Chapter 2
Main Types of Organometallic Derivatives

Abstract This chapter describes the various functional derivatives that form the backbone of transition metal chemistry. In each case, the coordination modes of the involved ligand are presented, then the main synthetic routes, the reactivity, and the most useful analytical techniques are described. For metal hydrides, the more specific points concern the η^2-H_2 complexes and the influence of spectator ligands on the acidity–basicity of hydrides in solution. For metal carbonyls, the high lability of the structures is stressed with its consequences for their analysis by IR or ^{13}C NMR. For metal alkyls or aryls, the various decomposition pathways are discussed with a special emphasis on the β-H elimination of importance for polymerization catalysis. The section is completed by a presentation of the uses of the zirconium–carbon bond in organic synthesis. The section on metal carbenes starts by a thorough discussion of the factors favoring the singlet or triplet ground states in free carbenes. Their complexation by transition metals leads to electrophilic (Fischer) or nucleophilic (Schrock) complexes with very different reactivities. Their role in the metathesis of alkenes is highlighted. A similar presentation of metal carbynes and their role in the metathesis of alkynes completes this section. The final section describes some specific π-complexes, η^4-diene-iron-tricarbonyls, ferrocene and η^6-arene-chromium-tricarbonyls which are widely used in organic synthesis.

Keywords Metal hydrides • Metal carbonyls • Metal alkyls • Metal carbenes • π-complexes

2.1 Metal Hydrides

For a long time, the existence of stable metal hydrides was controversial because the M–H bond is highly reactive and was difficult to detect before the emergence of proton NMR spectroscopy. The main coordination modes of hydrogen are indicated below.

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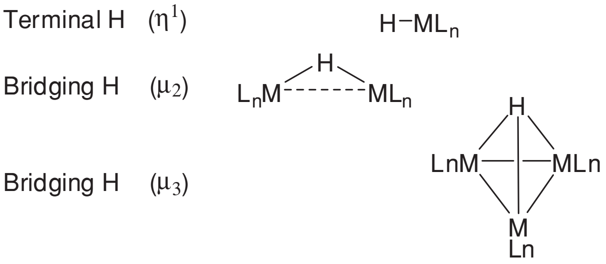
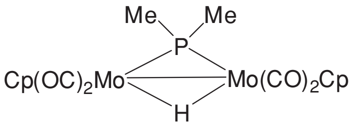
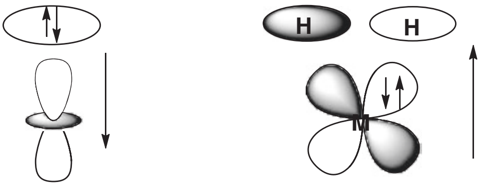


The bridging hydrides are considered as protonated M–M bonds (μ_2) or protonated clusters (μ_3). The M–H–M bond is always bent: M–H–M angle between ca. 80 and 120 °. These bridging species are a little bit delicate to handle for the electron counts. The best way is to count the number of electrons of the ML_n units, count the M–M bond if existing, then add the electrons of H and other bridging ligands.



Mo	6 e
Me_2P	3 e
CO	2 e
Cp	5 e
H	1 e

Here, each metal unit has 15e, the Mo–Mo bond counts for 1, the two bridging ligands share their 4e between the two molybdenum atoms. The other important case concerns the η^2-H_2 complexes discovered by Kubas in 1984 [1]. The bonding can be decomposed into a donation from the H–H σ bond to the d_{z^2} empty orbital of the metal and a back donation from the d_{xz} orbital of the metal to the σ* antibonding orbital of H–H. In order to avoid the cleavage of H–H, this backbonding must be suppressed or minimized. This can be achieved when using metal centers with low d electron counts and electron-accepting ancillary ligands like CO, etc. The existence of the H–H bond in these complexes is established by IR spectroscopy (the stretching frequency of η^2-H–H corresponds to a band around 2700 cm^{-1}), by proton NMR (replacing H–H by H–D and measuring the H–D coupling), and by neutron diffraction.

