

Organometallic Aspects of the Fischer-Tropsch Synthesis

By Wolfgang A. Herrmann*

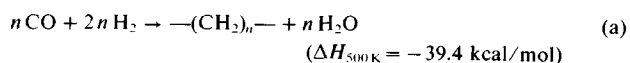
In memoriam Rowland Pettit

The Fischer-Tropsch Synthesis counts among the industrial-scale processes having a versatile and broad product range, and has for decades offered the most attractive possibility for the use of coal as a source of heating oil and fuels. This conceivably simple reaction, the catalytic hydrogenation of carbon monoxide, generally leads to simple hydrocarbons as well (*i.e.* short chain olefins) that have been sought as chemical feedstocks since the oil crisis of the seventies, but fails to provide the large-scale, economic process required, due in large part to the minimal selectivity of traditional Fischer-Tropsch processes. In an effort to solve this problem current research in this sector is concerned not only with the optimization of old and the development of new catalytic systems, but also increasingly with the elucidation of numerous relevant reaction mechanisms. This article will discuss, from the viewpoint of an organometallic chemist, the significance of typical model reactions, both with regard to some fundamental aspects of synthesis gas chemistry, and in comparison with previous views concerning the mechanism of the Fischer-Tropsch Synthesis. The importance of various unique classes of complexes that have been studied in the context of Fischer-Tropsch chemistry is also evaluated with regard to their importance in the synthesis of hydrocarbons from carbon monoxide and hydrogen. It emerges that the primary steps of the reductive oligomerization of carbon monoxide are best described by the carbide/methylene mechanism, as originally proposed by *Hans Fischer* and *Franz Tropsch*.

1. Introduction

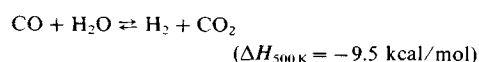
The versatile and technically well-established Fischer-Tropsch Synthesis^[1-3] has recently joined olefin metathesis^[4] as one of the most attractive and productive areas of organometallic research. The mechanistic features of the Oxo-synthesis have long since been explained^[5], and the elegant model studies of *Casey*, *Katz*, *Grubbs*, and *Schrock* into the mechanism of olefin metathesis have reached their culmination point. Nevertheless, the mechanistic steps of the catalytic hydrogenation of carbon monoxide continue to be strongly debated.

At first glance the Fischer-Tropsch synthesis obeys the trivial-looking, idealized equation (a)



giving in an exothermic reaction a plethora of products including straight chain alkanes, alkenes, alcohols, aldehydes, carboxylic acids, esters, as well as arenes. The highly selective Union Carbide process, a rhodium- and ruthenium-catalyzed ethylene glycol synthesis^[6], as well as the predominantly nickel-catalyzed production of methane from synthesis gas ("CO methanation")^[7], are notable special cases of CO hydrogenation. It is still not known, however, whether these processes involve uniform reaction sequences. The comprehensive mechanisms proposed for the catalytic formation of Fischer-Tropsch products are partic-

ularly speculative, since the classical, low-selectivity synthesis normally employs heterogeneous alkaline iron and cobalt melt- or precipitation catalysts, under which conditions a confusing array of parallel and subsequent reactions appears to occur. The spectrum of products is virtually always dominated by aliphatic and α -olefinic hydrocarbons, but is strongly affected by rather small changes in pressure and temperature, the catalyst and its preparation and promoter content, as well as some parameters of the process-technology. For example, *Pichler* has shown that the use of specific ruthenium catalysts at high pressure (up to 2000 bar) and relatively low temperature leads to high-melting, straight chain paraffins ("polymethylenes") largely identical with Ziegler polyethylene, and with an average molecular weight of up to 240000. By way of contrast, rhodium catalysts yield low molecular weight oxygenated products^[2a,b]. In the Mobil process, the synthesis gas reaction induced by $\text{ZnO/Cr}_2\text{O}_3$ catalysts (high pressure) or copper-containing catalysts (medium pressure) is utilized for the synthesis of methanol, which, in turn, is subsequently converted into gasoline type hydrocarbons by means of zeolite supported catalysts. The activity and selectivity of the catalyst is particularly sensitive to the degree of alkalization, which is thought to increase the ability of the catalyst to chemisorb the reactants, as well as increase the rate of all carbon monoxide consuming reactions (CO reduction, water gas shift reaction, carbide formation, *etc.*). Finally the *water gas shift equilibrium*^[3b]



affects not only the composition of the coal-derived synthesis gas (CO/H_2) but also the nature and molecular weight distribution of the Fischer-Tropsch products.

[*] Prof. Dr. W. A. Herrmann
Institut für Anorganische Chemie der Universität
Universitätsstrasse 31, D-8400 Regensburg I (Germany)
New address:
Institut für Anorganische Chemie der Universität
Niederurseler Hang, D-6000 Frankfurt am Main 50 (Germany)

2. Present-Day Objectives of the Fischer-Tropsch Synthesis

The necessity of developing economically profitable alternative sources of chemical raw materials as a result of the oil crisis of the seventies has completely reversed the selectivity goal of the Fischer-Tropsch synthesis. The efficiency of a catalyst was previously measured in terms of the "degree of liquefaction", resulting from the production of liquid fuels from synthesis gas, whereas nowadays the achievement of as narrow as possible a product distribution is of particular interest (for example, short chain olefins as chemical feedstocks, $C_5 \dots C_{11}$ olefins for conversion into softener alcohols, $C_9 \dots C_{10}$ aliphatics as detergent raw materials). Economic estimates lead to the conclusion that a complete replacement of petroleum products by hydrocarbons derived from synthesis gas is not possible, at least at present, in the Federal Republic of Germany. Although short-, medium length, and long-chain alkenes bring far higher returns as chemical feedstocks than as fuels and heating oils, this reversion would result in a 6–7-fold increase in the demand for hard coal (4 t per 1 t primary product, *i. e.* 600 million tons per year). Hence, the Fischer-Tropsch synthesis could compete with petroleum only if the process selectivity could be considerably improved, and if crude oil were to be scarce and coal comparatively cheap. The last two of these conditions are already met with in some countries, *e. g.*, South Africa and Australia. Therefore, allowing for a certain amount of flexibility in the demand for basic chemicals, a new generation Fischer-Tropsch synthesis must be marked by high selectivity in order to compete effectively. It is generally agreed, that the development of new types of catalysts deserves primary attention. In view of the advanced state of our technical knowledge of the classical Fischer-Tropsch synthesis the emphasis will be on the use of alkalized heterogeneous catalysts, but a great deal of effort will be directed towards the development of homogeneous catalysts^[8] with their potential for selective product control. This goal seems to be within reach now that the metal-induced model reactions discussed in this article have not only characterized numerous previously unknown classes of compounds, but also decidedly increased our understanding of the elementary steps of carbon monoxide hydrogenation.

3. Limiting Conditions for Reaction Mechanisms

Every possible reaction mechanism for the Fischer-Tropsch synthesis must fulfil the following limiting conditions: 1) The reaction formally obeys polymerization kinetics giving a Schultz-Flory product molecular weight distribution. 2) α -Olefins and alcohols are primary products. ^{14}C -Tracer studies^[1b,9] have established that saturated hy-

drocarbons arise independently by olefin hydrogenation subsequent to the actual chain growth process. Beyond that, there is no doubt α -olefins as well as alcohols and aldehydes are incorporated into growing chains. 3) The chain termination steps do not deactivate the catalytic center, for the rate of chain growth normally remains unchanged for weeks. 4) The formation of hydrocarbons from synthesis gas according to eq. (a) results in the reduction of carbon monoxide to CH_2 building blocks with concomitant formation of water (!).

4. The Carbide/Methylene Mechanism

In one of their first publications, *Fischer and Tropsch* considered CO hydrogenation as a "Polymerisation von Methylen-Gruppen" wherein surface carbide species were formulated as the pivotal precursors of the methylene groups^[10a]. Since the discovery and complete characterization of stable transition metal-methylene complexes with terminal **1**^[11, 12] and with bridging CH_2 -functions **2**^[13, 14] (Fig. 1), this viewpoint has been revived through results of elegant experiments. Thus, nickel, cobalt, and ruthenium-based catalysts were doped with labeled carbon using the Boudouard disproportionation of ^{13}CO and were then treated with $^{12}\text{CO}/\text{H}_2$ mixtures under Fischer-Tropsch (F-T) conditions. The resulting product mixture consists mainly of $^{13}\text{CH}_4$ and hydrocarbons containing *several* (!) ^{13}C -atoms in one and the same molecule^[10b].

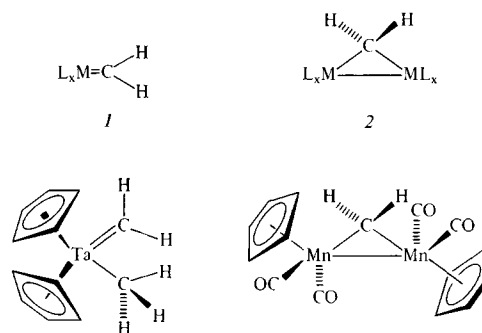
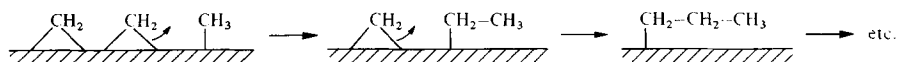


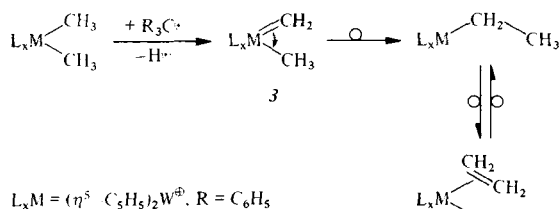
Fig. 1. Typical methylene complexes of type **1** with terminal ligands and of type **2** with bridge-bound ligands. The mononuclear tantalum complex is accessible by selective deprotonation of the cationic precursor $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_3)_2]^+$ [11, 12], while the methylene bridge of the dinuclear manganese complex is achievable with diazomethane [13, 14].

