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Mechanistic Features of Catalytic Carbon Monoxide Hydrogenation Reactions

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I. Introduction

At moderate temperatures, the plausible products of a stoichiometric or catalytic hydrogenation of carbon monoxide include methanol, formaldehyde, and methane as well as a virtually unlimited array of saturated hydrocarbons, olefins, aromatic hydrocarbons, and oxygenated (especially hydroxyl) derivatives of these hydrocarbons. All have been observed in catalytic reactions with the exception of formaldehyde whose formation is not thermodynamically favored over a wide range of temperatures and pressures. On the other hand, formaldehyde precursors, transition metal formyl complexes, can be generated in stoichiometric reactions of metal carbonyls with hydrides or hydride transfer reagents such as BR_3H^-, and some of these formylmetal complexes have been converted to free formaldehyde by acidification with strong acids. Presented in Table I are some relevant thermodynamic data and in Figures 1 and 2 are the temperature and pressure dependencies of equilibrium constants for some CO hydrogenation reactions.

In the catalytic regime for carbon monoxide hydrogenation, there are three commonly referenced reactions: (1) the methanol synthesis reaction,[1-4]

$$CO + 2H_2 \rightarrow CH_3OH \qquad (1)$$

(2) the methanation reaction[5,6]

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

and (3) a synthesis reaction

$$CO \xrightarrow{H_2} C_aH_b + C_cH_d(OH)_e + C_fH_gCHO + C_hH_iCOOH \qquad (3)$$

which is actually a complex set of reactions and is often referred to as the Fischer–Tropsch synthesis reaction[7-13] where the reaction products may consist of a range of hydrocarbons, very high molecular weight polymethylenes, a range of olefins, a range of aromatic hydrocarbons, a range of alcohols or polyols, aldehydes or acids, and cross mixtures of these ranges. It is a synthesis distinguished by lack of selectivity that reflects a myriad of competing reactions. A so-called selective Fischer–Tropsch synthesis, an unknown element today (with the possible exception of polymethylene synthesis) but a desirable technological achievement, will be mechanistically differentiable from the Fischer–Tropsch synthesis and should receive a distinctive name when discovered. From the standpoint of understanding these important hydrogenation reactions, five formal types of reactions may be considered: (i) hydrogen atom transfer from metal surface atoms or from surface intermediates to carbon whereby a carbon–hydrogen bond is formed, (ii) net hydrogen atom transfer to oxygen resulting in oxygen–hydrogen bond formation, (iii) carbon–carbon bond formation, (iv) carbon–oxygen bond scission, and (v) carbon–oxygen bond formation.[14] All these formal types of reactions can be operative in Fischer–Tropsch synthesis, only (i) and (ii) are operative in methanol synthesis (although methanol syntheses generate at least traces of methane), and (iii) and (v) are not significant reactions in a methanation reaction. Although methane itself is not

TABLE I. Thermodynamic Data for Molecules Involved in CO Hydrogenation Reactions[a]

molecule(g)	$\Delta G_f°$, kcal/mol	$\Delta H_f°$, kcal/mol	$S°$, cal/(deg mol)
CO	−32.81	−26.42	47.30
CO_2	−94.26	−94.05	51.06
H_2O	−54.64	−57.80	45.11
H_2CO	−26.3	−25.95	52.26
CH_3OH	−38.69	−48.07	56.8
CH_4	−12.14	−17.89	44.50
C_2H_4	+16.28	+12.45	52.45
C_2H_6	−7.86	−20.24	54.85
C_2H_5OH	−40.30	−56.24	67.4
CH_3CHO	−31.96	−39.73	63.5
$CH_2OHCH_2OH(\ell)$	−77.12	−108.58	39.9
$\overline{CH_2CH_2O}$	−2.79	−12.58	58.1
CH_3OCH_3	−27.3	−44.3	63.72
CH_3CHCH_2	+14.99	*4.88	63.8
C_3H_8	−5.61	−24.83	64.51
$CH_3CH_2CH_2OH$	−38.95	−61.55	77.63
C_6H_6	+30.99	+19.82	64.34

[a] Data selected from the Joint Army–Navy–Air Force Thermodynamic Tables (JANAF Tables) and "The Chemical Thermodynamics of Organic Compounds" by D. R. Stull, E. F. Westrum, Jr., G. C. Sinke; Wiley, New York, 1969.

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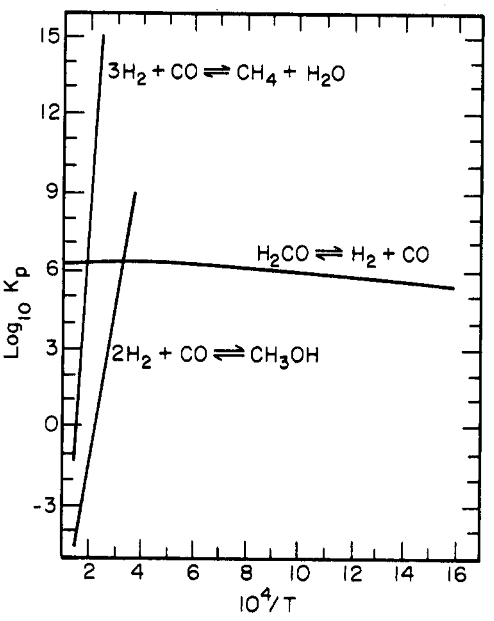


Figure 1. Equilibrium constants for three H_2 + CO reactions presented as a function of temperature.

reactive under typical CO hydrogenation conditions, most other hydrocarbons are reactive and can undergo subsequent dehydrogenation, isomerization, and aromatization reactions. Such reactions are significantly affected by the nature of the catalyst support. For the purposes of this review, we shall consider only the five formal reactions described above as they comprise the key mechanistic steps in these CO hydrogenation reactions.

Fischer-Tropsch synthesis reactions are commonly characterized in review articles as synthesis reactions in which the products have a Flory-Schultz type of molecular weight distribution.[12] Many catalytic systems do but others do not,[13b] particularly those effected at low pressures or high temperatures where methane is a major product. A problem here in characterization may be one of semantics. What is the definition of a Fischer-Tropsch reaction—one that has a Flory-Schultz molecular weight distribution of hydrocarbon products or any relatively nonselective CO hydrogenation reaction? Can we define it mechanistically—is there a single set of elementary reactions operative, to varying degrees, in Fischer-Tropsch synthesis reactions or is there more than one mechanistic set? In fact, only a formal and limited definition is feasible now. We define a Fischer-Tropsch synthesis reaction here as a CO hydrogenation reaction that minimally includes three of the aforementioned *formal* elementary steps: carbon-hydrogen and carbon-carbon bond formation as well as carbon-oxygen bond scission. This definition allows for substantive mechanistic differences among Fischer-Tropsch reactions and delineates the minimal and key formal reaction steps. In a sense, the methanation reaction is a limiting case of Fischer-Tropsch synthesis where a surface methyl species is intercepted selectively by a surface hydride species. In a Fischer-Tropsch synthesis reaction, there probably is a number of different surface intermediates each of which may react with an identical intermediate or with a different one, hence leading potentially to a mixture of products. High mobility of at least some of these surface species is a necessary feature of these reactions. An enlightening set of experiments[11] has indicated possible mobility features of surface intermediates in a CO hydrogenation reaction: Using a pure zirconia catalyst, the major hydrocarbon product was methane; only small amounts of methanol, dimethyl ether, hydrocarbons, and aromatic hydrocarbons were detected as products. In sharp contrast, a simple physical mixture of the zirconia catalyst with a zeolite yielded a mixture of hydrocarbons that consisted largely of aromatic hydrocarbons and contained virtually no methane.

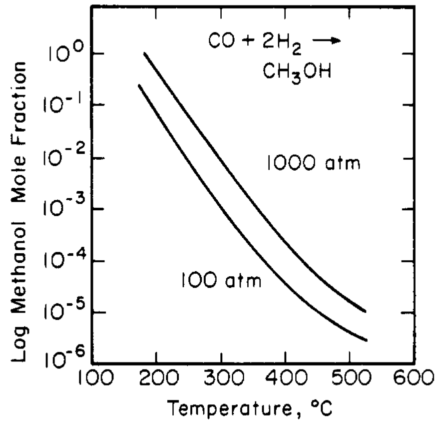
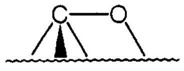


Figure 2. Temperature dependence of equilibrium methanol concentration in $2H_2$ + CO reaction systems is presented at two different pressures.

The organization of this mechanism discussion is in terms of the formal reaction steps enumerated above. Each of five elementary steps (C-O bond scission or formation, O-H bond formation, C-H bond formation, and C-O bond formation) is considered in separate sections *as a first or an early step* in the hydrogenation sequence. In each section, subsequent steps comprising C-H and O-H bond formation are also considered. The C-H bond formation is factored into two sections, one treating the first step, formation of a formylmetal complex, and the second, the steps subsequent to a formylmetal intermediate. The fifth reaction step, carbon-carbon bond formation, is considered lastly—not because such steps are necessarily final steps exclusive of termination steps but simply to separate this common reaction step from the others. In all these sections, possible surface intermediates are compared with relevant species established in mononuclear and polynuclear (cluster) metal coordination chemistry. Solution-state reactions, stoichiometric and catalytic, are generally more susceptible to mechanistic studies because of the relatively long lifetime of intermediates (relative to surface reactions), and established solution-state chemistry of CO (and of CO + H_2) with transition metal complexes can be suggestive of plausible intermediates and of reaction sequences for the analogous surface chemistry.

