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Carbonyl Coupling Reactions Using Transition Metals, Lanthanides, and Actinides

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Contents

I. Introduction

The use of metals in carbon–carbon bond forming reactions is well-known. Recent advances in organometallic chemistry have produced many useful and highly specific carbon–carbon bond forming reactions that are extremely useful in organic chemistry. An intensively studied class of carbon–carbon bond forming reactions are the Fischer–Tropsch reactions where large hydrocarbons can be built from CO. The use of carbonyl-containing compounds in organometallic chemistry is extremely widespread. Organometallic systems have been shown that are able to couple coordinated carbonyls. Synthetic organic chemists have benefitted greatly as well, from the use of "inorganic" systems to effect reductive carbonyl coupling. The uses of low-valent titanium in organic carbonyl coupling reactions have been previously reviewed.[1,2] The purpose of this paper is to review the uses of transition metals, lanthanides, and actinides in effecting either heterogeneous or homogeneous carbonyl coupling reactions in which a carbon–carbon bond is created from two carbonyls.

II. Carbonyl Coupling Reactions in Organic Chemistry

Many examples of carbonyl coupling reactions have been demonstrated with electron-rich transition metals, lanthanides, and actinides. The metals used most commonly are the early transition metals, lanthanides, and actinides, for which the metal–oxygen bond strengths are greatest. In order to provide electron-rich metal centers, a large variety of reductive methods for generating low-valent metal species have been employed. These reductions commonly use metal halides as convenient, reducible metal sources. A large number of reducing agents have also been employed, including many metal activation procedures pioneered by our research group. Among the most common reducing agents are alkali metals, Zn, Mg, metal hydrides, and lithium reagents.

The vast majority of uses of transition metals to effect the reductive coupling of coordinated carbonyls employ highly oxophilic early transition metals. A thermodynamic gauge of metal oxophilicity can be seen by examining the standard heats of formation for classes of binary metal oxides. The MO_2 oxides are known for most early transition metals, lanthanides, and actinides, and thermodynamic data for most of these metals exist. Examination of the standard heats of formation give a good indication of comparative metal oxophilicity (Figure 1). It can be seen that metal oxophilicity increases as one proceeds to the left of the transition metals.

Two classes of reductive carbonyl coupling reactions have been observed in heterogeneous systems where the organic molecules have been isolated. Coupling of two carbonyls may proceed to give either pinacols or alkenes. The reduction of carbonyls to pinacols is a well-established reaction, particularly for aromatic ketones, which are more readily reduced than aliphatic ketones. Much more recent (the first report of this type of reaction was from Schreibmann in 1970[3]) are the reports of the reductive coupling of ketones to alkenes. In fact, these reductive couplings of ketones to alkenes almost always proceed via metallopinacols (vide infra), and when the reactions run to partial completion are quenched, pinacols can be isolated.

A. Carbonyl Couplings To Give Pinacols

The coupling of ketones to give pinacols is a very old, well-established reaction in organic chemistry. This reaction has been demonstrated photochemically (most commonly with aryl ketones). It can be accomplished with a variety of metal reducing agents. The alkali metals have been used extensively for this purpose. The use of a Mg/MgI_2 mixture (said to produce MgI in situ), demonstrated by Gomberg and Bachmann in 1927,[4] is still commonly used. Another very common route to pinacols from carbonyl compounds is by using Al/Hg.[3] This reaction is even used in undergraduate organic synthesis laboratory courses. The synthesis of pinacols from carbonyl compounds is generally thought of as taking place via reduction of the carbonyl to a radical anion (ketyl), followed by radical coupling to give a

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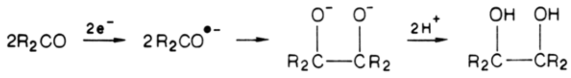


$$2R_2CO \xrightarrow{2e^-} 2R_2CO^{\bullet-} \longrightarrow R_2\overset{O^-}{C}-\overset{O^-}{C}R_2 \xrightarrow{2H^+} R_2\overset{OH}{C}-\overset{OH}{C}R_2$$

pinacol dianion, which is subsequently protonated by the medium or upon quenching.

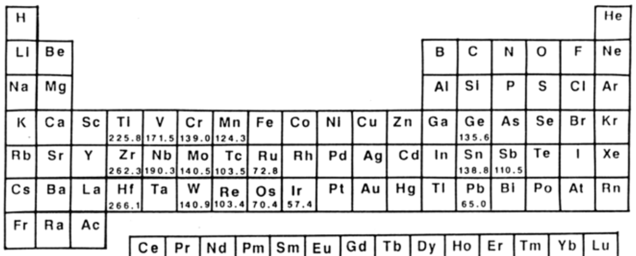


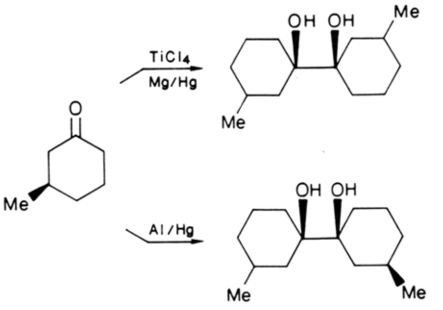
Figure 1. Standard enthalpies of formation (–kcal/mol) for MO_2 oxides.

TABLE I. Heterogeneous Reagents for Pinacol-Forming Reactions

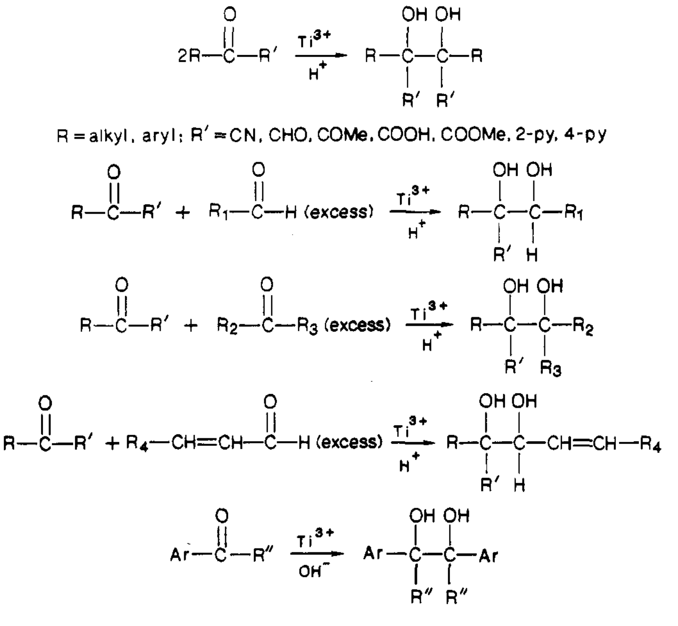
metal compd	redox agent	ketone amt	Ar[a]	R[a]	ref
acidic $CrCl_2$	none		?[b]	?[b]	7
acidic VCl_2	none		?[b]	?[b]	7
ammoniacal $TiCl_3$	none	0.19	?		8
aq $TiCl_3$ acidic	none	1		X[c]	9
aq $TiCl_3$ alkaline	none	1	X	X[c]	9
Al/Hg	none	?	X	X	3
$TiCl_4$	Mg, 0.5 *t*-BuOH	0.5		X[d]	15
$TiCl_4$	Mg, *t*-BuOH	1		X[d]	15
$TiCl_4$	Mg/Hg	0.67	X	X	13
$TiCl_3$	*t*-BuLi	?		P	13
$TiCl_3$	*n*-BuLi	?		P	13
$TiCl_3$	DIBAL	?		P	13
$TiCl_4$	Zn		X	X	23
$CpTiCl_3$	0.75 $LiAlH_4$	1		X	13
$(C_6Me_6)Ti(AlCl_4)_2$	none	0.5		X	13
Cp_2Ti	none	?		P	13
$Cp_2Ti(CO)_2$	none		P		14
VCl_3	1.5 Mg, *t*-BuOH	1		X[d]	15
Ce	I_2	0.5	X[e]	X[f]	16
Ce	ICH_2CH_2I	0.5	X[g]		16
CeI_3	K	0.5	X[g]		16
Ce	C_6H_5I	0.5	X[h]		16
Ce	$TiCl_4$	0.5	X[g]		16
SmI_2	none	1	X	X	17
$(PhCC)_2Yb$	none	2	P[i]		18
$(C_6F_5)_2Yb$	none	0.87	X[i]		18

[a] Key: X = coupled to give $R_2C(OH)C(OH)R_2$; P = poor yield. [b] α,β-Unsaturated ketone or aromatic or unsaturated aldehyde. [c] Activated ketone RCOR′: R = CN, CHO, COMe, COOH, COOMe, 2-py, 4-py. [d] Enone mesityl oxide. [e] Ph_2CO did not react. [f] Cyclododecanone gave cyclododecanol (70%). [g] Demonstrated only for PhCOMe. [h] PhCOMe, *p*-BrC_6H_4COMe. [i] Benzophenone.