Other results support the conclusion that carbon monoxide rapidly dissociatively chemisorbs on F-T catalysts to give carbide species, which then react with hydrogen to give oxygen-free CH_x intermediates ($x = 1-3$) and in this way result in chain growth (Scheme 1)^[10b]. Mention should be made in this context that surface-bound CH_2 groups can also become involved in competitive olefin metathesis^[4, 10b]. Furthermore, carbidization of the catalyst under

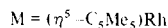
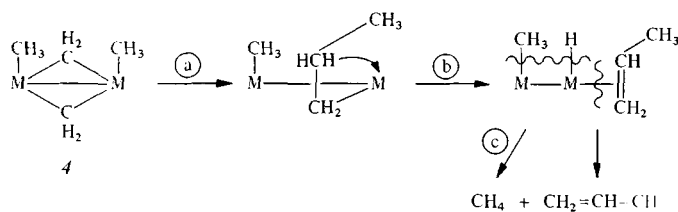


Scheme 1.

real F-T conditions is well known^[1a]. The mechanistic viability of the insertion of a methylene group into a metal-methyl bond finally leading to polymerization as outlined in Scheme 1, could recently be verified in a stoichiometric model reaction of an electrophilic CH₂-complex **3** with the help of labeling studies^[15a]. Beyond that, the products of



the thermolysis of dinuclear μ -methylene-methyl complex **4** impressively confirm the methylene insertion step^[15b]: At 350 °C the *cis*-isomer yields primarily methane (48%), ethylene (20%), ethane (2%), and propene (30%); only traces of propane and C₄+ hydrocarbons are formed, while cyclopropane is not formed at all. Control experiments rule out the participation of π -bonded C₅(CH₃)₅ ligands in the synthesis of the observed hydrocarbons. Of particular importance is the predominance of propene over propane— α -olefins are among the primary products of the Fischer-

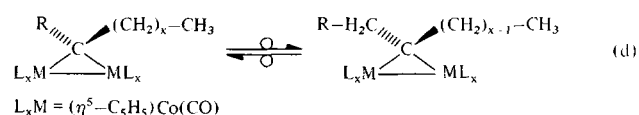
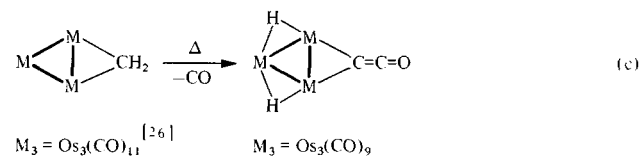
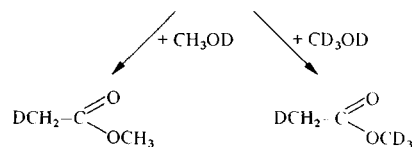
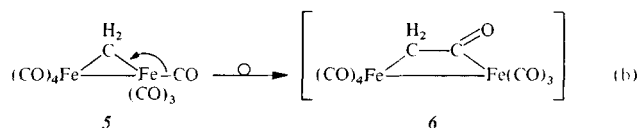


Scheme 2. (a)–(c), see text.

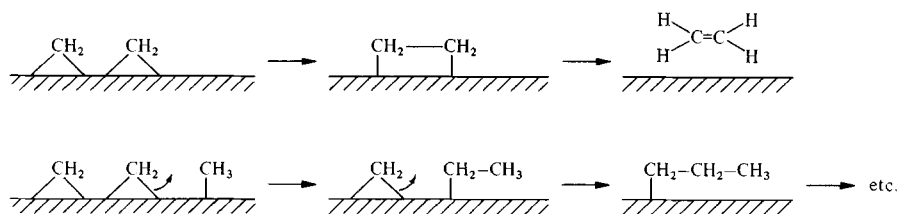
Tropsch synthesis! The most pertinent aspects of the thermal decomposition of the dinuclear system **4** are summarized in Scheme 2; they include the initial double CH₂-insertion (a) (C—C coupling), and the two conceivably most important termination steps under real Fischer-Tropsch conditions, *e.g.*, the kinetically highly favored β -hydrogen elimination (b) and the dinuclear alkyl/hydrogen reductive elimination (c) (giving alkanes; in this case, methane). The latter process liberates the olefin, in this case propene. Bis(μ -alkylidene) complexes *without* additional alkyl ligands generally decompose to give only olefins, resulting from carbene dimerization^[15c]. The mode of coordination of CH₂-species attached to surfaces (**1** or **2**) remains uncertain, especially considering the fact that specific dinuclear metal complexes can contain both terminal as well as bridging methylene ligands^[16]. Recent HMO calculations indicate that the C-atoms of the surface-bound bridging methylenes are not tetrahedrally coordinated, as in **2**, but are planar coordinated^[23a], whereas in all isolable dinuclear complexes reported in the literature a distorted tetrahedral structure is found, irrespective of whether a metal-metal bond is present at the same time or not^[14].

4.1. Dimetallacyclopropanes

Dimetallacyclopropanes **2** comprise a structurally and spectroscopically well established class of compounds and represent the most simple available model systems for the simulation of the chemistry of surface-bound methylene or alkylidene species. They are marked by an especially high tendency toward incorporation of olefins (\rightarrow olefin homologation) and acetylene derivatives^[14b], as well as a high reactivity *vis-à-vis* hydrogen (\rightarrow methane)^[14b] and protic acids ($\rightarrow\mu$ -methylidyne complexes)^[14b]. A μ,η^2 -ketene intermediate **6** (CO-insertion) is proposed to account for the interesting formation of methyl acetate (80%) in the decomposition of the μ -methylene iron complex **5** with methanol according to eq. (b); nothing is known, however, about the fate of the complex fragment^[17a]. This reaction may provide a starting point for a better understanding of catalytic *alcohol homologation* processes. Also worth mentioning in this respect is the observed carbonylation of a bridging methylene group to give the corresponding ketenylidene function [eq. (c)]^[17b]. Should recent reports of an as yet mechanistically poorly understood isomerization of an alkylidene chain along a metal-metal unit turn out to be a general pathway [eq. (d)]^[17c], then this process offers yet another model for the isomerization of mobile alkylidene species on metal surfaces^[18]. The equilibrium (d) allows the bridging methylene with the lowest degree of substitution [R(CH₂)_{x+1}CH] to be achieved^[17c]. Model studies have established that elimination of an alkylidene species from the metal centers is strongly favored by β -hydrogen migration (\rightarrow olefins), but is much less favorable than decarbonylation if it should happen that the complex displays CO ligands at the same time^[14b].



The most convincing support of the carbide/methylene mechanism was provided by a detailed investigation, *inter alia*, of the Fischer-Tropsch catalyst-induced decomposi-



Scheme 3.

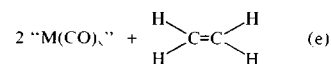
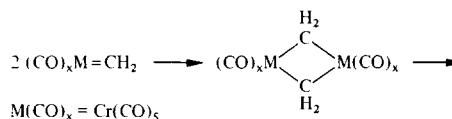
tion of gaseous diazomethane^[10c]. Exclusively ethylene and dinitrogen are formed on Ni-, Pd-, Fe-, Co-, Ru-, and Cu-surfaces in the temperature range 25–250 °C at atmospheric pressure. Therefore, in the absence of other reac-

tants, only dimerization and no polymerization of the surface absorbed CH₂-fragments occurs (Scheme 3, top). On the other hand, reaction of a mixture of H₂/CH₂N₂ over Co-, Fe-, and Ru-catalysts leads to a wide variety of hydrocarbons (primarily linear alkanes and olefins) with the isomer and molecular weight distribution of typical Fischer-Tropsch reactions! The results for H₂/CH₂N₂ and H₂/CO reactions under comparable conditions, illustrated in Figure 2, suggest the same polymerization mechanism as in Scheme 3 (bottom). Besides CO-activation (→ carbide→methylene) the dissociative chemisorption of H₂ is also a prerequisite for this mechanism: If the catalyst surface (e.g. copper) is not capable of this latter process then no Fischer-Tropsch reactivity is observed, and, as expected, CH₂N₂ decomposition gives only ethylene, even in the presence of H₂^[10c]. The production of CH₄^[19a] in the reaction of H₂ (ca. 12 bar, benzene, 60 °C) with the isolable model complex (μ-CH₂)Fe₂(CO)₈ does not contradict this mechanism, since multiple CH₂-insertions are not possible in this monomethylene system. Furthermore, the selective formation of ethylene in the reduction of coordinated carbon monoxide with AlH₃^[19b] is probably attributable to the methylene complex as formulated in eq. (e): Thus, Cr(CO)₆ gives exclusively ethylene, in a rapid reaction (15 min, 22 °C), even with a large excess of AlH₃; only after acidification of the reaction mixture with H₂SO₄ are methane and ethane formed.

Finally, in accord with the chain growth formalism of Scheme 3 (bottom) it is found that the composition of the product gases of the F-T synthesis over different catalysts is identical with that of the hydrocarbon mixture obtained upon treatment of the expended catalyst with acid^[19c].

4.2. Carbide Clusters

The metal-induced decomposition of carbon monoxide leading to formation of cluster complexes with “naked” C-



atoms as ligands is no longer a curiosity in organometallic chemistry. The rupture of the C—O bond, especially on metal surfaces, may be facilitated by the coordination of

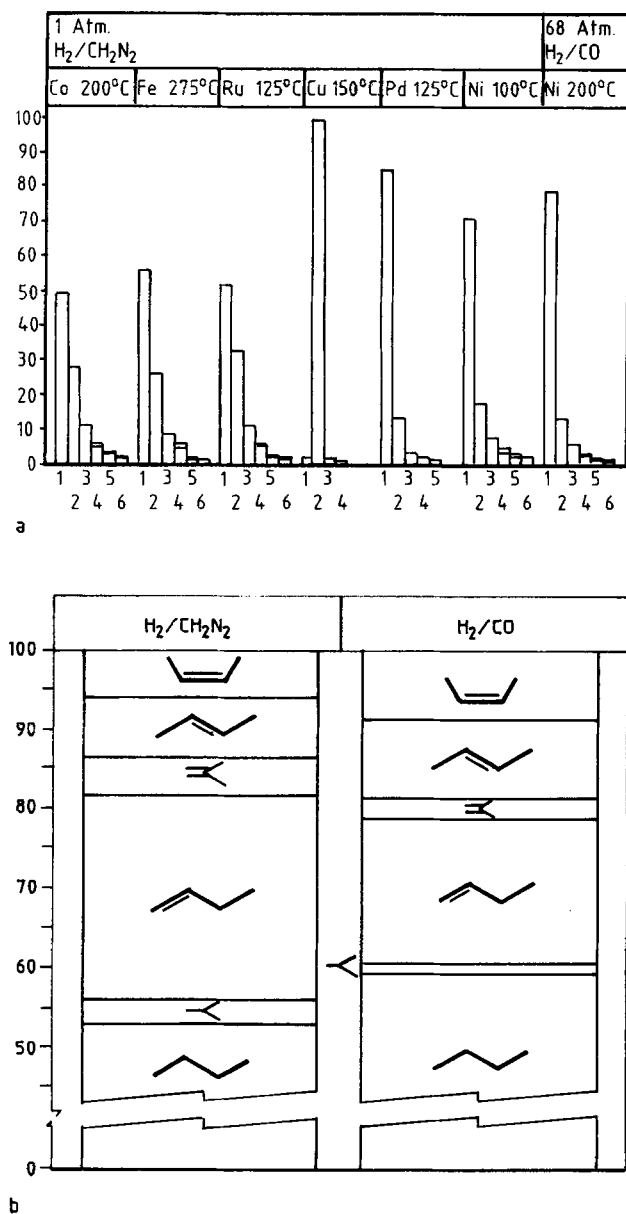
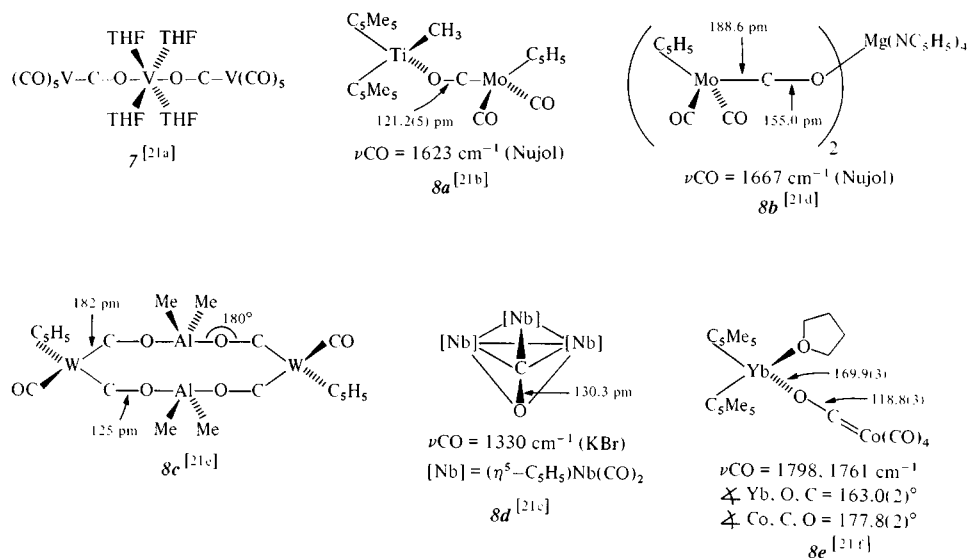
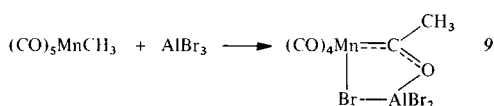