II. Carbon-Oxygen Bond Scission



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Carbon-oxygen bond scission in CO hydrogenation reactions may occur at any point in the overall reaction sequence. We consider here the case where this scission occurs before any carbon-hydrogen bond formation steps and then consider the possible steps subsequent to C-O bond scission. Chemisorption of carbon monoxide on metal surfaces initially involves bonding of the CO carbon atom to one or more surface metal atoms. As the temperature is raised, intermediates similar to 1 can be formed. In fact, there are specific models of such an intermediate in metal carbonyl clusters (see Figure 3). At higher temperatures, cleavage of the carbon-oxygen bond can occur and, under some conditions with the less electropositive metals, the resultant chemisorbed oxygen atom may react with CO to form gaseous CO_2.[15] The CO bond-breaking process proceeds more readily on the surfaces of electropositive metals like iron where the chemisorption process is dissociative in character at 300 K. Ruthenium does not effect cleavage of the carbon-oxygen bond under moderate conditions but does at the elevated temperature and pressure conditions that are employed for CO hydrogenation

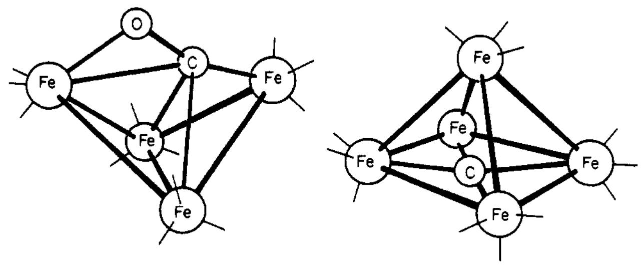
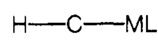


Figure 3. Two cluster structures presented here are representative of various stages in the dissociative chemisorption of carbon monoxide on a metal surface. The structure to the left shows a cluster framework arrangement for $[Fe_4(CO)_{13}H]^-$ in which one of the carbonyl ligands is bonded through both the carbon and the oxygen atoms. The positions of the other 12 carbonyl ligands are spatially shown by the lines that project out from each of the four iron atoms, and the hydride ligand bridges the lower two iron atoms. This very interesting cluster structure is suggestive of an intermediate state in the conversion of a chemisorbed carbon monoxide molecule to a dissociatively chemisorbed state with disjoint carbon and oxygen atoms on a metal surface. The figure to the right depicts the framework atoms in the cluster carbide, $CFe_5(CO)_{15}$. The cluster has an exposed μ_5-C ligand that extends below the basal plane of the square pyramidal array of five iron atoms. The individual carbon and oxygen atoms of the 15 carbonyl ligands are not shown, but the basic stereochemistry of the ligand array is shown by lines that project out from each of the five iron atoms.

reactions. In fact, recent studies indicate that the first step in Fischer–Tropsch synthesis reactions catalyzed by iron, ruthenium, cobalt, and nickel is the cleavage of the carbon–oxygen bond.[16-20] The oxygen atom from the CO dissociation step may appear in a CO_2 product or with electropositive metals like iron may appear initially in a metal oxide surface phase and ultimately in the product, H_2O. There is no explicitly established analog of this elementary step in molecular metal coordination chemistry although some metal carbonyl complexes on pyrolysis generate so-called metal carbide clusters[21] in which the carbidic carbon atom is bonded only to metal atoms. The carbidic carbon atom, in some cases, appears to be formed from a CO ligand although a definitive labeling reaction has not been reported. Labeling studies have established a "solvent" molecule as the source of the carbide carbon atom in some metal carbide cluster syntheses.[22]

The elementary step subsequent to CO bond scission may be carbon–hydrogen bond formation or carbon–carbon bond formation. Obviously, the former predominates in the methanation reaction as, for example, in a low-pressure metal surface catalyzed hydrogenation or in the high-pressure and -temperature nickel surface catalyzed hydrogenation. Nevertheless, some higher hydrocarbons are always produced although the yields may be very low, but we defer consideration of the carbon–carbon bond formation and the production of higher hydrocarbons until a later section of this discussion.

In the conversion of a surface carbon atom to methane, there probably will be intermediate states of CH, CH_2, and CH_3 species bound to surface metal atoms. All three species are known as ligands in mononuclear transition metal coordination chemistry as shown in **2-4**. In the carbyne or alkylidyne complexes, **2**, the parent methylidyne derivative is unknown but the RCM analogs are established.[23-25] For this set, nothing is known about the ease of converting, *with H_2 as the reactant,* a methylidyne to a methylene metal complex or a methylene to an alkyl metal complex,[26] although the reaction of alkyl metal complexes with hydrogen to yield methane is well established.[27] However, metal clusters appear to be better models, albeit simple models, of chemisorption states, and the chemistry of the cluster derivatives, namely the CH, CH_2, and CH_3 species as well as C (carbide) species, would seem a more relevant reference state here.



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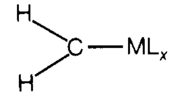

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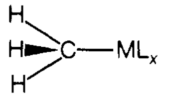

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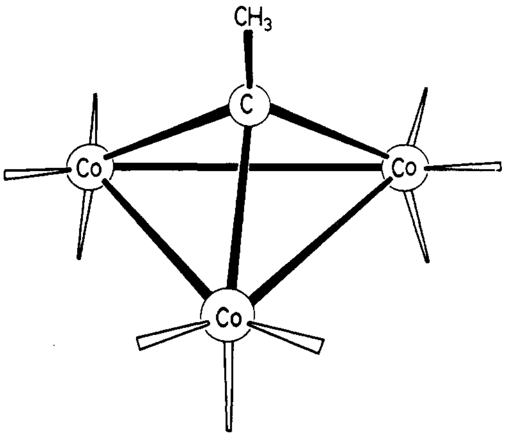


Figure 4. In this figure the spatial arrangement of the framework atoms in the μ_3-ethylidyne cluster, $CH_3CCo_3(CO)_9$, is shown. The spatial positions of the nine carbonyl ligands, three carbonyl ligands terminally bonded to each cobalt atom, are shown by the lines that project from the cobalt atoms.

There is only one class of a metal cluster in which a carbidic or bare carbon atom is bound to metal atoms so as to project out, in an exposed manner, away from the basic metal atom framework; the carbide carbon atoms in $Fe_5C(CO)_{15}$ and its derivatives like $Fe_5C(CO)_{14}^{2-}$ and $Fe_5C(CO)_{15-x}L_x$, $Ru_5C(CO)_{15}$, and $Os_5C(CO)_{15}$ lie below the base of the square-pyramidal array of metal atoms (Figure 3).[28-30] The carbide carbon atom in $Fe_5C(CO)_{15}$ has been shown by Tachikawa[31] to be nonreactive toward hydrogen up to ~80 °C where this iron cluster decomposes. In contrast, the carbon species generated by the dissociative chemisorption (at elevated temperatures) of CO on metals like nickel and ruthenium react with hydrogen gas at 25 °C to generate hydrocarbons.[16,17]

Metal clusters with a bound CH species (and the analog CR species with R = alkyl or aryl) are well established. The common form is a trimetallic cluster in which all three metal atoms are bonded to the carbon atom to give a tetrahedral CM_3 framework, as in $CH_3CCo_3(CO)_9$ (Figure 4).[32] Although the reaction of these HC (or RC) cluster complexes with hydrogen is little explored, the critical step of hydrogenation to give methane (or alkane) has been demonstrated in a photoactivated hydrogenation and in a thermal hydrogenation of a μ_3-alkylidyne ligand. Geoffroy and Epstein have reported the quantitative formation or methane and $Co_4(CO)_{12}$ from the photochemical reaction of hydrogen and $HCCo_3(CO)_9$.[33] For the thermal reactions, Bergman and Stuhl[34] have shown that hydrogen converts $RCCo_3(CO)_9$ to alkane (RH), alkene (R–H), $Co_4(CO)_{12}$, and traces of cobalt metal. The point at which Co–Co bonds are broken and re-formed in these reactions is not known. Also, the cluster $CH_3OCRu_3H_3(CO)_9$ is converted at 130 °C to dimethyl ether and $Ru_3(CO)_{12}$ in a high-pressure (~30 atm) atmosphere pf CO and hydrogen.[35] In this hydrogenation process, intermediate carbene and alkyl derivatives are presumably generated as speculatively noted in (4)

$$CH_3OCRu_3H_3(CO)_9 \overset{CO}{\rightleftharpoons} CH_3O\overset{H}{C}Ru_3H_2(CO)_{10}$$
$$\overset{CO}{\rightleftharpoons} CH_3OCH_2Ru_3H(CO)_{11} \overset{CO}{\rightleftharpoons} CH_3OCH_3 + Ru_3(CO)_{12} \qquad (4)$$

although some cluster fragmentation and re-formation may occur at some stage(s). The alkoxyalkylidyne ruthenium, and also an analogous osmium, complex was prepared in a two-step synthesis from methyl fluorosulfate and $HM_3(\mu_2\text{-}CO)(CO)_{10}^-$ (re-

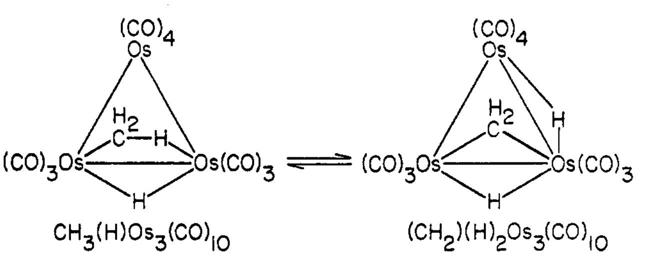


Figure 5. This is a representation of the remarkable equilibrium solution of two cluster molecules, one a methylene and the other a methyl species, which rapidly interconvert. The methylene structure on the right has been established by crystallographic analysis. The precise structure of the methyl derivative on the left has not as yet been crystallographically defined but NMR spectroscopic data have reasonably established that the methyl group unsymmetrically bridges between two osmium atoms with a three-center, two-electron C–H–Os interaction.

$$CH_3SO_3F + HM_3(\mu_2\text{-}CO)(CO)_{10}^- \rightarrow SO_3F^- + HM_3(\mu_2\text{-}COCH_3)(CO)_{10} \quad (5)$$

$$HM_3(\mu_2\text{-}COCH_3)(CO)_{10} + H_2 \xrightleftharpoons{60\ ^\circ C} H_3M_3(\mu_3\text{-}COCH_3)(CO)_9 + CO \quad (6)$$

actions 5 and 6). Notable here are the intermediate complexes with alkoxyalkylidyne ligands that are edge bridging rather than face bridging. An analogously prepared iron μ_2-alkylidyne complex, $HFe_3(\mu_2\text{-}COCH_3)(CO)_{10}$, was not susceptible to facile conversion (reaction 6) to a μ_3-$COCH_3$ derivative.

Conversion of HCM_3 cluster complexes to H_2C– and H_3C–cluster species and to free methane is of substantial scientific interest, and the ease of such transformations and the reaction mechanism(s) should be explored in detail. The relative thermodynamics of hydrocarbon (or hydrocarbon fragment) dehydrogenation and hydrogenation are very sensitive to temperature and pressure conditions. Hence, the hydrogenation of the HCM_3 type of cluster should be explored under varying hydrogen pressure conditions to establish the critical thermodynamic as well as kinetic features.

Carbene or methylene, CH_2, and methyl derivatives of molecular metal clusters are limited to one fully characterized example each with both derivatives arising from a solution equilibrium between them.[36] The reaction of diazomethane with the cluster hydride, $H_2Os_3(CO)_{10}$, produces $Os_3(CO)_{10}CH_4$[37] which in solution exists as an equilibrium mixture of the methyl species $H(CH_3)Os_3(CO)_{10}$ and the μ_2-methylene species, $H_2(CH_2)Os_3(CO)_{10}$[38] (Figure 5). The methyl derivative is especially interesting because it looks like a snapshot of an incipient carbon–hydrogen bond breaking (or bond making) process; the CH_3 group bridges between two metal atoms but in an unsymmetric fashion with an Os–C–H–Os multicenter interaction.[36,39] Rapid and selective exchange of C–H hydrogen atoms occurs in the methyl derivative with the hydrogen atom in the hydride site that bridges the side to the right (Figure 5) in the methylene derivative.[36]

Hydrogenation of the above methyl and methylene cluster derivatives has not been reported. Solutions of these species when heated yield the carbyne or methylidyne derivative $HCOs_3H_3(CO)_9$ (eq 7), which has a tetrahedral Os_3C core,

$$CH_2Os_3H_2(CO)_{10} \text{ (or } CH_3Os_3H(CO)_{10}) \rightarrow HCOs_3H_3(CO)_9 + CO \quad (7)$$

three edge-bridging hydride ligands, and a set of three terminal carbonyl ligands associated with each osmium atom.[36] Thus, in this case, dehydrogenation of the CH_3 (and CH_2) species occurs at elevated temperatures. Presumably, hydrogenation to give methane would prevail under high hydrogen and carbon monoxide pressure conditions; the presence of CO might facilitate the hydrogenation (hydrogen transfer from Os to C), and $Os_3(CO)_{12}$, or $H_2Os_3(CO)_{11}$, would then be the predominant coproduct as in (4) above which is fully analogous.