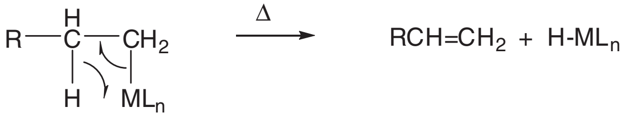


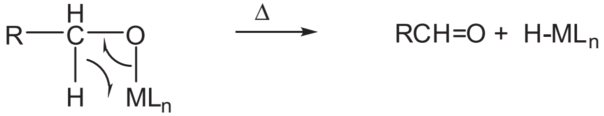
Donation H_2 to M Back-donation M to H_2

The synthesis of hydrides is classical in most cases: oxidative addition of H_2, reduction of M–Cl by $LiAlH_4$ or other source of H^-, protonation, hydrogenolysis of M–M bonds, etc. A good example is the synthesis of the Schwartz reagent which is useful for the hydrozirconation of alkenes:

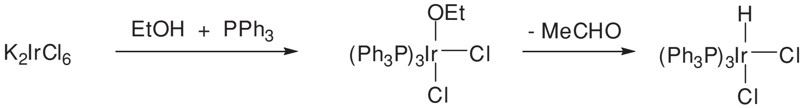
$$Cp_2ZrCl_2 \xrightarrow{LiAlH_4} Cp_2Zr(H)Cl + Cp_2ZrH_2 \xrightarrow{CH_2Cl_2} Cp_2Zr(H)Cl$$

Apart from these classical routes, it is also possible to get hydrides using the so-called β-H elimination. It operates with metal alkyls and metal alkoxides when β-H is available, and also with metal formates and metal hydroxycarbonyls.





This route from alkoxides works only with nonoxophilic metals, mainly from the platinum group (Ru, Rh, Pd, Ir, Pt), for example:



As already mentioned, the best method for detecting the M–H bond is proton NMR spectroscopy. The hydride resonance appears between 0 and −50 ppm (Me_4Si), in a range which is empty for organic groups. The only exception is for d^0 and d^{10} metal hydrides which resonate at low fields (δ positive). The M–H bond is relatively strong; the bond dissociation energy (BDE) varies between 37 and 65 kcal mol^{-1}. Generally, these hydrides are poorly soluble in water and not compatible with this solvent. Nevertheless, $[HCo(CO)_4]$ is an acid as strong as sulfuric acid whereas $[HRe(C_5H_5)_2]$ is a base comparable to ammonia. It must be noted, however, that $[HCo(CO)_4]$ is a genuine hydride in the gas phase (−0.75 e on H). More general and precise data can be measured in acetonitrile as the solvent:

Some pKa in CH_3CN:

$[HCr(CO)_3Cp]$ 13.3 $[HMo(CO)_3Cp]$ 13.9 $[HW(CO)_3Cp]$ 16.1 As can be seen, the hydride character increases with the atomic weight of the metal.

$[HCo(CO)_4]$ 8.4 $[HCo(CO)_3(PPh_3)]$ 15.4

The influence of the other ligands on the metal is enormous. H is more basic when L is a better donor.

Some of the most useful reactions of metal hydrides are given hereafter:

$$M{-}H + CCl_4 \rightarrow M{-}Cl + CHCl_3$$

$$M{-}H + CO_2 \rightarrow M{-}C\,(O)\,OH$$

$$M{-}H + H_2C{=}CH_2 \rightarrow M{-}CH_2{-}CH_3$$

$$M{-}H + HC \equiv CH \rightarrow M{-}CH{=}CH_2$$

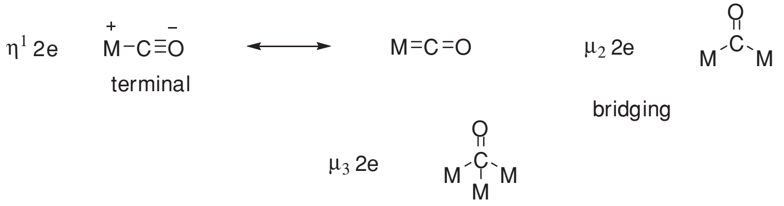
The third reaction is the reverse of the β-H elimination. Metal formyls [M–CHO], which are the primary products of the insertion of CO into the M–H bonds, are unstable in most cases but are important catalytic intermediates.

2.2 Metal Carbonyls

Metal carbonyls have been known since the end of the nineteenth century and are widely used in the chemical industry. A listing of the main stable metal carbonyls is given here. Most of them obey the 18e rule. A notable exception is vanadium hexacarbonyl which is a reactive blue radical which cannot dimerize for steric reasons. Several heavy clusters of osmium are also known [2].