It should be noted that the specific reaction conditions and reagents used can have profound effects on the results of these carbonyl coupling reactions. Mundy et al. have demonstrated unequivocally that the stereochemistry of the pinacol resulting from the reductive coupling of (*R*)-(+)-3-methylcyclohexanone is different when the Al/Hg reagent or the $TiCl_4$/(Mg/Hg) reagent (vide infra) is used.[5] These two reagent systems are probably the most commonly used in pinacol synthesis. The product resulting from the use of the titanium reagent is the one expected for Ti(IV) coordination to



SCHEME I. Pinacol Preparations with Aqueous Ti^{3+}



two oxygen atoms. The mechanistic course of the Al/Hg reaction is considerably more difficult to rationalize but is clearly different from that of the titanium system.

1. Aqueous Systems

Interestingly, the synthesis of pinacols from ketones is one of the first reactions in which transition metals were used for the coupling of organic carbonyl species. The use of a Zn/Cu couple was reported by Griner to couple unsaturated aldehydes to pinacols as early as 1892.[6] Early reports also exist on the use of chromium and vanadium,[7] as well as ammoniacal $TiCl_3$[8] based reducing agents in order to effect this type of reaction. These early reports were all accomplished under aqueous conditions (Table I).

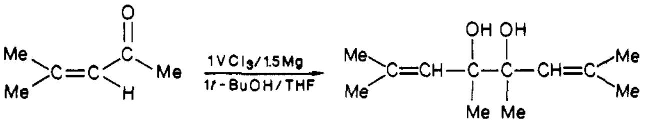
Aqueous conditions are still used quite extensively in the work of Clerici and Porta.[9] Commercially available aqueous $TiCl_3$ has been used in acidic solutions to couple aliphatic or aromatic ketones or aldehydes containing "activating" (i.e., strongly electron-withdrawing groups that stabilize the radical intermediate) groups (Scheme I). Some of the activating groups used include CN, CHO, COMe, COOH, COOMe, 2-pyridyl, and 4-pyridyl. In addition, these activated carbonyl compounds can also undergo cross-coupling reactions with unactivated carbonyl compounds when the unactivated compound is in excess or is used as the reaction solvent. This has proved to be an excellent way to prepare unsymmetrical pinacols.[10] Simple unactivated aromatic ketones and aldehydes have been homocoupled by a very similar methodology, with the exception that the $TiCl_3$ solution is used under alkaline conditions.[11,12] The reducing ability of this titanium reagent system is quite pH dependent and has been shown to increase with increasing alkalinity. Thus, the stronger alkaline reductant is capable of coupling unactivated aromatic carbonyls but is still ineffective for unactivated aliphatic carbonyl compounds.

2. Nonaqueous Systems

(a) Titanium and Vanadium. With the exception of the previously reported aqueous systems, all of the examples of reductive coupling of carbonyls to pinacols have been conducted in nonaqueous solvents. A variety of reduced titanium species have been reported to couple carbonyls to pinacols. The most common sources of titanium are the titanium chlorides $TiCl_3$ and $TiCl_4$; however, the organometallic complex $CpTiCl_3$ has also been used. A number of different reducing agents have been employed including Mg, Mg/Hg, RLi, DIBAL, $LiAlH_4$, and Zn. By far the most common of these is the Mg/Hg reductant pioneered by the work of Corey, Danheiser, and Chandrasekaran.[13]

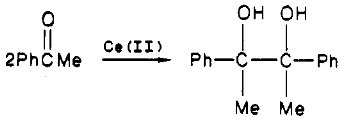
The well-characterized Ti(II) complexes Cp_2Ti,[13] $Cp_2Ti(CO)_2$,[14] and $(C_6Me_6)Ti(AlCl_4)_2$[13] have all been reported to carry out the reductive carbonyl coupling reaction to give pinacols, but only $(C_6Me_6)Ti(AlCl_4)_2$ has succeeded in giving acceptable yields.

In addition to the previously reported aqueous vanadium reduction, low-valent vanadium species prepared by reduction of VCl_3 with Mg have been reported to couple carbonyls to pinacols.[15] The only compound reported to be reduced by this material, however, is the unsaturated ketone mesityl oxide ($(CH_3)_2C{=}CHC(O)CH_3$). The pinacol was obtained in 75% yield.



(b) Lanthanides. The standard enthalpies of formation for the lanthanides and actinides are among the most negative known for any MO_2 metal oxides (Figure 1). In addition to their oxophilicity, the lanthanides and actinides possess several other features that make their potential for carrying out interesting organic transformations great. A great disservice has been done by calling the f elements "rare earths". The natural abundance of most lanthanides, uranium, and thorium is greater than quite a few transition metals, and many main-group elements as well. The availability of f orbitals, particularly for the actinides for which the 5f orbitals are not as "buried" as in the 4f lanthanides, enables transformations unknown for the transition metals. The f elements exhibit large coordination numbers and high kinetic lability (compared with transition metals). For these reasons, the lanthanides and actinides have also proven effective for reductive carbonyl coupling reactions.

A variety of low-valent (presumably Ce(II)) cerium moieties, both heterogeneous and homogeneous, have been used to couple aromatic and aliphatic ketones and aldehydes to pinacols.[16] The reagent used for most of



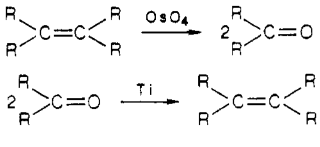
this work was Ce/I_2. These low-valent cerium compounds are somewhat unique in that they are prepared oxidatively from cerium metal, rather than reductively from metal halides as with most transition-metal systems. The Ce/I_2 reagent was shown to couple aromatic aldehydes and ketones and cyclic aliphatic ketones in high yield. Only two exceptions were noted. Benzophenone failed to react at all, and cyclododecanone gave a 70% yield of the reduced product cyclododecanol but no pinacol. All of the reagent systems prepared from cerium metal (see Table I) gave good yields (>68%) of pinacol from acetophenone.

The soluble SmI_2 compound, which was also prepared oxidatively from samarium metal and ICH_2CH_2I, gave high (>85%) yields of pinacols from aromatic and aliphatic ketones and aldehydes.[17] All reactions were quite fast. Aromatic aldehydes and ketones reacted in seconds, aliphatic aldehydes reacted in hours, and aliphatic ketones required 1 day. The functionalities NO_2, CN, COOH, OMe, and NMe_2 were tolerated on aromatic aldehydes. This shows the exceptional selectivity of this reagent. The only compound attempted that did not give high pinacol yields was acetaldehyde. In this case, ethyl acetate was found to be the major product.

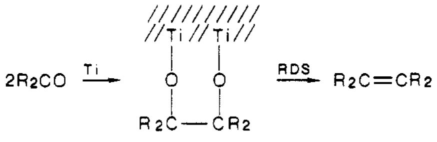
The compounds formulated as YbR_2 (R = PhCC, C_6F_5) were shown to form benzopinacol from benzophenone.[18] These ytterbium compounds were prepared by transmetalation from the corresponding dialkylmercury compounds and were not characterized in any way. The resulting solutions were filtered to remove precipitated mercury. The $(PhCC)_2Yb$ compound gave benzopinacol in 14% yield, whereas $(C_6F_5)_2Yb$ gave benzopinacol in 84% yield (based on initial mercurial). These ytterbium compounds were not effective in the reductive coupling of aromatic aldehydes or of aliphatic ketones or aldehydes.

B. Carbonyl Couplings To Give Olefins

While the reduction of carbonyl compounds to give pinacols is an old, well-established reaction, the use of carbonyl compounds in the synthesis of olefins is much more recent. Many important contributions to the development of this reaction have been reported by McMurry (vide infra). The first report of coupling two carbonyls to give a olefin was disclosed in the work on pinacol preparation by Schreibmann[3] (vide supra). Although yields were not reported, Schreibmann noted the isolation of tetraphenylethylene from the reaction of benzophenone with Al/Hg; *trans*-2,3-diphenyl-2-butene from acetophenone; and *trans*-stilbene from benzaldehyde. This reaction forming alkenes from carbonyls—usually employing early-transition-metal compounds in low oxidation states—may be thought of as the formal inverse of the well-known oxidative cleavage reactions of alkenes involving late transition metals in high oxidation states (e.g., OsO_4 and $KMnO_4$).