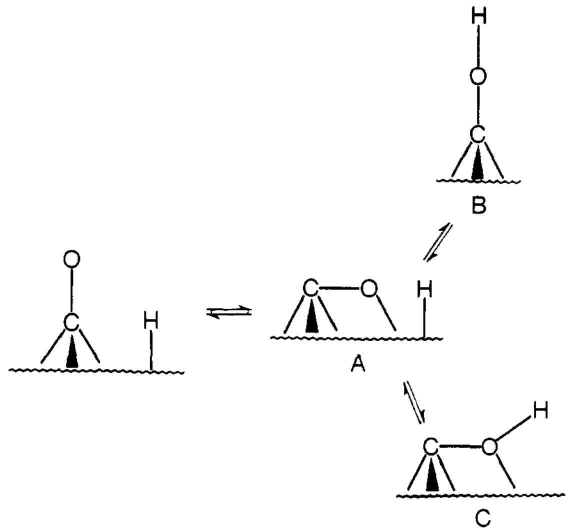
Several other cluster and dinuclear metal methylene complexes have been reported. $Ru_3(CH_2)(CO)_{10}H_2$ is a minor product of the reaction of $Ru_3(CO)_{12}$ with $NaBH_4$, although it was not isolated in spectroscopically pure form.[40] Three dinuclear metal derivatives with bridging methylene groups, $(\mu_2\text{-}CH_2)Rh_2(CO)_2(\eta^5\text{-}C_5H_5)_2$,[41] $(\mu_2\text{-}CH_2)_3Ru_2(PMe_3)_6$,[42] and $\mu_2\text{-}(CH_2)Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$,[43] have been synthesized and crystallographically characterized. In the complex $[(CH_3)_3P]_3Ru(\mu_2\text{-}CH_2)_3Ru[P(CH_3)_3]$, where there are three symmetrically bridging CH_2 groups, protonation gives $\{[(CH_3)_3P]_3Ru(\mu_2\text{-}CH_2)_2Ru[P(CH_3)_3]_3\}^{2+}$ where there are two. Monoprotonation of the former yields $\{[(CH_3)_3P]_3Ru(\mu_2\text{-}CH_2)_2(\mu_2\text{-}CH_3)Ru[P(CH_3)_3]_3\}^+$ which has two symmetrically bridging CH_2 groups and one bridging CH_3 group that *may* be symmetric in form.[42b] No chemistry relating to hydrogenation or dehydrogenation reactions of these methylene complexes has been reported.

Presumably, a carbide cluster like $Fe_5C(CO)_{15}$ with an exposed rather than a central or cage carbon atom, the various methylidene clusters like $HCCo_3(CO)_9$ and $HCOs_3H_3(CO)_9$, and the methyl and methylene osmium clusters discussed above may be reasonable models of the intermediate surface states in the conversion of CO to CH_4 wherein the first step is C–O bond cleavage. However, the chemical reactivity of C, CH, CH_2, and CH_3 bridging ligands may be different in the two regimes of cluster and surface chemistry. In fact, the ease of hydrogenation of surface carbon, generated by dissociative CO chemisorption on metals like ruthenium, to give hydrocarbons suggests that the activation energy in the sequence of steps $C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4$ is very low. Once the carbon surface species is generated, hydrogenation can proceed even at 20 °C. On the other hand, the susceptibility to hydrogenation of a C ligand in a cluster with an exposed carbide atom is very low if not zero in the $Fe_5C(CO)_{15}$ experiment. Furthermore, the temperatures required for hydrogenation of the triply bridging HC and RC ligands in cobalt and ruthenium clusters is high (>100 °C). Perhaps the C and HC surface species on the irregular surfaces of real heterogeneous catalysts are bonded not to four or five and to three metal atoms, respectively, but to fewer. Such C or HC metal species would be less coordinately saturated and should have higher reactivities. Important research objectives are (1) the synthesis of coordinately unsaturated clusters with μ_3 or μ_2 C ligands and μ_2 HC ligands and (2) a comparison of the hydrogenation rates of these ligands with those of the (presently) conventional μ_5-C and μ_3-HC ligands and with metal surface carbon intermediates generated from dissociative CO chemisorption.

Not all metal surface catalyzed methanation reactions or hydrogenation reactions that yield only hydrocarbons necessarily will follow a reaction cycle in which the carbon–oxygen bond is cleaved first, even for those catalytic systems (e.g., Co, Ni, and Ru) in which the *major* reaction cycle does involve this bond cleavage reaction as the first step. It is possible that another sequence, which has as a first step carbon–hydrogen bond formation, is competitive at least under some reaction conditions. In fact, there is a study[20] of the nickel-catalyzed methanation reaction that indicates two types of catalytic cycles are operative: the dominant high-temperature cycle based on a first step involving dissociative chemisorption of CO and a second, low-temperature cycle in which there is a direct hydrogenation of the chemisorbed CO *molecule*.

III. Oxygen–Hydrogen Bond Formation

In principle, the first step in a CO hydrogenation reaction could be transfer of hydrogen from the surface metal atoms to the oxygen atom, and we consider this possible first step in this section. The geometric features of such a reaction potential surface could be quite varied. Two plausible sequences are illustrated in (8). Hydrogen transfer from a metal (metal hydride) site to the oxygen atom would appear an unlikely event, but hydrogen transfer from a M-OH surface site (metal oxide or metal oxide–metal catalyst) is certainly feasible. Of the labeled intermediates in (8), only C has not been established yet in cluster coordination chemistry. Intermediate B, a hydroxymethylidyne species with the carbon atom bound to three metal atoms, is defined spectroscopically for one cluster ($(\mu_3\text{-HOC})Co_3(CO)_9$)[44] obtained by the low-temperature (−20 °C) acidification of anionic $[(\mu_3\text{-OC})Co_3(CO_9)]^-$.[45,46] This hydroxymethylidyne cluster is unstable as a solid or in solution; the cluster decomposes rapidly at 20–40 °C to yield (solution phase) $HCo(CO)_4$ and $Co_4(CO)_{12}$. Thus, the thermodynamic implications for this isolated example of a $(\mu_3\text{-HOC})M_3$ cluster suggest that oxygen–hydrogen bond formation may not be an especially favorable first step in surface catalyzed CO hydrogenation reactions that do not proceed by an initial CO dissociative chemisorption step and that (to anticipate later discussion) do not involve an electropositive metal like zinc. However, neither is the alternative step of carbon–hydrogen formation to give a formyl metal species an especially favorable step (see next section). In fact, the rate-determining step in transition metal catalyzed CO hydrogenation reactions that do not have C–O bond scission as the first step may be the formation of either a >COH or -CHO surface intermediate.[47]



(8)

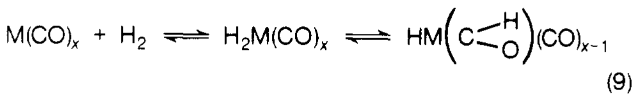
Protonation of anionic metal carbonyls at low temperatures will probably serve as a relatively general synthesis route to bridged COH ligands. Hodali and Shriver[48a] have prepared $(\mu_2\text{-HOC})HFe_3(CO)_{10}$ by a protonation of $HFe_3(CO)_{11}^-$ at −90 °C. This complex with an edge bridging COH ligand decomposes above −30 °C as does the $(\mu_3\text{-HOC})Co_3(CO)_9$ complex. In contrast, the $\mu_2\text{-CH}_3OC$ iron derivative is quite stable,[48a] as is the analogous $\mu_3\text{-CH}_3OC$ derivative of $Co_3(CO)_9$.[49]

The oxygen atoms of carbon monoxide molecules coordinated to one or several metal atoms are weakly basic sites and can bond, for example, to strong Lewis acids, protic acids, and carbonium ions.[50] Shriver and co-workers[51] have established that such acid–base interactions can occur in mononuclear and polynuclear metal carbonyls in the presence of a strong Lewis acid like a boron trihalide. Because electron transfer from metal to carbon monoxide is more effective if the carbonyl ligand is bridge bonded rather than terminally bonded, the acid–base interaction in polynuclear metal carbonyls is such that the Lewis acid is almost invariably bound to an oxygen atom of a bridging carbonyl.[50] Such complexation will reduce the effective C–O bond order and may facilitate subsequent reduction (hydrogenation) reactions of this doubly bound CO molecule. This possibility is not adequately documented but some supportive data exist. A remarkably facile hydrogenation of carbon monoxide to hydrocarbons can be effected with $Ir_4(CO)_{12}$ as the catalyst precursor, in the presence of an aluminum halide.[53] It has been proposed that species with Ir–C–O–Al interactions may be active intermediates in the catalytic reaction. In addition, alane, AlH_3, which is a strong Lewis acid, has been shown to complex and reduce coordinated CO in $Ru_3(CO)_{12}$ to give hydrocarbons.[54]

IV. Carbon-Hydrogen Bond Formation

A. Metal-Formyl Intermediate

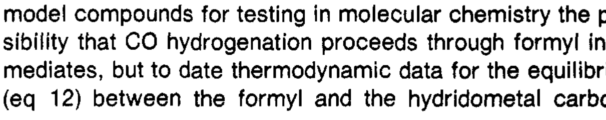
One of the most attractive first steps to set out for a catalytic CO hydrogenation reaction is hydride transfer from a metal atom to a carbonyl ligand to form a formyl intermediate (eq 9). This hydride transfer to the carbonyl carbon atom has a fully documented analog in the facile formation of acylmetal complexes from alkylmetal carbonyl complexes (eq 10) which forms the very mechanistic key to the myriad of catalytic hydroformylation, carboxylation, and carboalkoxylation reactions, some of which are of substantial technological importance.



$$M(CO)_x + H_2 \rightleftharpoons H_2M(CO)_x \rightleftharpoons HM\left(C\begin{smallmatrix}H\\O\end{smallmatrix}\right)(CO)_{x-1} \quad (9)$$

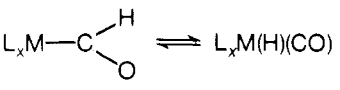
$$CH_3M(CO)_x \xrightarrow{CO} CH_3\overset{O}{C}M(CO)_x \quad (10)$$

Transition metal-formyl complexes have been prepared, isolated, and studied in recent years because of the increased interest in CO hydrogenation reactions.[55-60] None has been prepared directly from hydrogen and a molecular metal carbonyl or from a hydridometal carbonyl complex, but Lewis acids like AlX_3 or BX_3, which Shriver and co-workers[48b] have shown promote CO insertion in alkylmetal complexes, might promote such reactions. Of the synthetic procedures known, the most general and effective procedure comprises the reaction (eq 11) of a metal carbonyl with a hydride ion transfer reagent such as BR_3H^-.[57] In fact, the essence of nearly all formylmetal complex syntheses is hydride ion transfer to a metal carbonyl, and these formyl derivatives are themselves hydride donors, a point of some potential mechanistic importance as discussed later.