$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^-$	$[Cr(CO)_6]$	$[Mn_2(CO)_{10}]$	$[Fe(CO)_5]$	$[Co_2(CO)_8]$	$[Ni(CO)_4]$
	$[V(CO)_6]$			$[Fe_2(CO)_9]$	$[Co_4(CO)_{12}]$	
				$[Fe_3(CO)_{12}]$	$[Co_6(CO)_{16}]$	
$[Zr(CO)_6]^{2-}$	$[Nb(CO)_6]^-$	$[Mo(CO)_6]$	$[Tc_2(CO)_{10}]$	$[Ru(CO)_5]$	$[Rh_2(CO)_8]$	$[Pd(CO)_4]^{2+}$
			$[Tc_3(CO)_{12}]$	$[Ru_2(CO)_9]$	$[Rh_4(CO)_{12}]$	
				$[Ru_3(CO)_{12}]$	$[Rh_6(CO)_{16}]$	
$[Hf(CO)_6]^{2-}$	$[Ta(CO)_6]^-$	$[W(CO)_6]$	$[Re_2(CO)_{10}]$	$[Os(CO)_5]$	$[Ir_2(CO)_8]$	$[Pt(CO)_4]^{2+}$
				$[Os_2(CO)_9]$	$[Ir_4(CO)_{12}]$	
				$[Os_3(CO)_{12}]$	$[Ir_6(CO)_{16}]$	

As seen earlier, CO which is isoelectronic with N_2, has a high-lying axial lone pair at C which plays the major role in the coordination with a transition metal. The coordination mode can be η^1, μ_2, or μ_3



In some very rare instances, the coordination can also involve the two degenerate π bonds to give 4e and 6e complexes. Metal carbonyls are highly fluxional and can adopt several structures in the solid state and in solution. The classical example is $[Co_2(CO)_8]$ which displays bridging COs in the solid state but none in solution. This difference can be detected by IR spectroscopy.

2069, 2055, 2032 cm^{-1}

solid state: $\nu(CO)$ 2071, 2044, 2042, $\underbrace{1866,\ 1857}_{\text{bridging COs}}$ cm^{-1}

In the same vein, the axial and equatorial COs of the trigonal bipyramidal [Fe(CO)$_5$] cannot be distinguished by ^{13}C NMR in solution at room temperature due to their rapid interchange by Berry pseudorotation as discussed earlier. Their separation occurs at −38 °C in the solid state.

As seen previously, CO has two orthogonal π^* accepting orbitals, hence the existence of a strong backbonding in metal carbonyls. This backbonding has several consequences: (1) the C–O bond is lengthened: it increases from 1.128 Å in free CO to 1.13–1.18 Å in metal carbonyls; (2) the weakening of the CO bond can be monitored by IR spectroscopy since the CO stretching frequency is proportional to the square root of the force constant. In free CO, ν(CO) 2143 cm^{-1}, $k = 19.8$ mdyne/Å, in M–CO (terminal) ν(CO) 1900–2100 cm^{-1}, $k = 17$–18 mdyne/Å; (3) the M–C bond is strengthened and becomes shorter: in [Me–Mn(CO)$_5$], Me–Mn 2.185 Å, Mn–CO 1.80 Å. Overall, CO is one of the strongest π-acceptor ligand; the order is: $\mathrm{NO > CO > RNC \approx PF_3 > PCl_3 > P(OR)_3 > PR_3 \approx SR_2 > RCN > RNH_2 \approx OR_2}$.

The M–CO bond is relatively weak but its strength varies significantly according to the metal: in [Fe(CO)$_5$], the Fe–C bond strength is 27.7 kcal mol^{-1}, in [Cr(CO)$_6$], the Cr–C bond strength is 37 kcal mol^{-1}, in [Mo(CO)$_6$], the Mo–C bond strength is 40 kcal mol^{-1}, and in [W(CO)$_6$], the W–C bond strength is 46 kcal mol^{-1}. As a consequence, metal carbonyls are ideal substrates for substitution reactions. Also, in many cases, clusterization takes place easily by partial loss of CO under heating or irradiation by UV light:

$$\left[\mathrm{Co_2(CO)_8}\right] \xrightarrow{70\,^\circ\mathrm{C}} \left[\mathrm{Co(CO)_3}\right] \rightarrow \left[\mathrm{Co_4(CO)_{12}}\right]$$

$$\left[\mathrm{Fe(CO)_5}\right] \xrightarrow{h\nu} \left[\mathrm{Fe_2(CO)_9}\right]$$

The best analytical tool to detect metal carbonyls is IR spectroscopy. The CO stretching frequencies are in the range 1900–2100 cm^{-1} for terminal COs and 1700–1850 cm^{-1} for μ_2CO's. The technique is both very sensitive and very fast (time constants in the range of 10^{-15} s.), so that it takes a snapshot of the molecule before it can fluctuate. In so doing, it gives information on the local symmetry of the complex. Here are some indications on the correlation between symmetry and CO stretching modes.