Fig. 2. a) Molecular weight distribution of hydrocarbon fractions formed from H₂/CH₂N₂ and H₂/CO on F-T catalysts. Alkanes and olefins are presented together corresponding to their chain lengths (abscissa). The block starting from the zero line represents the proportion of linear hydrocarbons, while the proportion of branched isomers are represented by the upper sections. Ordinate: Wt.-%. b) Comparison of the C₄-hydrocarbon fractions obtained from H₂/CH₂N₂ and H₂/CO, resp. (39% cobalt/silica catalyst, 210 °C, 1 bar). Ordinate: Wt.-%. (After [10c].)

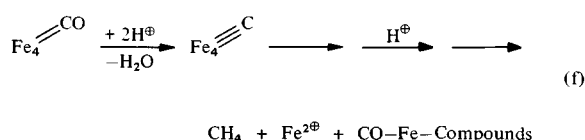
both atoms^[20], as has been demonstrated in a series of structurally well-characterized multinuclear complexes (e.g. **7** and **8**; THF = tetrahydrofuran)^[21]. The η^2, μ_3 -complexation in the niobium cluster **8d** leads to an extreme lengthening of the C—O distance (ca. 130 pm)^[21c]. The ytterbium(III) complex **8e** is an illustrative example, revealing the oxophilic character of lanthanoid elements. Here too, the C—O bond of the carbonyl bridge is significantly weakened as compared with the usual type of complexation^[21f].



Besides O-complexation, the activating effect of Lewis acids has also been well investigated since the time that *Shriver et al.* carried out their formative studies in this sector^[22a, b]. Thus, the addition of aluminum tribromide increases the rate of the intramolecular methyl migration by orders of magnitude. In the resulting X-ray structurally



characterized product **9** the “ambiphilic” Lewis acid stabilizes not only the free coordination site on the transition metal formed as a result of methyl migration, but also complexes the basic acetyl function through the electron-deficient aluminum atom. Alumina surfaces show a comparable effect on the rate of methyl-to-carbonyl transfer to that observed for AlBr_3 in solution^[28].

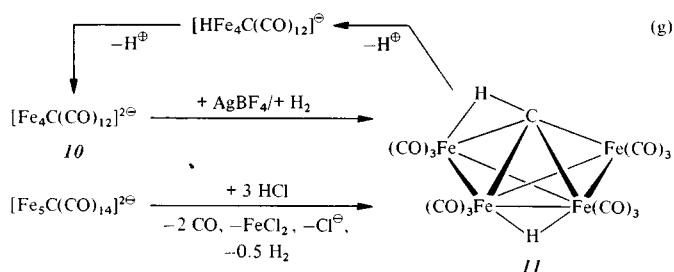


Treatment with Brønsted acids allowed an anionic carbonyl complex to be smoothly decomposed with formation of CH_4 and H_2 [eq. (f)]. It was proven by deuterium label-

ing experiments, that the hydrocarbon hydrogens came from the added acid^[22c]. Accordingly, the mononuclear and dinuclear complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Li}$ and $\text{Mg}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2 \cdot x\text{THF}$ produce methane, ethylene, and ethane as a result of $\eta^2, \mu(\text{C, O})$ -coordination, even at low temperatures. The formation of cationic $\text{Fe}=\text{CH}_2$ species in this reaction has been postulated^[22d]. The plausibility of these proposed mechanisms, however, is diminished by the normally low yields of hydrocarbons produced in the course of such reactions. In the light of this, strongly

oxophilic centers should favor carbide formation. However, it is exactly such transition metals, from groups IV and V, which strangely enough hinder Fischer-Tropsch reactivity.

Muetterties has recently developed rational synthetic methods for the generation of carbide complexes^[23], and, moreover, has shown^[24a] that structurally characterized compounds with four-fold coordinated anionic carbide C-atoms react with H_2 under oxidative conditions to give CH-functionalities [eq. (g)], and are thus to be seriously considered as key species in the formation of CH_2 -moieties from CO. Alternatively, it proved possible to form C—H bonds by protonation [eq. (f) and (g)]. Rapid hydrogen ex-



change between the CH and the Fe—H groups would indicate the importance of such processes on metal surfaces. The fully-characterized $\mu_4, \eta^2\text{-CH}$ -three-center bond^[24a, b] in

the “butterfly” molecule **11** (see Fig. 3) appears to approach the energetically most favorable form of methyldi-nyne complexation on top of specific metal surfaces^[24c], and emphasizes the importance of M—H interactions in

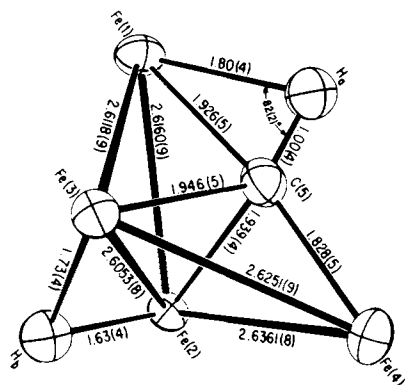
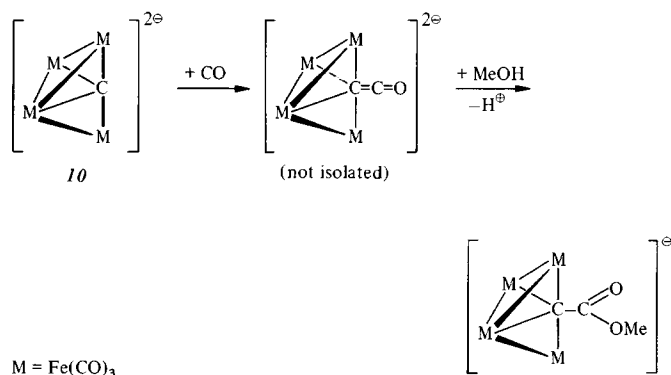


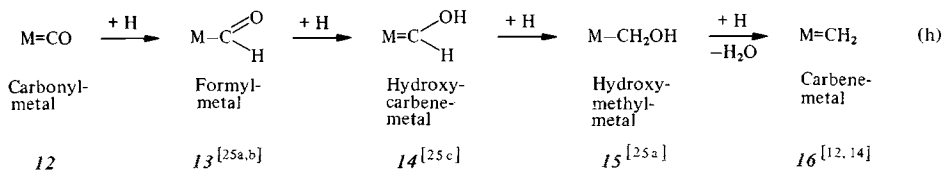
Fig. 3. Structural section from the μ_4, η^3 -methyldi-nyne cluster **11**. For sake of clarity the carbonyl ligands have been omitted; bond lengths in pm (after [24b]; reproduced by permission of the American Chemical Society).

catalytic processes. Besides oxidative addition of H_2 , carbide clusters (such as **10**) are also capable of carbonylation^[24d].

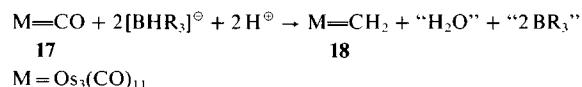


4.3. Stepwise CO-Hydrogenation

A much discussed alternative approach to methylene species is the *stepwise* hydrogenation of (in **12** metal-coordinated) carbon monoxide, a reaction sequence [(h)] which should involve the structural types **13**–**15**^[12, 14, 25], that are now preparatively available as more or less stable mono- and



dinuclear complexes. Starting from the trinuclear osmium complex **17**, and using spectroscopy and [2H]-labeling experiments, the entire sequence **12**–**16** has been established by consecutive reaction with H^- and H^+ as shown in the following equation^[26]:



Of particular significance here is the observation, that the *hydride* hydrogen from the reductant $K[BH(O-i-C_3H_7)_3]$ appears in the methylene group of **18**, whereas the subsequently added phosphoric acid (H^+) is required for the detachment of the carbonyl oxygen. Consistent with this finding, formation of the methylene cluster **18** does not occur when these reagents are added to the carbonyl complex **17** in the opposite order. The intermediate anionic formyl complex $Os_3(CO)_{11}[C(=O)H]^\ominus$ produced by H^- -addition is characterized by a 1H -NMR signal observed at $\delta = 16.0$ as well as by an intense ν_{CO} band at 1577 cm^{-1} ^[26].

