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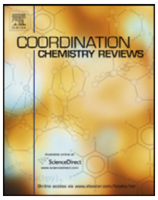

Review

# Homogeneous syngas conversion

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ABSTRACT

Recent approaches to the homogeneous conversion of synthesis gas to organic chemicals and fuels are reviewed. Progress in this field is placed in the context of important industrially practiced transformations, such as the Fischer–Tropsch process for conversion of synthesis gas to higher alkanes, as well as previous attempts to produce a viable homogeneous alternative. Approaches to homogeneous syngas conversion discussed in some detail include the reduction of transition metal carbonyl complexes by main group hydrides or transition metal hydrides; unusual routes to formyls including radical-based late transition metal chemistry; early metal and lanthanide reductive couplings; cluster chemistry; and Lewis acid-assisted transformations. Our current research combines a number of these concepts in an attempt to convert syngas selectively to multicarbon organic fragments.

## 1. Introduction

Syngas ($H_2 + CO$) is readily obtained from natural gas, coal and biomass, so its conversion to organic products constitutes a potentially attractive alternative to petroleum-derived fuels and chemicals. Research in the field has been going on for a century or more: Sabatier reported methanation over nickel in 1902, and Fischer and Tropsch obtained liquid hydrocarbons in 1926. While $C_1$ products, methane (which one would never *want* to make from syngas) and methanol (which *is* produced from syngas, over a

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*Abbreviations:* 9-BBN, 9-borabicyclo(3.3.1)nonane; bpy, 2,2′-bipyridine; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; $CP_3$, $CH_3C(CH_2CH_2PPh_2)_3$; ET, electron transfer; Fp, $[CpFe(CO)_2]^+$; FT, Fischer–Tropsch; GTL, gas-to-liquids; OEP, octaethylporphyrinato; $P_1$, *tert*-butylimino-tris(pyrrolidino)phosphorane (*t*BuNP(pyrrolidino)$_3$); syngas, synthesis gas (CO and $H_2$); TMP, tetrakis-(2,4,6-trimethylphenyl)porphyrinato; TXP, tetrakis-(3,5-dimethylphenyl)porphyrinato.

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copper–zinc catalyst, on an immense scale), can be generated efficiently and selectively, conversion of syngas to more complex $C_{2+}$ products, whether hydrocarbons or oxygenates, is more problematic. The main issue is selectivity: the Fischer–Tropsch reaction generates a Schultz–Flory distribution of hydrocarbons, for which the ability to select for any particular desired range of products, such as diesel, is strictly limited. As a consequence, historically it has not been economically competitive with petroleum, and has been practiced on a large scale only under special geopolitical circumstances. (More recently the relative cost and availability of methane and coal compared to oil have made the economics look much better, and giant-scale gas-to-liquid (GTL) projects are underway in the Middle East and elsewhere.) Only limited success in selective formation of higher alcohols and other oxygenates has ever been achieved.

Substituting homogeneous for heterogeneous catalysts appears an attractive possibility. In general, homogeneously catalyzed reactions tend to be more selective than their heterogeneous counterparts; also homogeneous catalysts can often be readily adjusted (by changing ligands, for example) to tailor the product distribution, taking advantage of the detailed mechanistic understanding that can often be obtained, whereas rational modification of heterogeneous catalysts is more difficult. Research in homogeneously catalyzed syngas conversion first spiked in response to the oil crisis of the 1970s; the subsequent relaxation of oil prices, coupled with the significant technical hurdles that were quickly recognized, caused interest to wane somewhat, although a significant level of activity has always been maintained. More recently there has been a major revival of interest, a consequence of the economic trends mentioned above as well as the recognition of new possible opportunities; hence a review on this topic appears quite timely.

## 2. General mechanistic considerations

While there is still considerable controversy over the mechanism(s) of heterogeneously catalyzed Fischer–Tropsch chemistry, dissociation of the C–O bond to form a surface carbidic species is most commonly invoked. Such a process is almost surely inaccessible for a monometallic metal complex; for this reason metal clusters have frequently been tested as homogeneous catalysts, although it is far from clear whether they remain intact under reaction conditions. The mechanisms of the two cases are probably quite different, as manifested (at least in part) by the fact that oxygenates, not hydrocarbons, are by far the more common products in the latter case [1].

For an organometallic chemist, the &ldquo;obvious&rdquo; first step of a homogeneously catalyzed CO hydrogenation would be migratory insertion of CO into a metal–hydride bond; however, by now it is well established that the strength of the latter makes this elementary step highly endoenergetic [2]. The extreme conditions required for previously reported examples of homogeneous CO hydrogenation are most likely a consequence of this barrier, at least in part. Attack of a nucleophilic hydride on coordinated CO constitutes a much more facile method for formation of the first C–H bond, but integration of such a step into a viable overall catalytic process has been problematic. C–C bond formation also presents some difficulties, although there are known methods for overcoming those in the context of CO chemistry, particularly with the aid of Lewis acid co-catalysts.

## 3. Homogeneous catalytic CO hydrogenation

The topic has been reviewed previously [3–5], and we will only briefly summarize some of the earlier discoveries. Homogeneously catalyzed hydrogenation and oligomerization of CO was first reported (in patents) by Dupont in the early 1950s, using cobalt catalysts operating under extremely high pressures (1500–5000 atm) of syngas [6,7]. In the 1970s and early 1980s complexes of other metals, including Rh, Fe, Ru, and Ir, were reported to similarly catalyze hydrogenation of CO [4]; all require high pressures (generally over 1000 atm) and produce mostly methanol with only very small yields of $C_{2+}$ products, mostly ethylene glycol. The mildest conditions for the homogeneous reaction were found using $Ru_3(CO)_{12}$ as the precatalyst (although it and other polynuclear complexes probably do not remain intact), at pressures as low as 100 atm, but again yielding methanol as by far the major product.

As noted above, heterogeneously catalyzed conversion of syngas to methanol is a very efficient process, so the main interest in these systems is the formation of higher products. Systems that yield significant amounts of such products require (or are greatly enhanced by) the presence of a Lewis or Brønsted acid. (Lewis acidic additives enhance heterogeneously catalyzed Fischer–Tropsch reactions as well [8].) For example, ethane and higher hydrocarbons could be obtained using $Ir_4(CO)_{12}$ in a NaCl/$AlCl_3$ melt [9–11], or Os and Rh carbonyl complexes with $BBr_3$ or $AlBr_3$ [12,13]. Similarly, whereas $Ru_3(CO)_{12}$ is active for methanol synthesis in many organic solvents, it only produces significant amounts of ethylene glycol (as the diester) in carboxylic acid solvents [14]. A plausible mechanism for the latter transformation is condensation of an intermediate Ru hydroxymethyl group and the acid to produce a stabilized carboxymethyl group (transition metal hydroxymethyl groups are generally unstable, but undergo facile condensation reactions with acids under mild conditions [15]) which could be carbonylated to ultimately produce the $C_2$ product [4,16]. Rh carbonyl catalysts can give ethylene glycol selectivities up to 75% at 200–230 °C, under 2200–2400 psi of 1:1 $H_2$/CO, and with the addition of Lewis bases and alkali cations [4,5,17,18].

The extreme conditions required for these reactions might result from the difficulty of forming the first C–H bond, the substantial thermodynamic instability of formaldehyde (a very probable precursor to ethylene glycol), or perhaps both. It is not clear whether the former step involves (kinetically disfavored) intramolecular insertion of CO into an M–H bond or intermolecular attack of a (weakly nucleophilic) metal hydride on a metal carbonyl complex. It seems likely that the alkali cations favor the formation of glycol by facilitating the insertion of CO into intermediate M–C bonds by binding to the carbonyl oxygen. Lewis bases could facilitate the reaction in several possible ways: driving migratory insertion; producing a more nucleophilic metal hydride by coordination or deprotonation; or deprotonating a metal hydride to form an anionic species which can add to intermediate formaldehyde to produce a hydroxymethyl complex that subsequently undergoes CO insertion [4,5]. Studies on the effect of base strength on the formation of glycol support the last proposal [19–21]. In reactions with combined rhodium and ruthenium catalysts, 10 times more Ru than Rh was required and the product selectivity for $C_1$ vs. $C_2$ was dependent on Rh and independent of Ru, suggesting that Ru serves as the hydride source while CO reduction and coupling occurs on the Rh center [5,22]. The ruthenium hydride species $[HRu_3(CO)_{11}]^-$ has been observed under catalytic conditions and could serve as a hydride source for carbonyl reduction [3].

Addition of halides to these systems often enhances the production of ethanol, but this is most probably attributable to formation of methyl halides (either from metal hydroxymethyls or directly from methanol) which can be converted to acetic acid (as in the Monsanto and Cativa processes) and thence hydrogenated to ethanol [4,5].

More recently, while little additional experimental work has been published on these catalytic systems, calculations have been used to gain insight into the reaction mechanisms [23]. DFT calculations on $HCo(CO)_4$ found an intermediate in which formaldehyde binds in $\eta^2$ fashion to $HCo(CO)_3$ and then forms either a hydroxymethyl or methoxy complex, a key branch point which determines whether $C_1$ or $C_2$ hydrogenation products are formed. For Co the methoxy is favored; this would lead to the production of methanol rather than ethylene glycol [24,25]. A computational study for $HRh(CO)_4$ at the MP2 level supports a similar formaldehyde insertion, but in this case the hydroxymethyl species is favored over formation of the methoxy species [25]. which would explain why Rh is the most selective catalyst for the formation of $C_2$ products. The first step of the reaction was taken to be insertion of CO into the Rh–H bond and calculated to be endothermic by 28.2 kcal/mol, consistent with the known difficulty of carbonyl insertions into metal hydrides and with the harsh conditions required for the reaction. However, the alternate possibility of intermolecular nucleophilic attack of hydride from one $HRh(CO)_4$ on CO of another, to form $[Rh(CO)_4][HRh(CHO)(CO)_3]$, was not investigated; from there protonation of the formyl would yield a methoxycarbene hydride which could undergo facile hydride migration to yield the hydroxymethyl precursor to ethylene glycol. A methoxycarbene was calculated to be of comparable stability to the other reactive intermediates, but discarded because of the high barrier to its formation directly from a Rh(III) formyl dihydride (which the authors considered as the only possible precursor to its formation, despite the fact that there is no evidence that Rh(III) is ever formed in the reaction; indeed, under the reducing conditions of the reaction formation of Rh(III) seems unlikely).

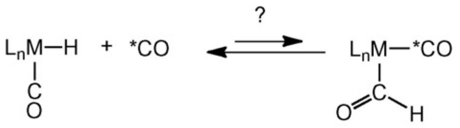
Recent DFT calculations on $Ru(CO)_5$-catalyzed Fischer–Tropsch chemistry indicated that the formation of saturated alkyl chains is energetically more favorable with at least two metal centers in a cluster [26]; the key factor is the ability to form *bridging* methylene groups which can then couple into the growing alkyl chain. It is generally believed that bridging methylene, methine, and carbide groups are important intermediates in the heterogeneously catalyzed reaction [1,8]; recently it has been shown that two adjacent supported Ru centers can catalyze the FT reaction, but an isolated one cannot [27].

## 4. Models for homogeneous catalysis: early studies

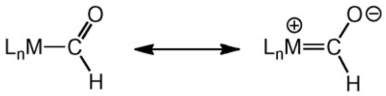
Besides the attempts at direct conversion of syngas outlined in the previous section, a great deal of effort during the 1970s and early 1980s was centered on models for putative FT intermediates, in the hope of elucidating mechanistic insight that could be applied to rational design of homogeneous catalysts, and perhaps to improvement of heterogeneous catalysts as well. Much of this work has been previously reviewed [28,29]; we will only summarize a few highlights and general trends of these early studies.

### 4.1. CO reduction

To reduce CO to hydrocarbon products C–O bonds must be broken and replaced with C–H bonds, no matter how the reaction mechanism proceeds, but until the 1970s no partially reduced CO ligands were known: only CO itself and fully reduced $CH_3$ [30]. Metal formyl complexes were widely postulated as plausible intermediates in the reduction of CO, possibly formed by CO insertion into M–H bonds [31], just as metal acyl complexes are formed by migratory insertion of CO into a M–$CH_3$ bond [32,33]; but hydride carbonylation is generally accepted to be thermodynamically unfavorable and not a feasible route to formyl complexes [34–36]. Because this is a thermodynamic and not a kinetic problem, the reverse reaction is quite facile: formyl complexes commonly undergo decarbonylation (Scheme 1), making their isolation and characterization difficult [30,32,33]. Only one example of reversible CO insertion, into a thorium hydride bond, has been clearly established; the formyl ligand is stabilized by $\eta^2$ coordination to the oxophilic thorium center [37]. Because migratory insertion is not a viable synthetic route to formyls other options must be used.



**Scheme 1.**



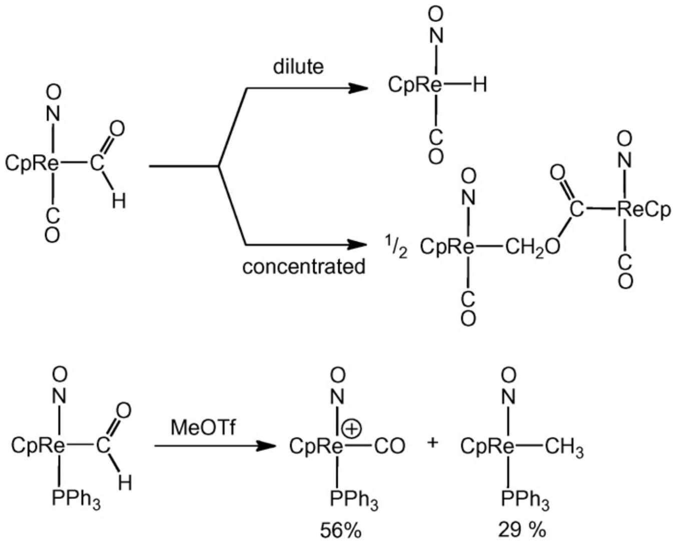
**Scheme 2.**

#### 4.1.1. CO reduction with main group hydrides

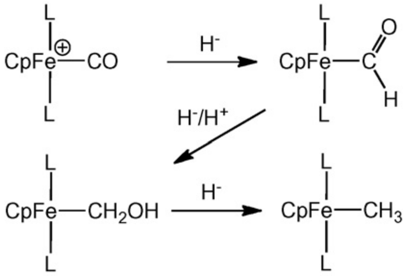
CO molecules coordinated to electrophilic metal centers are susceptible to nucleophilic attack, and it is thus that most metal formyl complexes have been made; earlier work on this approach has been thoroughly reviewed [30]. The first reported transition metal formyl complex, $[Fe(CO)_4(CHO)]^-$ was synthesized by addition of nucleophilic $[Fe(CO)_4]^{2-}$ to formic acetic anhydride [38]. Anionic formyl complexes tend to be much more kinetically stable than their neutral analogs. Many anionic formyls have been synthesized using the strong hydride donor $LiHBEt_3$. In some cases even bis-formyls can be formed in this manner from the reduction of two CO ligands; such is the case for $[Li][CpRe(NO)(CHO)_2]$, obtained from $[CpRe(NO)(CO)_2][BF_4]$ and 2 $LiHBEt_3$ [30,39–41]. The earliest neutral formyls were Os complexes (synthesized via exotic, non-general routes [30,42–44]); the most studied neutral formyls are CpRe(NO)(L)(CHO) (L = CO, $PPh_3$) formed from the carbonyl cation and a borohydride reagent [39,40,45,46]. The $PPh_3$ complex is unusually stable and decomposes only at temperatures greater than 90 °C; it has also been structurally characterized by x-ray crystallography [47]. Formyl complexes are potent hydride donors in their own right, further illustrating that they are high energy intermediates compared to the starting carbonyl complexes [48].