Most of the mechanistic work done on these reductive carbonyl coupling reactions (vide infra) leads to the conclusion that these reactions proceed via metallopinacols. The initial step of these reactions then is very similar to those described previously in the reductive carbonyl coupling reactions to give pinacols. The difficulty comes in the deoxygenation of the resulting metallopinacols, which McMurry has shown is the rate-determining step of this transformation.[19] The reagent systems used for the alkene-forming reactions are generally more highly reduced (lower oxidation states) and employ more oxophilic materials than do the comparable systems used for pinacol formations. This is borne out by the fact that aqueous Ti(III) solutions can be used in the formation of pinacols from carbonyl compounds, whereas air/H_2O-sensitive Ti(0) or Ti(II) systems are required for the alkene-forming reactions.



1. Titanium

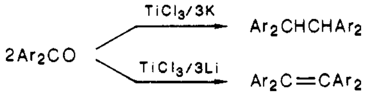
The oxophilicity of titanium has been exploited in the well-known reductive carbonyl coupling reactions pioneered by McMurry[19-21] and others[22,23] using low-valent titanium. There have been a large number of different methods reported for generating these low-valent titanium species (Table II), many developed by McMurry's group, each of which has its own unique characteristics.

Virtually all of the methods reported couple aromatic ketones to olefins, but not all are effective in coupling aliphatic ketones (which are harder to reduce). However, McMurry reported[24] that the titanium prepared by reducing $TiCl_3$ with potassium by the procedure developed by Rieke and Hudnall[25] gave 1,1,2,2-tetraarylalkanes from aromatic ketones. This method was preferred by McMurry over the previously reported $LiAlH_4$ reduction. These tetraarylalkanes were reported to arise from further reduction of tetraarylalkenes.

$$2Ar_2CO \xrightarrow{TiCl_3/3K} Ar_2C{=}CAr_2 \rightarrow Ar_2CHCHAr_2$$

In order to attempt to combat irreproducibility problems, the use of $LiAlH_4$ as a reducing agent for the titanium systems of McMurry's was subsequently changed. The initial report on the use of $LiAlH_4$ as a reducing agent was improved by use of potassium as a reductant (vide supra). For reasons of safety, the use of lithium instead of potassium was subsequently recommended.

The results using lithium reductions were reported to be "nearly as effective"[26] as potassium reductions. Two important differences were noted however: First, the lithium reductions did not proceed to completion, and excess lithium remained.[24] This procedure was modified slightly by Richardson[27] in that the excess lithium was removed from the titanium slurry by filtration. This modified preparation of titanium was shown to be effective in the reductive carbonyl coupling of haloaromatic ketones. Second, the titanium reagent prepared by lithium reduction reduced aromatic ketones to alkenes[24,27] rather than the alkanes found by the potassium reductions (vide supra).[24]



The reductant McMurry currently prefers is a Zn–Cu couple.[28] McMurry has gone back to using $LiAlH_4$ (in the presence of NEt_3) for the coupling of keto esters, however.[29]

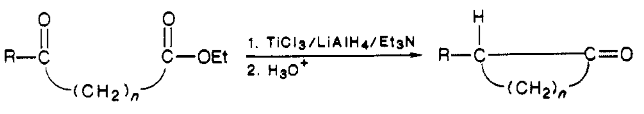


TABLE II. Heterogeneous Reagents for Alkene-Forming Reactions

metal compd	reducing agent	ketone amt	Ar[a]	R[b]	ref
Al/Hg	none	?	X		3
$TiCl_3$	0.4 $LiAlH_4$	0.40	X	X	19
$TiCl_3$	0.5 $LiAlH_4$	0.5	X	X	20
$TiCl_4$	0.5 $LiAlH_4$[c]	0.20		X	34
$TiCl_3$	0.5 $LiAlH_4$[c]	0.10[d]		X	29
$TiCl_3$	0.5 $LiAlH_4$	1	X		30
$TiCl_4$	0.75 $LiAlH_4$	1	X		30
$TiCl_3$	3.2 K	0.25		X	32
$TiCl_3$	3.2 K	1	X		30
$TiCl_3$	3.5 K	0.25	X[e]	X	24
$TiCl_4$	4.3 K	1	X		30
$TiCl_4$	4.2 Li	1	X		30
$TiCl_3$	3.5 Li	0.25	X[f]	X	26
$TiCl_3$	<3 Li + Li[g]	?	X	X	24
$TiCl_3$	<3 Li[h]	0.25[i]	X		27
$TiCl_4$	2 BuLi	?	X		23
$TiCl_4$	2 Zn	0.66	X		23
$TiCl_4$	2 Zn[c]	0.20		X	34
$TiCl_4$	2 Zn[j]	0.93		X	33
$TiCl_3$	2.3 ZnCu	0.18	X	X	28
$TiCl_3$	1.7 Mg	1	X		30
$TiCl_4$	2 Mg	?	X		23
$TiCl_4$	2.2 Mg	1	X		30
$TiCl_3$·3THF	2.5 Mg	2	X	P	22
$TiCl_3$·3THF	4 Mg	5		X	22
$TiCl_4$	Mg/Hg	?	X		5
$TiCl_3$ or $TiCl_4$	$LiBH_4$	?	?		20
$TiCl_3$ or $TiCl_4$	CaH_2	?	?		20
$TiCl_3$ or $TiCl_4$	LiH	?	?		20
WCl_6	2 *n*-BuLi	0.25–0.5	X	P	35
WCl_6	$LiAlH_4$	0.5	X	P	36
WCl_6	$NaAlH_4$	0.5	X	P	36
WCl_6	Zn	0.5	X	P	36
WCl_6	4 e^-	2	X		37
UCl_4	4 Na/K	2		X	40
UCl_4	2 $[(TMEDA)Li]_2[Naph]$	2		X	43
$ThCl_4$	2 $[(TMEDA)Li]_2[Naph]$	2		X	43

[a] Key: X = coupled to give $Ar_2C{=}CAr_2$; ? = not reported; P = poor yield. [b] Key: X = coupled to give $R_2C{=}CR_2$; P = poor yield. [c] +0.2 NR_3. [d] Keto ester. [e] Coupled to give $Ar_2CHCHAr_2$. [f] Cross-coupling between aryl and alkyl ketone. [g] Reduction did not proceed to completion; excess Li remained. [h] Filtered to remove excess Li. [i] Haloketone. [j] +0.83 pyridine.

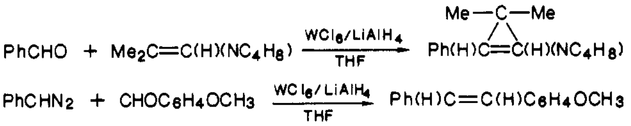
Many of the stoichiometries reported ideally generate Ti(0) species, while others generate Ti(II) species—assuming that the reductions proceed to completion. The actual oxidation state of the species responsible for the reductive coupling of ketones remains speculative. Dams, Malinowski, and Geise have investigated the stoichiometries involved in the reduction of $TiCl_4$ as well as $TiCl_3$.[30,31] They conclude that the optimum ratio of ketone (benzophenone) to titanium is 1:1 in all cases. Furthermore, the stoichiometries for reduction of $TiCl_3$ and $TiCl_4$ were investigated with the reducing agents Li, K, Mg, and $LiAlH_4$. In all cases the stoichiometries found were those corresponding to reduction to Ti(0), allowing for a slight excess of reductant due to impurities.

	$TiCl_3$ (*m*), equiv	*m*/3	$TiCl_4$ (*n*), equiv	*n*/4
Li			4.2	0.95
K	3.2	1.1	4.3	1.1
Mg	1.7	0.57	2.3	0.58
$LiAlH_4$	0.5	0.17	0.75	0.19

2. Tungsten

Next to titanium, the metal receiving the most attention in reductive ketone-coupling reactions is tungsten. In fact, one of the first reports of the use of a metal in a reductive ketone-coupling reaction was that of Sharpless et al. in 1972 who used WCl_6 + 2*n*-BuLi.[35] In general, tungsten reagents are not as effective as titanium reagents, particularly for aliphatic carbonyl compounds (Table II).