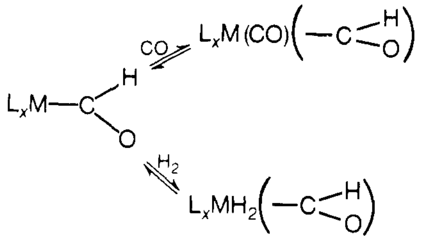
$$BR_3H^- + (\eta^5\text{-}C_5H_5)Re(CO)_2(NO)^+ \longrightarrow BR_3 + (\eta^5\text{-}C_5H_5)Re\left(C\begin{smallmatrix}H\\O\end{smallmatrix}\right)(CO)NO) \quad (11)$$

The recent studies of formylmetal complexes have provided model compounds for testing in molecular chemistry the possibility that CO hydrogenation proceeds through formyl intermediates, but to date thermodynamic data for the equilibrium (eq 12) between the formyl and the hydridometal carbonyl complexes have not been obtained. It is known that formylmetal complexes decompose (at widely varying rates) to form the hydridometal carbonyl complex, but equilibrium information is lacking for moderate conditions of pressure and temperature and for conditions typical of catalytic CO hydrogenation reactions. Since for the generalized equilibrium (eq 12), cited above, the formyl complex has two fewer electrons than the hydridometal carbonyl, high CO or H_2 pressures should favor the formyl complex as illustrated in eq 13. Essential to an understanding of CO hydrogenation reactions are thermodynamic data



$$L_xM{-}C\begin{smallmatrix}H\\O\end{smallmatrix} \rightleftharpoons L_xM(H)(CO) \quad (12)$$

for equilibria like (12) and (13) over a range of temperature and pressure conditions. Essential also are chemical studies that



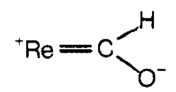
(13)

would demonstrate the reduction *by hydrogen* (*H_2*) of formylmetal complexes to organic products like methane or methanol. Reduction of formylmetal species to alkylmetal complexes by strong reducing reagents like borane etherate may be relevant to basic metal oxide catalyzed reactions, e.g., ZnO where the active Zn-H intermediate is a strong hydride ion transfer species, but such reductions do not demonstrate the feasibility of reaction steps for a formylmetal intermediate in transition metal catalysis of *hydrogen* (H_2) reduction of CO.

Available information for formylmetal complex chemistry does suggest several quite different and possible scenarios for methanol synthesis from CO and H_2 at basic oxide surfaces or multiphase surfaces like ZnO-Cu. Such catalysts produce methanol from CO + H_2 in a remarkably efficient and selective fashion (only traces of methane are found). The key spectroscopic observation is that ZnO reacts with hydrogen to form Zn-H surface species probably at anion vacancy sites.[61] Since zinc hydrides are effective and strong hydride ion transfer reagents, surface Zn-H species should, on the basis of established formylmetal syntheses, generate surface -CH-O species if a surface bound CO species is present. Because ZnO alone will produce methanol from CO + H_2, there must be some type of Zn-CO surface species under methanol synthesis conditions. With the more effective ZnO-Cu catalyst, the carbon monoxide may be bound initially at copper sites.[62] The active copper sites are probably more like copper(I) than copper(0) sites; the former more effectively binds carbon monoxide. Klier and co-workers propose dissolution of Cu(I) in the ZnO matrix because they found no evidence for a separate copper oxide phase.[62] Actually, carbon dioxide is added in small amounts to the synthesis gases for optimal yields with the commercial ZnO-Cu-Al_2O_3 catalyst, and a possible role of CO_2 is to help sustain active copper(I) sites under the reducing conditions of methanol synthesis.

Some transition metals from the later periodic groups, e.g., iridium, palladium and platinum, can also catalyze the synthesis of methanol at high pressure and temperature although not with the selectivity of ZnO based catalysts.[4,5] The mechanism of these metal catalyzed reactions is unknown. Here the first step also could be formation of a surface formyl species, but there is no evidence for such an intermediate. A key experiment in these metal surface catalyzed syntheses of methanol is the hydrogenation of a $^{13}C-^{16}O$ and $^{12}C-^{18}O$ mixture because the nonappearance of the cross product, $^{13}CH_3{}^{18}OH$, would establish that no CO bond scission occurs in the catalytic cycle or the converse observation and conclusion.[63a] Deuterium isotope effects have been interpreted in terms of a rate-determining H_2 dissociation on ZnO-Cr_2O_3 (zinc chromite) surfaces.[63b]

Cluster formyl chemistry is presently an unknown area, and hence there are no cluster stereochemical models. The analog acyl group is known only as a terminal ligand in molecular coordination chemistry.[63e] A formyl radical chemisorbed on a metal surface could be bound to one or more surface metal atoms or could be bound through both the carbon and the oxygen atoms.[64] The structure of a mononuclear rhenium formyl derivative has been established by crystallographic studies,[55b] and the rhenium carbon distance is very short, 2.06 Å, suggesting a significant contribution from forms like:

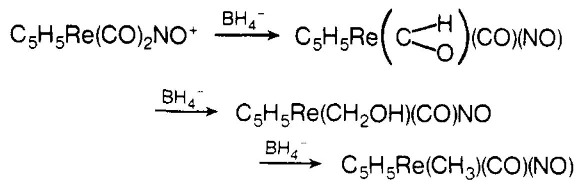


B. Possible Reaction Sequences Subsequent to a Formyl Intermediate

Given the assumption that reaction of CO and H_2 on metal or metal oxide surfaces can generate a metal-formyl species in an early step, the cogent issues are: (i) what surface species are then sequentially formed, (ii) does H atom transfer always proceed directly from a metal site to a carbon (or carbon—oxygen) site, (iii) is a series of H atom transfers the base of subsequent intermediate formation or do other surface radicals play significant roles? Each of these issues is assessed first in hypothetical form and then with relation to established or suspected reaction sequences. Largely we ignore discussion of C-C bond formation reactions here although such reactions may readily occur with intermediates considered in this section. Carbon-carbon bond forming reactions are discussed in the next section.

Without concern for the source of H we may graphically represent a series of H atom transformations of a formylmetal intermediate and a set of intermediate rearrangements as shown in Scheme I. The question of the number and kinds of metal atom interactions with individual intermediates is ignored for the initial purposes of the scheme; e.g., species B could be bound through both the carbon and the oxygen atoms to surface metal atoms. Because C-C bond formation reactions are presently ignored, only three "free" products are considered, namely, formaldehyde, methanol, and methane, and formaldehyde formation is a thermodynamically insignificant reaction.

Precedents exist for all intermediates, A-E, shown in Scheme I. Essentially all relevant information for these intermediates comes from mononuclear metal coordination chemistry. Cluster structural models for these possible intermediates exist today only for D and E where the OCH_3 ligand bridges between two metal atoms as in $H(CH_3O)Os_3(CO)_{10}$[65] and where the CH_3 ligand unsymmetrically bridges two metal atoms in the previously cited $H(CH_3)Os_3(CO)_{10}$[38] molecule. For the mononuclear models, much of the information is derived from the chemistry of η^5-$C_5H_5Re(CO)_2NO^+$ and its phosphine derivative η^5-$C_5H_5Re[P(C_6H_5)_3](CO)NO^+$. Reduction of the dicarbonyl cation by borohydride ion, controlled by stoichiometry and solvent medium, yields the formyl, hydroxymethyl, and methyl derivatives (eq 14);[66] interestingly, the hydroxymethyl derivative

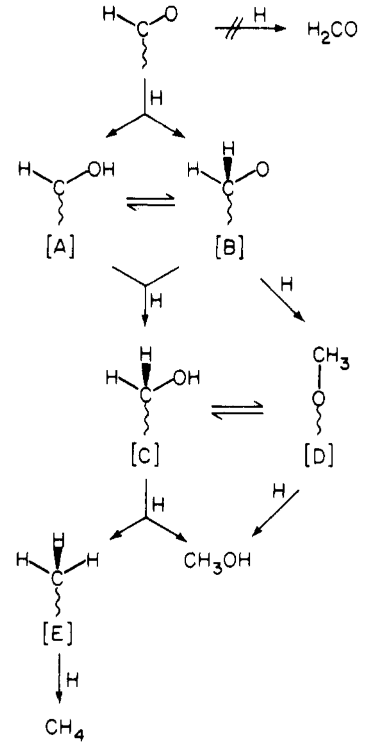


$$C_5H_5Re(CO)_2NO^+ \xrightarrow{BH_4^-} C_5H_5Re\left(C{<}^{H}_{O}\right)(CO)(NO) \xrightarrow{BH_4^-} C_5H_5Re(CH_2OH)(CO)NO \xrightarrow{BH_4^-} C_5H_5Re(CH_3)(CO)(NO) \quad (14)$$

is an air-stable and relatively thermally stable crystalline solid.[67] Protonation of the formyl complex, $C_5H_5Re(CHO)[P(C_6H_5)_3]NO$ apparently gave the hydroxymethylene $C_5H_5Re(CHOH)[P(C_6H_5)_3]NO^+$, a thermally unstable complex; the corresponding methylation reaction with CH_3SO_3F gave the stable methoxymethylene complex, isolated and characterized as the SO_3F^- salt.[69,70]

An alternative to the hydroxymethylene surface intermediate A is some kind of formaldehyde complex B. One example of a CH_2O derivative of a mononuclear metal complex is known: reaction of an aqueous formaldehyde solution with $Os(CO)_2[P(C_6H_5)_3]_2$ yields $Os(CO)_2[P(C_6H_5)_3]_2(\eta^2$-$CH_2O)$ which has the structure shown in Figure 6 wherein the formaldehyde is bound through both the carbon and oxygen atoms.[71] This formaldehyde complex reverts on temperature elevation to a

SCHEME I



formylosmium hydride complex (eq 15). No experimental data have been reported for the reduction of a formymetal derivative

$$\mathrm{Os(CO)_2[P(C_6H_5)_3]_2(\eta^2\text{-}CH_2O)} \longrightarrow \mathrm{Os(CO)_2[P(C_6H_5)_3]_2\left(C\begin{smallmatrix}H\\O\end{smallmatrix}\right)(H)} \quad (15)$$

to a CH_2O derivative and for a subsequent reduction of the latter by hydrogen (H_2) in molecular coordination chemistry. However, a tentative indication of hydrogen atom addition to the formaldehyde derivative to yield a $-CH_2OH$ metal derivative (eq 16) has been described,[71] but the CH_2OH derivative was not obtained

$$\mathrm{Os(CO)_2[P(C_6H_5)_3]_2(\eta^2\text{-}CH_2O) + CF_3COOH} \rightarrow \mathrm{Os(CO)_2(CH_2OH)(O_2CCF_3)[P(C_6H_5)_3]_2} \quad (16)$$

in pure form and was only spectrally studied.