Two resonance structures, one best described as a formyl and the other as a carbene, contribute to the stability of these species, making the oxygen relatively nucleophilic (Scheme 2) [30], capable of coordinating to electrophiles or attacking electrophilic CO ligands on other metal centers [28–30,41,49]. Addition of an electrophile ($H^+$ or $Me^+$) can initiate formyl disproportionation, in which a cationic carbene complex is generated and then accepts a hydride from a second equivalent of formyl, resulting in formation of a metal alkyl species [48,50]. Coordination of an electrophile makes the formyl easier to reduce. Reagents such as $NaBH_4$ or $LiAlH_4$, can result in multiple reductions of a carbonyl ligand; once the first hydride is delivered the B or Al atom can coordinate to the formyl oxygen forming a carbene that is then further reduced by a hydride from $BH_3$ or $AlH_3$. Depending on the conditions, species such as $CpRe(NO)(CO)_2^+$ and $CpFe(CO)_3^+$ can be reduced either to formyl, hydroxymethyl, or methyl species (Schemes 3–5) [45,46,50–52]. The wide array of products that can be obtained from these type of hydride reductions has been discussed in Cutler's review [29].

Hydroxymethyl species have proven to be the most unstable intermediate, and are difficult to isolate in the reduction sequence. Only a few well-characterized examples have been reported, notably for Re [53,54], Os [55], Ru [56–58], and Fe [51,52,59]; they tend to undergo rapid β-hydride elimination to produce formaldehyde and metal hydride rather than carbonylation and/or further



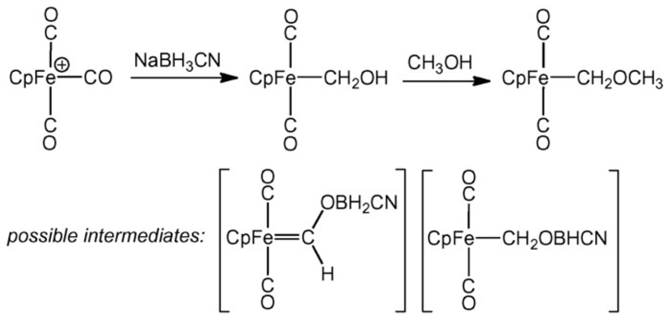
Scheme 3.



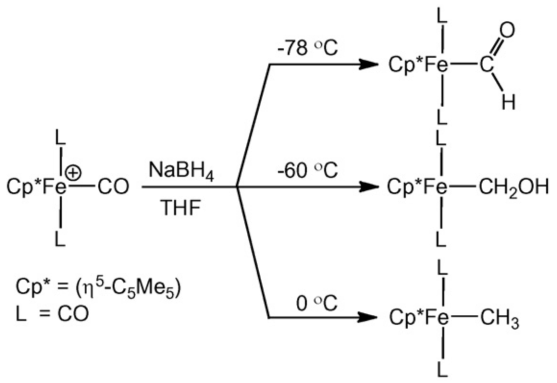
Scheme 4.

reduction, although there are some exceptions, as in the example of Scheme 6. These complexes are sensitive to bases and decompose to eliminate formaldehyde. Some react with acids HX, to eliminate water and form a more stable $MCH_2X$ [60]. This may be the reason for the improved selectivity for ethylene glycol esters in acid medium (vide supra): $MCH_2X$ intermediates are more likely to survive long enough to undergo carbonylation and subsequent reduction.

Of course, none of these reactions are likely to be applicable to a practical catalytic scheme, as the main group hydride reagents are not readily accessible from dihydrogen. For that reason, transition metal hydrides that exhibit similar nucleophilic character and *can* be generated directly from $H_2$ attracted considerable interest.



Scheme 5.



Scheme 6.

### 4.1.2. CO reduction with transition metal hydrides

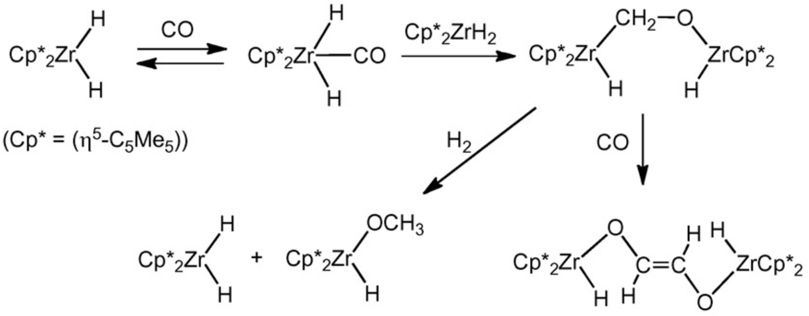
Nucleophilic character of transition metal hydrides appears to be in part a consequence of position in the periodic table; some early transition metal hydrides exhibit the strongest such behavior [61], which has been exploited for a number of stoichiometric reductions of CO. Most prominent among these are the reactions of $Cp^*_2ZrH_2$, as shown in Schemes 7 and 8. Treatment with CO gas forms some $Cp^*_2Zr(H)_2(CO)$, which accepts a hydride from $Cp^*_2ZrH_2$, leading to a variety of reduced species under extremely mild conditions, in one case even forming a C–C bond (Scheme 7) [62–64]. The zirconocene dihydride species can also reduce CO coordinated to separate metal centers, forming zirconoxycarbene-type species (Scheme 8) [65,66]. In a similar vein, the rather less nucleophilic $Cp_2NbH_3$ reacts with $Cr(CO)_6$, at only slightly elevated temperature, to produce ethane [67,68]. (In a report of relevance to homogeneous syngas conversion catalysis, Dombek showed that the proposed intermediate $[HRu(CO)_4]^-$ can reduce $[CpRe(CO)_2NO]^+$ to the corresponding formyl [69]).

However, these systems also are not viable candidates for catalytic processes: there would be no way to break the extremely strong M–O bonds formed by highly electropositive early transition metals and close a catalytic cycle. It is quite possible that some or all of the known catalytic reactions that produce alcohols proceed via this route; but those require fairly extreme conditions, as discussed above — most probably a consequence of the much weaker nucleophilicity of the late transition metal carbonyl hydrides that would have to provide the reducing power.

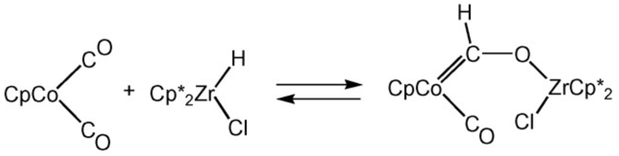
### 4.2. C–C bond formation

CO migratory insertion into metal alkyls is ubiquitous throughout the transition metals, but it is not always so facile as desired for a catalytic process, depending on the nature of both the alkyl group and the metal. For example, the carbonylation of $Mn(CO)_5(Me)$ to $Mn(CO)_5(COMe)$ proceeds under an atmosphere of CO [70], but the insertion of oxygenated alkyls, such as $CH_2OCH_3$, is much slower; and even unsubstituted Re alkyls are highly resistant to carbonylation: until recently there were only a few examples in the literature (none for the parent $Re(CO)_5(Me)$), all requiring harsh conditions [71–76].

Carbonylation can be driven by the addition of good ligands, usually phosphines, to trap the vacant site left from alkyl migration. For CO oligomerization, CO itself must sufficiently drive carbonylation. A much more promising approach was first demonstrated by Shriver: addition of Lewis acids such as $AlX_3$ (X = Br, Cl) or $BF_3$ to FpMe or $Mn(CO)_5(Me)$ under CO results in rapid methyl migration and CO uptake, yielding an acyl product bound to the Lewis acid, which can be removed by hydrolysis (Scheme 9) [77–80]. A similar reaction affords one of the rare examples of migratory



Scheme 7.



Scheme 8.

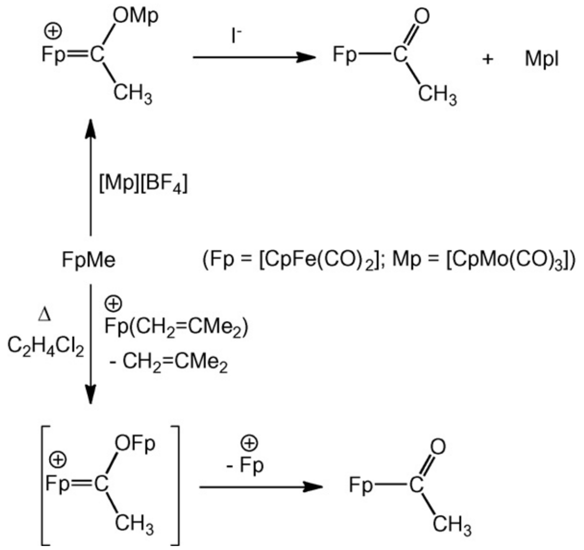
insertion at Re [71]. Although these very strong Lewis acids will probably, as for early transition metals, form irreversibly strong M–O bonds, the extremely high enhancement of reactivity (at least three orders of magnitude for the $Mn(CO)_5(Me)/AlX_3$ case [79,80]) suggests that weaker Lewis acids or even Brønsted acids could well be compatible with catalytic syngas conversion. In fact, Shriver was able to show that significant rate enhancements for carbonylation can be obtained by using moderately strong Brønsted acids with $Mn(CO)_5(CH_3)$ (very strong acids cleave the M–C bond) [78].

A few examples which use transition metal-based Lewis acids to effect similar transformations have also been reported; for example, FpMe undergoes C–C coupling in the presence of $Fp^+$ or $[CpMo(CO)_3]^+$ (Scheme 10) [81–84]. While the exact mechanism of these reactions is not known, the intermediate species in which the transition metal Lewis acid center is bound to the acyl oxygen can be observed. The reaction proceeds considerably faster with the Mo complex, which would be expected to be more electron-deficient and hence a better Lewis acid than the Fe complex.

The most probable route to the first C–C bond on the way to a $C_{2+}$ product is migratory insertion of CO into a M–C single bond to yield an acyl intermediate. There are other possibilities, such as coupling of CO with a less-reduced M=C species, illustrated by the reaction of CO with $[Fp{=}CH_2]^+$ to form the isolable $\eta^2$-ketene $[Fp(CH_2{=}C{=}O)]^+$. The simple methylidene, however, is likely much more reactive than the more relevant $[Fp{=}CH(OMe)]^+$. Addition of a nucleophile to the carbonyl carbon of the ketene gives a metal alkyl which could undergo further transformation (Scheme 11) [85,86].

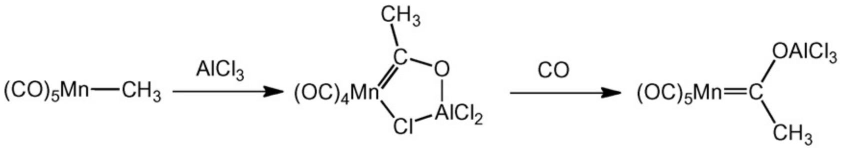
### 4.3. *Closing the cycle: release of $C_{2+}$ and regeneration of M(CO)*

While there are now examples of metal complexes undergoing all of the individual transformations necessary to catalyze the reduction and coupling of CO with $H_2$, few if any can accomplish all of the steps, and none under a single set of conditions. In virtually every case compounds that are good at one particular step are incapable of another key step, illustrating the subtle balance that exists between compounds that are too electron-poor or too electron-rich and either too reactive or too stable; the window for a compound that is &ldquo;just right&rdquo; is very small. Until recently, Cutler's Fp system was the closest to being able to perform all of the necessary transformations. $[Fp(CO)]^+$ is reduced to $Fp(CH_2OCH_3)$ by the fairly weak borohydride $NaBH_3CN$ in methanol (although the yield is only 40%) [51]; reaction of this complex with CO does *not* result in carbonylation, although it will carbonylate upon addition of $PPh_3$ (or the dicarbonyl analog can be synthesized by an alternative route). $Fp(C(O)CH_2OCH_3)$ reacts with strong electrophiles at the acyl oxygen, forming cationic oxycarbenes that can be converted to organic $C_2$ species such as acetaldehyde, glycolaldehyde derivatives, or methyl acetate, depending on reagent used (Scheme 12) [29,87–89].

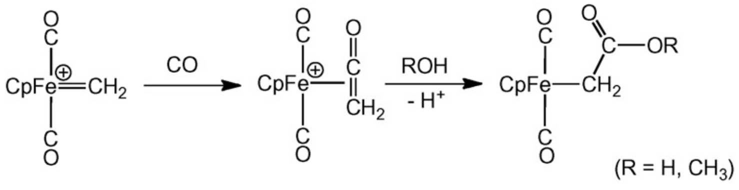


Scheme 10.

Although this does not comprise even a complete stoichiometric cycle (as CO migratory insertion does not occur without the addition of phosphine), it is close enough to suggest that one metal center might be capable of performing all of the necessary trans-



Scheme 9.



Scheme 11.

formations. However, it illustrates perhaps the biggest challenge to catalysis (besides the fact that borohydrides cannot be generated from $H_2$): the incompatibility of the hydrides and protons needed to promote the transformations. The Fp system, which is too electron-rich to undergo facile carbonylation and requires the use of borohydrides for carbonyl reduction, still reacts only with fairly strong electrophiles, such as $[Me_3O][BF_4]$ or $[H{\cdot}OEt_2][BF_4]$, to release $C_2$ products; in a catalytic system they would just react with the strong hydrides required to reduce the carbonyl ligands and leave the CO untouched. As already remarked, known catalytic systems probably overcome this problem by using very high temperature and pressure to compensate for the milder reagents.

## 5. Current research trends

Many of the more recent approaches to homogeneous syngas conversion are continuations of the model studies described above, particularly the use of strong main group hydride reagents as well as highly nucleophilic early transition metal hydrides for formation of the first C–H bond. While a number of interesting twists have been reported, the fundamental challenges associated with these approaches still remain. A number of new directions have been opened up, including studies of multimetallic species and clusters, and the ability of less oxophilic mid and late transition metal hydrides to transfer H to CO. It is beyond the scope of this review to present all of these results, or to consider more than a handful in any detail; rather we will try to summarize the main interests that the research community has been pursuing, and to indicate the approaches that appear to us most promising.