The results of Fujiwara et al. showed that, at least for tungsten, the reductive coupling of benzaldehyde could proceed, at least in part, via a carbene mechanism.[36] When benzaldehyde was allowed to react with the reagent prepared from $WCl_6/LiAlH_4$ in the presence of an enamine [1-(2-methylpropenyl)pyrrolidine], a cyclopropane [1-(2,2-dimethyl-3-phenylcyclopropyl)-pyrrolidine] was obtained in low yield. Phenyldiazomethane reacted with *p*-methoxybenzaldehyde in the presence of the same tungsten system to give a 12% yield of *p*-methoxystilbene. The Fischer carbene complex $(CO)_5W{=}C(Ph)OCH_3$ effected the coupling of benzaldehyde to stilbene in moderate yield (42%). A transient NMR peak at δ 8.8 was assigned to the α-H of the proposed tungsten alkylidene intermediate in the reaction of benzaldehyde with the $WCl_6/LiAlH_4$ reagent.



$$PhCHO + Me_2C{=}C(H)(NC_4H_8) \xrightarrow[THF]{WCl_6/LiAlH_4} Ph(H)C\overset{Me-C-Me}{\triangle}C(H)(NC_4H_8)$$

$$PhCHN_2 + CHOC_6H_4OCH_3 \xrightarrow[THF]{WCl_6/LiAlH_4} Ph(H)C{=}C(H)C_6H_4OCH_3$$

An interesting contrast to the chemical reductions described previously is the electrochemical work by Petit, Mortreux, and Petit. They report that low-valent tungsten species produced *electrochemically* by controlled-potential electroreduction of WCl_6 at a platinum cylindrical grid cathode and an aluminum foil anode can effect quantitative reductive coupling of benzaldehyde to stilbene.[37] The coupling proceeded well in THF, DMSO, and DMF, but use of CH_2Cl_2 as a solvent gave styrene instead. CH_2Cl_2 under these conditions has been shown to produce in situ carbenic species.[38] The coupling yields of aliphatic aldehydes were poor. Best results were obtained when the PhCHO was present during the reduction of WCl_6. If PhCHO was added after the electroreduction of WCl_6, stilbene was obtained in only 10% yield. Constant-potential coulometry indicated that 4 equiv of electrons was passed/mol of WCl_6, with or without PhCHO.

3. Other Metals

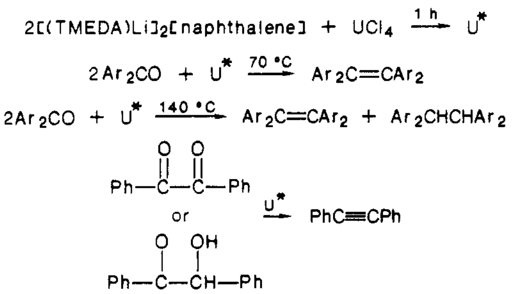
Dams, Malinowski, and Geise also studied the nature of the metal on the reductive coupling of benzophenone.[39] These results are reproduced in Table III. Titanium appears to play a unique role in this reductive coupling reaction. Yields for the other metals that gave any indication of reactivity were unacceptably low.

Recent work in our research group has shown that active uranium and thorium can be used to accomplish the reductive carbonyl coupling of aromatic ketones very effectively.[40–44] Active uranium prepared by Na/K reduction of UCl_4 in DME,[40] as well as active uranium and thorium prepared in hydrocarbon solvents, have been used.[41–44] The chemistry of the active metals prepared in hydrocarbon (typically aromatic) solvents is much cleaner and more controllable. These active actinides react with oxygenated solvents, and active uranium has been shown to produce ethylene and

TABLE III. Comparison of the Effectiveness of Reduced Metals on the Coupling of Benzophenone to Tetraphenylethylene[39]

metal halide	reducing agent	% yield
$TiCl_3$	0.5 $LiAlH_4$	93
$TiCl_4$	0.8 $LiAlH_4$	90
WCl_6	1.2 $LiAlH_4$	30
$MoCl_5$	1.0 $LiAlH_4$	18
$ZrCl_4$	0.9 $LiAlH_4$	11
$NbCl_5$	1.0 $LiAlH_4$	10
VCl_3	0.7 $LiAlH_4$	8
$MgCl_2$	2.5 K	0
$CoCl_2$	0.4 $LiAlH_4$	0
$NiCl_3$	0.35 $LiAlH_4$	0
$FeCl_3$	0.65 $LiAlH_4$	0
$CuCl_3$	0.4 $LiAlH_4$	0
$CrCl_3$	0.6 $LiAlH_4$	0
$ZnCl_2$	2.5 K	0
$MnCl_2$	0.4 $LiAlH_4$	0
$SnCl_2$	0.35 $LiAlH_4$	0
$AlCl_3$	3.0 $LiAlH_4$	0
$HfCl_4$	0.6 $LiAlH_4$	0
$TaCl_5$	1.0 $LiAlH_4$	0

SCHEME II. Preparation and Reactivity of Active Uranium (U*)



methyl vinyl ether from DME.[41–43] Active uranium and thorium can be prepared in hydrocarbon solvents by using the hydrocarbon-soluble reducing agent [(TMEDA)Li]$_2$[naphthalene] (which can be prepared on a preparative scale).[43] Active uranium and thorium couple carbonyls in the stoichiometry 2:1 carbonyl to metal.[43] This is in contrast to transition-metal systems where 1:1 carbonyl to metal center is the rule (vide supra). We have used this increase in coordinating ability of actinides in order to reduce benzil and benzoin to diphenylacetylene[44]—a transformation attempted using titanium by two authors without success.[24,45] Furthermore, at elevated temperatures C–H activation takes place to form metal hydride species. When the carbonyl coupling takes place in the presence of these hydrides, tetraarylethanes result[41–43] (Scheme II).

.The reaction of cyclopentanone, cyclohexanone, and cycloheptanone cocondensed with Mg atoms has been studied.[46] Pinacols were isolated in low yields from the resulting product mixtures. Detailed studies on the cycloheptanone system showed evidence of carbenoid species generated from the deoxygenation of cycloheptanone by Mg or a Mg complex.

Miller and DeKock have studied the reactions of metal atom vapors cocondensed with cyclohexanone.[47] The metals studied were Ti, Cr, Co, Ni, Nd, and U. In no case were appreciable yields of bicyclohexylidene observed, in contrast to the heterogeneous reduction systems of McMurry. With the exception of titanium, all of the metals studied produced aldol condensation products as the major products. In the titanium reaction, the major product observed was the pinacol (71%). Pinacols were observed (24–27%) in the reactions of Cr, Nd, and U, whereas the aldol condensation product was observed in 70–76% yields. The late transition metals Co and Ni produced no observable amounts of pinacol.

TABLE IV. Homogeneous Reagents for Carbonyl Coupling Reactions

metal compd	ketone amt	Ar[a]	R[b]	ref
$(C_6H_6)_2Ti$	0.5	X	X	48
$Cp_2Ti(CO)_2$	0.5	*c*		14
$[CpTiCl_2(THF)_{1.5}]$	excess		X[d]	49
$W(CO)_6$	0.5	P		36
$W(CO)_5PPh_3$	0.5	P		36
$W(CO)_5NH_2C_6H_{11}$	0.5	P		36
$W(CO)_5{=}C(Ph)OCH_3$	0.5	P		36
$[W(CO)_5Cl]NEt_4$	0.5	P		36
$[W(CO)_5Cl]NEt_4 + AlCl_3$	0.5	P		36
$W_2(O\text{-}i\text{-}Pr)_6(py)_2$	1.		?	80
$Mo(CO)_6$	0.5	P		36

[a] Key: X = coupled to give $Ar_2C{=}CAr_2$; P = poor yield. [b] Key: X = coupled to give $R_2C{=}CR_2$; ? = yield not reported. [c] See text. [d] Paraformaldehyde.

M	alkene, %	aldol, %	pinacol, %
Ti	8	21	71
Cr	2	70	27
Nd		76	24
U	3	71	26
Co		91	
Ni		31	

III. Organometallic Carbonyl Coupling Reactions

The question of which metal oxidation state is responsible for the reductive ketone-coupling reaction, and the proposed role of zerovalent metals in the heterogeneous reactions (vide supra), prompted investigations into the use of organometallic complexes of well-defined oxidation states for this transformation. The complexes known to couple organic ketones to alkenes are shown in Table IV. By far, the vast majority of complexes used for well-characterized coordinated carbonyl couplings have been those of the group 4 metals.

A. Titanium

The bis(arene)titanium complex $(\eta^6\text{-}C_6H_6)_2Ti$ was shown to be highly active toward reductive ketone coupling reactions for both aromatic and aliphatic ketones.[48] In addition, it is the only metal complex known that will reduce the α-diketone benzil to diphenylacetylene. This complex has also been shown to be extremely effective in other types of deoxygenation reactions such as the reduction of allylic and benzylic alcohols to olefins and the conversion of epoxides to olefins.