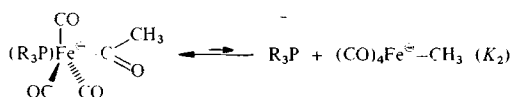
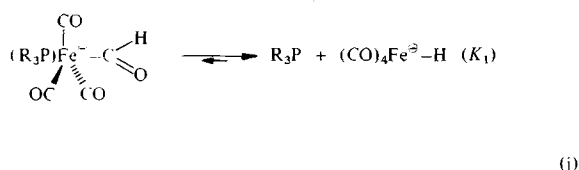
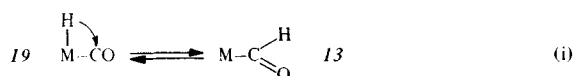
4.4. Formyl Complexes

Since the extensive studies of *Casey*^[25a] and *Gladysz*^[25b], structurally well-characterized mono- and multinuclear complexes with up to two η^1 -bound formyl functionalities per metal are readily accessible in large quantities by reduction of the appropriate cationic or neutral metal carbonyl precursor with commercially available hydride reagents. Formyl ligands can easily be detected 1H -NMR spectroscopically by means of low field signals in the region $\delta > 10$ ppm. Complex *anions* of this kind are chemically characterized by a pronounced hydride reactivity: Thus the extensively investigated iron complex $[L(CO)_3Fe[C(=O)H]]^\ominus$ ($L = P(OC_6H_5)_3$) is suitable not only for the smooth reduction of 2-butanone to 2-butanol (92%), but also for hydride transfer to neutral Fischer carbenes or carbonylmetal compounds, for example $(CO)_5W=C(OCH_3)C_6H_5$ or $Re_2(CO)_{10}$ ^[25a]. Moreover, reactivity studies suggest participation of the oxo-carbene structure $M=C(O^-)H$ in the ground state of anionic formylmetal systems. In the absence of appropriate reactants the irreversible decarbonylation typical of neutral formyl complexes normally dominates, whereby generally good yields of metal hydride derivatives result according to the scheme $M-C(=O)H \rightarrow M-H + CO$ ^[25a, b]. Occasionally, metalformyls also undergo intermolecular Claisen-Tischtschenko-type dismutation reactions. Thus, the neutral formylmanganese complex of composition *mer*-(CO)₃[$P(OCH_3)_3$]₂Mn[C(=O)H] decomposes above $0^\circ C$ with CO_2 - and CO-elimination and concomitant formation

of both the known mononuclear methyl derivative *mer*-(CO)₃[$P(OCH_3)_3$]₂MnCH₃ (40%) and the novel dinuclear complex $Mn_2(CO)_6[P(OCH_3)_3]_4$ (8%). This observation nicely points to a general, metal-centered pathway starting from formyl and leading to methyl functionalities^[25d].

4.5. The Formyl/Hydrido(carbonyl) Equilibrium

The formation of the first C—H bond is of crucial importance to the stepwise, that is non-dissociative, CO reduction. Although the formyl/hydrido(carbonyl) equilibrium (i) has been cited for years as an analogous case to the well-established, completely reversible acetyl/methyl(carbonyl) system^[35] in the explanation of kinetic data for CO substitution in carbonyl(hydrido)metal compounds, recent observations have strengthened the suspicion that the isomerization **19**→**13** does not occur to any appreciable extent for thermodynamic reasons. From model reactions [eq. (j)], carried out with isolable formyl and acetyl complexes, an equilibrium ratio of $K_1/K_2 > 10^5$ was ascertained, from which it follows that the kinetically moderately stable formyl species are thermodynamically less stable by a few orders of magnitude than the analogous acetyl complexes^[25a]. Consequently, whereas decarbonylation (see *e.g.* Section 4.4) as well as the formyl→hydrido(carbonyl) reaction **13**→**19** can practically always be achieved preparatively, the reverse “CO-insertion” (**19**→**13**), as formulated in eq. (i), has not yet been observed. It can be supposed that the 20–30 kcal/mol greater stability of the M—H bond compared with a M—CH₃ bond is responsible for the strongly divergent equilibrium relationship in eq. (j).

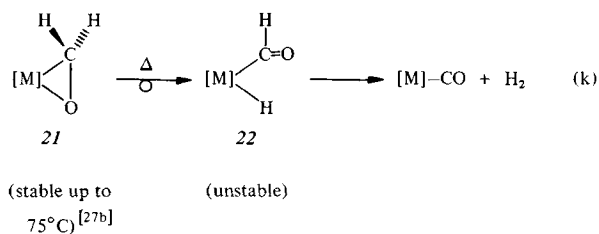
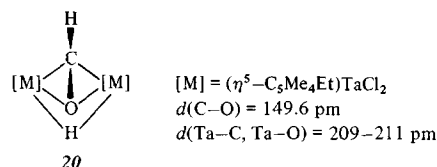


R = OC₂H₅

$$K_1 = \frac{[\text{R}_3\text{P}][(\text{CO})_4\text{Fe}^{\ominus}-\text{H}]}{[(\text{R}_3\text{P})_2(\text{CO})_3\text{Fe}^{\ominus}-\text{C}(\text{H})=\text{O}]}; \quad K_2 = \frac{[\text{R}_3\text{P}][(\text{CO})_4\text{Fe}^{\ominus}-\text{CH}_3]}{[(\text{R}_3\text{P})_2(\text{CO})_3\text{Fe}^{\ominus}-\text{C}(\text{CH}_3)=\text{O}]}$$

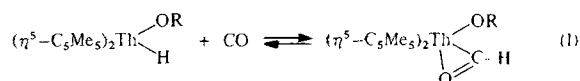
Nevertheless, it cannot be ruled out that formyl formation [eq. (i)] is favored on *heterogeneous* catalysts by an additional coordination of the formyl oxygen atom [cf. **20**→**22**, eq. (k)]^[27a,b], because Lewis acid effects of this kind also accelerate the formally analogous methyl group migration (CH₃—M—CO → M—C(=O)CH₃) by several orders of magnitude in homogeneous as well as heterogeneous systems (see Section 4.2).

Thus, the X-ray structurally characterized μ,η^2 -formyl complex **20** originates from addition of CO to the hydrido-precursor $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2]\text{H}_2$ ^[27a]; the equilibrium (l) has been demonstrated IR- and NMR-spectroscopical-



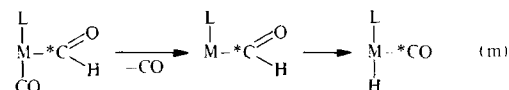
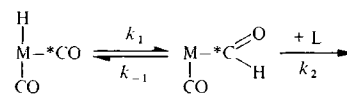
[M] = Os(CO)₂[P(C₆H₅)₃]₂

ly^[27c]. Moreover, destabilization of M—CO bonds by d⁰-metals should contribute to the preference for **13** [eq. (i)].



R = 1-*tert*-butyl-2,2-dimethylpropyl or 2,6-di-*tert*-butylphenyl

Several authors have recently commented^[27d] on the well-known, abnormally fast CO-substitution in anionic, neutral as well as cationic carbonyl(hydrido)metal complexes (*e.g.* HMn(CO)₅), and have suggested that precisely the kinetic character of such reactions is attributable to only *small* concentrations of formylmetal intermediates [eq. (m)]. Earlier observations of *Basolo*, *Heck*, and *Brown*, concerning the reactivity of H₂Fe(CO)₄, H₂Ru(CO)₄ and their derivatives, would suggest that the thermodynamic



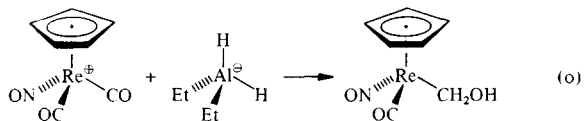
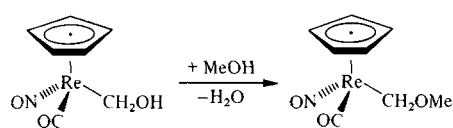
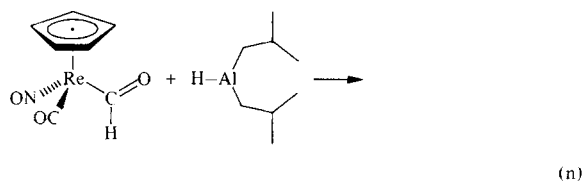
L = phosphane or phosphite, M = *e.g.* Mn(CO)₃ or HFe(CO)₂

instability of the formyl intermediate is a necessary prerequisite for the irreversible reaction of type **13**→**19** subsequent to substitution^[27d]. The question as to the realizability of the equilibrium (i) on catalyst surfaces remains unanswered.

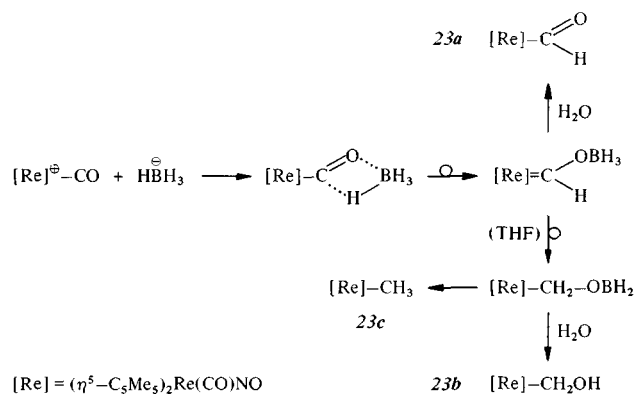
4.6. Hydroxymethyl, Methoxymethyl, Methoxy and Hydroxycarbene Complexes

In principle, starting from formyl complexes, further reduction can lead to hydroxymethyl derivatives. Thus *Casey*

et al. described the clean reaction (n), achieved on using the potent hydride transfer reagent diisobutylaluminum hydride ("DIBAL-H"). It is to be noted, however, that hydroxymethyl ligands are often preparatively more easily accessible [eq. (o)] *via* direct reaction of the corresponding carbonyl compound with hydride derivatives of boron and aluminum (*i.e.*, BH_3 , $[\text{H}_2\text{AlEt}_2]^-$, *etc.*)^[25a, b]. The most striking property of hydroxymethyl complexes is their behavior towards methanol, with which they react to give methoxymethyl derivatives [eq. (n)]^[25a].

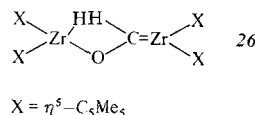
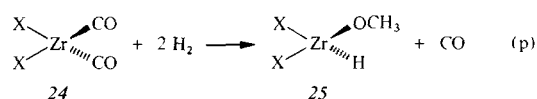


As model example for the stepwise reduction of coordinated carbon monoxide to isolable formyl, hydroxymethyl, and methyl ligands **23a–c**, *Sweet* and *Graham* have underscored the mechanism of the reaction of the complexation $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}(\text{CO})_2\text{NO}]^+$ with NaBH_4 in $\text{THF}/\text{H}_2\text{O}$ [29a]. Under similar conditions, but dependent upon the water content of the solvent, the reaction time and temperature, the analogues of **23a–c** had already been prepared in surprisingly high yields (up to 95%) from the corresponding cyclopentadienyl complex [29b].

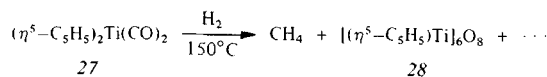


The first stoichiometric hydrogenation of complexed carbon monoxide in the homogeneous phase [eq. (p)] was achieved by altering the coordination atom in the li-

gand^[30a,b]. This reaction is not entirely resolved mechanistically; however, it does provide a convincing example of the pronounced oxophilicity of electron-deficient transition metals [here: Zr^{IV}] and for the strongly *hydridic* character (M^{δ+}—H^{δ-}) of their hydrido derivatives [here: (η⁵-C₅Me₅)₂ZrH₂ or (η⁵-C₅Me₅)₂Zr(CO)H₂]. If the conversion



24→**25** really proceeds intermolecularly, then formation of zirconoxycarbene intermediates **26** is likely, as have been isolated from the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ with $\text{W}(\text{CO})_6$ ^[30a]. Reduction of the carbonyltitanium compound **27** with H_2 gives *methane* with concomitant formation of the structurally characterized hexanuclear oxo complex **28**^[30b, c].