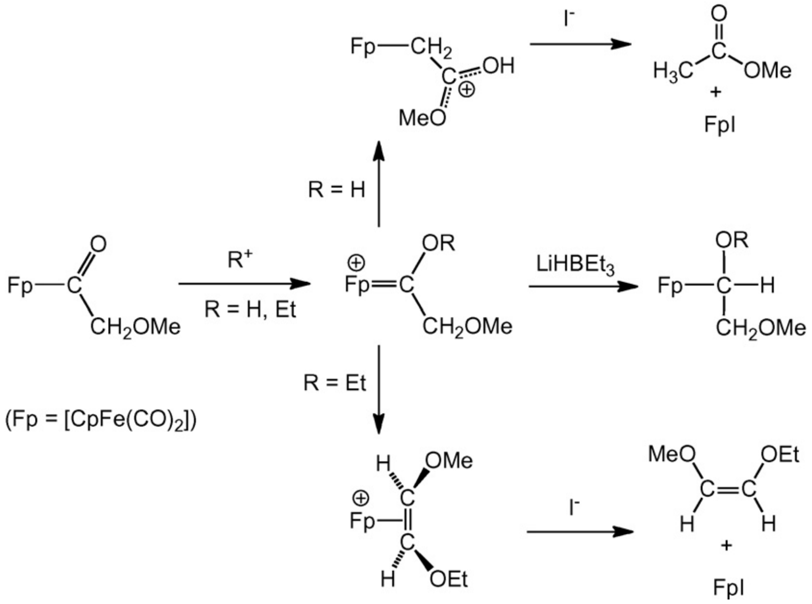
### *5.1. Generation of metal formyls and subsequent chemistry*

Most of the work in this area continues to involve complexes of metals in the middle of the transition series (groups 6–8), although some work on later metals has also led to interesting results, including in particular novel cluster [90] and monometallic [91,92] Pt and Ir [93] formyls. A review on theoretical investigations of CO reduction has appeared [23].

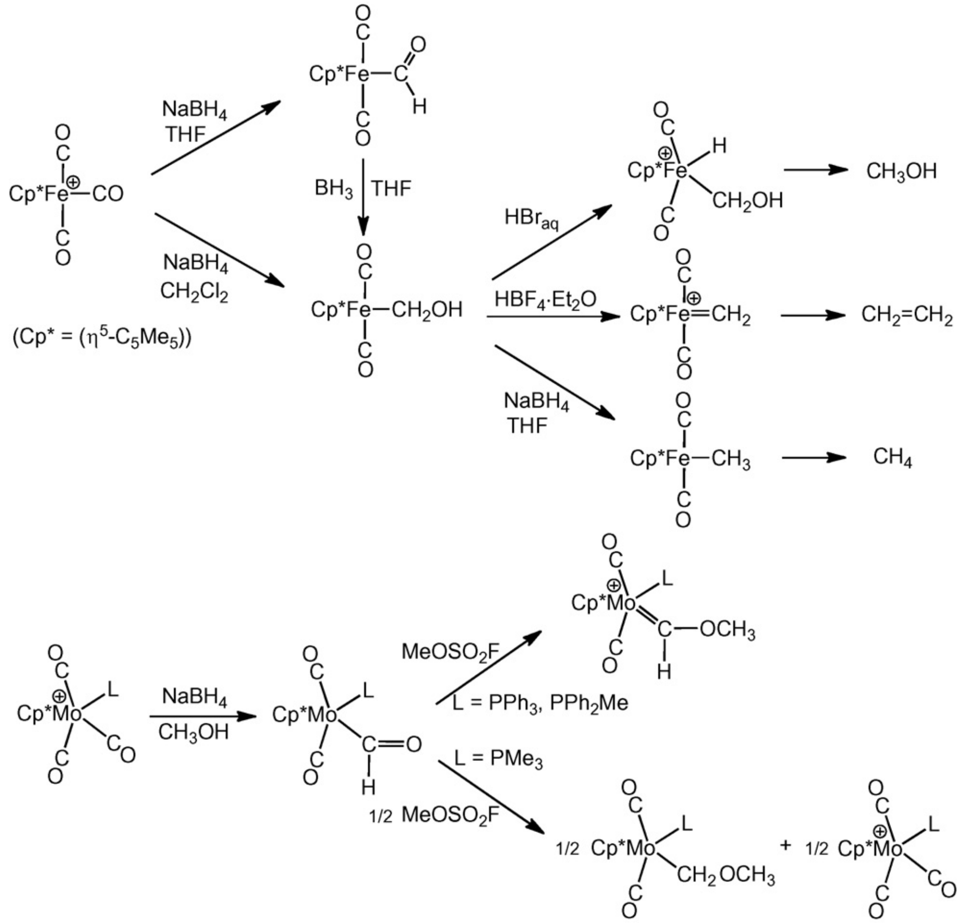
#### *5.1.1. Reduction by main group hydrides*

Astruc and co-workers have carried out an extensive series of studies on cationic CpFe and CpMo systems, finding that CO is reduced by $NaBH_4$ to a variety of species depending on solvent (Scheme 13) [52,94–98]. A short review of this work has appeared [99], and closely related chemistry has been reported by Cutler [100], Gibson [101], and Winter [102]. Despite being thermally unstable, $Cp^*Mo(CO)_2(PMe_3)(CHO)$ was crystallographically characterized [95]. On the other hand, $(C_5Ph_5)Fe(CO)(PMe_3)(CHO)$ [103] is an unusual example of a metalloformyl that is quite stable at room temperature, and it has also been structurally characterized [104]. Further elaborations of $C_1$ ligands via photochemical [105] and particularly electron-transfer reactions include studies on 1-electron reduced Fe methoxycarbene species [106]; 1-electron oxidative carbene coupling to form binuclear bridged species [107]; and ET reactions of carbenes and thioalkyl complexes [108]. Some stereochemically active $C_1$ derivatives were also examined [109,110]. These systems have also been investigated by computational modeling [111–114].

Continuing a program begun in 1984 [115], Gibson developed a convenient and general synthetic procedure for isolating a vari-



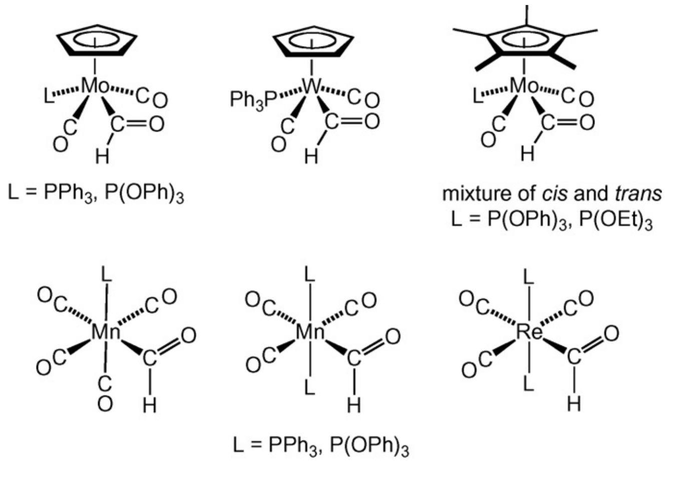
Scheme 12.



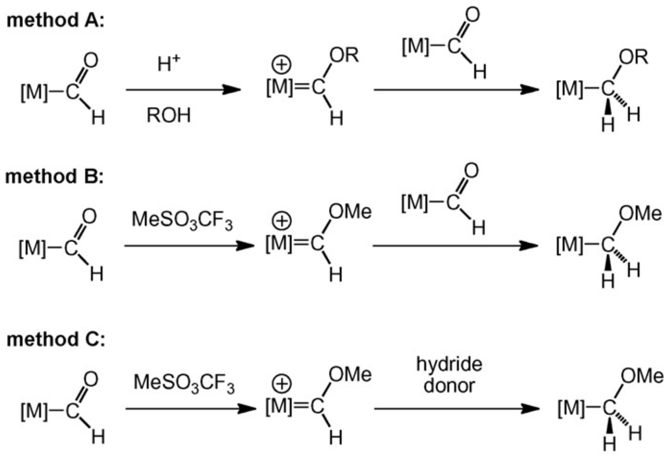
**Scheme 13.**

ety of neutral formyl complexes (Scheme 14), and compared their thermal stability [116]. While many of these had been reported previously, the use of MeOH as solvent to precipitate the formyl product facilitated their isolation and more thorough characterization. Others also used this methodology to access new formyl complexes [117–120]. Reaction of these neutral formyls with electrophiles led to hydroxycarbene, alkoxycarbene, alkoxymethyl, or metallacyclic [121] species (the latter being formed from a methylidene intermediate), depending on the electrophile and conditions used [122]. A more general route to secondary hydroxy-, alkoxy-, and aminocarbenes was later disclosed, which relies on an understanding of the hydride donor strength of the formyl: it must not be so hydridic as to reduce the carbene to the methoxymethyl species [123,124]; the latter may be obtained by hydride transfer either from an external donor or from the hydridic formyl starting material (Scheme 15) [125].

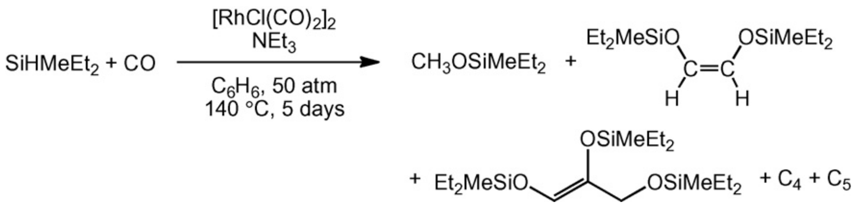
While silicon hydrides are generally not sufficiently nucleophilic to attack coordinated CO, there is at least one example (Scheme 16), where coordination of the Lewis acidic Si center to the resulting alkoxy species undoubtedly provides a major component of



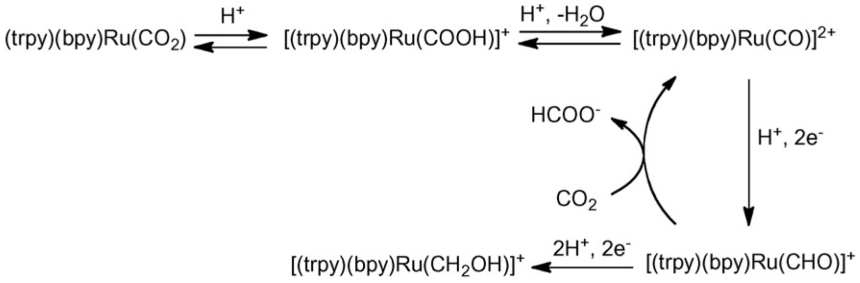
**Scheme 14.**



**Scheme 15.**



**Scheme 16.**



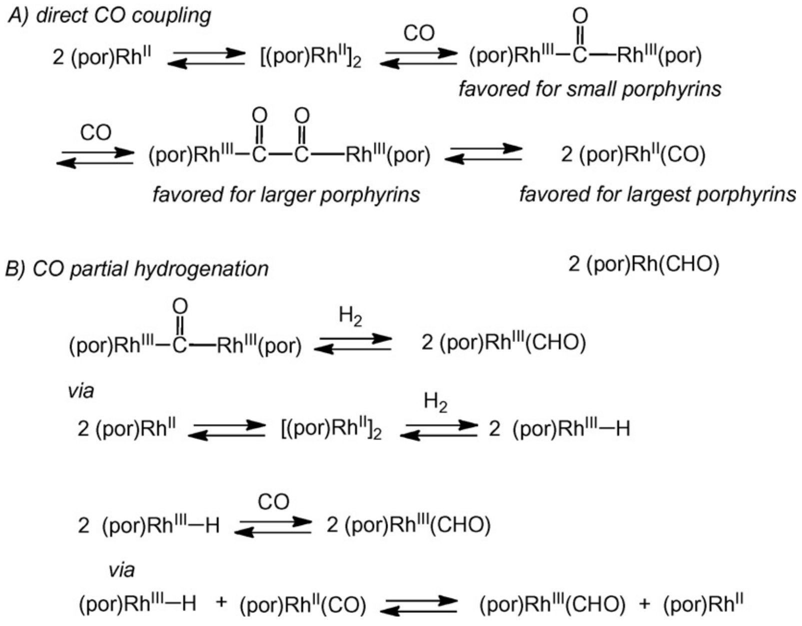
**Scheme 17.**

the driving force [126]. More generally, hydrosilylation of partially reduced CO species has been employed extensively as a model for CO hydrogenation chemistry; several recent reviews are available [127–132].

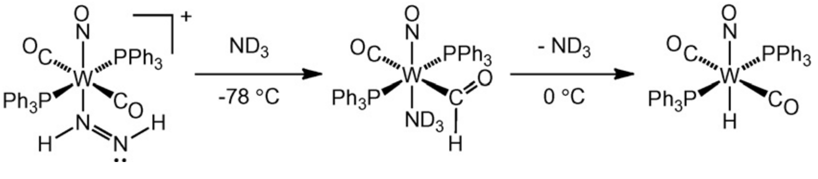
### 5.1.2. *Other routes to formyls*

The cationic formyl $[Ru(bpy)_2(CO)(CHO)]^+$ (bpy = 2,2′-bipyridine) was generated by the unusual route of 2-electron reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ in acid (Scheme 17); it can also be obtained by a more traditional $NaBH_4$ reduction route [133]. Its participation in $CO_2$ and CO reduction schemes has been investigated by both Tanaka and Gibson [15,134–139]. A larger variety of phenanthroline- and terpyridine-supported Ru formyls [140–142] undergo subsequent functionalization to acetoxymethyl and alkoxymethyl species [143,144].

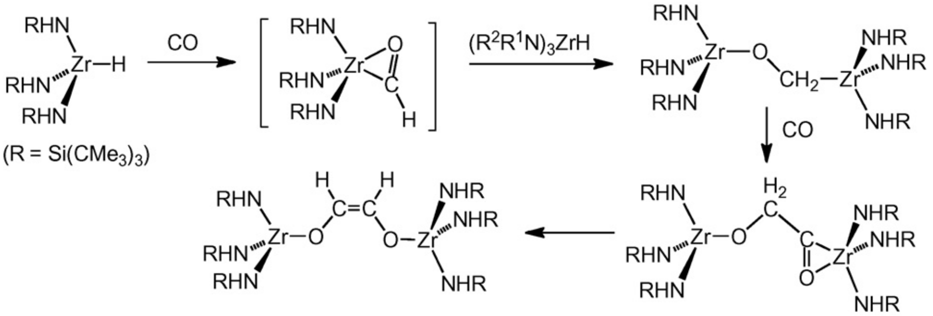
A very different mechanism, involving radical chemistry, accounts for the surprising reaction of octaethylporphyrin (OEP) rhodium hydride with CO to afford a Rh formyl [145]: the apparent insertion of CO into an M–H bond actually results from H-atom transfer (as opposed to hydride transfer) to a small amount of Rh–CO (Scheme 18) [146]. This system is a rare example of a late transition metal that is able to promote reduction of CO directly by $H_2$ (rather than by strong hydride sources). The chemistry can be modulated by steric effects of porphyrin substitution: (OEP)Rh, bearing a relatively small porphyrin ligand, exists predominantly as a dimetallaketone (bridging CO) species under CO; (TXP)Rh (TXP is tetrakis-(3,5-dimethylphenyl)porphyrinato), bearing a sterically more demanding ligand, disfavors the single CO bridge in favor of a dimetalladiketone (1,2-dionyl) species [147]; the largest porphyrinato ligands (such as tetrakis(2,4,6-trimethylphenyl)porphyrinato, TMP) disfavors bridging species altogether, instead giving Rh–CO species [148]. CO coupling and formyl formation were also found with salen [149,150] and bis(pyridine)–bis(amide) ligands [151]; some of the Rh–H species also readily insert formaldehyde, to give Rh–$CH_2OH$ species which react with water to liberate $CH_3OH$ and re-form the Rh(II) starting material (as a Rh–Rh bonded



**Scheme 18.**



Scheme 19.