There are several important mechanistic differences between this reagent and heterogeneous systems like those prepared by McMurry. In the coupling reaction of ketones, no pinacols were ever seen when $(\eta^6\text{-}C_6H_6)_2Ti$ was used. Furthermore, the reaction of pinacols with $(\eta^6\text{-}C_6H_6)_2Ti$ was much slower than the reaction of ketones. This is markedly different from the heterogeneous low-valent titanium systems where the rate-determining step in the reduction of ketones was shown to be the deoxygenation of the metallopinacol to form the alkene (vide supra).[19] For this reason, the mechanistic course of the homogeneous and heterogeneous reactions must be different. The homogeneous (η^6-$C_6H_6)_2$Ti complex reduces allyl and benzyl alcohols to the corresponding olefins, whereas the heterogeneous systems of McMurry produce mainly coupled products.

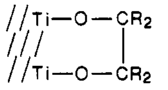
This (η^6-$C_6H_6)_2$Ti complex was prepared by codeposition of benzene with titanium vapor. It has not been used for other synthetic chemistry, most likely due to the difficulty in its preparation.

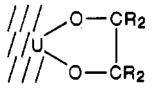
A related (π-arene)titanium(II) complex (η^6-C_6Me_6)-Ti$(AlCl_4)_2$ has been found to reductively couple ketones to pinacols (vide supra).[13] This complex is not effective for the formation of olefins, however.

Other titanium(II) species have been found to be effective in the reductive coupling of carbonyls to olefins. The complex $Cp_2Ti(CO)_2$ was shown by Chen, Chan, and Shaver to give pinacols and olefins from aromatic aldehydes in good yields.[14] Interestingly, the reaction of $Cp_2Ti(CO)_2$ with benzophenone gave diphenylmethanol (benzhydrol) (26%), diphenylmethane (44%), and 1,1,2,2-tetraphenylethane (17%) after 30 h in refluxing THF, but no tetraphenylethylene was observed in this reaction. Aliphatic aldehydes were reduced to the corresponding alcohols by $Cp_2Ti(CO)_2$.

The Ti(III) compound $[CpTiCl_2(THF)_{1.5}]$ formed ethylene and the $[CpTiCl_2]_2O$ oxide compound, upon reaction with an excess of paraformaldehyde.[49] The $[CpTiCl(\mu\text{-}O)]_4$ compound crystallized with $[CpTiCl_2]_2O$, and its formation was suggested to occur via hydrolysis of $[CpTiCl_2]_2O$ in the reaction workup.

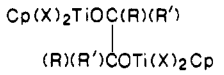
Reductive carbonyl couplings mediated by transition-metal systems are usually postulated as proceeding via a metallopinacol intermediate (vide supra). The investigations of heterogeneous titanium-induced carbonyl couplings studied in detail by McMurry and Geise suggest the intermediacy of a dinuclear metallopinacol.[31] This postulate is substantiated by the fact that these systems are only capable of reacting with one carbonyl per metal atom. The heterogeneous uranium systems that we have investigated show mononuclear metallopinacols (vide supra).[41-44] In homogeneous organometallic systems, however, mononuclear transition-metal metallopinacols can be observed. There are several examples of the reaction of an early transition metal with a carbonyl-containing compound and subsequent isolation of mononuclear or dinuclear metallopinacols.


dinuclear


mononuclear

Reaction of $Cp_2Ti(CO)_2$ with diethyl ketomalonate, $(EtOOC)_2CO$, resulted in reductive coupling of the carbonyls and isolation of a mononuclear metallopinacol.[50] A maximized 40% yield of complex was only obtained when a large excess of diethyl ketomalonate over $CpTi(CO)_2$ was used. This complex was structurally characterized and showed the expected structure for a mononuclear metallopinacol. No formation of alkene was noted from this complex.

The reaction of the organic carbonyl-containing compounds $(CH_3)_2CO$, $Ph(CH_3)CO$, and PhCHO with the Ti(III) compounds $CpTiX_2$ (X = Cl, Br) or their THF complexes gave rise to yellow crystalline products.[51] These products were formulated as dinuclear metallopinacols on the basis of analytical, molecular weight, and IR data.

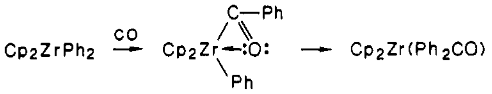


$$\begin{array}{l}\mathrm{Cp(X)_2TiOC(R)(R')} \\ \qquad\qquad | \\ \mathrm{(R)(R')COTi(X)_2Cp}\end{array}$$

This structure was later confirmed crystallographically.[52] The reaction with benzophenone took a different course, however. The reversible reaction with benzophenone gave a monomeric complex, which gave benzophenone upon dissolution in THF, hydrolysis, alcoholysis, or thermal decomposition. Reversibility was never seen for the other carbonyl compounds, and hydrolysis or alcoholysis always gave pinacols.

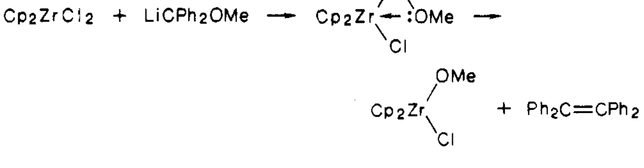
B. Zirconium and Hafnium

Although analogous metallopinacols of benzophenone have been postulated in the reductive coupling of benzophenone to tetraphenylethylene, no metallobenzopinacols have been isolated. This is presumably due to the increased steric bulk of the phenyl group over the alkyl groups typically isolated, although electronic factors could also play a role. Complexes of benzophenone have been isolated by Erker; however, they were not prepared from benzophenone.[53] Thermolysis of phenylbenzoylzirconacene $Cp_2Zr(Ph)COPh$ (prepared via carbonylation of Cp_2ZrPh_2) at 70 °C gave the



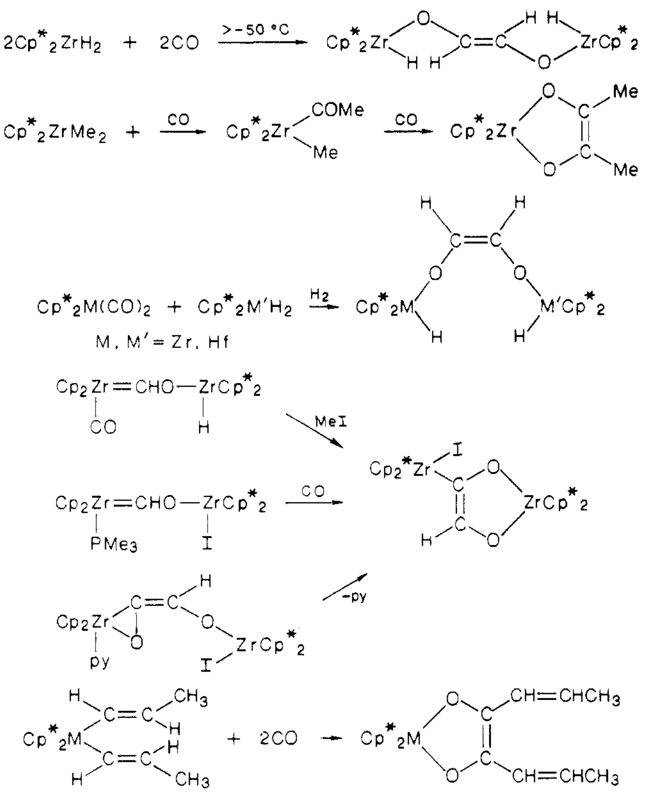
η^2-benzophenone complex $Cp_2Zr(Ph_2CO)$, which exists in equilibrium with the thermodynamically favored dimer. The X-ray crystal structure of this dimer has been reported.[54] Treatment of this complex with water or protic acids gave benzhydrol.

The zirconacene benzhydryl methyl ether complex $Cp_2Zr(Cl)CPh_2OMe$ (prepared from Cp_2ZrCl_2 and $LiCPh_2OMe$ in Et_2O), which shows coordination of the ether oxygen to the zirconium, exhibits an interesting thermally induced rearrangement.[55-57] At ambient temperature, slow reaction of this complex ($t_{1/2}$ = 48 h) gives $Cp_2Zr(Cl)OMe$ and tetraphenylethylene. These same products can be produced by treatment of the previously described benzophenone complex $Cp_2Zr(Ph_2CO)$ with MeCl. These results show that coordinated benzophenone can be induced to couple to give tetraphenylethylene.