Generation of an OCH_3 intermediate from CO has been demonstrated in zirconium chemistry. The ziroconium(IV) hydride, $[\eta^5\text{-}C_5(CH_3)_5]_2ZrH_2$, reacts with CO at −80 °C to form a carbonyl adduct that yields $[\eta^5\text{-}C_5(CH_3)_5]_2ZrH(OCH_3)$ and $\{[\eta^5\text{-}C_5(CH_3)_5]_2ZrH\}_2(OCH{=}CHO)$ depending upon reaction conditions.[72,73] The proposed[72] reaction sequence for this chemistry is illustrated in Figure 7. This sequence (mechanistically suggestive for a CO hydrogenation scheme) may not be applicable to CO hydrogenation reactions catalyzed by the heavier (relatively electronegative) transition metals but may be of special relevance to the methanol synthesis reactions catalyzed by metal oxide or by metal oxide systems like ZnO–Cu where strongly hydridic metal intermediates are generated.

Thus, there is a substantial set of structural and chemical data that clearly show that all intermediates outlined in Scheme I are plausible and have coordination chemistry models. For the surface case, intermediates A through E are not all modelled in cluster chemistry but reasonable surface binding modes can be predicted.

(A) Hydroxymethylene intermediates should bridge metal sites as does the μ_2-alkoxymethylene ligand, $-C(OCH_3)C_6H_5$, in the cluster $Pt_2W[\mu_2\text{-}C(OCH_3)C_6H_5](CO)_6$.[74] Were the metal atoms of the surface strongly electropositive, bridging of both the carbon and the oxygen atoms of HCOH might occur; however, it is probably unlikely that hydroxymethylene intermediates are significant species in CO + H_2 reactions at a surface composed of strongly electropositive metal atoms.

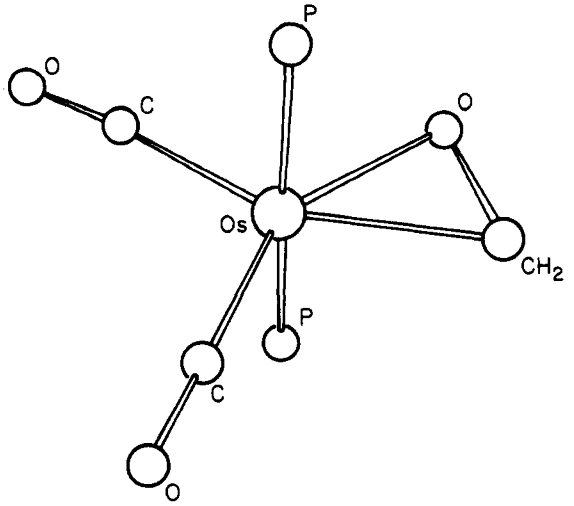


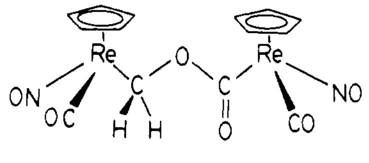
Figure 6. The skeletal array of atoms in the coordination sphere of a formaldehyde complex, $Os(\eta^2\text{-}CH_2O)(CO)_2[P(C_6H_5)_3]_2$, with the positions of the phenyl ligand atoms excluded for clarity. The structure may be considered as a six-coordinate complex with a bidentate formaldehyde ligand or alternatively as a pseudo-five-coordinate structure if the formaldehyde ligand is simply treated as a monodentate ligand. For the interaction of the formaldehyde ligand with the osmium center, the carbon–osmium and the oxygen–osmium distances are very similar, 2.19 and 2.04 Å, respectively. The carbon–oxygen distance in the formaldehyde ligand is very long, 1.59 Å.

(B) An H_2CO surface intermediate is unlikely to be bound only through oxygen and should be bonded to one or more metal surface atoms through both the carbon and oxygen atoms. The one example of an H_2CO ligand is the mononuclear osmium complex depicted in Figure 6; both the C and O atoms are bonded to the osmium atom.

(C) Hydroxymethyl intermediates should be bound to the metal surface through carbon and should bridge metal sites. For surfaces comprised of strongly electropositive metal atoms, the same qualifications cited in (A) above for the hydroxymethylene ligand above apply.

(D and E). Methyl and methoxy ligands should be bound through C and O atoms, respectively, to the surface metal atom and should bridge metal sites as established for cluster models.

Now we return to question (ii) posed at the beginning of this section: does H atom transfer in the conversion of a formyl metal complex always proceed from a metal site to a carbon (or carbon–oxygen) site? Actually, formyl metal complexes themselves are effective hydride transfer reagents. Moreover, Casey and co-workers[68] have demonstrated that $\eta^5\text{-}C_5H_5Re(CHO)(CO)(NO)$ upon standing at 20 °C (the complex is an oil at these temperatures) yields largely a dinuclear complex in which hydride transfer from one formyl ligand to the other has occurred, as shown in **5** (yet in dilute solution the complex decomposes slowly to $\eta^5\text{-}C_5H_5ReH(CO)_2(NO)$). In addition, metal oxide or metal oxide–metal surface catalysts will have surface OH groups that could potentially participate in the transformation of CO to hydrocarbon products; a noncomprehensive graphical represen-



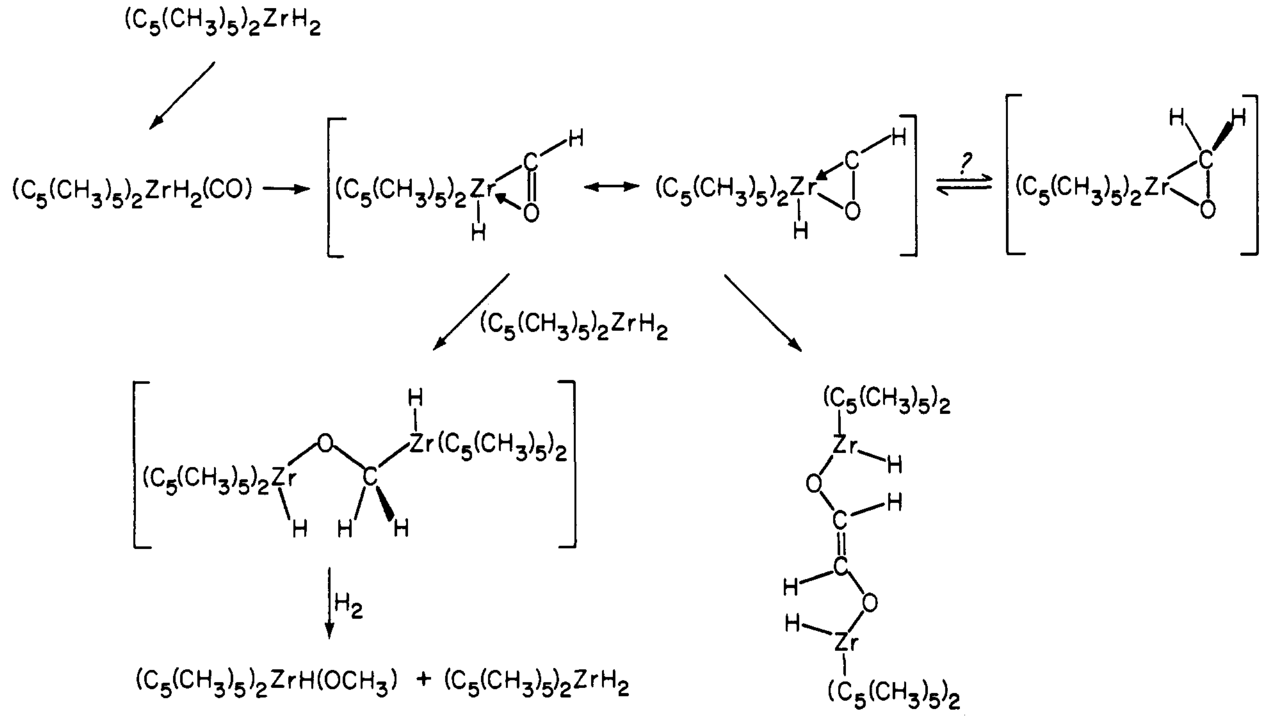


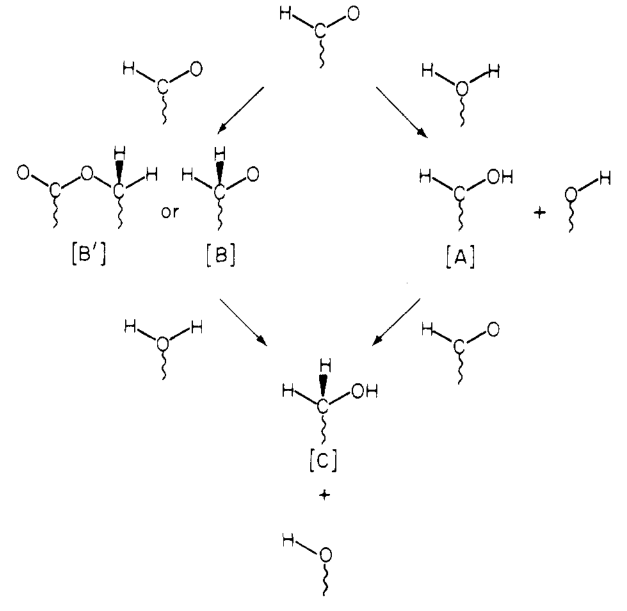
Figure 7. The zirconium hydride $[\eta^5\text{-}C_5(CH_3)_5]_2ZrH_2$ undergoes a remarkable series of transformations in the interaction with carbon monoxide. A proposed reaction scheme, as originally suggested by Bercaw and co-workers,[72] for this chemistry is illustrated above. In this representation, the possibility of an equilibrium between the formyl zirconium hydride species and a formaldehyde zirconium species is shown in the upper right although there are no data that explicitly define such a rearrangement. Formally similar reactions are observed for the related dimeric thorium and uranium dihydrides.

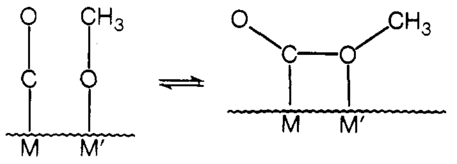
tation is shown in Scheme II. Since surface intermediates often have high surface mobility, *indirect* H atom transfer (H^+, H·, or H^-) from metal to carbon (or carbon-oxygen) sites should be considered mechanistically, especially for metal oxide surfaces.

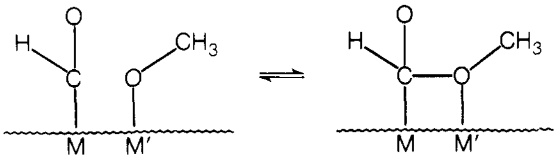
V. Carbon-Oxygen Bond Formation

Finally we come to issue (iii) raised and only partially answered in the preceding section; can other surface species participate in these reactions? Ichikawa,[75a] in his studies of metals like rhodium derived from metal clusters and supported on strongly basic metal oxides like ZnO, ZrO_2, and La_2O_3,[75b] has considered the attack of surface CH_3O^-, HO^-, and O^{2-} species on metal carbonyls and metal formyl intermediates with stabilization of the $MC(O)OCH_3$ intermediate by oxygen interaction with an adjacent metal center (eq 17 and 18). On hydrogenation, a surface bound methyl formate molecule would be produced, but this is known to form methanol on such catalysts. The analogous reaction with surface OH species would yield a surface C(OH)O species. These reactions are the surface equivalent of base conversion of CO to formate ion; the attack of carbon in M-C-O complexes by OH^- or CH_3O^- is well documented in coordination chemistry.[76-78] Hydrogenation of M-COOR or M-COOH species could occur by hydride ion transfer reactions from M'-H sites where M' is either the electropositive metal atom associated with the oxide phase or the transition metal atom.