Scheme 20.

dimer) [151]. Complexes with linked porphyrins generate formyl species under CO/$H_2$, probably with two Rh–CO species cleaving $H_2$ homolytically in a concerted fashion [152], in contrast to the mechanism of mononuclear formyl formation, which involves H-atom abstraction from Rh–H by Rh–CO [146]. Sulfonated analogues were also reported, which facilitate the same chemistry in degassed water [153,154] and methanol [155]; the chemistry proceeds much faster in water [153]. Unfortunately this chemistry has yet to yield significant amounts of free CO-derived organic products; one reason could be that the very strong Rh–C bonds [35] (which provide the driving force for the CO reduction reactivity) are hard to cleave, reminiscent of the strong M–O bonds of early metals.

An unusual route to a formyl involves deprotonation of a bound diazene ligand, followed by an intramolecular hydride shift to an adjacent CO, giving an unstable formyl which undergoes decarbonylation (Scheme 19) [156]. An intramolecular H-transfer from formyl to CO has also been proposed [157].

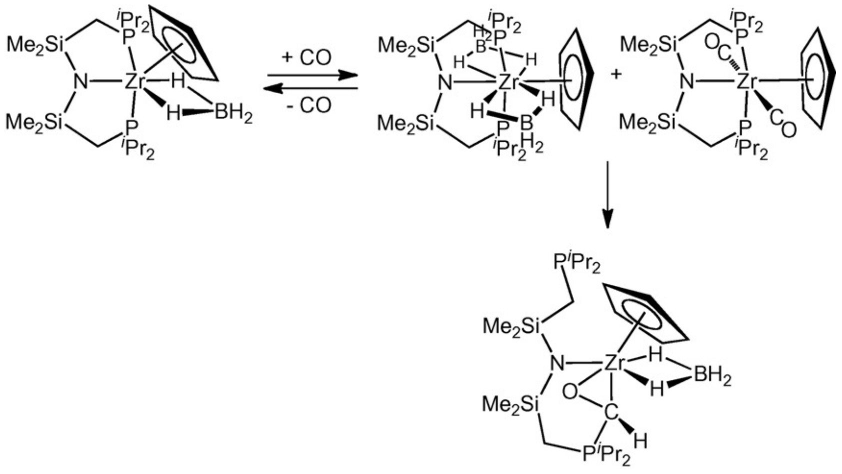
## 5.2. Early transition metal and lanthanide chemistry

Despite the fact that the high oxophilicity of these metals probably precludes any catalytic application, the CO reduction chemistry of these metals has continued to attract a high level of interest.

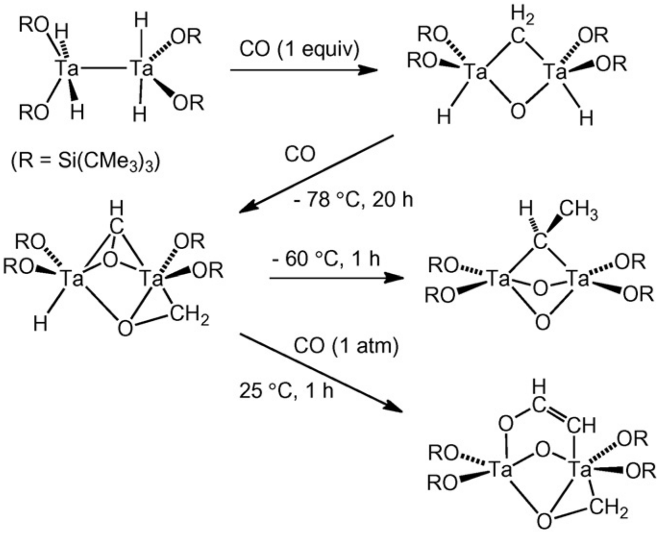
### 5.2.1. Nucleophilic hydrides

A few notable examples of CO reactions with Zr hydrides have been reported. Wolczanski (Scheme 20) [158] and Fryzuk (Scheme 21) [159] each utilized monomeric (boro)hydride precursors, while Floriani found that homobimetallic [($C_8H_8$)(OAr)ZrH]$_2$ (Ar = 2,6-$^t$Bu$C_6H_3$) reduced CO to bridging formaldehyde [160]. Curtis employed fulvalene as a binucleating supporting ligand to maintain proximal Zr centers, and similarly observed transformation of bridging Zr hydrides to bridging formaldehyde under CO [161]. This chemistry reflects the earlier work by Bercaw [62] and others [162] (Section 4.1.2), where reactive metal hydrides obtained by treating complexes with strong reductants followed by $H_2$ are able to reduce CO, in many cases giving C–C bonded species (such as the glycolaldehyde precursor in Scheme 20).

Such chemistry is not limited to Zr: similar reaction patterns have been observed with the dinuclear siloxy-Ta hydrides shown in Scheme 22 [163–165] as well as lanthanide hydrides of Yb [166] and Ce [167,168]. Starting from [1,2,4-($Me_3C$)$_3C_5H_2$]$_2$CeH, the terminal and bridging $C_1$ and $C_2$ products could be liberated from the metal



Scheme 21.



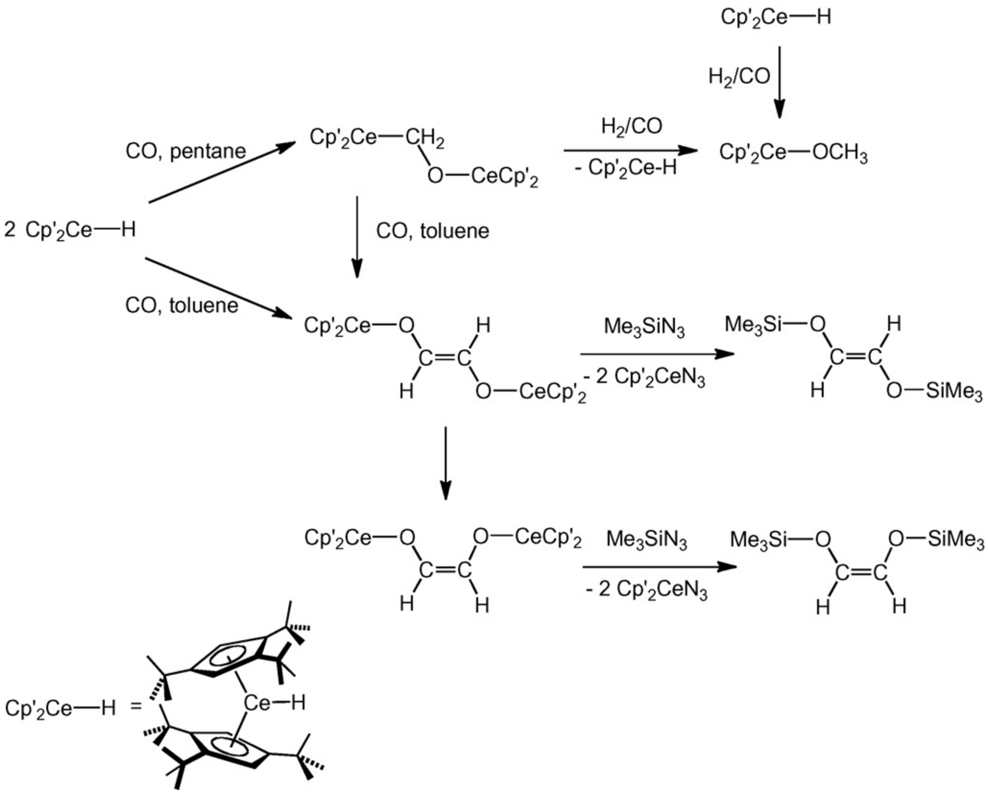
**Scheme 22.**

by treating with $Me_3SiN_3$ to give $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2CeN_3$ and silyl ethers (Scheme 23) [167,168].

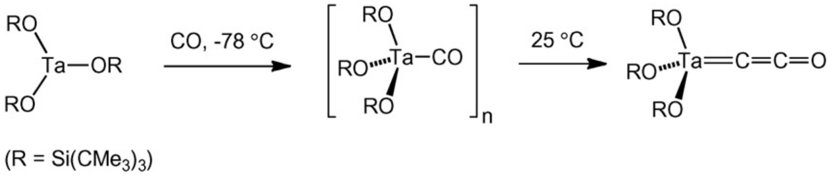
### 5.2.2. Non-hydridic reductive coupling of CO

Electron-rich metal complexes can react with CO in the absence of $H_2$ to give C–C coupled species that could, in principle, be converted to organic products; however, the precursor complexes require reducing agents much stronger than dihydrogen, so these reactions are probably not applicable to syngas conversion. Some examples: a tris(siloxy)$Ta^{III}$ complex reacts with CO to give a product with the unusual CCO ligand; the other O atom is removed as $silox_3Ta{=}O$ (Scheme 24) [164]. Lippard et al. have extensively studied reductive coupling of CO at V and Ta centers, where the coupled products can be removed by treatment with strong electrophiles such as $Me_3SiCl$ (Scheme 25); this work has been reviewed [169]. Gomez has studied the alkyl insertion and reductive coupling chemistry of CO on related cyclopentadienyl-ligated Ta and Nb systems [170].

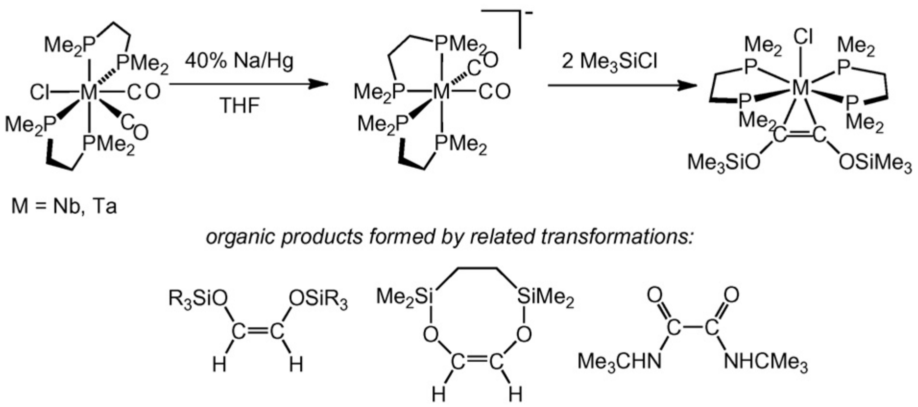
Complex products derived from coupling of CO by highly reduced metal centers include the ketenecarboxylate generated by $Sm^{II}$ (Scheme 26) [171]; Evans has also studied La analogues of this chemistry [172,173]. Cloke has found that $U^{II}$ reductively oligomerizes CO, giving first a dimeric ethynediolate complex inter-



**Scheme 23.**



**Scheme 24.**



Scheme 25.

mediate that proceeds to form the deltate and squarate complexes (Scheme 27) [174,175]; strong Lewis acid–base U–O interactions are implicated as crucial to this novel reactivity [176].

## 5.3. *Acid-promoted reactions*

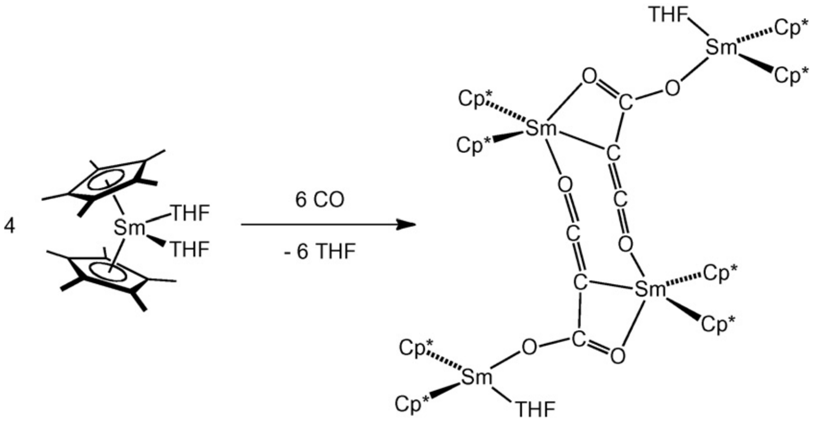
The positive effect of Lewis acid additives on homogeneous catalytic CO reduction as well as on migratory insertion reactions have been discussed above, as well as the probable role of such interactions in the early metal chemistry. Neutral boranes, normally weak hydride donors, reduce CO with the assistance of B–O interactions, as in the 9-BBN chemistry shown in Scheme 28 [177]; Shriver also demonstrated reduction of coordinated CO by $BH_3$, although the chemistry required the M–CO precursor to contain a metal alkyl bond, as acyl formation was a key first step [178].

Like Lewis acids, Brønsted acids can also assist in C–C bond formation: addition of the strong acid $[H{\cdot}(Et_2O)_2][BAr^F{}_4]$ to (Tp)W(O)(CO)(Me) gives (Tp)W(O)(=C(Me)OH)(MeCN) via promoted migratory insertion followed by protonation of the acyl to form a hydroxycarbene ligand [179]. Likewise, migratory insertion in $Ru(Me)(I)(CO)_2$(iPrN=CHCH=NiPr) is catalyzed by protons as well as Lewis acids (Ru- and Zn-based) [180]; although no bimetallic species were isolated, a mechanistic study implicated bridging diruthenium intermediates [181]. A number of studies on stabilization of formyls (and acyls) via binding to Lewis acids to have also been carried out [182–184].