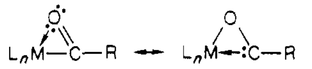


The group 4 metals zirconium and hafnium have been used quite extensively by Bercaw in effecting a variety of different types of carbonyl coupling reactions.[58-65] These reactions are summarized in Scheme III. The

SCHEME III. Organometallic Carbonyl Coupling Reactions of Zirconium and Hafnium

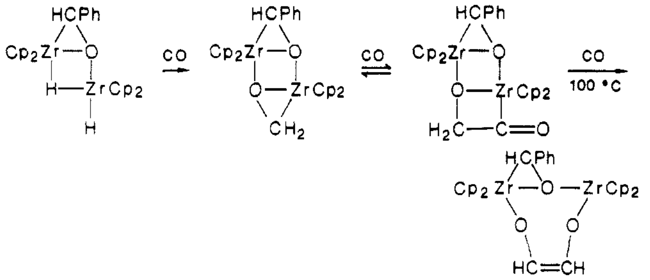


highly oxophilic nature of these metals gives rise to η^2-acyl coordination modes, whereby the metal center experiences coordination by both the carbon and oxygen of the carbonyl. This coordination mode can be written in terms of the following resonance structures:

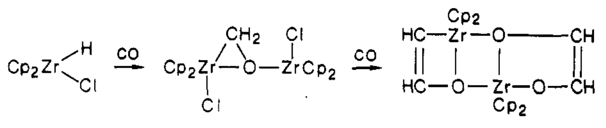


The importance of the oxycarbene resonance structure gives η^2-acyl species unique reactivity at the carbon atom of the carbonyl and permits the carbon–carbon bond formations that these organometallic complexes exhibit to occur.

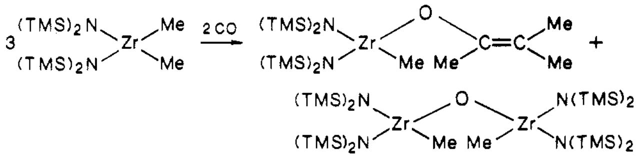
Carbonylation of the 1:1 adduct between monomeric Cp_2ZrH_2 and the (η^2-benzaldehyde)zirconacene unit ultimately gave a *cis*-enediolate complex in which the benzaldehyde ligand was resistant to attack of CO.[66,67]



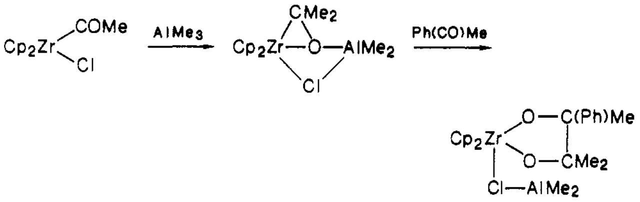
The carbonylation of $Cp_2Zr(H)(Cl)$ was reported to give the bridging formaldehyde complex $[Cp_2ZrCl]_2(\mu\text{-}CH_2O)$, which was further carbonylated slowly at atmospheric CO pressure in THF, giving a complex proposed to be an enediolate dimer.[68]



The reaction of $[(TMS)_2N]_2ZrMe_2$ with CO resulted in the formation of the zirconium oxide $[((TMS)_2N)_2ZrMe]_2O$ as well as the carbonyl coupling product $[(TMS)_2N]_2Zr(Me)(OC(Me){=}CMe_2)$.[69] Formation of this structurally characterized product by carbonyl coupling was confirmed by labeling experiments. Surprisingly, the hafnium analogue did not react with CO under these conditions.

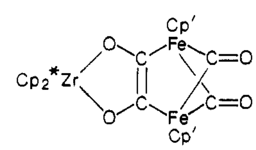


A zirconium–aluminum acetone complex has been cross-coupled with acetophenone to give a product arising from carbonyl coupling.[70] The aluminum reagent

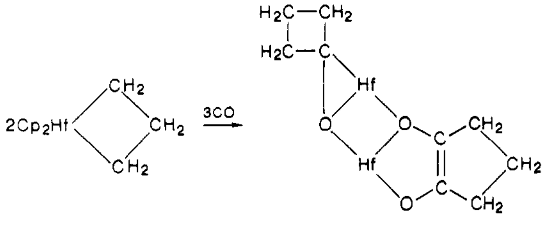


($AlMe_3$) was described as performing a dual role in this reaction. It acts as a reagent in the formation of the ketone complex (from an acetyl complex), and it stabilizes and prevents dimerization of the ketone complex by coordination to the ketone ligand. In the absence of coordinated aluminum, group 4 ketone complexes dimerize readily and are much less reactive than monomeric ketone complexes.

In 1982, Berry and Bercaw discovered a new type of coordinated carbonyl coupling whereby two carbonyls on different metal centers in a binuclear complex can be coupled upon addition of an early-transition-metal center.[71] Upon treatment of $[Cp'Fe(CO)_2]_2$ ($Cp' = \eta^5\text{-}C_5H_4R$) with 0.5 equiv of $[Cp^*_2ZrN_2]_2N_2$ ($Cp^* = C_5Me_5$) the trinuclear complex $Cp^*_2Zr(CO)_4Fe_2Cp'_2$ was isolated. This complex has been structurally characterized and the $ZrO_2C_2Fe_2$ unit found to be approximately coplanar. Removal of the Cp^*_2Zr moiety (as $Cp^*_2Zr(CO)_2$) by addition of CO uncouples the carbonyls of the dinuclear iron complex.



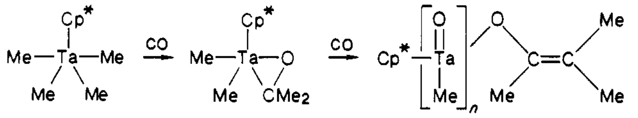
The hafnium metallocyclobutane complex $Cp_2Hf(CH_2)_3$ rapidly takes up 1.5 equiv of CO under ambient conditions to give an unusual product.[72]



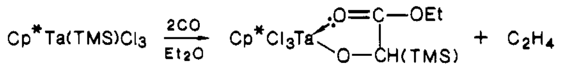
C. Niobium and Tantalum

Niobium and tantalum complexes have also been used to couple carbonyl ligands, although not nearly to the extent that group 4 metals have.

The Cp*TaMe$_4$ complex was the first complex of tantalum to exhibit carbonyl-coupling reactions.[73] When this complex was treated with CO, 1 equiv was rapidly taken up, giving an η^2-acetone complex. This complex absorbs a second mole of CO more slowly at 25 °C to give an oligomeric enolate complex resulting from carbonyl coupling. This result was verified by ^{13}C labeling. Crossover experiments (with CD$_3$) were also conducted, showing that the reaction was intramolecular and that there was no methyl group scrambling. Reaction of the acetone complex with hydrogen quantitatively converted the acetone ligand into an alkoxide, which demonstrates that the Ta–C bond is cleaved (at least with H$_2$) more rapidly than is the Ta–O bond.



The complex Cp*Ta(TMS)Cl$_3$ reacts with two CO in ether, giving a complex resulting from carbonyl coupling and ether cleavage.[74] This was confirmed by ^{13}C labeling. The intermediacy of a silaacyl was suggested by NMR and IR. The silaacyl complex was stable for hours at room temperature in solution but rapidly reacts further in the presence of excess CO. No analogous CO insertion takes place in THF; however, 2-methyltetrahydrofuran does effect the corresponding reaction.



The use of niobium and tantalum complexes to couple carbonyl ligands is illustrated by the reduction of the seven-coordinate complexes M(CO)$_2$(dmpe)$_2$Cl (M = Nb, Ta; dmpe = 1,2-bis(dimethylphosphino)ethane] having cis carbonyl ligands.[75,76] When Ta(CO)$_2$(dmpe)$_2$Cl was treated with excess Mg in the presence of (C$_5$R$_5$)MCl$_2$ (M = Zr, R = Me; M = Ti, R = H, Me) followed by addition of (TMS)Cl, the complex Ta[(TMS)OC≡CO(TMS)](dmpe)$_2$Cl was isolated.[75] This was the first structurally characterized example of an acetylene diether complex. An improved synthesis reported later reduced M(CO)$_2$(dmpe)$_2$Cl (M = Nb, Ta) with 40% Na/Hg in THF or DME, followed by filtration and addition of TMSY (Y = Cl, CF$_3$SO$_3$) to give M[(TMS)OC≡CO(TMS)](dmpe)$_2$Y.[76] Chromatography on alumina resulted in uncoupling of the acetylene diether ligand.