SCHEME II




(17)


(18)

VI. Carbon-Carbon Bond Formation

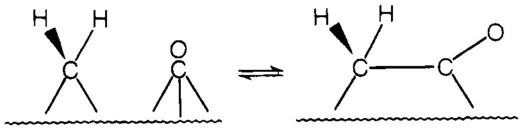
Exclusive of the highly selective methanation reaction and the methanol synthesis reaction, catalytic hydrogenation of carbon monoxide produces a range of hydrocarbons and hydrocarbon derivatives. Carbon-carbon bond formation is a pervasive and important step in these catalytic reactions. The obvious questions to be asked are "at what stage or stages do carbon-carbon bond making reactions occur?", and "is the reaction singular in character or is more than one mechanism operative?". Typically, the carbon-carbon bond-making process has been identified as a CO insertion[79] into a metal alkyl surface intermediate, based on the unsupported assumption that CO hydrogenation reactions are mechanistically analogous to hydroformylation[80] reactions. This process which generates an acyl species (eq 19) and increases the chain length by one

$$\mathrm{R{-}M}_x \overset{\mathrm{CO}}{\rightleftharpoons} \mathrm{R{-}M}_x\mathrm{{-}CO} \rightleftharpoons \mathrm{RCOM}_x \qquad (19)$$

cannot easily account for the generation of substantial amounts of large hydrocarbons even when coupled with subsequent steps like those depicted in eq 20. In fact, any of the one-carbon in-

$$\mathrm{RCOM}_x \overset{\mathrm{H}}{\rightleftharpoons} \mathrm{RCOM}_x\mathrm{H} \rightleftharpoons \mathrm{R}\underset{\bullet}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{OM}_x \qquad (20)$$

termediates discussed in earlier sections may undergo CO insertion reactions as schematically depicted in eq 21-25. There is precedent for the carbene or methylene CO insertion reac-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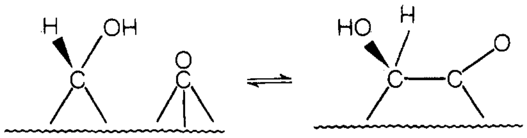
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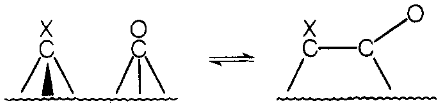
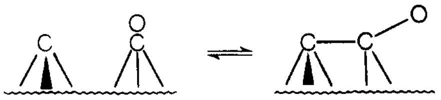

(X = H, OH) (23)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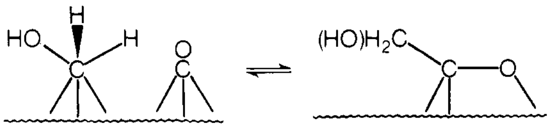
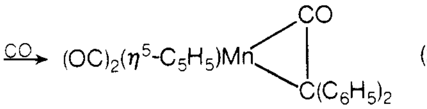
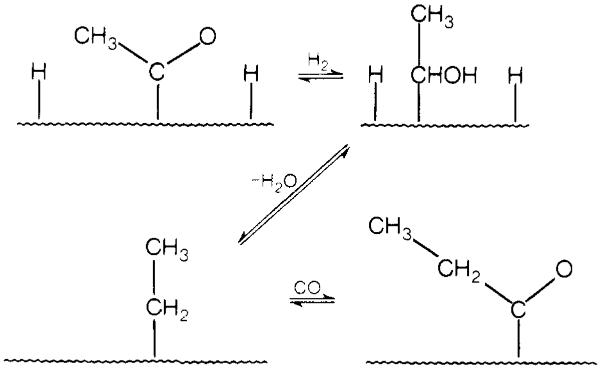

(25)

tions, e.g., CO insertion in the mononuclear manganese carbene (eq 26) to give a manganacyclopropanone structure.[81]

$(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$


(26)

A study of μ_2-methylene and μ_3-methylidyne metal cluster reactions with carbon monoxide and with carbon monoxide and hydrogen would greatly assist a more objective assessment of reaction schemes like (21)-(23). Further hydrocarbon chain length increase by such reactions is precluded (catalytic hydroformylations of olefins do not lead to chain length increase beyond the single carbon (CO) addition). A sequence like (27) in which chain length may increase has been suggested as steps subsequent to the acylation step.[82] Although such processes as outlined in (27) may be operative with some catalytic processes, it is unlikely that this relatively complicated scheme can account for the formation of high molecular weight hydrocarbons, e.g., polymethylene.[83-86] Furthermore, the last step in (27) must be in competition with a hydrogen atom transfer especially if the preceding steps all proceed with reasonable rates; this would lead to a predominant formation of low molecular weight alkanes. However, high molecular weight hydrocarbon polymers can be produced with some catalysts.


(27)

Since most Fischer-Tropsch reactions are effected with metals that dissociatively chemisorb carbon monoxide, at least at the temperatures of the catalytic reaction, the carbon-carbon formation reaction or reactions should be referenced to the carbon surface intermediate formed in the dissociative chemisorption step. There could be an association of this surface carbide so as to generate hydrocarbons of varying chain length as hydrogen atom transfer proceeds, but such an association is unlikely to account for hydrocarbon polymer formation. A more attractive stage for carbon-carbon bond formation is after partial hydrogenation of the carbon surface intermediate. Specifically, CH, CH_2, and CH_3 surface species which should be in rapid equilibrium at the synthesis temperatures (reasoning from the osmium cluster data) should react to form carbon-carbon bonds provided close approach of such species is feasible under reaction conditions. Carbon-carbon bond formation with CH, CH_2, and CH_3 could in principle generate all possible classes of hydrocarbons. Termination steps could include (a) hydrogen atom transfer from the metal to a carbon atom to form a saturated hydrocarbon, (b) a β-hydride abstraction to yield an olefin, (c) dehydrogenation reactions of cyclohexyl ring radicals to ultimately give aromatic hydrocarbons, and (d) carbon monoxide insertion and then hydrogen atom transfer to form an aldehyde or further hydrogen atom transfer to form alcohols. A set of comparable microscopic rate constants would ensure a molecular weight distribution in the product hydrocarbons or hydrocarbon derivatives that would fit the observed distributions.

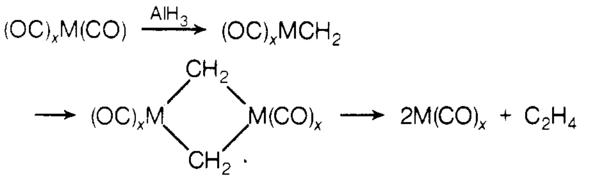
Mobility of CH, CH_2, and CH_3 surface species is certainly plausible. A CH_3 or CH_2 species need only have an activation barrier—for a bending from a bridging to a terminal (sitting atop a metal atom) surface site—that is less than ca. ~10 kcal/mol to adequately allow for the C-C bond formation process discussed above. In fact, since a facile $CH_2 \rightleftharpoons CH_3$ interconversion has been demonstrated for the CH_2 and CH_3 osmium cluster derivatives,[36] $CH_2Os_3H_2(CO)_{10}$ and $CH_3Os_3H(CO)_{10}$, we need in principle demonstrate only a mobility of either the CH_2 or CH_3 surface species. However, both probably have surface mobility. Presently, there are little data available from metal cluster chemistry that would support this contention. Nevertheless, the barrier to intramolecular methyl group exchange between terminal and bridging sites in $(CH_3)_2Al(\mu_2\text{-}CH_3)_2Al(CH_3)_2$ is very low, $\Delta H^{\ddagger} = 15.6 \pm 0.2$ kcal/mol.[87,88] Studies of methyl or methylene group exchange in metal cluster models have not been made simply because few such cluster derivatives have been prepared. Synthetic, structural, and chemical studies of metal clusters with CH_3 or CH_2 groups represent a major scientific challenge.

A CH surface species should be less mobile than the CH_2 and CH_3 species. Mobility is nonetheless a possibility for a CH surface species. Established is a facile interconversion of μ_2 and μ_3 forms of the $COCH_3$ ligand in a ruthenium cluster (eq 28).[35] An analogous process on a metal surface could permit sur-

$$(\mu_2\text{-}CH_3OC)Ru_3H(CO)_{10} + H_2$$
$$\overset{60\ ^\circ\mathrm{C}}{\rightleftharpoons} (\mu_3\text{-}CH_3OC)Ru_3H_3(CO)_9 + CO \qquad (28)$$

face migration of a bound CH species.

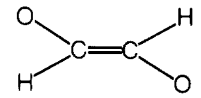
With respect to the carbon–carbon bond formation process based on initial interaction of CH, CH_2, and CH_3 surface species, model cluster studies could at least enable the identification, at a molecular mechanistic level, of the reactions of metal bound species of the CH, CH_2, and CH_3 class. In one relevant study where coordinated carbon monoxide was reduced with alane, $AlH_3\cdot(OR_2)_x$, to give high yields of ethylene, the intermediacy of a methylene metal complex was postulated and the methylene metal complex was proposed to dimerize as shown in (29).[54]



$$(OC)_xM(CO) \xrightarrow{AlH_3} (OC)_xMCH_2 \longrightarrow (OC)_xM(CH_2)_2M(CO)_x \longrightarrow 2M(CO)_x + C_2H_4 \quad (29)$$

The importance of surface methylene species must be overwhelmingly significant in certain catalytic CO + H_2 reactions as, for example, in the formation of high molecular weight polymethylene.

