate, whereas benzoyl peroxide, butyl chloride, bromide, and iodide, and octyl chloride were purchased from MCB. Sodium bicarbonate was obtained from Fisher. Nitrogen, argon, carbon dioxide, hydrogen, and carbon monoxide were purchased from AIRCO Corp. AIBN was obtained from Aldrich and recrystallized from methanol prior to use. KOH was purchased from Mallinckrodt Chemicals and used as received.

Synthesis of the Catalyst Precursors. $[PPN][O_2CR]$ (R = H or CH_3),[29] $(\mu\text{-H})M_2(CO)_{10}^-$ (M = Cr or W),[31] $[PPN][(CO)_5MCl]$,[31] and $[PPN][(CO)_5WO_2CR]$ where R = H or CH_3[8] (PPN = bis(triphenylphosphine)nitrogen(1+)) were prepared and purified according to the previously described methods.

Reaction of $[PPN][(CO)_5WCl]$ with NaOMe. $[PPN][(CO)_5WCl]$ (0.0551 g) and 0.06 g of NaOMe were mixed in 10 mL of THF under a nitrogen atmosphere. The reaction mixture was refluxed and monitored via FTIR spectroscopy. After 0.5 h of reflux, an orange solution with IR bands at 1912 (s), 1844 (m), 1807 (w), and 1712 (w) cm^{-1} was observed. After 3 h of additional reflux, peaks due to $(\mu\text{-H})[W_2(CO)_{10}]$ (1938 (vs) and 1879 (m) cm^{-1}) and a yellow solid (decomposition products) were observed in the reaction mixture.

Reaction of $[PPN][(CO)_5WCl]$ with $NaHCO_3$. $[PPN][(CO)_5WCl]$ (0.045 g) and 0.0976 g of $NaHCO_3$ were mixed with 10 mL of THF under nitrogen. The reaction mixture was refluxed for 3 h, and no change was observed by FTIR spectroscopy. A brown oil was observed on the walls of the flask, but it was found to be decomposition products (no carbonyl bands).

Reaction of $HW(CO)_5^-$ with $(CO)_5WCl^-$. $[PPN][HW(CO)_5]$ (0.055 g), 0.0594 g of $PPN(CO)_5WCl$, and 0.1091 g of $NaHCO_3$ were stirred in 10 mL of THF. The reaction mixture was refluxed; bands attributed to $(CO)_5WCl^-$, $HW(CO)_5^-$, and $(\mu\text{-H})[W_2(CO)_{10}^-]$ were observed. The amount of $(CO)_5WCl^-$ did not change during the reaction period, but the disappearance of $HW(CO)_5^-$ gave rise to the formation (>90%) of $^1/_2$ equiv of $(\mu\text{-H})W_2(CO)_{10}^-$. Decomposition products (yellow solid) were also observed on the walls of the reactor.

Kinetic Study of the Reaction between $[PPN][(CO)_5WCl]$ and H_2. In a typical reaction, 0.37 g of $[PPN][(CO)_5WCl]$ was dissolved in 35 mL of THF and transferred to a 300-mL Parr reactor inside an Argon-filled drybox. The reactor was brought outside the drybox and pressurized with hydrogen. The vessel was rapidly heated to the desired temperature (150 °C), and the reaction time was started. Samples were withdrawn into Teflon-capped vials and rapidly transferred to the IR cell. The reactor was repressurized to its original value (900 psi in all cases) with additional hydrogen. Ten samples were taken for each kinetic run. The reaction was followed by the appearance of the peak due to the bridging hydride $(\mu\text{-H})[M_2(CO)_{10}]^-$ at 1938 cm^{-1} for M = W and at 1940 cm^{-1} for the chromium derivative. Calibration plots were made that indicated a linear relationship between the absorbance of the band at 1938 cm^{-1} and the concentration of $(\mu\text{-H})[W_2(CO)_{10}]^-$ in the range studied (10^{-2}–10^{-3} M).

Kinetic Study of the Reaction of $(CO)_5WO_2CH^-$ with *n*-BuCl. These reactions were carried out in a Fisher-Porter tube (equipped with a sampling device) under a pressure of 80–85 psi and a temperature of 50 °C. Fifteen milliliters of a solution of 5×10^{-3} M of $(CO)_5WO_2CH^-$ in THF (to which 0.3 mL of *n*-BuCl had been previously added) was transferred under nitrogen to the reactor. A water thermostated bath was used to rapidly heat the tube to the desired temperature. The reactor was left in the bath with occasional shaking during the reaction period. Samples were withdrawn into Teflon-capped vials and analyzed via FTIR. The appearance of *n*-BuO_2CH was followed by the band at 1726 cm^{-1}. Ten samples were collected, and calibrated plots indicated a linear relationship between the absorbance of the band at 1726 cm^{-1} and the concentration of *n*-BuO_2CH.

Catalytic Reactions. In a typical run, 0.14 mmol of catalyst was dissolved in 15 mL of degassed THF. After addition of the internal standard (isooctane), the alkyl halide and the alkali-metal salt, the solution was placed inside a drybox and transferred to a 300-mL Parr reactor. This vessel was then removed from the drybox and pressurized up to 300 psi (at 25 °C) with pure CO_2. Molecular hydrogen was used to achieve final pressure of 600 psi. The reactor was heated by means of a mantle equipped with a Parr temperature controller Model 4831. When the temperature inside the reactor (measured with a thermocouple type J (iron–constantan) reached 150 °C, the reaction time was started. At the end of the reaction period (normally 24 h) the heating was discontinued and the reactor placed in an ice bath for 1 h. At this time a gas sample was taken by allowing the gas to escape and collecting it by using a gas sampling device. After the reactor was put inside the drybox, the vessel was opened and the reaction solution transferred to an IR cell and to a septum-capped vial in order to be analyzed by GC (the column used for analysis of liquid samples was 10% picric acid over Chromosorb (2 m × $^1/_8$ in.) and 100 (2 min) to 120 °C at 5 °C/min, inlet pressure 21 psi of He; for gas samples the column used was carbosphere (100 (1.5 min) to 160 °C (2 min) at 25 °C/min).

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 86-03681) is greatly appreciated.

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