Another tantalum complex has been used recently for reductive coupling of CO. The (silox)$_3$Ta complex (silox = t-Bu$_3$SiO$^-$) (prepared by reducing (silox)$_3$TaCl$_2$ with Na/Hg) reacts with 0.5 equiv of CO at ambient temperature to give a structurally characterized complex formulated as (silox)$_3$Ta=C=C=Ta(silox)$_3$ according to the following stoichiometry:[77]

$$4(\text{silox})_3\text{Ta} + 2\text{CO} \rightarrow 2(\text{silox})_3\text{Ta}{=}\text{O} + [(\text{silox})_3\text{Ta}]_2(\mu\text{-C}_2)$$

This reaction was shown to proceed via an oligomeric [(silox)$_3$Ta=C=O]$_n$ tantalum species and the ketenylidene complex (silox)$_3$Ta=C=C=O by exhaustive ^{13}CO-labeling experiments.[78]

D. Chromium, Molybdenum, and Tungsten

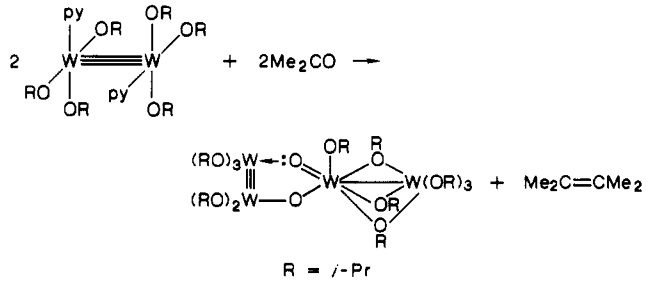
A thermally induced reductive coupling reaction of the acyl carbonyls of bis(η^6-acylbenzene)chromiums has been reported.[79] This report differs somewhat from the others described, in that the carbonyls are not coordinated to the metal in the original complex. The reaction is, however, postulated to take place via coordinated carbonyls. These thermolyses take place at or below the melting point of the particular complexes. The reaction occurs best with the neat complex, although small yields can be obtained in solution. Interestingly, chromium atoms dispersed in a benzophenone matrix and warmed to 135 °C effected very little coupling. The intermediacy of a metallopinacol was ruled out on the basis that these reactions work best with electron-donating groups, thus destabilizing the pinacol. This same trend was taken as indicative that the arene is still coordinated to the metal when the coupling takes place.

$$(\eta^6\text{-PhCOR})_2\text{Cr} \longrightarrow \text{PhCOR} + \text{PhCH}_2\text{R} + \text{Ph(R)C}{=}\text{C(R)Ph} + \text{PhC}{\equiv}\text{CPh}$$

		PhCOR	PhCH$_2$R	Ph(R)C=C(R)Ph	PhC≡CPh
R = H	135 °C	tr		54.7%	
R = Ph	150 °C	40.3%	15.6%	37.6%	
	135 °C				6.3%

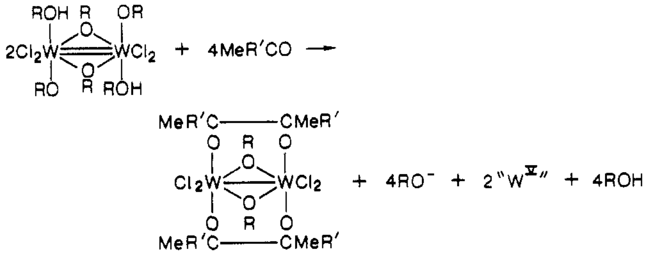
Zerovalent organometallic complexes of tungsten and molybdenum have been shown to couple benzaldehyde to stilbenes in moderate yields.[36] In all cases the yields of stilbenes (E + Z) were less than 63%. W(CO)$_6$ was the most effective complex studied for this transformation. Although the yields are considerably lower than for titanium systems, these complexes have the advantage of being "relatively stable to air".

Dinuclear tungsten complexes with metal–metal bonds have also been used in a few instances to couple carbonyl compounds.[80-82] Multiple metal–metal bonds are able to serve as electron sources, and the dinuclear center is able to serve as a template for assembly of substrate molecules. The fact that carbonyl compounds coordinate well to metal centers facilitates this type of reductive carbonyl coupling reaction. The W$_2$(O-i-Pr)$_6$(py)$_2$ compound with a tungsten–tungsten triple bond has been shown to couple acetone to 2,3-dimethyl-2-butene with the resulting formation of W$_4$O$_2$(O-i-Pr)$_{12}$.[80] The tungsten complex here effects the oxygen extrusion from acetone, but the exact mechanism is not clear.



R = i-Pr

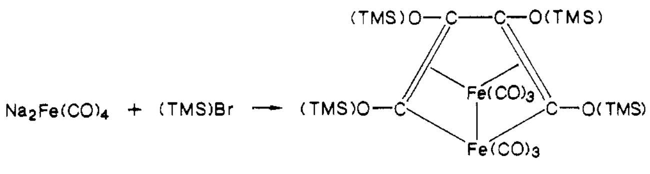
Another multiply bonded tungsten system W$_2$Cl$_4$(μ-OR)$_2$(OR)(ROH)$_2$ (W=W) has been used by Cotton and co-workers to reductively couple two ketones resulting in a complex with a tungsten–tungsten single bond and two pinacol bridges.[81,82] This resulting complex, which has been structurally characterized, is an excellent model for the postulated intermediate in the reactions of McMurry (although the heterogeneous titanium systems may not contain metal–metal bonds). In fact, it is the only structurally characterized example of a dinuclear metallopinacol prepared via reductive coupling of ketones. This reaction proceeds with acetone or methyl ethyl ketone and works with various analogues of the tungsten complex. Reaction of the tungsten complex with 2-pentanone gave a product appearing to be the monopinacol-bridged tungsten complex but was not structurally characterized. Interestingly, this mono(pinacol) complex exhibited much greater solubility in organic solvents (acetone, $CHCl_3$, CH_2Cl_2) than the analogous bis(pinacol) complexes. This reaction seems to be very sensitive to the steric bulk of the ketone used. Thus, the formation of a bis(pinacol) with methyl ethyl ketone vs the formation of a mono(pinacol) with methyl propyl ketone was observed. Attempts to prepare complexes of non-methyl ketones were unsuccessful. The reaction is initiated by displacement of the coordinated ROH ligands by ketone and to this end is greatly facilitated by the presence of acid. The reaction is proposed to occur with the following stoichiometry: half of the starting tungsten atoms forming product, and half supplying electrons and ending up in some other oxidized form.



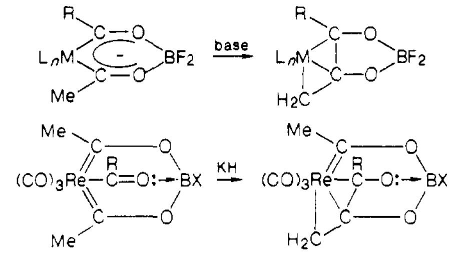
E. Iron, Manganese, and Rhenium

In addition to the use of highly oxophilic early transition metals to effect reductive carbonyl coupling, transition metals that are not as oxophilic may be used under the proper conditions. The use of these less oxophilic transition metals is normally accomplished by use of anionic complexes, or strongly donating ligands.

The first example of a coordinated carbonyl-coupling reaction was demonstrated by Bennett et al. in 1973.[83] When $Na_2Fe(CO)_4$ was treated with (TMS)Br (TMS = Me_3Si), the resulting product contained a ferracyclopentadiene ring with all olefinic carbons substituted by (TMS)O groups. This complex was structurally characterized and was a reformulation of the original report of $(TMS)_4Fe_2(CO)_8$ (prepared analogously from (TMS)I).

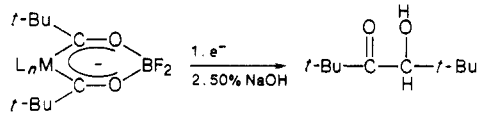


Lukehart has observed the coupling of coordinated acyl ligands upon treatment of metalla-β-diketonate complexes with base.[84-87] The reaction typically proceeds by removal of a proton from the acetyl group, with resulting carbonyl coupling giving an anionic complex. The coupled carbon atoms and the exo-methylene carbon atom generated from deprotonation of the original acetyl methyl group bond to the metal as an allylic ligand. The ML_n fragment can be CpFeCO (Fp), $(CO)_4Mn$, or $(CO)_4Re$. The R group is typically methyl or isopropyl but can also be a cyclohexene prepared from a Diels–Alder reaction on a metallodienophile. A variety of bases can be used such as KH, tetramethylpiperidine, and pyridine. The kinetic deprotonation occurs at the methyl group; however, at low temperatures in nonethereal solvents (CH_2Cl_2) deprotonation of the isopropyl group for the $Re(CO)_4$ analogue has been observed.