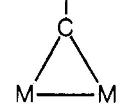
A very interesting and relatively new CO + H_2 reaction catalyzed by molecular anionic rhodium and cobalt carbonyl complexes[89,90] leads to ethylene glycol formation, in high yield at very high pressures with the rhodium catalysts where principal coproducts are methanol and glycerol.[89] A virtual myriad of reaction sequences can be envisioned for a glycol synthesis; of special interest here is the possibility of hydroxymethylene dimerization in these molecular rhodium complex catalyzed reactions. For this system, model studies of hydroxymethylene, CH(OH), clusters, and also of CO insertion reactions for formyl, hydroxymethyl, and formaldehyde metal complexes are necessary before relative probabilities for various reaction sequences can be realistically assessed. Note also the possible relevance of the previously mentioned zirconium chemistry (see Figure 7) where a



ligand was generated in the reaction of $[\eta^5\text{-}C_5(CH_3)_5]_2ZrH_2$ with CO. Similar chemistry has been demonstrated for the related thorium and uranium hydrides (dimers).[91]

VII. Conclusions

At this stage of experimental study and of mechanistic understanding in the catalytic carbon monoxide hydrogenation reactions, the focus should be on the elementary steps that must be present in these catalytic reactions, namely, C–H, O–H, and C–C bond formations and C–O bond scission and C–O bond formation. Within the framework of the experimental mechanistic information for CO hydrogenation reactions, we submit that a structural, thermodynamic, and chemical comparison of possible intermediates in the surface catalyzed reactions with isolable coordination complexes that emulate the suspected intermediates should provide ultimately not only a better understanding on a molecular scale of the surface catalyzed CO hydrogenation reactions but also a clearer perception of boundary conditions in analogies between the coordination chemistry of metal surfaces and molecular metal complexes. Consistently, we have sought comparisons based on metal cluster rather than mononuclear metal coordination chemistry simply because we still consider a polynuclear complex to be generally more effective than a mononuclear transition metal complex as a catalyst for CO hydrogenation, and also as a model for a catalytic intermediate[92–93] (which is not to say that a mononuclear metal complex cannot be a catalyst for CO hydrogenation reactions). Reduction of the CO bond order in the active metal complex should facilitate the hydrogenation process; the μ_2-CO, μ_3-CO, and η^2-OC type of interactions, **6–8**, feasible only in polynuclear metal complexes are more effective in CO bond order reduction than the conventional two-center M–CO type of binding that prevails in mononuclear metal carbonyl complexes. Furthermore, scission of the carbon–oxygen bond required in hydrocarbon formation will be difficult without both M–O and M–C interactions for CO or for the partially reduced CO ligand.[92]



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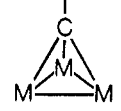

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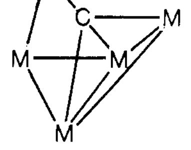

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Consideration of the available information for surface catalyzed CO hydrogenation reactions and for model systems from molecular coordination chemistry does not allow a definitive characterization of the stoichiometric and intimate mechanisms of the hydrogenation reactions. There are, however, sufficient data on which to base some generalizations and to provide focal points for future studies.

The hydrogenation of CO catalyzed by surfaces composed of metal atoms that are relatively electropositive, e.g., iron, ruthenium, cobalt, and nickel, appear to proceed largely through a first step of dissociative CO chemisorption to yield some kind of surface C species that is far more reactive than the exposed carbon ligands in clusters like $Fe_5C(CO)_{15}(\mu_5\text{-}C$ ligand). Hydrogenation of the surface carbon can yield methane (methanation reaction), or the intermediate CH, CH_2, or CH_3 species may interact to generate higher hydrocarbons (Fischer–Tropsch synthesis reactions). The precise nature of the C–C bond formation steps is not defined, but the very complexity of products in a typical metal catalyzed CO hydrogenation reaction suggests that C–C bond formation may involve all or many of the implicated CH_x intermediates although one may be dominant as in CH_2 association in the polymethylene synthesis reaction. Termination steps include hydrogenation of alkyl intermediates, β-hydride abstraction in alkyl intermediates, and CO "insertion" followed by hydrogenation particularly with rhodium catalysts; one may dominate or there may be a combination of termination steps. The role of catalyst supports, potential significance in product distribution, is addressed only for the case of basic metal oxide supports.

Carbon monoxide apparently does not chemisorb with scission of the C–O bond on metals like palladium and platinum even under the typical conditions of CO hydrogenation reactions. Nevertheless, these metals are CO hydrogenation catalysts and they tend to produce methanol; this is particularly evident in reactions catalyzed by palladium supported on silica. No mechanistic information is available for these systems which, in fact, are quite amenable to detailed examination: infrared studies, CO labeling experiments, and trapping of suspected surface intermediates. If here the methanol synthesis sequence proceeds without C–O scission and if all reduction steps do not involve the support in a mechanistically significant fashion, then formyl, hydroxymethylene (or H_2CO species), and hydroxymethyl (or methoxy) surface species would appear to be plausible intermediates. Hydrocarbon formation which necessarily involves CO bond scission may arise from any of these intermediates by steps in which oxygenated intermediates, prior to an OCH_3 state, become O and C bonded to the metal surface—or by an initial dissociative reaction of the CO molecule. It is difficult to fully discount the latter possibility despite literature statements. A careful study of doubly labeled CO chemisorption and desorption from palladium and platinum surfaces at the conditions typical of the catalytic reaction is a critical, definitive test of the associative chemisorption hypothesis for CO on palladium and platinum (CO chemisorption on these metals even at higher temperatures is largely reversible, but C–O bond dissociation could occur in a largely reversible fashion, hence the need for the labeled ^{13}CO and $C^{18}O$ experiments).

Basic metal oxides are catalysts for CO hydrogenation and some like ZnO exhibit a good selectivity for methanol formation. Mixed basic metal oxide–metal systems can achieve a nearly fully selective hydrogenation of CO to methanol. Especially notable is the ZnO–Cu system now commercially used in methanol production and also Ichikawa's rhodium metal catalysts (derived from rhodium clusters and supported on basic oxides) which are selective at atmospheric pressure. In the ZnO–Cu catalyzed reaction, a key set of reactions is the generation of a ZnH surface species with subsequent transfer to a CO carbon atom of a carbonyl surface species that is predominately a Cu(I)–CO complex. Transformation of the formyl surface intermediate to methanol could then follow formal sequences outlined in Schemes I and II. However, the alternative scheme for these catalyst systems that contain a basic metal oxide whereby a surface carbonyl intermediate is attacked by surface OH or OCH_3 species to give a $-C(O)OCH_3$ or $-C(O)OH$ surface species must receive careful consideration. Trapping of surface intermediates with appropriate organic reactants, a type of study now in progress as in the Bell and the Klier research studies of the Fischer–Tropsch and the methanol synthesis reactions, respectively, could provide the necessary differentiating information. On a general basis, mechanistic considerations and mechanistic studies must recognize the potential role of *all* surface intermediates in the basic reductive (H transfer reaction) and the C–C bond formation phases of CO hydrogenation reactions. Also, the potential for mechanistic diversity in the CO–H_2 catalytic reaction systems must be considered.

The perceptive model coordination studies of Casey,[57,59,68] Gladsyz,[55,58,60,69] Roper,[71] Graham,[66] Hermann,[41,43a] and others have contributed substantially to the construction of mechanistic regimes for CO hydrogenation reactions. This type of modelling, especially in the cluster regime, can still add significantly to the resolution of mechanistic features in the surface catalyzed reactions. Reactions of the model intermediates and thermodynamic studies of these complexes and their key reactions will provide a much more substantial coordination chemistry background for future discussions of the intimate mechanistic features of surface catalyzed CO hydrogenation reactions.

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VIII. References and Notes

(1) J. Wender, *Catal. Rev.-Sci. Eng.*, **14,** 97 (1976).
(2) C. L. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, New York, 1970, Chapter 14.
(3) W. J. Thomas and S. Portalski, *Ind. Eng. Chem.*, **50,** 967 (1958).
(4) M. L. Poutsma, L. F. Elek, P. A. Ibarbia, A. D. Risch, and J. A. Rabo, *J. Catal.*, **52,** 157 (1978).
(5) M. A. Vannice, *Catal. Rev.-Sci. Eng.*, **14,** 153 (1976).
(6) (a) G. A. Mills and F. W. Steffgen, *Catal. Rev.*, **8,** 159 (1973); (b) V. M. Vlasenko and G. E. Yuzefovich, *Russ. Chem. Rev.*, **39,** 728 (1969); (c) C. Masters, *Adv. Organomet. Chem.*, **17,** 61 (1979).
(7) D. L. King, *J. Catal.*, **51,** 386 (1978).
(8) H. Pichler and H. Schultz, *Chem. Ing.-Tech.*, **42,** 1162 (1970).
(9) B. K. Nefedov and Y. T. Eidus, *Russ. Chem. Rev.* (*Engl. Transl.*), **34,** 272 (1965).
(10) H. Storch, N. Golumbr, and R. Anderson, "The Fischer-Tropsch and Related Syntheses", Wiley-Interscience, New York, 1951.
(11) C. D. Chang, W. H. Lang, and A. J. Silvestri, *J. Catal.*, **56,** 268 (1979).
(12) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **15,** 136 (1976).
(13) (a) Y. T. Eidus, *Russ. Chem. Rev.*, **36,** 338 (1967). (b) A recent study of CO hydrogenation with supported Rh and Rh-Fe catalysts indicated a high selectivity to the production of two carbon products; cf. M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, **54,** 120 (1978).
(14) Historically, two mechanisms have been proposed for the Fischer-Tropsch process. The carbide theory was first proposed by Fischer and Tropsch in 1926. According to this theory, adsorbed carbon monoxide is reduced to surface carbide which can then be hydropolymerized to hydrocarbons. This mechanism, however, is not consistent with the Flory-Schultz distribution of molecular weights found for the products of the Fischer-Tropsch process. A second mechanism involves the formation of unstable intermediates containing C, H, and O atoms such as the formation of an HCOH surface complex. This has recently been discussed by Henrici-Olivé and Olivé.[12] In recent years, the carbide theory has been revised to include initiation, propagation, and termination steps. The modified theory is consistent with the Flory-Schultz distribution of molecular weights. For detailed discussions of the above mechanistic hypotheses, cf. (a) F. Fischer and H. Tropsch, *Brenst.-Chem.*, **7,** 97 (1926); (b) O. C. Elvins and A. W. Nash, *Nature* (*London*), **118,** 154 (1926); (c) H. Pichler, *Adv. Catal.*, **4,** 271 (1952); (d) ref. 19.
(15) B. G. Broden, T. N. Rhodin, C. Brucker, R. Benbow, and Z. Hurych (*Surf. Sci.*, **59,** 593 (1976)) discuss the character of CO chemisorption on metals at 300 K.
(16) G. Low and A. T. Bell, *J. Catal.*, **57,** 397 (1979).
(17) J. G. Ekerdt and A. T. Bell, *J. Catal.*, in press.
(18) J. McCarty, P. Wentrcek, and H. Wise, cited in ref 17.
(19) P. Biloen, J. N. Helle, and W. H. M. Sachtler, *J. Catal.*, **58,** 95 (1979).
(20) J. A. Rabo, A. P. Risch, and M. L. Poutsma, *J. Catal.*, **53,** 295 (1978).
(21) For a comprehensive review of metal carbide clusters, see M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, in press.
(22) For example, synthesis of trigonal prismatic $Rh_6C(CO)_{15}{}^{2-}$ in $^{13}CCl_4$ leads to a specific ^{13}C labeling of the carbide carbon atom; cf. V. G. Albano, P. Chini, S. Martinengo, D. J. A. McCaffrey, D. Strumulo, and B. T. Heaton, *J. Am. Chem. Soc.*, **96,** 8106 (1974). There is no labeling study of cluster carbide synthesis that unequivocally demonstrates that CO is the source of the carbide carbon atom.
(23) G. Huttner, A. Frank, and E. O. Fischer, *Isr. J. Chem.*, **15,** 133 (1977).
(24) G. Huttner, H. Lorenz, and W. Gartzke, *Angew. Chem., Int. Ed. Engl.*, **13,** 609 (1974).
(25) M. R. Churchill and W. J. Young, *J. Chem. Soc., Chem. Commun.*, 321 (1979).
(26) There is a somewhat special example of hydrogenation of a carbene to a hydrocarbon derivative: $(\eta^5\text{-}C_5H_5)_2W{=}C{-}O{-}Zr(H)(\eta^5\text{-}C_5Me_5)_2 + 2H_2$ (170°) $\rightarrow (\eta^5\text{-}C_5H_5)_2WH_2 + CH_3OZr(H)(\eta^5\text{-}C_5Me_5)_2$. Cf. P. T. Wolczanski, R. S. Threlkel, and J. E. Bercaw, *J. Am. Chem. Soc.*, **101,** 218 (1979).
(27) Many peralkyl complexes, e.g., $Ta(CH_3)_5$, react with hydrogen to yield methane. Mechanistically, these reactions are a bit of a puzzle because the metal atom in these complexes is in the highest plausible oxidation state (concerted four-center reactions may obtain here) and these should be carefully anlayzed for detailed mechanistic information.
(28) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84,** 4633 (1962).
(29) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 2606 (1975).
(30) $Os_6(CO)_{16}C(MeC_2Me)$ also has an exposed carbide carbon ligand (μ_4-C ligand). Cf. C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. H. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 421 (1978).
(31) M. Tachikawa and E. L. Muetterties, unpublished data.
(32) P. W. Sutton and L. Dahl, *J. Am. Chem. Soc.*, **89,** 261 (1967).
(33) G. L. Geoffroy and R. A. Epstein, *Inorg. Chem.*, **16,** 2795 (1977).
(34) R. Bergman and L. S. Stuhl, personal communication.
(35) J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 214 (1979).
(36) (a) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99,** 5225 (1977); (b) ibid., **100,** 6544 (1978); (c) ibid., **100,** 7726 (1978).
(37) This refers to a physical mixture, one component of which, the methylene derivative, has been isolated in single crystal form and structurally characterized by crystallographic studies.
(38) A. J. Schultz, J. M. Williams, R. B. Calvert, J. R. Shapley, and G. D. Stucky, *Inorg. Chem.*, **18,** 319 (1979).
(39) Unsymmetric M–C–H–M interactions also arise in monomolecular complexes like methyl allyl iron structures; cf. J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100,** 7407 (1978).
(40) C. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 477 (1977).
(41) W. A. Hermann, C. Kruger, R. Goddard, and I. Bernal, *Angew. Chem., Int. Ed. Engl.*, **16,** 334 (1977).
(42) (a) R. A. Andersen, R. A. Jones, G. Wilkinson, M. Hursthouse, and K. M. Malik, *J. Chem. Soc., Chem. Commun.*, 865 (1977); (b) M. B. Hursthouse, R. A. Jones, K. M. Abdul Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, **101,** 4128 (1979).
(43) (a) W. A. Hermann, B. Reiter, and H. Biersack, *J. Organomet. Chem.*, **97,** 245 (1975); (b) M. Cresurick, I. Bernal, and W. A. Herrmann, *ibid.*, **172,** C39 (1979).
(44) G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 396 (1979).
(45) G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 397 (1979).
(46) S. A. Fieldhouse, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *J. Chem. Soc., Chem. Commun.*, 181 (1970).