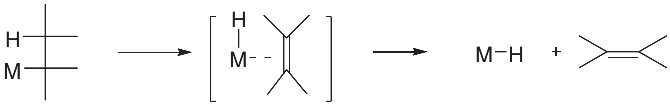
Complex	Symmetry	ν(CO) modes
[Ni(CO)$_2$L$_2$]	C_{2v}	2
Trans [RuX$_2$(CO)$_2$L$_2$]	D_{2h}	2
[CpMn(CO)$_3$]	C_{3v}	2
[Fe(CO)$_3$L$_2$] (axial L)	D_{3h}	1
[XMn(CO)$_5$]	C_{4v}	3
Trans [Mo(CO)$_4$L$_2$]	D_{4h}	1
[Ni(CO)$_4$]	T_d	1
[Cr(CO)$_6$]	O_h	1

It is possible to understand this correlation between the symmetry of a complex and the number of visible CO stretching modes on a simple example. Let us consider the *cis* and *trans* octahedral complexes [M(CO)$_2$L$_4$]. The two COs can vibrate in phase or out of phase. Thus, two bands would be expected in both cases. But in the *trans* case, the in phase vibration induces no change in the dipole moment of the molecule and cannot be detected by IR.

The other technique for the detection of metal carbonyls is ^{13}C NMR spectroscopy. The carbonyl resonances appear in the range 190–230 ppm. But this spectroscopy is slow (time constants in the range of 10^{-1} s.) and gives no reliable information on the local symmetry under standard conditions. For example, at room temperature, the trigonal bipyramidal [Fe(CO)$_5$] gives only one CO resonance at 210 ppm.

2.3 Metal Alkyls and Aryls

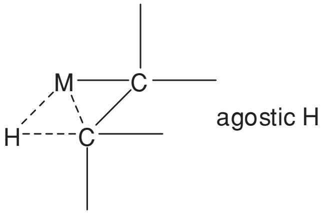
The metal–carbon σ bond is moderately strong (30–65 kcal/mol) but, in general, kinetically unstable because several pathways exist for its decomposition. As a general rule, the orders of thermodynamic stability are M–H > M–R, M–Ar > M–R, and M–Rf(perfluoroalkyl) > M–R. The most efficient decomposition pathway is the β-H elimination:



In order to confer some kinetic stability to the metal–alkyl bond, it is necessary to block this decomposition pathway. There are several possibilities:

(1) To use alkyl groups without β-H: CH$_3$, CH$_2$Ph, CH$_2$CMe$_3$, CH$_2$SiMe$_3$, CH$_2$CF$_3$, etc.
(2) To block the approach of β-H to the metal by steric hindrance or geometrical constraint (R = –C≡C–H linear)
(3) To block the formation of the alkene (when R is 1-norbornyl, the alkene cannot form at the bridgehead according to the Bredt rule)
(4) To block the formation of the alkene–hydride intermediate by using a stable 18e complex that cannot generate the needed vacancy by release of one of its L ligand. For example, in [CpFe(CO)$_2$Et], both Cp and CO are strongly bonded to iron due to a complementary push–pull electronic effect and the Fe–Et bond is stable.

In some cases, even when the β-H elimination appears possible (the M…H interaction can be detected either by spectroscopy or neutron diffraction), the decomposition does not proceed further and the metal alkyl becomes reasonably stable. This type of β-H interacting with the metal is called agostic. The species can be viewed as a loose η^2 complex of the C–H bond.



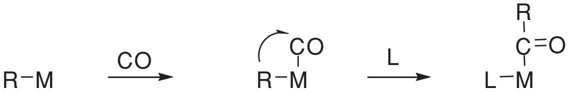
The orbital scheme is similar to that of the η^2-H_2 complexes. In order to stabilize this kind of complexes, it is necessary to suppress the back donation of electrons from the metal to the σ^* orbital of the C–H bond. This can be achieved by using d^0 metal centers. This is the reason why metals like Ti^{+4} and Zr^{+4} are used in olefin polymerization catalysis and in organic synthesis because both need reasonably stable alkyl complexes as we shall see later.