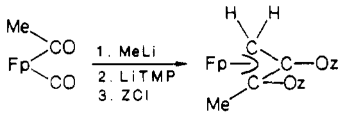
R = Me, *i*-Pr; X = F, Cl

The related di-*tert*-butyl complex, which has no acidic hydrogens, can be reduced either chemically (with Na/Hg, sodium naphthalenide, or sodium benzophenone ketyl) or electrochemically, generating a complex in which acyl ligand coupling has taken place.[88]

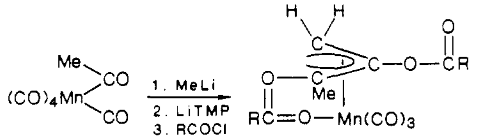


This complex was not isolated, but workup with 50% NaOH gave isolated pivaloin. The isolation of organic products which retain the coupled C–C bond from organometallic carbonyl coupling reactions is quite unusual.

In most of the work by Lukehart, the metalla-β-diketonate is coordinated by a BF_2 group. This BF_2 group is not essential for the reductive carbonyl coupling however. Work has also been done by Lukehart on coupling of carbonyls not coordinated by BF_2 groups.[89] This reaction proceeds by attack of MeLi on a coordinated carbonyl, forming an anionic complex. Deprotonation of this anionic complex is effected by lithium tetramethylpiperidide, followed by quenching with (TMS)Cl, MeCOCl, or PhCOCl.



Z = TMS, MeCO, PhCO

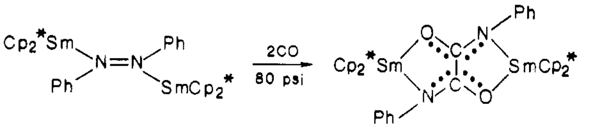


R = Me, Ph

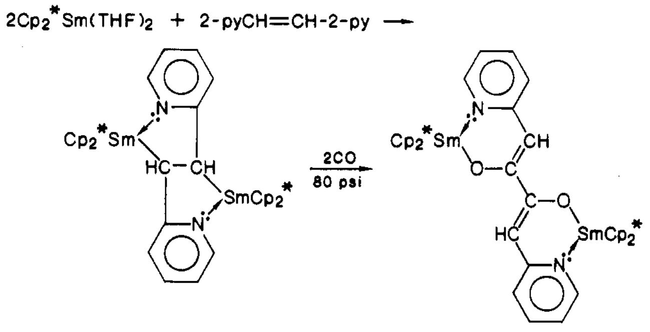
F. Lanthanides

A number of interesting carbonyl couplings have been demonstrated for the lanthanides. As the group 4 metals zirconium and hafnium have been used to prepare enediolate complexes, so have the lanthanides. The lanthanide complex $[Cp^*{}_2SmH]_2$ reacts readily with CO to form enediolate complexes that were isolated as triphenylphosphine oxide adducts.[90] Both *cis*- and *trans*-enediolate complexes were isolated, and the cis complex was found to isomerize to the trans complex in solution.

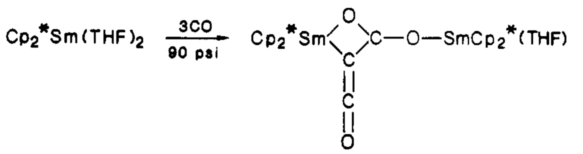
Another formal CO dimerization utilizing lanthanides studied by the Evans group is the double insertion of CO into a samarium azobenzene complex.[91] This interesting azobenzene complex is prepared by the reaction of azobenzene with $Cp*_2Sm(THF)_2$. This azobenzene complex reacts with CO to give a product consisting of the insertion of two CO groups into the N=N double bond of the azobenzene complex!



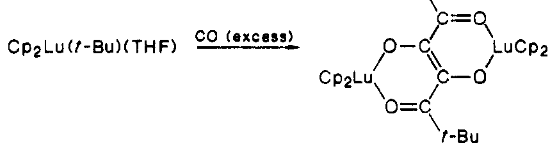
A similar result has been recently reported whereby the same samarium complex activates the alkene RCH=CHR (R = 2-pyridyl) toward double CO insertion to give a complex containing the $RCHC(O)C(O)CHR^{2-}$ unit.[92]



A complex consisting of a formal CO trimerization has also been prepared by the Evans group.[93] This complex can formally be derived from three CO molecules by two one-electron reductions [2Sm(II) → 2Sm(III) + $2e^-$] plus the appropriate couplings. The formation of this complex also requires the cleavage of at least one CO group.



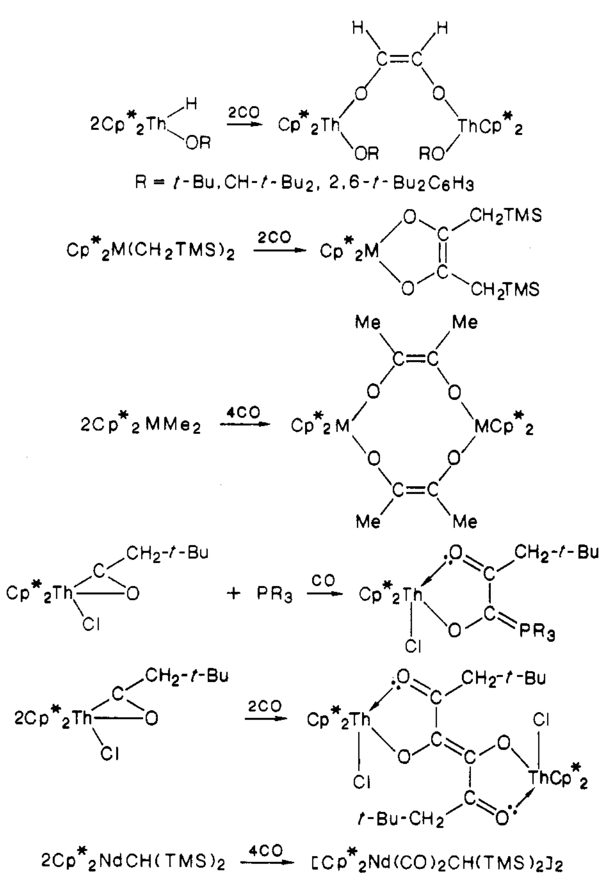
Not only have dimerizations and trimerizations been effected by lanthanides, but the Evans group has also succeeded in carrying out a tetramerization of CO using a lanthanide metal.[94] The reaction of excess CO with Cp_2Lu(*t*-Bu)(THF) at room temperature gave rise to a metal enedionediolate complex whereby the formal coupling of four carbonyls has taken place.



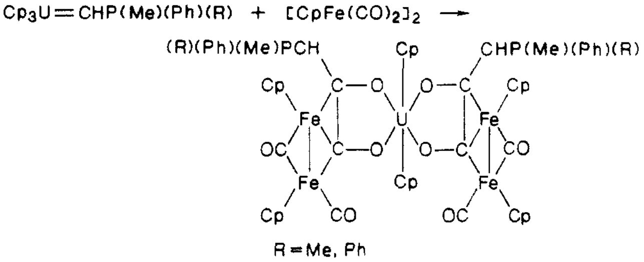
G. Actinides

Coordinated carbonyl couplings have been demonstrated for actinides closely resembling their group 4 transition-metal counterparts by Marks and co-workers (Scheme IV).[95–103] A number of analogues of enediolates have been prepared. With group 4 transition metals and lanthanides, both *cis*- and *trans*-enediolates have been synthesized. In contrast, actinides have shown only *cis*-enediolates. Bis(enediolates) have been prepared with uranium and thorium, which have no counterparts in group 4 organometallics. This shows quite illustratively how the larger, f elements can extend the scope of organometallic chemistry. Particularly noteworthy in this regard is the formal tetramerization of CO effected by the lanthanides and actinides to form enedionediolates. The structure of the thorium enedionediolate has the thorium atoms contained in a 5-membered ring, whereas the lanthanide enedionediolate complex previously described has the lutetium atoms contained within 6-membered rings. A neodymium (lanthanide) enedionediolate complex has also been prepared by the Marks group, but its structure has not been elucidated as to which type of enedionediolate coordination it exhibits.[101]

SCHEME IV. Organometallic Carbonyl Coupling Reactions of Lanthanides and Actinides (M = Th, U)



Just as the $[Cp*_2ZrN_2]_2N_2$ complex was shown to couple the carbonyl ligands of $[Cp'Fe(CO)_2]_2$, the uranium phosphoylide complex $Cp_3U{=}CHPR_3$ also effects carbonyl coupling in the analogous complex $[CpFe(CO)_2]_2$.[104] In this case, however, the uranium complex is able to couple carbonyl ligands in two $[CpFe(CO)_2]_2$ moieties. Each iron complex gives rise to a $\eta^1{:}\eta^3$-allyl ligand created by bond formation between a carbonyl group bonded to iron and $CHPR_3^-$, plus coupling of bridging and terminal carbonyls in the iron dimer. This transformation clearly shows the incredible power of actinides in effecting unusual types of carbonyl coupling



reactions with no precedent in transition-metal chemistry.

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