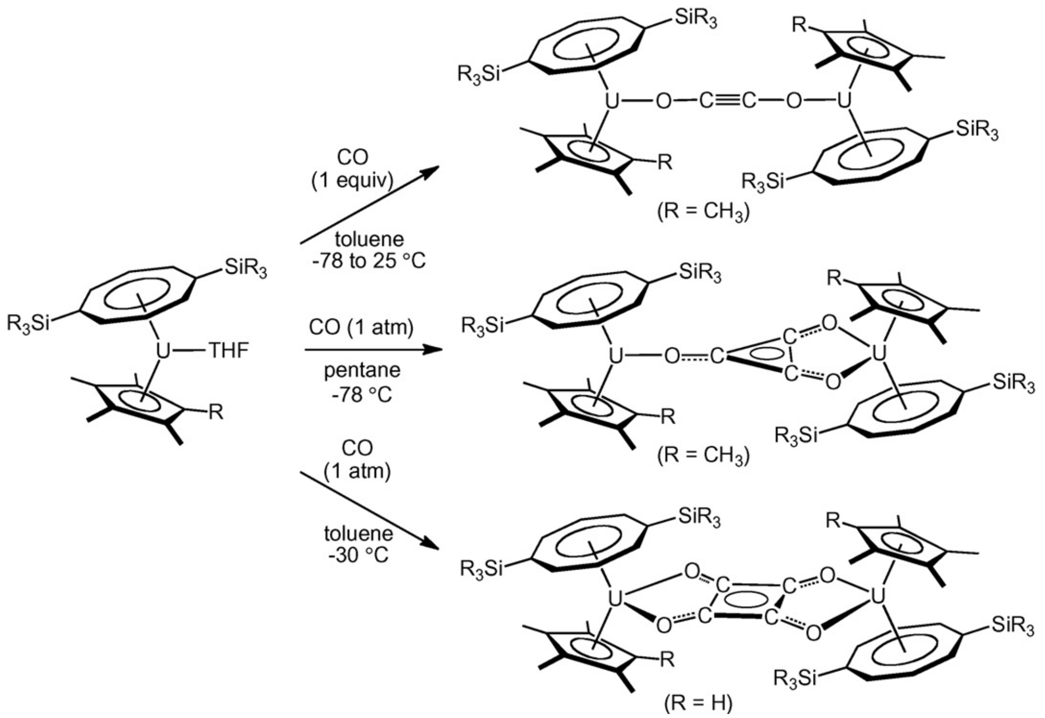
## 5.4. *Reactions of later transition metal hydrides*

As already noted, there are problems with generating the first C–H bond by nucleophilic attack of hydride on coordinated CO: main group hydrides are not readily formed from dihydrogen; early transition metal hydrides lead to irreversibly strong M–O bonds; later transition metal hydrides in general are insufficiently nucleophilic. There are some exceptions to the last generalization, to be sure; a number of examples of C–H bond formation have been reported wherein hydride complexes of Fe [94], Mo [185,186] and W [187,188] react with a second metal carbonyl complex. By far the most promising results are those of the DuBois group, which first showed in 1993 that hydridobis(diphosphine) complexes of the group 10 metals, $[HM(PP)_2]^+$, can reduce a variety of electrophilic carbonyl complexes to generate formyl species, although the latter are not always stable to reaction conditions (Table 1) [189]. The analogous neutral Rh(I) hydrides are even stronger nucleophiles [190]. Because these complexes can be generated directly from $H_2$ in the presence of base, by heterolytic activation (Scheme 29), and since the less electropositive group 10 metals will not form prohibitively strong bonds to oxygen, this chemistry appears potentially viable for incorporation into catalytic schemes.

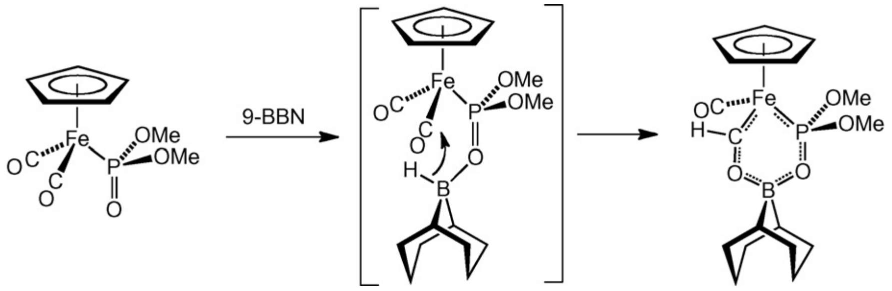
Subsequent work by DuBois has generated detailed thermodynamic understanding of how the &ldquo;hydricity&rdquo; of a given complex depends on the metal and ligands [191–193]. For example, hydride strength increases down the periodic table, with Ni–H [194,195] species being poorer hydride donors by ~10–12 kcal/mol compared to their Pd [196] and Pt [197–200] analogues; Rh [201–204] hydrides appear similarly more potent than Co [205] hydrides. Theoretical investigations generally give good agreement, successfully predicting the distortions that seem to cause the highly ligand-dependent properties [206–208]. DuBois et al. also examined the thermodynamic hydricity of formyl complexes themselves [209], making it possible to predict in advance the required strength of a potential hydride



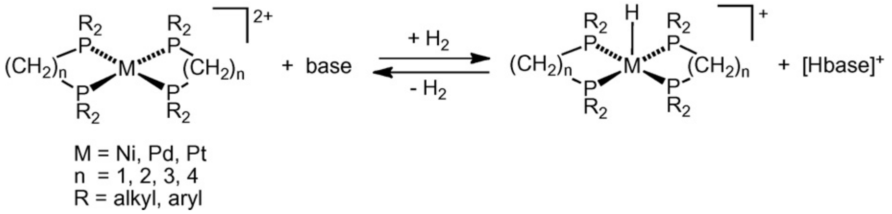
Scheme 26.



Scheme 27.



Scheme 28.

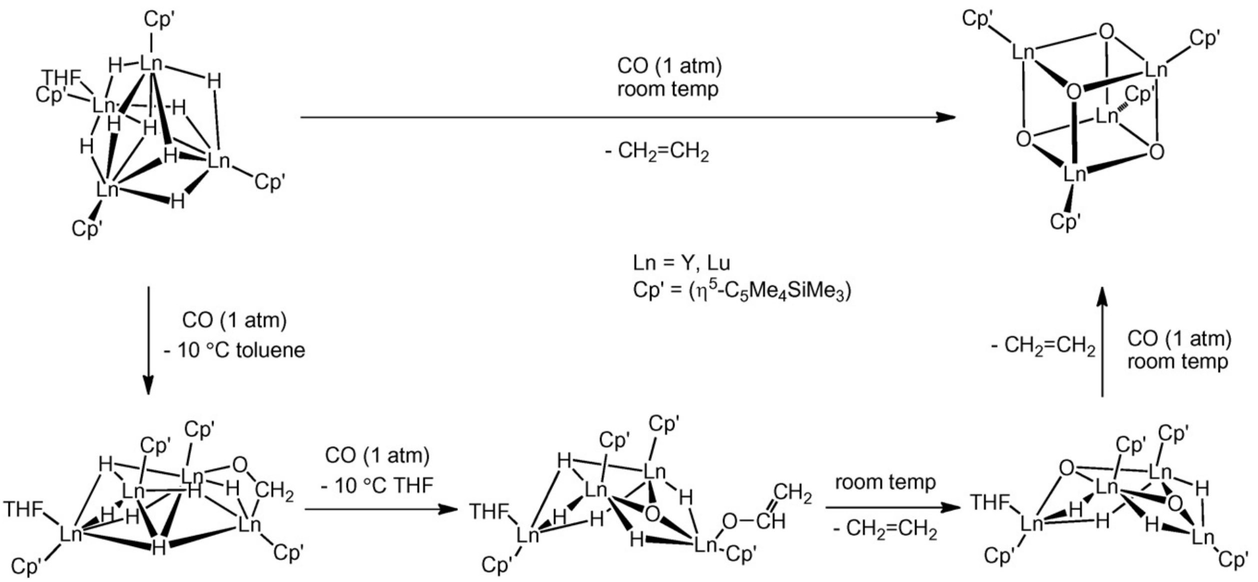


Scheme 29.

**Table 1**
Reactions of transition metal carbonyl cations with nucleophilic group 10 metal hydrides.

| Carbonyl reactants | Product of reduction with $[HNi(dmpe)_2][PF_6]$ | Product of reduction with $[HPt(dmpe)_2][PF_6]$ |
|---|---|---|
| $[Cp^*Mo(CO)_3P(OMe)_3]^+$ | *cis*-$Cp^*Mo(CO)_2P(OMe)_3H$ | *cis*-$Cp^*Mo(CO)_2P(OMe)_3(CHO)$ |
| $[Mn(CO)_5PPh_3]^+$ | *cis*-$Mn(CO)_4(PPh_3)H$ | *cis*-$Mn(CO)_4(PPh_3)(CHO)$ |
| $[CpRe(CO)_2NO]^+$ | $CpRe(CO)(NO)(CHO)$ | $CpRe(CO)(NO)(CHO)$ |
| $[CpRe(CO)(NO)(CH_3CN)]^+$ | $CpRe(CO)(NO)H$ | $CpRe(CO)(NO)(CHO)$ (a) |
| $[CpRe(CO)(NO)(PPh_3)]^+$ | No reaction | $CpRe(PPh_3)(NO)(CHO)$ |
| $[(CpRe(CO)(NO)(PEt_3)]^+$ | No reaction | $CpRe(PEt_3)(NO)(CHO)$ |
| $[Cp^*Re(CO)_2NO]^+$ | $Cp^*Re(CO)(NO)(CHO)$ | $Cp^*Re(CO)(NO)(CHO)$ |
| $[Cp^*Ru(CO)_3]^+$ | $Cp^*Ru(CO)_2(CHO)$ (a) | $Cp^*Ru(CO)_2(CHO)$ (a) |
| $[(CP_3)Ru(CO)_3]^{2+}$ | $[(CP_3)Ru(CO)_2H]^+$ | $[(CP_3)Ru(CO)_2(CHO)]^+$ |

*Notes*: $CP_3 = CH_3C(CH_2CH_2PPh_2)_3$. (a) Formyl decomposes to corresponding hydride during reaction.



**Scheme 30.**

donor needed for reduction of any chosen transition metal carbonyl.

The kinetics of hydride transfer from mid-transition metal hydrides have been studied by Bullock and co-workers [210,211]; again there are effects due to both the metal and ligand. Third-row metal hydrides deliver hydride faster than first-row complexes, by 3–5 orders of magnitude, but second row complexes are even faster (by a factor of 3–5). More electron-donating ligands increase the rate of hydride transfer greatly. Homolytic bond dissociation energies show no correlation with the kinetics of hydride transfer (a heterolytic process). A later publication on kinetic isotope effect showed a wide range of values based on the ligands, with an inverse kinetic isotope effect in some cases [212].

### 5.5. Metal cluster complexes

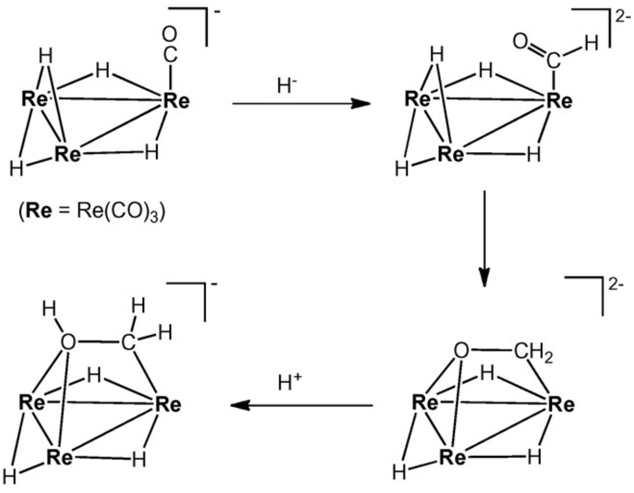
This approach to CO reduction has attracted continuing interest: a cluster complex could exhibit metal surface reactivity patterns, while heterobimetallic systems combining early and late transition metals might provide the advantages of metal-support co-catalysis, believed to operate in F–T catalysts (which consist of late transition metals supported on early transition metal or main group metal oxides such as $TiO_2$, $Al_2O_3$, etc.). Comprehensive reviews have appeared on the synthesis and reactivity of early-late heterobimetallic complexes [213–215], and on C–C bond forming reactions on heterobimetallic scaffolds [216].

A number of hydrido-cluster complexes, of both early and late transition metals, give interesting CO reduction chemistry. The lanthanide tetramers shown in Scheme 30 react with CO at 1 atm at ambient temperature to effect deoxygenation and C–C bond formation, extruding ethylene, an unusual product in homogeneous CO reduction chemistry [217]. These hydride clusters also react with CO coordinated to other transition metals [218]. Sequential addition of strong hydride and proton sources to a trirhenium cluster affords a triply-bridging $-CH_2OH$ group (Scheme 31) [219]. Treatment of $[CpFe(CO)]_4$ and derivatives with strong hydride reductants generates a new cluster containing two bridging acetylene molecules derived from CO; intermediates include a bis-methylidyne species which can be reduced to induce C–C coupling (Scheme 32) [220–222]. Other examples include an $Os_3$ cluster [223], a heterometallic $WOs_3$ cluster [224], and several Co and Ru clusters [225,226].

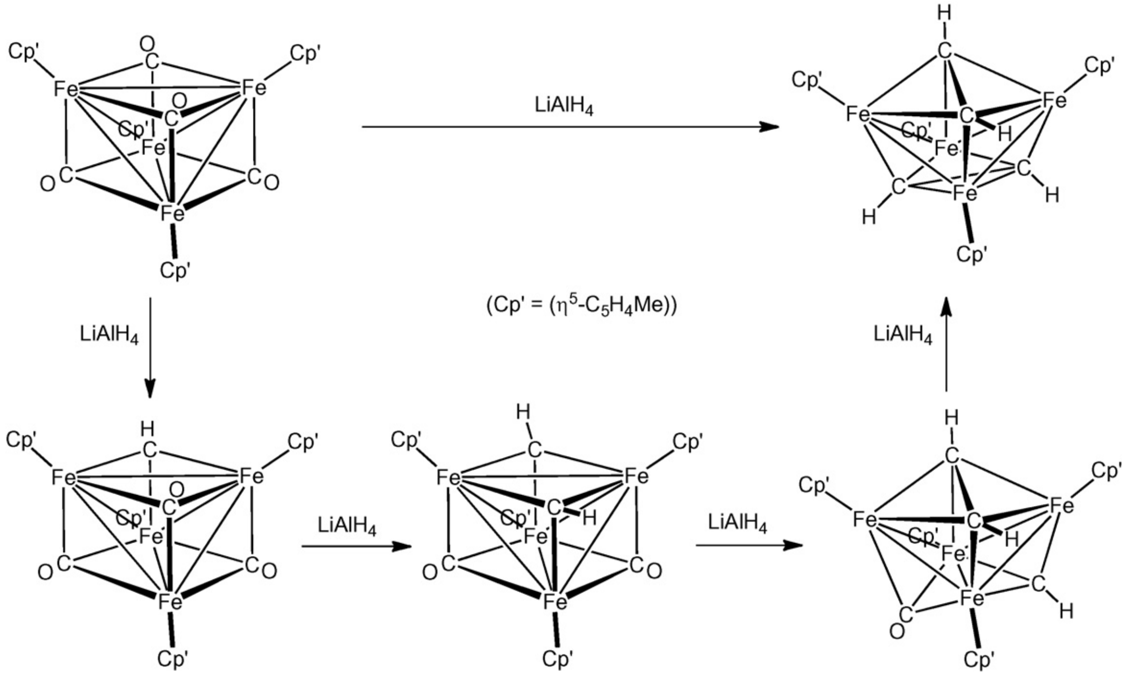
### 5.6. Multicomponent systems: our current research program

The main focus of current work in our group is to design systems with two or more reactive centers working together in concert, for several reasons. Most generally, a combination of two different metal centers will be more likely to be able to activate both CO and $H_2$ and achieve the desired reactivity than a single one. Secondly, the combination of transition metal complexes with Lewis or Brønsted acids appears to be beneficial in several different ways, promoting both transfer of H to CO and C–C bond forming reactions. Lastly, the possibility of intramolecularly connecting the acid to the metal center, and thus using the chelate effect to enhance acid promotion, offers additional opportunities.