On using nucleophilic, H₂O-resistant hydridoniobium complexes [e.g., (η⁵-C₅H₅)₂NbH₃] for the reduction of electrophilic carbonylmetal compounds M(CO)_x, Labinger *et al.*^[31a, b] observed selective alkane formation in specific cases [e.g. Cr(CO)₆, 2 h, 45 °C]; labeling experiments indicated that ethylene is the initial product, which is subsequently catalytically hydrogenated to ethane^[31a]. The spec-

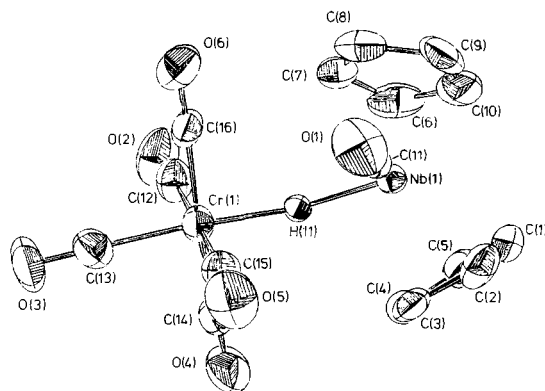
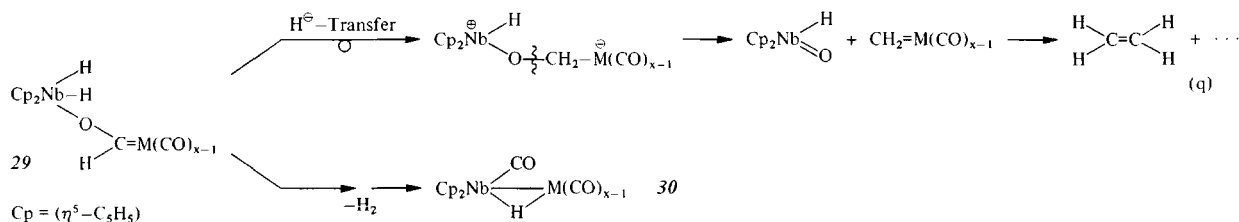


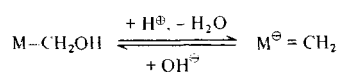
Fig. 4. Molecular structure of the μ -hydrido complex (η^5 -C₅H₅)₂Nb(CO)—H—Cr(CO)₅ (type **30**), which is accessible as stable product by photolysis of (η^5 -C₅H₅)₂NbH₃ and Cr(CO)₆. The formation of such compounds can be explained in terms of an oxycarbene intermediate (type **29**) through hydrogen transfer. Selected molecular data: Nb(1)—Cr(1) 345.3(2), Cr(1)—H(11) 118.2(102), Nb(1)—H(11) 182.4(99) pm; Cr(1), H(11), Nb(1) 137.4(54)°; $R_{\text{int}} = 0.045$, $R_{\text{min}} = 0.077$. (*W. A. Hermark, M. L. Ziegler et al., unpublished results 1980/81*).

troscopically identified initial dinuclear products of type **29**, however, open the possibility for side reactions [eq. (q)], which often lead to stable μ -hydrido complexes **30**

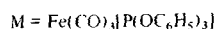
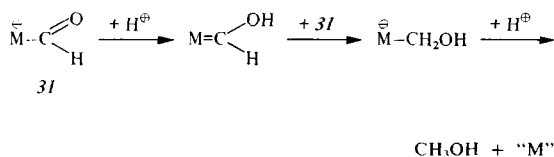


(Fig. 4)^[31b-d]. Naturally, CO-reductions with hydrido-transition metal complexes have proven to be much more complex than those with hydrides of the main group elements of comparable reducing strength (*e.g.*, Red-Al[®], K-Selectride, *etc.*). Nevertheless, owing to their extreme tendency to hydrolyze, the latter are only suitable for stoichiometric reactions.

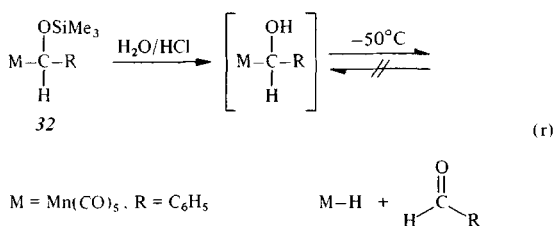
Methylene complexes $\text{M}^+=\text{CH}_2$ are related to their hydroxymethyl precursors by the acid/base equilibrium



The protonation of anionic formyl derivatives such as **31** possibly involves hydroxycarbene complexes according to the overall sequence



Nevertheless, the primary formation of formaldehyde and its subsequent reduction by the hydride donor **31** cannot be ruled out^[32]. Although the occurrence of free formaldehyde under real Fischer-Tropsch conditions is often not explicitly taken into consideration^[2a], there is mass spectroscopic evidence for its presence among the initial products^[33a]. According to a recent report concerning the protodesilylation of **32**, α -hydroxyalkyl complexes can be expected to irreversibly decompose to free aldehyde and the corresponding metal hydride [eq. (r)]^[34].

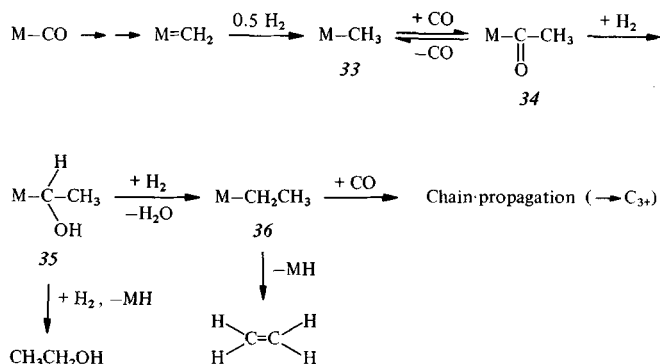


It was very recently reported that free formaldehyde is capable of acting as a hydride donor toward ketones or higher aldehydes in the sense of metal-catalyzed Cannizzaro reactions with formation of the corresponding alcohols^[33b]. Zirconocene dichloride-catalyzed reductive CO-

oligomerization with diisobutylaluminum hydride gives a mixture of methanol, ethanol, 1-propanol, and 1-butanol (1.0:0.10:0.15:0.03)^[33c]. Even octacarbonyldicobalt behaves as a weak catalyst for methanol formation from synthesis gas, but in this case rather drastic reaction conditions (300 bar, 200°C) are required to achieve acceptable yields^[33d].

5. The Carbon Monoxide Insertion Mechanism

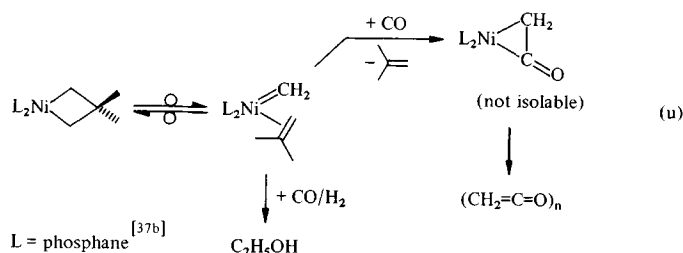
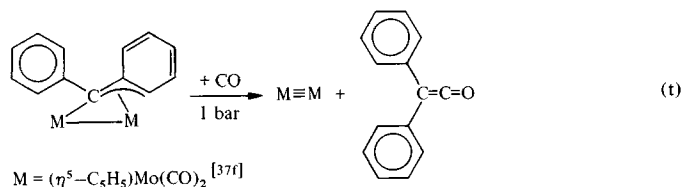
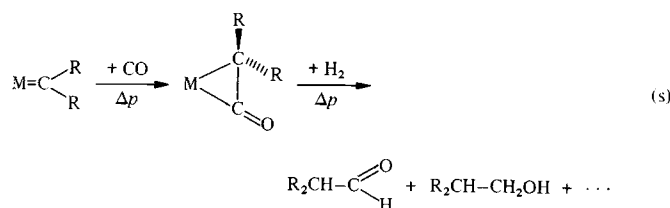
The most popular mechanism, but which according to the current state of our knowledge is presumably at best dominant in the synthesis of oxygen-containing F-T products, is based upon "CO-insertion"^[35] into a metal-carbon bond as the fundamental chain growth step (alkyl migration)^[2a]. According to this mechanism, the first $\text{M}-\text{CH}_3$ group **33** is formed by reduction of a metal-bound formyl intermediate, as outlined in principle in eq. (h). Subsequent reduction of the resulting acetyl moiety to an ethyl moiety is viewed as the key reaction along the path to consecutive incorporation of CO. If decarbonylation **34**→**33** is faster than alkyl transfer, then the formation of higher products will not result. A most important aspect of this



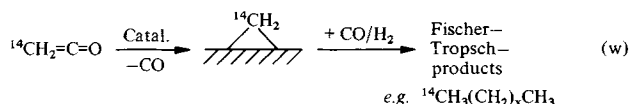
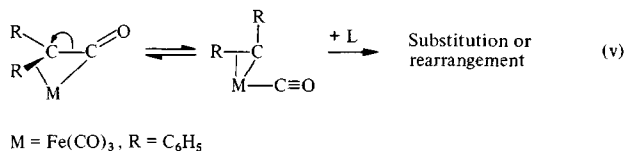
sequence is the reduction of α -hydroxyalkyl intermediates (*e.g.*, **35**) with cleavage of the metal-to-carbon bond to give alcohols, as well as β -hydrogen abstraction in the alkyl state (*e.g.*, **36**) to give α -olefins in competition with chain growth. On the other hand, alcohol formation could also arise from metal carbene species: mononuclear model systems for both hydrogenolytic cleavage of the carbene intermediate^[36] and CO-addition have hitherto been established [eqs. (s)–(u)]^[37a, b, f].

The latter reaction gives primarily the corresponding, in some cases isolable, structurally well-characterized ketene complexes (*cf.* Fig. 5)^[14a, 37a]. Decisive for the course of the reaction (u), is the metallocyclobutane/metal-olefin-me-

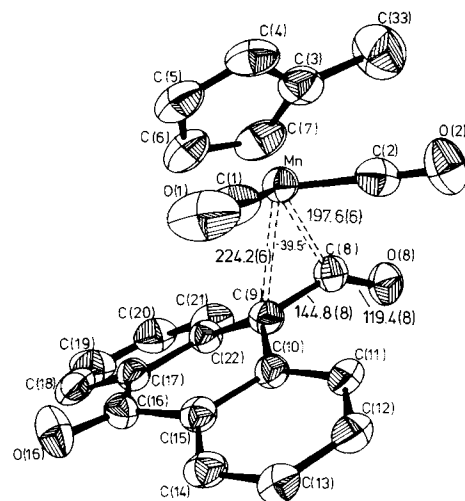
thylene equilibrium, that is also established for metallocycles of platinum^[37b]. The observation of intramolecular CO-exchange in multiply metal-bonded ketenes suggests



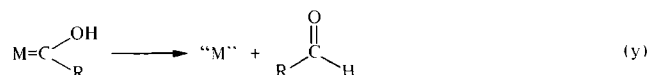
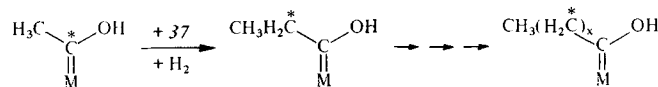
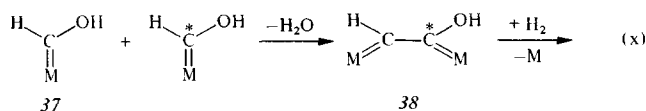
reversible cleavage of a ketene C—C bond within the coordination sphere of the metal as in eq. (v) (Fig. 6)^[37c]. Thus surface-bound ketenes could also take part in chain growth. In this connection, it should be remembered that incorporation of the methylene fragment from ketene into F-T products has been known for some time [eq. (w)]^[5a].