(47) However, the next step—formation of a CH(OH) or H_2CO surface species—also could be a slow step.

(48) (a) H. A. Hodali and D. F. Shriver, *Inorg. Chem.*, **18**, 1236 (1979); (b) S. B. Butts, E. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, *J. Am. Chem. Soc.*, **101**, 5864 (1979).

(49) D. E. Seyferth, J. E. Hallgren, and P. L. K. Hong, *J. Organomet. Chem.*, **50**, 265 (1973).

(50) N. E. Kim, W. J. Nelson, and D. F. Shriver, *Inorg. Chim. Acta*, **7**, 393 (1973).

(51) J. F. Kristoff and D. F. Shriver, *Inorg. Chem.*, **13**, 499 (1974).

(52) B. K. Nicholson, B. H. Robinson, and J. Simpson, *J. Organomet. Chem.*, **66**, C3 (1974).

(53) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).

(54) C. Masters, C. van der Woude, and J. A. van Doorn, *J. Am. Chem. Soc.*, **101**, 1633 (1979).

(55) (a) W. Tam, W.-K. Wong, and J. A. Gladysz, *J. Am. Chem. Soc.*, **101**, 1589 (1979); (b) W.-K. Wong, W. Tam, C. E. Strouse, and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 530 (1979).

(56) S. R. Winter, G. W. Cornett, and E. A. Thompson, *J. Organomet. Chem.*, **133**, 339 (1977).

(57) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976).

(58) J. A. Gladysz and W. Tam, *J. Am. Chem. Soc.*, **100**, 2545 (1978).

(59) C. P. Casey and S. Neumann, *J. Am. Chem. Soc.*, **100**, 2544 (1978).

(60) J. A. Gladyz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, C1 (1977).

(61) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772, 3781 (1969).

(62) See the discussions and experiments of K. Klier and co-workers: S. Mehta, G. W. Simmons, K. Klier, and R. G. Herman, *J. Catal.*, **57**, 339 (1979); R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, and S. B. Bulko, *ibid.*, **56**, 407 (1978), and references therein.

(63) (a) The isotopic exchange reaction of $^{13}C-^{16}O$ with $^{12}C-^{18}O$ has been established using ZnO catalysts; cf. G. Carnisio, F. Garbassi, G. Petrini, and G. Parravano, *J. Catal.*, **54**, 66 (1978). (b) The isotope effects in the synthesis of methanol upon substitution of hydrogen by deuterium using a zinc chromite catalyst has been examined.[63c,d] (c) T. V. Belysheva, F. S. Shub, V. D. Kuznetsor, and M. I. Temkin, *Kinet. Catal.* (*Engl. Transl.*), **19**, 296 (1978). (d) T. V. Belysheva, F. S. Shub, and M. I. Temkin, *ibid.*, **19**, 661 (1978). (e) The stereochemistry of the acyl ligand in $Rh_6(CO)_{15}$-$[C(O)C_2H_5]$ is not established; cf. P. Chini, S. Martinengo, and G. Garlaschelli, *J. Chem. Soc., Chem. Commun.*, 709 (1972).

(64) Our molecular orbital analysis of molecules or molecular fragments on surfaces has been extended to the formyl radical but a meaningful comparison of a terminal with a bridging position is difficult because no reference formyl data are available for bond distance elongation on going from a terminal to a bridging site. With a fixed bond distance, bridging sites are explicably the more stable (R. M. Gavin, unpublished data).

(65) B. F. G. Johnson, P. A. Kilty, and J. Lewis, *J. Chem. Soc. A*, 2859 (1968).

(66) J. R. Sweet and W. A. G. Graham, *J. Organomet. Chem.*, **173**, C9 (1979).

(67) In fact, the cyclic reaction sequences

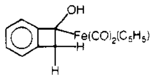
$$\mathrm{ReCH_2OH} \xrightarrow{\mathrm{CH_3OH}} \mathrm{ReCH_2OCH_3} \xrightarrow[\mathrm{H^+}]{\mathrm{H_2O}} \mathrm{ReCH_2OH}$$

have been demonstrated.[68]

(68) C. P. Casey, M. A. Andrews, and D. R. McAlister, *J. Am. Chem. Soc.*, **101**, 3371 (1979).

(69) W. K. Wong, W. Tam, and J. A. Gladsyz, *J. Am. Chem. Soc.*, **101**, 5442 (1979).

(70) An earlier report of an unstable hydroxymethylene was by A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95**, 5430 (1973).



(71) K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, *J. Am. Chem. Soc.*, **101**, 503 (1979).

(72) (a) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 2716 (1978). (b) P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, to be published. See also a reductive coupling of CO by a tantalum complex by C. D. Wood and R. R. Schrock, *ibid.*, **101**, 5421 (1979).

(73) For related early transition metal stoichiometric hydrogenation of CO see: (a) J. A. Labinger, K. S. Wong, and W. R. Scheidt, *J. Am. Chem. Soc.*, **100**, 3254 (1978); (b) G. Fachinetti, C. Fioran, A. Roselli, and S. Pucci, *J. Chem. Soc., Chem. Commun.*, 269 (1978).

(74) The crystal structure of the alkylalkoxycarbene complex $Pt_2W[\mu_2$-$C(OCH_3)(C_6H_5)](CO)_6(P\,^tBu_2CH_3)_2$ reveals that the carbene occupies a bridging site; cf. T. Ashworth, M. Berry, J. Howard, M. Lugana, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 45 (1979).

(75) (a) M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 566 (1978); *Chem. Lett.*, 335 (1976); *Bull. Chem. Soc. Jpn.*, **51**, 2273 (1978); *J. Catal.*, **59**, 67 (1979). (b) Selective methanol formation proceeds with the Ichikawa catalysts at atmospheric pressure to near-equilibrium methanol concentrations, but with acidic oxides, oxygenated products decrease sharply.

(76) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

(77) E. L. Muetterties, *Inorg. Chem.*, **4**, 1841 (1965).

(78) D. J. Darensbourg and J. A. Froelich, *J. Am. Chem. Soc.*, **99**, 5940 (1977).

(79) Mechanistically, this is a methyl migration rather than CO insertion. For analogous examples in coordination chemistry, cf. H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 7224 (1978).

(80) See R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, p 215, and references therein.

(81) W. A. Hermann and J. Plank, *Angew. Chem.*, **90**, 555 (1978).

(82) G. Henrici-Olivé and S. Olivé, *J. Mol. Catal.*, **3**, 443 (1977/78).

(83) A. Guyer, P. Guyer, F. Schneider, and H. R. Marfurt, *Helv. Chim. Acta*, **38**, 798 (1955).

(84) A. Guyer, J. Jutz, and P. Guyer, *Helv. Chim. Acta*, **38**, 971 (1955).

(85) H. Köbel and K. K. Bhattacharyya, *Justus Liebigs Ann. Chem.*, **618**, 67 (1958).

(86) (a) H. R. Arnold, F. S. Fawcett, and W. W. Gilbert, U.S. Patent 2 825 704 (1958). (b) H. R. Arnold, F. S. Fawcett, and B. W. Howk, U.S. Patent 2 825 705 (1958).

(87) T. L. Brown and K. C. Williams, *J. Am. Chem. Soc.*, **88**, 5460 (1966).

(88) E. A. Jeffrey and T. Mole, *Aust. J. Chem.*, **22**, 1129 (1969).

(89) W. E. Walker et al., U.S. Patents 3 878 216, 3 878 290, 3 878 292 (1975).

(90) W. F. Gresham, British Patent 655 237 (July 1951); *Chem. Abstr.*, **46**, 7115h (1951).

(91) J. M. Manriquez, P. J. Fagan, T. J. Marks, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, **100**, 7112 (1978), and references therein.

(92) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); **85**, 451 (1976); *Science*, **196**, 839 (1977).

(93) E. L. Muetterties, T. N. Rhodin, E. Band, C. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).