The work summarized above provides fairly clear guidelines for a viable approach to selective homogeneous syngas conversion based on a two-catalyst system, where one metal complex acts as a scaffold for CO reduction, while the other delivers hydride. The metal carbonyl must be sufficiently electrophilic to accept a hydride, and the second sufficiently nucleophilic to donate one; but neither can be so oxophilic that strong M–O bond formation would preclude catalysis. The clear first-choice candidates are cationic



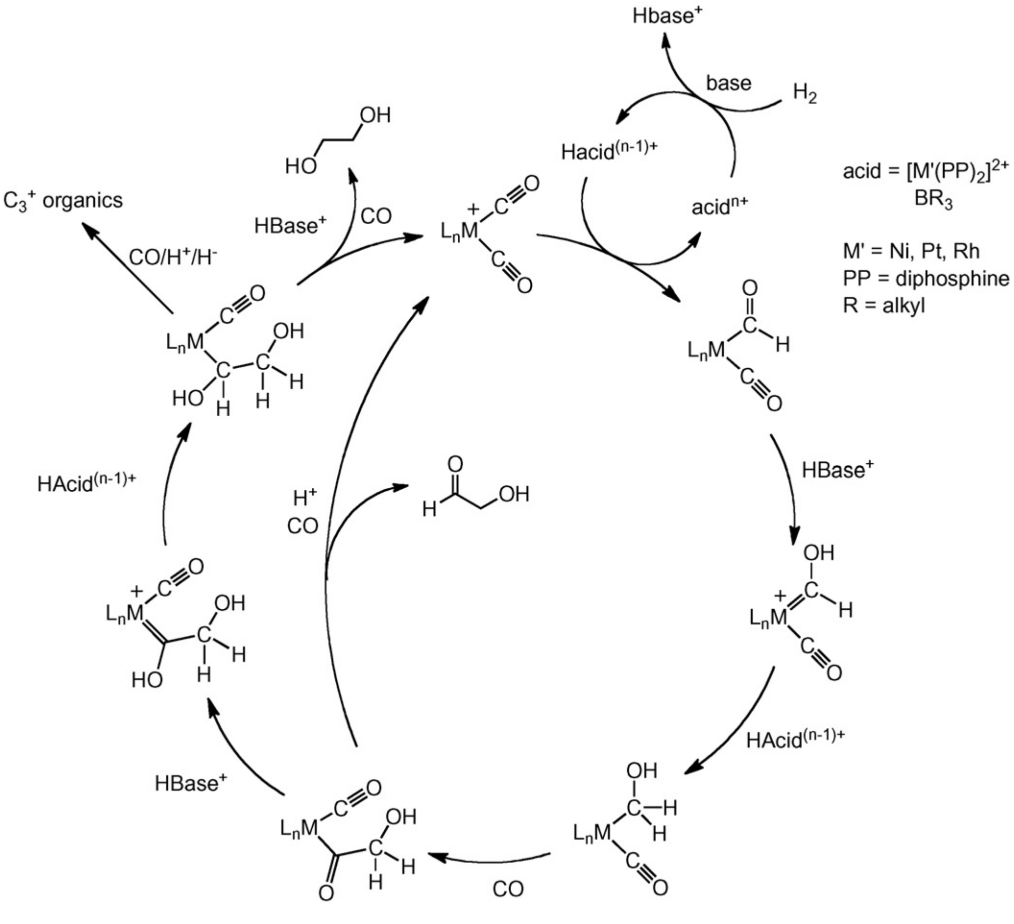
**Scheme 31.**



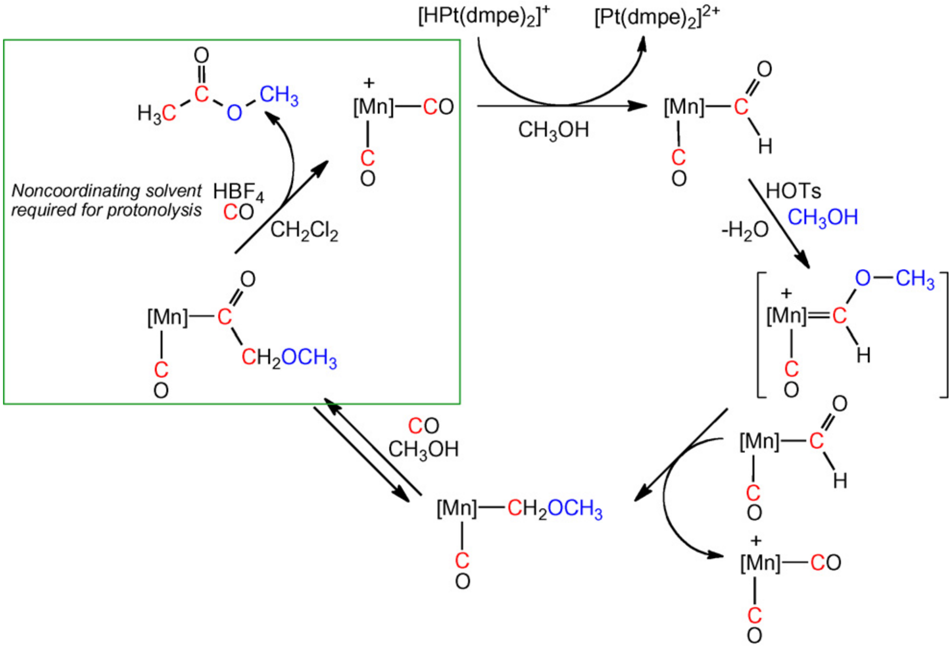
Scheme 32.

mid-transition-metal carbonyl complexes and DuBois's late transition metal bis(diphosphine) complex dications, respectively; one hypothetical sequence of reactions that such a combination might catalyze is shown in Scheme 33.

A proof-of-concept was accomplished using the combination of $[(PPh_3)Mn(CO)_5]^+$ and $[HPt(dmpe)_2]^+$, which react readily to generate a formyl, although it is quite unstable. However, treatment of $[(PPh_3)Mn(CO)_5]^+$ with $[HPt(dmpe)_2]^+$ in



Scheme 33.

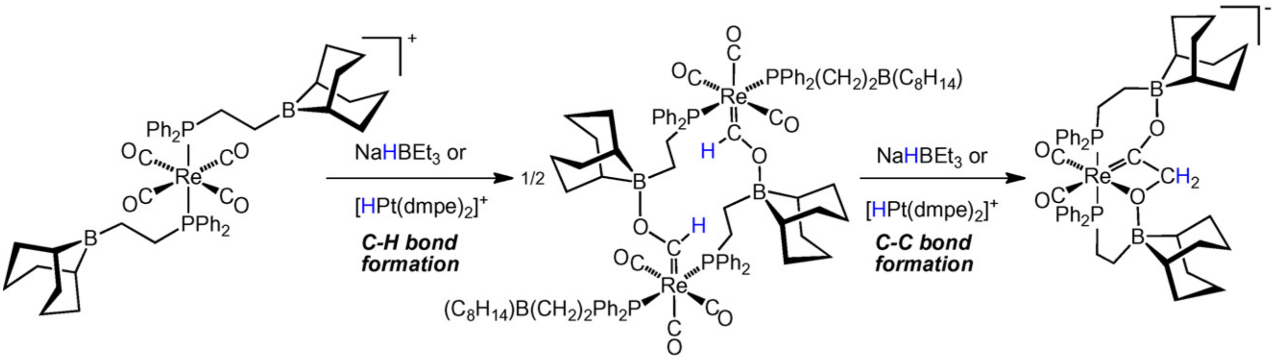


Scheme 34.

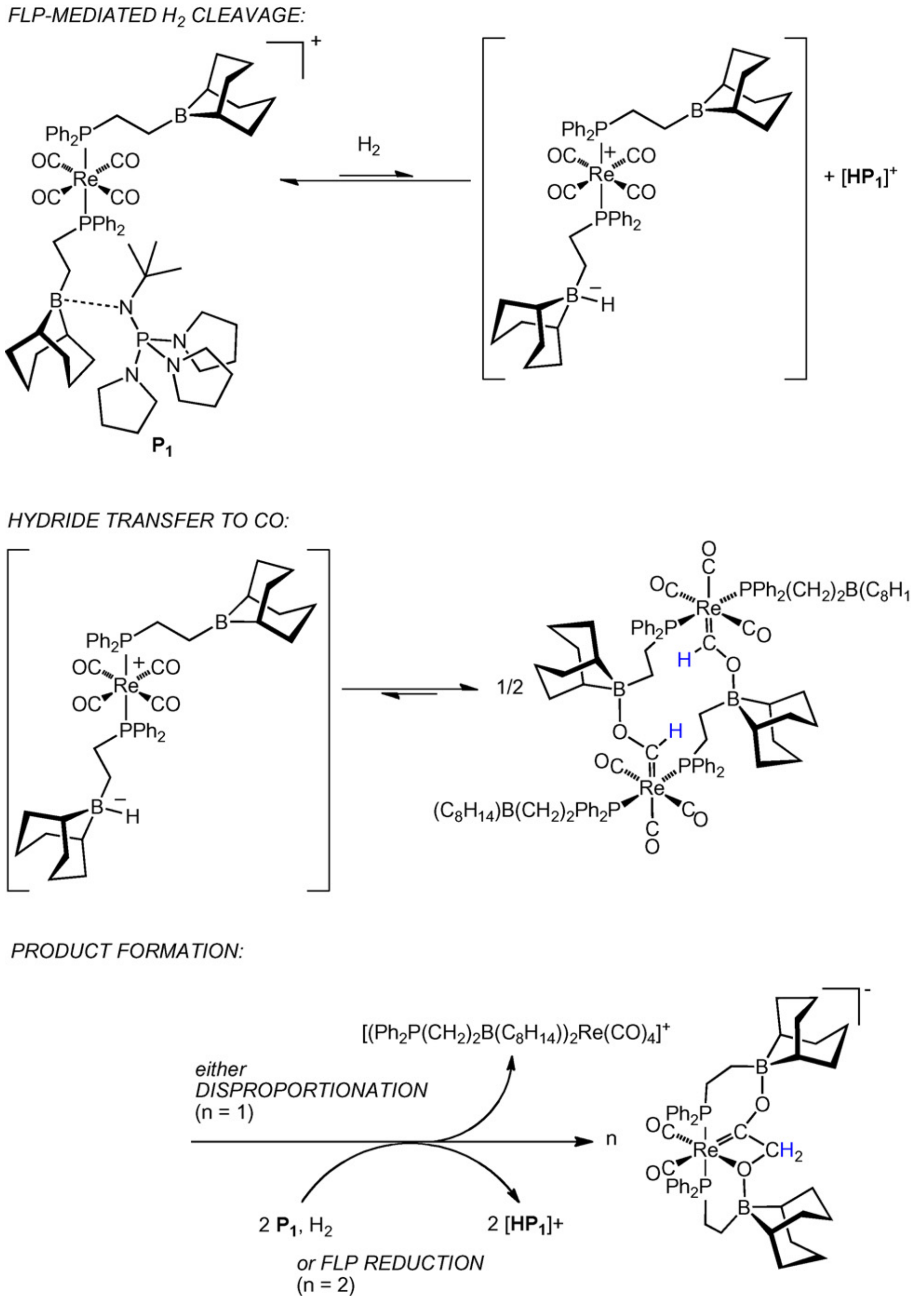
MeOH followed immediately by *p*-toluenesulfonic acid produced $(PPh_3)Mn(CO)_4(CH_2OCH_3)$, which undergoes migratory insertion under 1 atm CO to afford $(PPh_3)Mn(CO)_4(COCH_2OCH_3)$. Treatment of $(PPh_3)Mn(CO)_4(COCH_2OCH_3)$ with MeOTf or $[Et_3O][BF_4]$ leads, via a alkoxycarbene intermediate, to elimination of dialkoxy-substituted olefins, but reaction with HOTf produces methyl acetate [184]. The overall reaction (Scheme 34), when combined with hydrolysis of methyl acetate, amounts to the direct synthesis of acetic acid from syngas, a highly interesting transformation, although it cannot (yet) be operated catalytically because of the incompatibility of the reducing Pt–H with highly electrophilic reagents required to effect some of the steps. A better-balanced system that can operate with weaker reagents will be needed for a successful catalyst.

One approach to facilitate CO reduction, and thus enable weaker reagents to function, is to incorporate a Lewis acid into the secondary coordination sphere of the metal carbonyl cation. Such &ldquo;amphoteric&rdquo; ligands have been examined earlier in this context, although their mode of action may not be as straightforward as anticipated. For example, addition of a phosphine ligand with an appended dialkylaluminum group to $HMn(CO)_5$, in hopes of inducing the elusive intramolecular migratory insertion of CO into an M–H bond, did indeed afford a C–H bonded product; but mechanistic studies showed clearly that a completely different pathway was involved [227,228]. To minimize such complications, a pendant Lewis acidic borane moiety was attached to a hydride-free carbonyl cation, *trans*-$[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4][BF_4]$, which proved to be easily reduced by $[HPt(dmpe)_2]^+$, giving first a formyl/boroxycarbene intermediate that subsequently undergoes further reduction and C–C coupling, to generate the anionic boroxy(boroxymethyl)carbene shown in Scheme 35 [229]. In this case the Lewis acid seems to be facilitating both the initial reduction *and* a second hydride transfer and subsequent C–C bond formation event. Extensive additional studies have been carried out to shed light on the parameters of Lewis acid promotion in these several processes: while the first C–H bond can be formed with intermolecular acid assistance, intramolecular attachment is required to induce the second hydride transfer and subsequent C–C bond formation. Only one Lewis acid is required for this latter step, and studies varying the length of the connector concluded that shorter linkers were optimal [230].

Although an overall catalytic reaction is probably not possible here, owing to the unacceptably high B–O bond strength, the reduction of the metal carbonyl complex by $H_2$ should be potentially catalytic in Pt. While trying to demonstrate that possibility, an unexpected metal-free cycle for $H_2$ cleavage and hydride transfer was discovered: the sterically bulky phosphazene base tBuNP(pyrrolidino)$_3$ (**P$_1$**) is strong enough to directly cleave $H_2$



Scheme 35.