Alternatively, it is possible to form ketene functionalities by carbene transfer to carbonyl-metal compounds^[37e]. The synthetic step **34**→**36** has been established in the reduction of mononuclear acetyliron and acetyl ruthenium complexes with borane, and thus, in principle, could take place in catalytic cycles as well^[37d]. The possibility of *selective* formation of oxygen-containing products by CO insertion



shift with concomitant formation of free aldehyde [eq. (y)] is also to be expected for surface-bound hydroxycarbene complexes^[25c, 40]. It is not certain whether this reaction, in the sense of a $d'' \rightarrow d''-2 \rightarrow d''$ process, involves a hydrido(acyl) intermediate ($d''-2$).

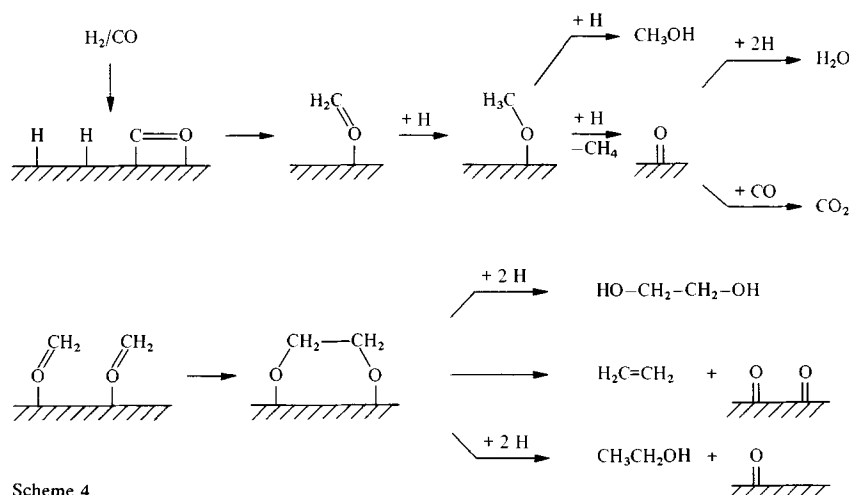


Model reactions for the reverse of eq. (y) are as yet unknown; this is unfortunate since their feasibility would not only give strong support to the mechanistic involvement of aldehydes in the Fischer-Tropsch synthesis but also would

graduation reactions considered here have been verified starting from isolable hydroxycarbene complexes of type 39. It must be conceded, however, that the failure of these reactions to occur may possibly be due to coordinative saturation of the available substrates. Polynuclear systems bridged by hydroxyalkylidene functionalities and bearing supporting ligands that are prone to easy elimination could in fact basically change this pattern.

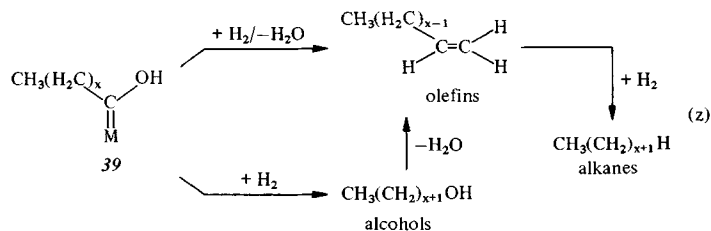
7. The Oxide Mechanism

The most recent mechanism put forward for the Fischer-Tropsch process, namely the "Oxide Mechanism" proposed by R. S. Sapienza^[42] (Brookhaven National Laboratory) at an ACS meeting in August 1981, suffers from the grave disadvantage that it is quite speculative and, as yet, there is no suitable model system warranting its support. The general concept of this mechanism is that chain growth is accomplished on metal oxide surfaces and that the carbon atoms to be connected with each other do not touch the metal centers of the catalyst. In this context, formaldehyde is believed to be formed as the initial product



Scheme 4.

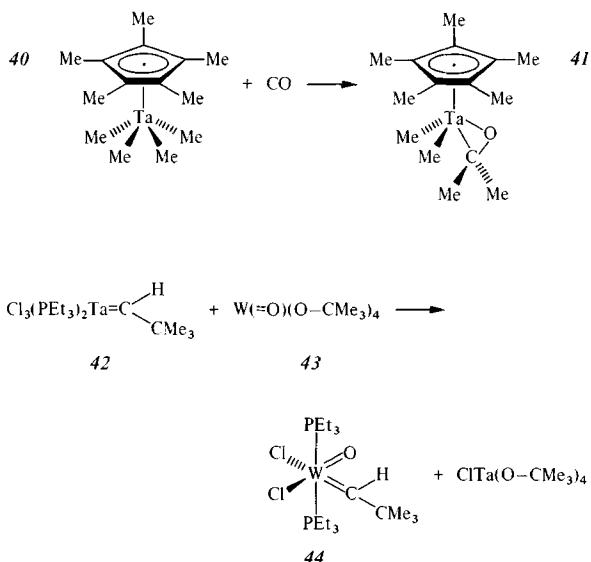
furnish an elegant synthetic route to hydroxycarbene complexes of which only scattered examples have so far been reported. Both these aspects represent a true challenge to the organometallic chemist.



A crucial test for the usefulness of the hydroxycarbene or hydroxymethylene model [eq. (x)] are the terminating steps outlined in eq. (z): None of the most conceivable de-

and is anchored to the catalyst surface by means of the oxygen atom only. According to this view, the stability of the metal-to-oxygen linkage decidedly governs the product pattern (Scheme 4): After reductive coupling of the formaldehyde groups, hydrocarbons (in the case of strong M—O bonds) or oxygenates (in the case of weak M—O bonds) are formed. There is little doubt that the formation of oxidic surface layers has an effective influence upon the product pattern, but to overlook any possible metal-centered reaction steps would seem far too much of an oversimplification. Both the "Oxide Mechanism" as well as a related mechanism emphasizing the importance of hydroxy groups anchored to the catalyst surface^[43] are inconsistent with the basic observation that even pronounced oxophilic metals (Ta^{I}) and metals in higher oxidation states (W^{IV}) do not bind simple *O,C*-ligands exclusively *via* the oxygen atom, and, conversely, that oxo(methylene)

complexes obviously do not display any tendency to rearrange to aldehyde or keto derivatives. A typical example in support of this assessment is the well-characterized η^2 -acetone complex **41**, which is formed by means of CO-insertion into the metal-methyl bond of the precursor molecule **40**^[44]. In addition, the *Floriani* group has shown that C-coordination survives in the course of cycloaddition reactions between diphenylketene and certain titanium complexes^[45]. Finally, the neopentylidene group of **42** is not transferred from tantalum to the oxo ligand of the carbene acceptor molecule **43**, but rather to its metal center. The



catalytic activity of the “tetraivalent” tungsten compound **44** (olefin metathesis) is exclusively due to a phosphane dissociation pre-equilibrium and, thus, proceeds immediately in the center of the molecule but does not involve peripheral ligands^[46].

8. Closing Remarks—Future Trends

What have we learned in the foregoing discussion? Organometallic model reactions have uncovered numerous, in part entirely new fundamental pathways in synthesis gas chemistry. Moreover, they have provided detailed knowledge of simple organometallic species, *e.g.* formyl and μ -methylene compounds. The mechanistic concept of the Fischer-Tropsch synthesis becomes clearer now in that the reaction principles regarding carbide, methylene, hydroxymethyl, formyl and hydroxycarbene complexes are far better understood than a few years ago. Therefore, unrealistic pathways for synthesis gas reactions can be excluded on the basis of such knowledge. There is increasing evidence that the carbide/methylene mechanism should be considered as offering the best description of reductive oligomerization of carbon monoxide giving oxygen-free products. Since there is no unambiguous proof for the hydrido(carbonyl) \rightarrow η^1 -formyl interconversion, caution has to be exercised in focusing on the participation of formyl intermediates in the chain-growth process, at least from the viewpoint of a critical organometallic chemist, because this im-

portant question is lacking a comprehensive, clear answer.

We should not forget that several striking experimental results still await elucidation. For example, all mechanisms that have hitherto been considered by various researchers do not sufficiently explain the fact that increasing H₂/CO pressure ratios favor the formation of alcohols under the conditions of heterogeneous F-T catalysis. In addition, both the participation of the side product water in the initial steps of the Fischer-Tropsch synthesis [eq. (a)] and the possibility of consecutive CO insertion reactions into methylene- and alkyl-metal bonds remain unclear. A comprehensive mechanism for carbon monoxide hydrogenation yielding oxygenates as well as the mechanistic explanation of alcohol homologation processes offer serious problems. Here, model studies involving carbonylation of metallacycles should provide a means of throwing some light on these questions.

Dinuclear μ -methylene complexes will undoubtedly play a pivotal role in further model studies. In this context it should be investigated whether combination of typical Fischer-Tropsch metals (*e.g.* transition metals of group VIII) with the pronounced oxophilic, electron-deficient early transition metals (*e.g.* group IV and V-metals such as Ti, Nb, and Ta) renders catalytic CO/H₂ reactions possible. Finally, carbide cluster compounds that are nowadays easily accessible require further investigations into their capability for initiating Fischer-Tropsch-type reactions. Immobilized, polymer-supported catalytic centers^[41] are expected to demonstrate the borderline between heterogeneously and homogeneously catalyzed synthesis gas reactions and to reveal the importance of multi-site activation in the course of the F-T process. It should prove possible to recognize the interrelationship with other kinds of catalytic reactions such as the olefin metathesis.

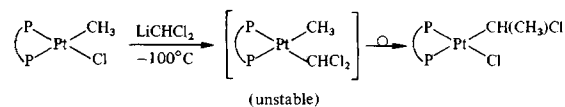
At present, considerable interest is attached to the stepwise improvement of heterogeneous catalysts in order to gradually approach the new selectivity goal mentioned in the Introduction. These developments should not have been neglected here; therefore, we conclude our review by pointing out the quintessence of two outstanding papers which nicely demonstrate future trends. Thus, the selectivity for C₂- to C₅-olefins is enhanced from 40 to 55% (H₂:CO = 2:1; 200 °C) if ruthenium carbonyl, Ru₃(CO)₁₂, is used in place of the usual precursors RuCl₃ or Ru(NO)(NO₃)₃ for the preparation of Ru/ γ -Al₂O₃ catalysts. Even more informative is the result that addition of the standard promoter potassium to the “Ru₃(CO)₁₂”/ γ -Al₂O₃ catalyst once again enhances the process selectivity for low molecular weight olefins (80% at 1% K-content); at the same time, the overall activity of the catalyst for CO hydrogenation is found to decrease to a very large extent (*ca.* 50%)^[47]. This striking contradictory effect—selectivity *versus* activity—is less pronounced in the case of the conventional “RuCl₃”/ γ -Al₂O₃ catalyst. From these results, it is suggested that addition of potassium suppresses surface-induced hydrogen dissociation and, at the same time, stabilizes the adsorbed carbon monoxide, thus decreasing the activity for hydrogenation of CO. The enhancement of the olefin selectivity indicates that the surface-anchored alkyl intermediates experience an acceleration in β -hydrogen ab-

straction^[47]. Another study has shown that ruthenium/zeolite catalysts (e.g., Ru/zeolon; 3% Ru; Si/Al = 5:1) suffer from decreasing activity for syn-gas methanation with increasing acidity of the catalyst support—an observation which directly corresponds to increasing electron-deficiency of the catalytically active metal^[48]. These and related findings are certainly interesting for the tailoring of new Fischer-Tropsch catalysts.

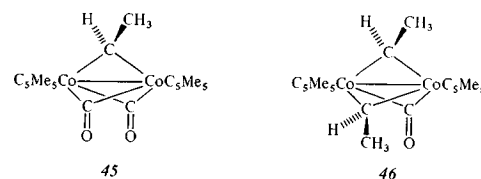
The results of my group that have been mentioned in this review arise from the enthusiasm of my coworkers, whose work I greatly appreciate. Generous support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the BASF Aktiengesellschaft, the Hoechst Aktiengesellschaft, the Chemische Werke Hüls, the Degussa Hanau, the Humboldt Foundation, and the Karl-Winnacker Foundation is also gratefully acknowledged.

Received: September 22, 1981 [A 399 IE]
German version: *Angew. Chem.* 94 (1982) 118
Translated by Dr. J. M. Huggins, Regensburg

- [1] For some excellent articles covering the Fischer-Tropsch Synthesis with specific emphasis upon process-technology see: a) C. D. Frohning, H. Kölbl, M. Ralek, W. Rottig, F. Schnur, H. Schulz, in J. Falbe: *Chemie-rohstoffe aus Kohle*, Thieme, Stuttgart 1977, Chapter 8, pp. 219–299ff; b) H. Pichler, H. Schulz, *Chemie-Ing.-Techn.* 42 (1970) 1162; c) H. H. Storch, N. Golumbic, R. B. Anderson: *The Fischer-Tropsch and Related Syntheses*, Wiley, New York 1951; d) C. D. Frohning, in Winnacker-Küchler: *Chemische Technologie*, 4th Edit., Hanser, München 1981, Vol. 5, pp. 518ff; e) C. D. Frohning in J. Falbe: *New Syntheses with Carbon Monoxide*, Springer, Berlin 1980.
- [2] a) G. Henrici-Olivé, S. Olivé, *Angew. Chem.* 88 (1976) 144; *Angew. Chem. Int. Ed. Engl.* 15 (1976) 136; *J. Mol. Catal.* 3 (1978) 443; 4 (1978) 379; b) C. Masters, *Adv. Organomet. Chem.* 17 (1979) 80; c) H. Pichler, *Adv. Catal.* 4 (1952) 272; a comprehensive review dealing with surface-centered Fischer-Tropsch type reactions has appeared since our manuscript was submitted for publication: Ch. K. Rofer-DePoorter, *Chem. Rev.* 81 (1981) 447.
- [3] For model reactions, see: a) E. L. Muetterties, J. Stein, *Chem. Rev.* 79 (1979) 479; b) P. C. Ford, *Acc. Chem. Res.* 14 (1981) 31.
- [4] For comprehensive reviews see: a) T. J. Katz, *Adv. Organomet. Chem.* 16 (1977) 283; b) N. Calderon, J. P. Lawrence, E. A. Ofstead, *ibid.* 17 (1979) 449; N. Calderon, E. A. Ofstead, W. A. Judy, *Angew. Chem.* 88 (1976) 433; *Angew. Chem. Int. Ed. Engl.* 15 (1976) 401; c) R. H. Grubbs, *Prog. Inorg. Chem.* 24 (1978) 1; d) R. Streck, *Chem. Ztg.* 99 (1975) 397.
- [5] Cf. a) J. P. Collman, L. S. Hegedus: *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill. Valley, Calif. 1980, Chap. 8, pp. 419ff.; b) F. A. Cotton, G. Wilkinson: *Advanced Inorganic Chemistry*, 4th Ed., Wiley, New York 1980, Chap. 30; *Anorganische Chemie*, 3rd Ed., Verlag Chemie, Weinheim 1980.
- [6] R. L. Pruett, *Ann. N. Y. Acad. Sci.* 295 (1977) 239; J. F. Knifton, *J. Am. Chem. Soc.* 103 (1981) 3959, and literature cited therein.
- [7] a) M. Araki, V. Poncet, *J. Catal.* 44 (1976) 439; b) C. P. Huang, J. T. Richardson, *ibid.* 51 (1978) 1, and literature cited therein.
- [8] For CO/H₂ reactions employing homogeneous catalysts, see [6] and a) G. Henrici-Olivé, S. Olivé, *Angew. Chem.* 91 (1979) 83; *Angew. Chem. Int. Ed. Engl.* 18 (1979) 77; b) W. Keim, M. Berger, J. Schlupp, *J. Catal.* 61 (1980) 359; c) B. D. Dombek, *J. Am. Chem. Soc.* 102 (1980) 6855; 103 (1981) 6508, and references cited therein.
- [9] H. Schulz, B. R. Rao, M. Elstner, *Erdöl Kohle* 23 (1970) 651, and references cited therein.
- [10] a) F. Fischer, H. Tropsch, *Brennst.-Chem.* 7 (1926) 97; b) P. Biloen, J. N. Helle, W. M. H. Sachtler, *J. Catal.* 58 (1979) 95; c) R. C. Brady III, R. Pettit, *J. Am. Chem. Soc.* 102 (1980) 6181.
- [11] a) R. R. Schrock, *J. Am. Chem. Soc.* 97 (1975) 6577; b) L. J. Guggenberger, R. R. Schrock, *ibid.* 97 (1975) 6578.
- [12] Review: R. R. Schrock, *Acc. Chem. Res.* 12 (1979) 98.
- [13] W. A. Herrmann, B. Reiter, H. Biersack, *J. Organomet. Chem.* 97 (1975) 245.
- [14] Reviews: a) W. A. Herrmann, *Angew. Chem.* 90 (1978) 855; *Angew. Chem. Int. Ed. Engl.* 17 (1978) 800; b) *Adv. Organomet. Chem.*, in press; c) *Pure Appl. Chem.*, in press.
- [15] a) J. C. Hayes, G. D. N. Pearson, N. J. Cooper, *J. Am. Chem. Soc.* 103 (1981) 4648. – The formation of the α-chloroethyl platinum complex according to the sequence



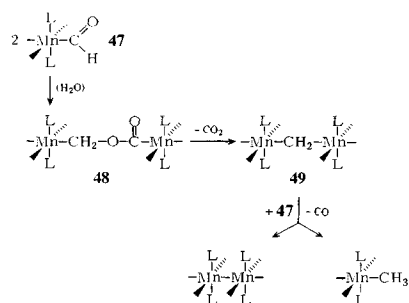
would also seem to involve a similar methylene insertion reaction. An alternative pathway including the free chlorocarbene, :C(H)Cl, is unlikely in this case: P. W. N. M. Van Leeuwen, C. F. Roobeek, R. Huis, *J. Organomet. Chem.* 142 (1977) 243. b) K. Isobe, D. G. Andrews, B. E. Mann, P. Maitlis, *J. Chem. Soc. Chem. Commun.* 1981, 809; c) M. Cooke, D. L. Davies, J. E. Guerschias, S. A. R. Knox, K. A. Mead, J. Roué, P. Woodward, *ibid.* 1981, 862. – Mono(μ-alkylidene) complexes having β-hydrogen substituents were shown to follow a further pathway of decomposition. For example, the μ-ethylidene derivative 45 produces, via 1,2-hydrogen shift, exclusively ethylene in virtually quantitative yield (250°C, solid state decomposition). On the other hand, the related bis(μ-ethylidene) complex 46 gives *cis*- and *trans*-2-butene (91%) under comparable conditions, with thermolytic degradation of this compound in toluene (110°C) yielding only ethylene (48%) and methane (52%); W. A. Herrmann, J. M. Huggins, unpublished results 1981; for the synthesis of



compounds belonging to this series see W. A. Herrmann, J. M. Huggins, Ch. Bauer, M. Smischek, M. L. Ziegler, H. Pfisterer, *J. Organomet. Chem.* (1982), in press.