**Scheme 36.**

heterolytically in combination with the borane, an example of a &ldquo;Frustrated Lewis Pair&rdquo; [231]. The reaction forms [**$HP_1$**]$^+$ and [$HBR_3$]$^-$ (unobserved), which quickly transfers hydride to the Re–CO fragment, eventually resulting in the second reduction and C–C coupling (Scheme 36) [232]. Ultimately we hope that a weaker Lewis acid, one which forms bonds to O sufficiently weak to permit closing a catalytic cycle, can promote the necessary C–H and C–C bond forming reactions by virtue of the extra benefit of the intramolecular interactions in these complex, three-component catalytic systems.

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## References

[1] P.M. Maitlis, J. Mol. Catal. A 204 (2003) 55.
[2] H. Berke, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 7224.
[3] B.D. Dombek, Adv. Catal. 32 (1983) 325.
[4] L. Marko, Transition Met. Chem. 17 (1992) 474.
[5] R. Whyman, A.P. Wright, J.A. Iggo, B.T. Heaton, J. Chem. Soc., Dalton Trans. (2002) 771.
[6] U.S. Pat., 2534018 (1950).
[7] U.S. Pat., 2636046 (1953).
[8] P.M. Maitlis, V. Zanotti, Chem. Commun. (2009) 1619.
[9] G.C. Demitras, E.L. Muetterties, J. Am. Chem. Soc. 99 (1977) 2796.
[10] H.-K. Wang, H.-W. Choi, E.L. Muetterties, Inorg. Chem. 20 (1981) 2661.
[11] J.P. Collman, J.I. Brauman, G. Tustin, G.S. Wann, J. Am. Chem. Soc. 105 (1983) 3913.
[12] H.-W. Choi, E.L. Muetterties, Inorg. Chem. 20 (1981) 2664.
[13] A.L. Lapidus, M.M. Savelev, L.T. Kondratev, E.V. Yastrebova, Izv. Akad. Nauk. SSSR, Ser. Khim. (1981) 1564.
[14] B.D. Dombek, J. Am. Chem. Soc. 102 (1980) 6857.

[15] D.H. Gibson, B.A. Sleadd, X.L. Yin, A. Vij, Organometallics 17 (1998) 2689.
[16] B.D. Dombek, J. Am. Chem. Soc. 102 (1980) 6855.
[17] R.L. Pruett, Ann. N. Y. Acad. Sci. 295 (1977) 239.
[18] Y. Kiso, M. Tanaka, T. Hayashi, K. Saeki, J. Organomet. Chem. 322 (1987) C32.
[19] Y. Kiso, K. Saeki, J. Organomet. Chem. 309 (1986) C26.
[20] Y. Kiso, K. Saeki, T. Hayashi, M. Tanaka, Y. Matsunaga, M. Ishino, M. Tamura, T. Deguchi, S. Nakamura, J. Organomet. Chem. 335 (1987) C27.
[21] Y. Kiso, K. Saeki, J. Organomet. Chem. 303 (1986) C17.
[22] R. Whyman, K. Gilhooley, S. Rigby, D. Winstanley, in: D.R. Fahey (Ed.), Industrial Chemicals via C1 Processes, ACS Symposium Series No. 328, American Chemical Society, Washington, DC, 1987, p. 108.
[23] M. Torrent, M. Sola, G. Frenking, Chem. Rev. 100 (2000) 439.
[24] L. Versluis, T. Ziegler, J. Am. Chem. Soc. 112 (1990) 6763.
[25] U. Pidun, G. Frenking, Chem. Eur. J. 4 (1998) 522.
[26] C. Welker, N.S. Phala, J.R. Moss, M. Claeys, E. van Steen, J. Mol. Catal. A 288 (2008) 75.
[27] M. Claeys, H. Hearshaw, J. Moss, E. van Steen, Stud. Surf. Sci. Catal. 130A (2000) 1157.
[28] W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 117.
[29] A.R. Cutler, P.K. Hanna, J.C. Vites, Chem. Rev. 88 (1988) 1363.
[30] J.A. Gladysz, Adv. Organomet. Chem. 20 (1982) 1.
[31] H. Pichler, H. Schulz, Chem. Ing. Tech. 42 (1970) 1162.
[32] A. Wojcicki, Adv. Organomet. Chem. 11 (1973) 87.
[33] F. Calderazzo, Angew. Chem. Int. Ed. 16 (1977) 299.
[34] S.L. Van Voorhees, B.B. Wayland, Organometallics 6 (1987) 204.
[35] M.D. Farnos, B.A. Woods, B.B. Wayland, J. Am. Chem. Soc. 108 (1986) 3659.
[36] C. Floriani, Pure Appl. Chem. 55 (1983) 1.
[37] P.J. Fagan, K.G. Moloy, T.J. Marks, J. Am. Chem. Soc. 103 (1981) 6959.
[38] J.P. Collman, S.R. Winter, J. Am. Chem. Soc. 95 (1973) 4089.
[39] C.P. Casey, M.A. Andrews, J.E. Rinz, J. Am. Chem. Soc. 101 (1979) 741.
[40] W. Tam, W.-K. Wong, J.A. Gladysz, J. Am. Chem. Soc. 101 (1979) 1589.
[41] C.P. Casey, M.A. Andrews, D.R. McAlister, J.E. Rinz, J. Am. Chem. Soc. 102 (1980) 1927.
[42] T.J. Collins, W.R. Roper, J. Chem. Soc., Chem. Commun. (1976) 1044.
[43] T.J. Collins, W.R. Roper, J. Organomet. Chem. 159 (1978) 73.
[44] K.L. Brown, G.R. Clark, C.E.L. Headford, K. Marsden, W.R. Roper, J. Am. Chem. Soc. 101 (1979) 503.
[45] J.R. Sweet, W.A.G. Graham, J. Organomet. Chem. 173 (1979) C9.
[46] W.K. Wong, W. Tam, C.E. Strouse, J.A. Gladysz, J. Chem. Soc., Chem. Commun. (1979) 530.
[47] H. Berke, G. Weiler, Angew. Chem. Int. Ed. 21 (1982) 150.
[48] W.-K. Wong, W. Tam, J.A. Gladysz, J. Am. Chem. Soc. 101 (1979) 5440.
[49] C.P. Casey, M.A. Andrews, D.R. McAlister, J. Am. Chem. Soc. 101 (1979) 3371.
[50] W. Tam, G.Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong, J.A. Gladysz, J. Am. Chem. Soc. 104 (1982) 141.
[51] T. Bodnar, E. Coman, K. Menard, A. Cutler, Inorg. Chem. 21 (1982) 1275.
[52] C. Lapinte, D. Astruc, J. Chem. Soc., Chem. Commun. (1983) 430.
[53] J.R. Sweet, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 2811.
[54] C.P. Casey, M.A. Andrews, D.R. McAlister, W.D. Jones, S.G. Harsey, J. Mol. Catal. 13 (1981) 43.
[55] C.J. May, W.A.G. Graham, J. Organomet. Chem. 234 (1982) C49.
[56] G.O. Nelson, Organometallics 2 (1983) 1474.
[57] C.E. Sumner, G.O. Nelson, J. Am. Chem. Soc. 106 (1984) 432.
[58] G.O. Nelson, C.E. Sumner, Organometallics 5 (1986) 1983.
[59] C. Lapinte, D. Catheline, D. Astruc, Organometallics 3 (1984) 817.
[60] D.H. Gibson, S.K. Mandal, K. Owens, W.E. Sattich, J.O. Franco, Organometallics 8 (1989) 1114.
[61] J.A. Labinger, J.E. Bercaw, Organometallics 7 (1988) 926.
[62] P.T. Wolczanski, J.E. Bercaw, Acc. Chem. Res. 13 (1980) 121.
[63] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 98 (1976) 6733.
[64] J.M. Manriquez, D.R. McAlister, R.D. Sanner, J.E. Bercaw, J. Am. Chem. Soc. 100 (1978) 2716.
[65] P.T. Wolczanski, R.S. Threlkel, J.E. Bercaw, J. Am. Chem. Soc. 101 (1979) 218.
[66] P.T. Barger, J.E. Bercaw, Organometallics 3 (1984) 278.
[67] K.S. Wong, J.A. Labinger, J. Am. Chem. Soc. 102 (1980) 3652.
[68] J.A. Labinger, K.S. Wong, W.R. Scheidt, J. Am. Chem. Soc. 100 (1978) 3254.
[69] B.D. Dombek, A.M. Harrison, J. Am. Chem. Soc. 105 (1983) 2485.
[70] R.J. Mawby, F. Basolo, R.G. Pearson, J. Am. Chem. Soc. 86 (1964) 3994.
[71] E. Lindner, G. von Au, Angew. Chem. Int. Ed. 19 (1980) 824.
[72] C.P. Casey, W.D. Jones, J. Am. Chem. Soc. 102 (1980) 6154.
[73] C.P. Casey, D.M. Scheck, J. Am. Chem. Soc. 102 (1980) 2723.
[74] K.E. Warner, J.R. Norton, Organometallics 4 (1985) 2150.
[75] B.D. Martin, K.E. Warner, J.R. Norton, J. Am. Chem. Soc. 108 (1986) 33.
[76] C.P. Casey, R.A. Widenhoefer, J.M. Oconnor, J. Organomet. Chem. 428 (1992) 99.
[77] S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson, D.F. Shriver, J. Am. Chem. Soc. 101 (1979) 5864.
[78] S.B. Butts, T.G. Richmond, D.F. Shriver, Inorg. Chem. 20 (1981) 278.
[79] S.B. Butts, S.H. Strauss, E.M. Holt, R.E. Stimson, N.W. Alcock, D.F. Shriver, J. Am. Chem. Soc. 102 (1980) 5093.
[80] T.G. Richmond, F. Basolo, D.F. Shriver, Inorg. Chem. 21 (1982) 1272.
[81] K. Sunkel, U. Nagel, W. Beck, J. Organomet. Chem. 251 (1983) 227.
[82] K. Sunkel, K. Schloter, W. Beck, K. Ackermann, U. Schubert, J. Organomet. Chem. 241 (1983) 333.
[83] S.J. LaCroce, A.R. Cutler, J. Am. Chem. Soc. 104 (1982) 2312.
[84] W.D. Jones, J.M. Huggins, R.G. Bergman, J. Am. Chem. Soc. 103 (1981) 4415.
[85] T.W. Bodnar, A.R. Cutler, J. Am. Chem. Soc. 105 (1983) 5926.
[86] T.W. Bodnar, E.J. Crawford, A.R. Cutler, Organometallics 5 (1986) 947.
[87] T. Bodnar, G. Coman, S. LaCroce, C. Lambert, K. Menard, A. Cutler, J. Am. Chem. Soc. 103 (1981) 2471.
[88] A. Cutler, T. Bodnar, E. Coman, S. LaCroce, C. Lambert, K. Menard, in: P. Ford (Ed.), ACS Symposium Series No. 152, American Chemical Society, Washington, DC, 1981, p. 279.
[89] E.J. Crawford, C. Lambert, K.P. Menard, A.R. Cutler, J. Am. Chem. Soc. 107 (1985) 3130.
[90] P. Leoni, F. Marchetti, L. Marchetti, M. Pasquali, S. Quaglierini, Angew. Chem. Int. Ed. 40 (2001) 3617.
[91] S. Reinartz, M. Brookhart, J.L. Templeton, Organometallics 21 (2002) 247.
[92] L. Schwartsburd, E. Poverenov, L.J.W. Shimon, D. Milstein, Organometallics 26 (2007) 2931.
[93] P.J. Alaimo, B.A. Arndtsen, R.G. Bergman, Organometallics 19 (2000) 2130.
[94] C. Lapinte, D. Catheline, D. Astruc, Organometallics 7 (1988) 1683.
[95] A. Asdar, C. Lapinte, L. Toupet, Organometallics 8 (1989) 2708.
[96] V. Guerchais, J. Chem. Soc., Chem. Commun. (1990) 534.
[97] K. Ferre, S. Le Mignot, S. Sinbandhit, L. Toupet, V. Guerchais, Chem. Commun. (2000) 1405.
[98] K. Ferre, G. Poignant, L. Toupet, V. Guerchais, J. Organomet. Chem. 629 (2001) 19.
[99] V. Guerchais, Eur. J. Inorg. Chem. (2002) 783.
[100] S.A. Levitre, A.R. Cutler, T.C. Forschner, Organometallics 8 (1989) 1133.
[101] D.H. Gibson, J.O. Franco, J.F. Richardson, Organometallics 12 (1993) 860.
[102] H. Adams, N.A. Bailey, J.T. Gauntlett, I.M. Harkin, M.J. Winter, S. Woodward, J. Chem. Soc., Dalton Trans. (1991) 1117.
[103] L.J. Li, A. Decken, B.G. Sayer, M.J. McGlinchey, P. Bregaint, J.Y. Thepot, L. Toupet, J.R. Hamon, C. Lapinte, Organometallics 13 (1994) 682.
[104] P. Bregaint, J.R. Hamon, C. Lapinte, Organometallics 11 (1992) 1417.
[105] S. Nlate, C. Lapinte, V. Guerchais, Organometallics 12 (1993) 4657.
[106] S. Nlate, V. Guerchais, C. Lapinte, J. Organomet. Chem. 434 (1992) 89.
[107] V. Mahias, S. Cron, L. Toupet, C. Lapinte, Organometallics 15 (1996) 5399.
[108] J.Y. Thepot, V. Guerchais, L. Toupet, C. Lapinte, Organometallics 12 (1993) 4843.
[109] M.A. Guillevic, P. Bregaint, C. Lapinte, J. Organomet. Chem. 514 (1996) 157.
[110] M.J. Tudoret, V. Guerchais, C. Lapinte, J. Organomet. Chem. 414 (1991) 373.
[111] M. Rosi, A. Sgamellotti, F. Tarantelli, C. Floriani, J. Chem. Soc., Dalton Trans. (1988) 249.
[112] D.A. Brown, N.J. Fitzpatrick, P.J. Groarke, N. Koga, K. Morokuma, Organometallics 12 (1993) 2521.
[113] D.A. Brown, W.K. Glass, M.M. Salama, J. Organomet. Chem. 474 (1994) 129.
[114] D.A. Brown, J.P. Deignan, N.J. Fitzpatrick, G.M. Fitzpatrick, W.K. Glass, Organometallics 20 (2001) 1636.
[115] D.H. Gibson, K. Owens, T.S. Ong, J. Am. Chem. Soc. 106 (1984) 1125.
[116] D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich, J.O. Franco, Organometallics 8 (1989) 498.
[117] A. Asdar, C. Lapinte, J. Organomet. Chem. 327 (1987) C33.
[118] P. Leoni, A. Landi, M. Pasquali, J. Organomet. Chem. 321 (1987) 365.
[119] P. Leoni, E. Aquilini, M. Pasquali, F. Marchetti, M. Sabat, J. Chem. Soc., Dalton Trans. (1988) 329.
[120] S.K. Mandal, J.A. Krause, M. Orchin, J. Organomet. Chem. 467 (1994) 113.
[121] D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich, J.F. Richardson, Organometallics 9 (1990) 424.
[122] D.H. Gibson, S.K. Mandal, K. Owens, J.F. Richardson, Organometallics 6 (1987) 2624.
[123] D.H. Gibson, S.K. Mandal, K. Owens, J.F. Richardson, Organometallics 9 (1990) 1936.
[124] D.H. Gibson, K. Owens, Organometallics 10 (1991) 1216.
[125] D.H. Gibson, K. Owens, S.K. Mandal, W.E. Sattich, J.O. Franco, Organometallics 10 (1991) 1203.
[126] N. Chatani, M. Shinohara, S. Ikeda, S. Murai, J. Am. Chem. Soc. 119 (1997) 4303.
[127] M. Akita, Nippon Kagaku Kaishi (1998) 783.
[128] M. Akita, Appl. Catal., A 200 (2000) 153.
[129] M. Akita, Y. Moro-oka, J. Synth. Org. Chem. Jpn. 50 (1992) 726.
[130] M. Akita, Y. Moro-oka, in: Y. Izumi, H. Arai, M. Iwamoto (Eds.), Science and Technology in Catalysis 1994, Elsevier, Amsterdam, 1995, p. 137.
[131] N. Chatani, S. Murai, Synlett (1996) 414.
[132] P.K. Hanna, B.T. Gregg, D.L. Tarazano, J.R. Pinkes, A.R. Cutler, Adv. Chem. Ser. (1992) 491.
[133] K. Toyohara, H. Nagao, T. Mizukawa, K. Tanaka, Inorg. Chem. 34 (1995) 5399.
[134] D.H. Gibson, Y. Ding, B.A. Sleadd, J.O. Franco, J.F. Richardson, M.S. Mashuta, J. Am. Chem. Soc. 118 (1996) 11984.
[135] D.H. Gibson, X. Yin, J. Am. Chem. Soc. 120 (1998) 11200.
[136] D. Ooyama, T. Tomon, K. Tsuge, K. Tanaka, J. Organomet. Chem. 619 (2001) 299.
[137] D.H. Gibson, H. He, Chem. Commun. (2001) 2082.
[138] K. Tanaka, D. Ooyama, Coord. Chem. Rev. 226 (2002) 211.
[139] D.H. Gibson, X. Yin, H. He, M.S. Mashuta, Organometallics 22 (2003) 337.
[140] D.H. Gibson, Y. Ding, J.G. Andino, M.S. Mashuta, J.F. Richardson, Organometallics 17 (1998) 5178.
[141] D.H. Gibson, J.G. Andino, S. Bhamidi, B.A. Sleadd, M.S. Mashuta, Organometallics 20 (2001) 4956.
[142] D.H. Gibson, J.G. Andino, M.S. Mashuta, Organometallics 25 (2006) 563.