- [16] a) W. A. Herrmann, *Xth Int. Conf. Organomet. Chem.*, Abstract S9, Toronto 1981; b) A. F. Dyke, S. A. R. Knox, K. A. Mead, P. Woodward, *J. Chem. Soc. Chem. Commun.* 1981, 861.
- [17] a) W. Keim, M. Röper, H. Strutz, *J. Organomet. Chem.* 219 (1981) C5; b) A. C. Sievert, D. S. Strickland, J. R. Shapley, G. R. Steinmetz, G. L. Geoffroy, *Organometallics*, in press; c) K. H. Theopold, R. G. Bergman, *J. Am. Chem. Soc.*, in press.
- [18] Chemistry of Metal Surfaces: a) E. L. Muetterties, *Angew. Chem.* 90 (1978) 577; *Angew. Chem. Int. Ed. Engl.* 17 (1978) 545; b) G. Ertl, *ibid.* 88 (1976) 423 and 15 (1976) 391, respectively.
- [19] a) C. E. Sumner, Jr., P. E. Riley, R. E. Davis, R. Pettit, *J. Am. Chem. Soc.* 102 (1980) 1752; b) C. Masters, C. van der Woude, J. A. van Doorn, *ibid.* 101 (1979) 1633; see also the comments in [14b]; c) M. Ritschel, W. Vielstich, *Chem.-Ing.-Tech.* 52 (1980) 327.
- [20] E. L. Muetterties, *Bull. Soc. Chim. Belg.* 84 (1975) 959; 85 (1976) 451.
- [21] a) M. Schneider, E. Weiss, *J. Organomet. Chem.* 121 (1976) 365; b) D. M. Hamilton, Jr., W. S. Williams, G. D. Stucky, *J. Am. Chem. Soc.* 103 (1981) 4255; c) W. A. Herrmann, H. Biersack, M. L. Ziegler, K. Weidenhammer, R. Siegel, D. Rehder, *ibid.* 103 (1981) 1692, references cited therein; d) S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, R. E. Hughes, *ibid.* 95 (1973) 4469; cf. J. M. Burlitch, R. B. Petersen, *J. Organomet. Chem.* 24 (1970) C65; e) R. R. Schrieke, J. D. Smith, *ibid.* 31 (1971) C46; G. J. Gainsford, R. R. Schrieke, J. D. Smith, *J. Chem. Soc. Chem. Commun.* 1972, 650; f) T. D. Tilley, R. A. Andersen, *ibid.* 1981, 985.
- [22] a) D. F. Shriver, *J. Organomet. Chem.* 94 (1975) 259; b) H. A. Hodali, D. F. Shriver, *Inorg. Chem.* 18 (1979) 1236, and references cited therein; c) K. Whitmire, D. F. Shriver, *J. Am. Chem. Soc.* 102 (1980) 1456; d) A. Wong, M. Harris, J. D. Atwood, *ibid.* 102 (1980) 4529.
- [23] a) E. L. Muetterties, *J. Organomet. Chem.* 200 (1980) 177; b) M. Tachikawa, R. L. Geerts, E. L. Muetterties, *ibid.* 213 (1981) 11.
- [24] a) M. Tachikawa, E. L. Muetterties, *J. Am. Chem. Soc.* 102 (1980) 4541; b) M. A. Beno, J. M. Williams, M. Tachikawa, E. L. Muetterties, *ibid.* 103 (1981) 1485; c) J. E. Demuth, H. Ibach, *Surf. Sci.* 78 (1978) L238; d) J. S. Bradley, G. B. Ansell, E. W. Hill, *J. Am. Chem. Soc.* 101 (1979) 7417; J. S. Bradley, G. B. Ansell, M. E. Leonowicz, E. W. Hill, *ibid.* 103 (1981) 4968.
- [25] Reviews: a) C. P. Casey, S. M. Neumann, M. A. Andrews, D. R. McAlister, *Pure Appl. Chem.* 52 (1980) 625; b) J. A. Gladysz in Y. Ishii, M. Tsutsui: *Fundamental Research in Homogeneous Catalysis*, Vol. 2, Plenum Publ. Co., New York 1978; J. A. Gladysz, *Aldrichim. Acta* 12 (1979) 13; c) E. O. Fischer (Nobel-Lecture), *Angew. Chem.* 86 (1974) 651; *Adv. Organomet. Chem.* 14 (1976) 1.—First authentic example of an anionic formyl complex: J. P. Collman, S. R. Winter, *J. Am. Chem. Soc.* 95 (1973) 4089. d) H. Berke, G. Weiler, *Angew. Chem.* 94 (1982) 135; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 150; this reaction requires the presence of catalytic amounts of water and is thought to proceed according

to the following scheme ($L = P(OCH_3)_3$; CO groups omitted for sake of clarity):



The unstable intermediate **48** is postulated in analogy with the formation of an isolable metalloester complex from a formylrhodium precursor [25e]. The μ -methylene species **49** that undergoes subsequent disproportionation appears the most plausible intermediate on the basis of ^1H -NMR spectroscopic as well as chemical evidence; e) C. P. Casey, M. A. Andrews, D. R. McAlister, J. E. Rinz, *J. Am. Chem. Soc.* **102** (1980) 1927.

- [26] G. R. Steinmetz, G. L. Geoffroy, *J. Am. Chem. Soc.* **103** (1981) 1278.
- [27] a) M. R. Churchill, H. J. Wasserman, *J. Chem. Soc. Chem. Commun.* **1981**, 274; b) K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, W. R. Roper, *J. Am. Chem. Soc.* **101** (1979) 503. – The iron complex of composition $\text{trans}(\text{CO})_2[\text{P}(\text{OMe})_3]_2\text{Fe}(\eta^2\text{-CH}_2\text{O})$ is formed from $(\mu\text{-N}_2)[(\text{CO})_2[\text{P}(\text{OMe})_3]_2\text{Fe}]_2$ and formaldehyde and was shown to adopt the same overall geometry as Roper's osmium complex $\text{trans}(\text{CO})_2\text{-}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Os}(\eta^2\text{-CH}_2\text{O})$ (**21**); H. Berke, W. Bankhardt, G. Huttner, J. von Seyerl, L. Zsolnai, *Chem. Ber.* **114** (1981) 2754. c) T. J. Marks, P. J. Fagan, E. A. Maatta, E. A. Minz, *Xth. Int. Conf. Organomet. Chem.*, Abstract 3DO5, Toronto 1981; P. J. Fagan, K. G. Moloy, T. J. Marks, *J. Am. Chem. Soc.* **103** (1981) 6559; d) R. G. Pearson, H. W. Walker, H. Mauermann, P. C. Ford, *Inorg. Chem.* **20** (1981) 2741.
- [28] D. F. Shriver *et al.*, *J. Am. Chem. Soc.* **101** (1979) 5864; **102** (1980) 5093, 5112.
- [29] a) J. R. Sweet, W. A. G. Graham, *Xth Int. Conf. Organomet. Chem.*, Abstract 2E13, Toronto 1981; b) J. R. Sweet, W. A. G. Graham, *J. Organomet. Chem.* **173** (1979) C9.
- [30] a) J. E. Bercaw *et al.*, *J. Am. Chem. Soc.* **98** (1976) 6734; **100** (1978) 2716; **101** (1979) 218; b) for a brief review, see: P. T. Wolczanski, J. E. Bercaw, *Acc. Chem. Res.* **13** (1980) 121; c) J. C. Huffman, J. G. Stone, W. C. Kru-sell, K. G. Caulton, *J. Am. Chem. Soc.* **99** (1977) 5829.
- [31] a) K. S. Wong, J. A. Labinger, *J. Am. Chem. Soc.* **102** (1980) 3652; b) J. A. Labinger, *Adv. Chem. Ser.* **167** (1978) 149; c) K. S. Wong, W. R. Scheidt, J. A. Labinger, *Inorg. Chem.* **18** (1979) 136; d) W. A. Herrmann, H. Biersack, M. L. Ziegler, P. Wülknitz, *Angew. Chem.* **93** (1981) 397; *Angew. Chem. Int. Ed. Engl.* **20** (1981) 388.
- [32] C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.* **100** (1978) 2544.
- [33] a) H. Kölbél, D. Hanus, *Chem.-Ing.-Tech.* **46** (1976) 1042; D. Kitzelmann, W. Vielstich, T. Dittrich, *ibid.* **49** (1977) 463; b) J. Cook, P. M. Maitlis, *J. Chem. Soc. Chem. Commun.* **1981**, 942; c) L. I. Shoer, J. Schwartz, *J. Am. Chem. Soc.* **99** (1977) 5831; d) J. W. Rathke, H. M. Feder, *ibid.* **100** (1978) 3623.
- [34] J. A. Gladysz, J. C. Selover, C. E. Strouse, *J. Am. Chem. Soc.* **100** (1978) 6766.
- [35] Review: F. Calderazzo, *Angew. Chem.* **89** (1977) 305; *Angew. Chem. Int. Ed. Engl.* **16** (1977) 299. – The first authentic example of true CO insertion reactions has been reported recently: H. Brunner, H. Vogt, *Angew. Chem.* **93** (1981) 409; *Angew. Chem. Int. Ed. Engl.* **20** (1981) 405.
- [36] C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.* **99** (1977) 1651.
- [37] a) W. A. Herrmann, J. Plank, *Angew. Chem.* **90** (1978) 555; *Angew. Chem. Int. Ed. Engl.* **17** (1978) 525; b) R. H. Grubbs, A. Miyashita, *Tetrahedron Lett.* **1981**, 1255; c) W. A. Herrmann, J. Gimeno, J. Weichmann, M. L. Ziegler, B. Balbach, *J. Organomet. Chem.* **213** (1981) C26; d) J. A. Van Doorn, C. Masters, H. C. Volger, *ibid.* **105** (1976) 245; e) W. A. Herrmann, J. Plank, M. L. Ziegler, K. Weidenhammer, *J. Am. Chem. Soc.* **101** (1979) 3133; f) for the conversion of a μ, η^3 -diphenylmethylene ligand into free diphenylketene cf. L. Messerle, M. D. Curtis, *ibid.* **102** (1980) 7789.
- [38] R. B. Anderson, L. J. Hofer, H. H. Storch, *Chem.-Ing.-Tech.* **30** (1958) 560.
- [39] H. Kölbél, J. Trapper, *Angew. Chem.* **78** (1966) 908; *Angew. Chem. Int. Ed. Engl.* **5** (1966) 843.
- [40] M. Ryang, I. Rhee, S. Tsutsumi, *Bull. Chem. Soc. Jpn.* **37** (1964) 341. – Hydroxycarbene complexes proved to be moderately stable in some cases, cf. E. O. Fischer, G. Kreis, F. R. Kreissl, *J. Organomet. Chem.* **56** (1973) C37.
- [41] P. Perkins, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **101** (1979) 3985.
- [42] Quoted by J. Haggin, *Chem. Eng. News* **59** (1981), No. 43, p. 22.
- [43] A. Deluzarche, J. Cressely, R. Kieffer, *J. Chem. Res. (M)* **1979**, 1657.
- [44] C. D. Wood, R. R. Schrock, *J. Am. Chem. Soc.* **101** (1979) 5421.
- [45] G. Fachinetti, C. Biran, C. Floriani, A. Chiesi Villa, C. Guastini, *Inorg. Chem.* **17** (1978) 2995.
- [46] J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, W. J. Youngs, *J. Am. Chem. Soc.* **102** (1980) 4515.
- [47] T. Okuhara, K. Kobayashi, T. Kimura, M. Misono, Y. Yoneda, *J. Chem. Soc. Chem. Commun.* **1981**, 1114.
- [48] D. G. Blackmond, J. G. Goodwin, Jr., *J. Chem. Soc. Chem. Commun.* **1981**, 125.

COMMUNICATIONS

Communications are brief preliminary reports of research work in all areas of chemistry which, on account of its fundamental significance, novelty, or general applicability, should be of interest to a broad spectrum of chemists. Authors of communications are requested to state reasons of this kind justifying publication on submission of their manuscript. The same reasons should be clearly apparent from the manuscript. In cases where the editorial staff decide, after due consultation with independent referees, that these conditions are not met, manuscripts will be returned to the authors with the request to submit them for publication in a specialist journal catering for scientists working in the field concerned.

Umpolung of Carbonyl Reactivity via Acetoxyalkyl Radicals**

By Bernd Giese* and Ulrich Erfort

The nucleophilic acetoxy radicals **7** can be generated from ketones **6** via the hydrazones **8** by mercuration (**8** → **9**) and reduction (**9** → **7**). The carbonyl carbon atom thus undergoes an umpolung from an acceptor to a donor^[5]. Generation of the radicals **7** in the presence of acrylonitrile leads to formation of the product **10** via a radical chain mechanism (see Table 1) in a reaction analogous to that of the unsubstituted alkylmercury salts^[2].

[*] Prof. Dr. B. Giese, U. Erfort
Institut für Organische Chemie und Biochemie
der Technischen Hochschule
Petersenstrasse 22, D-6100 Darmstadt (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.