[143] D.H. Gibson, B. Srinivas, B. Niemann, B.A. Sleadd, M.S. Mashuta, A. Vij, J.C. Gallucci, Organometallics 19 (2000) 4179.
[144] D.H. Gibson, J.G. Andino, M.S. Mashuta, Organometallics 24 (2005) 5067.
[145] B.B. Wayland, B.A. Woods, J. Chem. Soc., Chem. Commun. (1981) 700.
[146] R.S. Paonessa, N.C. Thomas, J. Halpern, J. Am. Chem. Soc. 107 (1985) 4333.
[147] V.L. Coffin, W. Brennen, B.B. Wayland, J. Am. Chem. Soc. 110 (1988) 6063.
[148] B.B. Wayland, A.E. Sherry, G. Poszmik, A.G. Bunn, J. Am. Chem. Soc. 114 (1992) 1673.
[149] A.G. Bunn, M.L. Wei, B.B. Wayland, Organometallics 13 (1994) 3390.
[150] D.J. Anderson, R. Eisenberg, Inorg. Chem. 33 (1994) 5378.
[151] M.L. Wei, B.B. Wayland, Organometallics 15 (1996) 4681.
[152] X.-X. Zhang, G.F. Parks, B.B. Wayland, J. Am. Chem. Soc. 119 (1997) 7938.
[153] X. Fu, B.B. Wayland, J. Am. Chem. Soc. 127 (2005) 16460.
[154] X. Fu, S. Li, B.B. Wayland, Inorg. Chem. 45 (2006) 9884.
[155] S. Li, S. Sarkar, B.B. Wayland, Inorg. Chem. 48 (2009) 8550.
[156] T.Y. Cheng, J.C. Peters, G.L. Hillhouse, J. Am. Chem. Soc. 116 (1994) 204.
[157] L. Luan, M. Brookhart, J.L. Templeton, Organometallics 11 (1992) 1433.
[158] C.C. Cummins, G.D. Van Duyne, C.P. Schaller, P.T. Wolczanski, Organometallics 10 (1991) 164.
[159] M.D. Fryzuk, M. Mylvaganam, M.J. Zaworotko, L.R. MacGillivray, Organometallics 15 (1996) 1134.
[160] P. Berno, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc., Chem. Commun. (1991) 109.
[161] C.J. Curtis, R.C. Haltiwanger, Organometallics 10 (1991) 3220.
[162] B.E. Kahn, R.D. Rieke, Chem. Rev. 88 (1988) 733.
[163] R.L. Miller, R. Toreki, R.E. LaPointe, P.T. Wolczanski, G.D. Van Duyne, D.C. Roe, J. Am. Chem. Soc. 115 (1993) 5570.
[164] D.R. Neithamer, R.E. Lapointe, R.A. Wheeler, D.S. Richeson, G.D. Vanduyne, P.T. Wolczanski, J. Am. Chem. Soc. 111 (1989) 9056.
[165] R. Toreki, R.E. Lapointe, P.T. Wolczanski, J. Am. Chem. Soc. 109 (1987) 7558.
[166] G.M. Ferrence, R. McDonald, J. Takats, Angew. Chem. Int. Ed. 38 (1999) 2233.
[167] E.L. Werkema, L. Maron, O. Eisenstein, R.A. Andersen, J. Am. Chem. Soc. 129 (2007) 6662.
[168] E.L. Werkema, L. Maron, O. Eisenstein, R.A. Andersen, J. Am. Chem. Soc. 129 (2007) 2529.
[169] E.M. Carnahan, J.D. Protasiewicz, S.J. Lippard, Acc. Chem. Res. 26 (1993) 90.
[170] M. Gomez, Eur. J. Inorg. Chem. (2003) 3681.
[171] W.J. Evans, J.W. Grate, L.A. Hughes, H. Zhang, J.L. Atwood, J. Am. Chem. Soc. 107 (1985) 3728.
[172] W.J. Evans, D.S. Lee, J.W. Ziller, N. Kaltsoyannis, J. Am. Chem. Soc. 128 (2006) 14176.
[173] W.J. Evans, B.L. Davis, Chem. Rev. 102 (2002) 2119.
[174] O.T. Summerscales, F.G.N. Cloke, P.B. Hitchcock, J.C. Green, N. Hazari, Science 311 (2006) 829.
[175] O.T. Summerscales, F.G.N. Cloke, Organometallic and Coordination Chemistry of the Actinides, Springer-Verlag, Berlin, Berlin, 2008, p. 87.
[176] A.S. Frey, F.G.N. Cloke, P.B. Hitchcock, I.J. Day, J.C. Green, G. Aitken, J. Am. Chem. Soc. 130 (2008) 13816.
[177] K. Kubo, H. Nakazawa, S. Nakahara, K. Yoshino, T. Mizuta, K. Miyoshi, Organometallics 19 (2000) 4932.
[178] R.E. Stimson, D.F. Shriver, Organometallics 1 (1982) 787.
[179] J.L. Cross, T.W. Crane, P.S. White, J.L. Templeton, Organometallics 22 (2003) 548.
[180] M.J.A. Kraakman, B. Deklerkengels, P.P.M. Delange, K. Vrieze, W.J.J. Smeets, A.L. Spek, Organometallics 11 (1992) 3774.
[181] B. Deklerkengels, J.H. Groen, M.J.A. Kraakman, J.M. Ernsting, K. Vrieze, K. Goubitz, J. Fraanje, Organometallics 13 (1994) 3279.
[182] G.D.W. Anderson, O.J. Boys, A.R. Cowley, J.C. Green, M.L.H. Green, S.A. Llewellyn, C.M. von Beckh, S.I. Pascu, I.C. Vei, J. Organomet. Chem. 689 (2004) 4407.
[183] S.A. Llewellyn, M.L.H. Green, A.R. Cowley, Dalton Trans. (2006) 1776.
[184] P.R. Elowe, N.M. West, J.A. Labinger, J.E. Bercaw, Organometallics 28 (2009) 6218.
[185] F. Liang, H. Jacobsen, H.W. Schmalle, T. Fox, H. Berke, Organometallics 19 (2000) 1950.
[186] F. Liang, H.W. Schmalle, T. Fox, H. Berke, Organometallics 22 (2003) 3382.
[187] J. Hock, H. Jacobsen, H.W. Schmalle, G.R.J. Artus, T. Fox, J.I. Amor, F. Bath, H. Berke, Organometallics 20 (2001) 1533.
[188] F. Furno, T. Fox, M. Alfonso, H. Berke, Eur. J. Inorg. Chem. (2001) 1559.
[189] A. Miedaner, D.L. DuBois, C.J. Curtis, R.C. Haltiwanger, Organometallics 12 (1993) 299.
[190] D.L. DuBois, D.M. Blake, A. Miedaner, C.J. Curtis, M.R. DuBois, J.A. Franz, J.C. Linehan, Organometallics 25 (2006) 4414.
[191] D.L. Dubois, Comm. Inorg. Chem. 19 (1997) 307.
[192] M.R. Dubois, D.L. Dubois, Acc. Chem. Res. 42 (2009) 1974.
[193] M.R. DuBois, D.L. DuBois, Chem. Soc. Rev. 38 (2009) 62.
[194] D.E. Berning, A. Miedaner, C.J. Curtis, B.C. Noll, M.C. Rakowski DuBois, D.L. DuBois, Organometallics 20 (2001) 1832.
[195] K. Fraze, A.D. Wilson, A.M. Appel, M. Rakowski DuBois, D.L. DuBois, Organometallics 26 (2007) 3918.
[196] J.W. Raebiger, A. Miedaner, C.J. Curtis, S.M. Miller, O.P. Anderson, D.L. DuBois, J. Am. Chem. Soc. 126 (2004) 5502.
[197] D.E. Berning, B.C. Noll, D.L. DuBois, J. Am. Chem. Soc. 121 (1999) 11432.
[198] C.J. Curtis, A. Miedaner, W.W. Ellis, D.L. DuBois, J. Am. Chem. Soc. 124 (2002) 1918.
[199] C.J. Curtis, A. Miedaner, J.W. Raebiger, D.L. DuBois, Organometallics 23 (2004) 511.
[200] A. Miedaner, J.W. Raebiger, C.J. Curtis, S.M. Miller, D.L. DuBois, Organometallics 23 (2004) 2670.
[201] A.J. Price, R. Ciancanelli, B.C. Noll, C.J. Curtis, D.L. DuBois, M.R. DuBois, Organometallics 21 (2002) 4833.
[202] J.W. Raebiger, D.L. DuBois, Organometallics 24 (2005) 110.
[203] M.T. Mock, R.G. Potter, D.M. Camaioni, J. Li, W.G. Dougherty, W.S. Kassel, B. Twamley, D.L. DuBois, J. Am. Chem. Soc. 131 (2009) 14454.
[204] A.D. Wilson, A.J.M. Miller, D.L. DuBois, J.A. Labinger, J.E. Bercaw, Inorg. Chem. 49 (2010) 3918.
[205] R. Ciancanelli, B.C. Noll, D.L. DuBois, M.R. DuBois, J. Am. Chem. Soc. 124 (2002) 2984.
[206] G. Kovacs, I. Papai, Organometallics 25 (2006) 820.
[207] X.J. Qi, Y. Fu, L. Liu, Q.X. Guo, Organometallics 26 (2007) 4197.
[208] M.R. Nimlos, C.H. Chang, C.J. Curtis, A. Miedaner, H.M. Pilath, D.L. DuBois, Organometallics 27 (2008) 2715.
[209] W.W. Ellis, A. Miedaner, C.J. Curtis, D.H. Gibson, D.L. DuBois, J. Am. Chem. Soc. 124 (2002) 1926.
[210] T.Y. Cheng, R.M. Bullock, Organometallics 14 (1995) 4031.
[211] T.Y. Cheng, B.S. Brunschwig, R.M. Bullock, J. Am. Chem. Soc. 120 (1998) 13121.
[212] T.Y. Cheng, R.M. Bullock, J. Am. Chem. Soc. 121 (1999) 3150.
[213] R.M. Bullock, C.P. Casey, Acc. Chem. Res. 20 (1987) 167.
[214] D.W. Stephan, Coord. Chem. Rev. 95 (1989) 41.
[215] N. Wheatley, P. Kalck, Chem. Rev. 99 (1999) 3379.
[216] V. Ritleng, M.J. Chetcuti, Chem. Rev. 107 (2007) 797.
[217] T. Shima, Z. Hou, J. Am. Chem. Soc. 128 (2006) 8124.
[218] Y. Takenaka, T. Shima, J. Baldamus, Z.M. Hou, Angew. Chem. Int. Ed. 48 (2009) 7888.
[219] T. Beringhelli, G. Dalfonso, G. Ciani, H. Molinari, Organometallics 6 (1987) 194.
[220] M. Okazaki, T. Ohtani, S. Inomata, N. Tagaki, H. Ogino, J. Am. Chem. Soc. 120 (1998) 9135.
[221] M. Okazaki, T. Ohtani, M. Takano, H. Ogino, Organometallics 23 (2004) 4055.
[222] M. Okazaki, T. Ohtani, H. Ogino, J. Am. Chem. Soc. 126 (2004) 4104.
[223] B.F.G. Johnson, J. Lewis, N. Prior, G. Schiavon, J. Cluster Sci. 3 (1992) 145.
[224] J.T. Park, J.R. Shapley, K. Lee, H. Song, J. Cluster Sci. 11 (2000) 343.
[225] D.S. Dumond, S. Hwang, M.G. Richmond, Inorg. Chim. Acta 160 (1989) 135.
[226] J.A. Partin, M.G. Richmond, J. Organomet. Chem. 353 (1988) C13.
[227] J.A. Labinger, J.S. Miller, J. Am. Chem. Soc. 104 (1982) 6856.
[228] D.L. Grimmett, J.A. Labinger, J.N. Bonfiglio, S.T. Masuo, E. Shearin, J.S. Miller, J. Am. Chem. Soc. 104 (1982) 6858.
[229] A.J.M. Miller, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 130 (2008) 11874.
[230] A.J.M. Miller, J.A. Labinger, J.E. Bercaw, Organometallics, in press.
[231] D.W. Stephan, G. Erker, Angew. Chem. Int. Ed. 49 (2010) 46.
[232] A.J.M. Miller, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 132 (2010) 3301.