The other decomposition pathways of the M–C bond are the reductive elimination involving alkyl or aryl groups and the α-H elimination that leads to carbene complexes as discussed later.

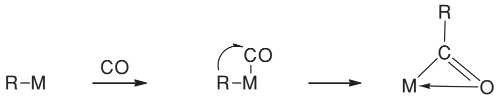
The spectroscopic detection of the M–C bond is not as easy as it is for hydrides and carbonyls. With NMR-active nuclei (spin ½), the ^1J (M–C) coupling is useful. The list of convenient metals is given here.

Spin 1/2	Isotopic abundance
^{103}Rh	100
^{183}W	14
^{187}Os	1.6
^{195}Pt	34

The most useful chemistry of the M–C bonds deals with the insertion of small molecules. Among them, carbon monoxide deserves special attention. The normal scheme is depicted hereafter.



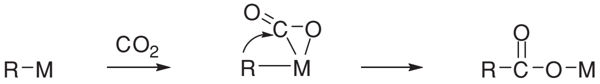
The CO stretching frequencies of the resulting acylmetal complexes appear around 1650 cm^{-1} like for an organic ketone. The situation is different with oxophilic metals from the left of the periodic table:



M = Ti(+4), Zr(+4), etc.

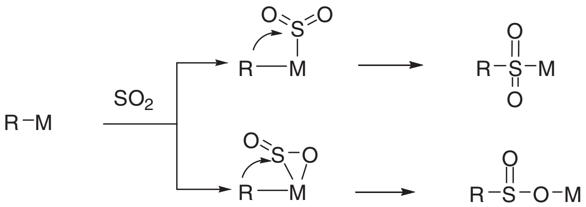
Here, the products are η^2-acyl complexes in which both carbon and oxygen are coordinated to the metal. The acyl group acts as a 3e ligand. The CO stretching frequency is much lower, around 1550 cm^{-1}.

The insertion of CO_2 has also some practical significance. CO_2 gives an η^2-complex and the nucleophilic alkyl attacks it at the positive carbon in the vast majority of cases:



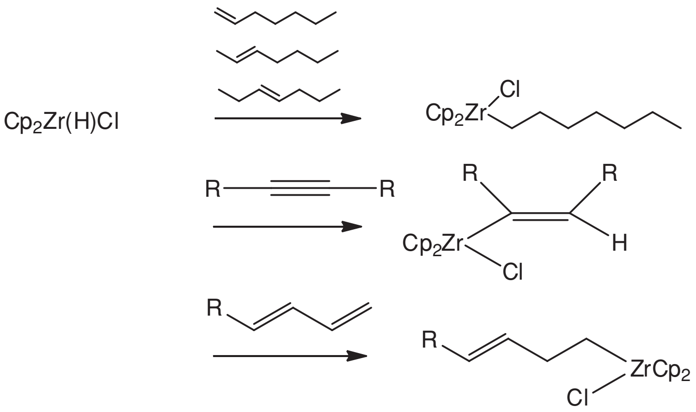
The attack at oxygen giving M–C(O)OR is observed in some rare cases with nonoxophilic metals.

The case of SO_2 is more subtle because there is still a lone pair at sulfur that is liable to give M ← SO_2 complexes. The other coordination mode is η^2 and the final products are either the metallasulfones M–S(O)$_2$R with thiophilic metals (nickel for example) or the sulfinates M–OS(O)R with oxophilic metals (titanium for example). An equilibrium between both types is sometimes observed.

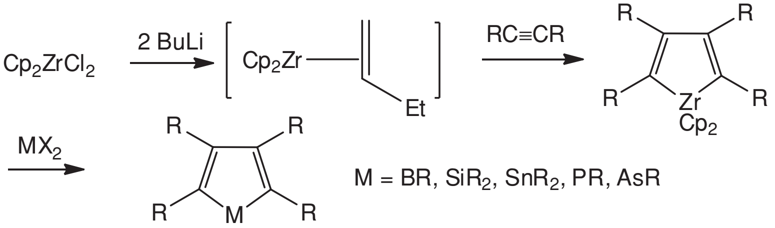


2.4 The Zirconium–Carbon Bond in Organic Synthesis

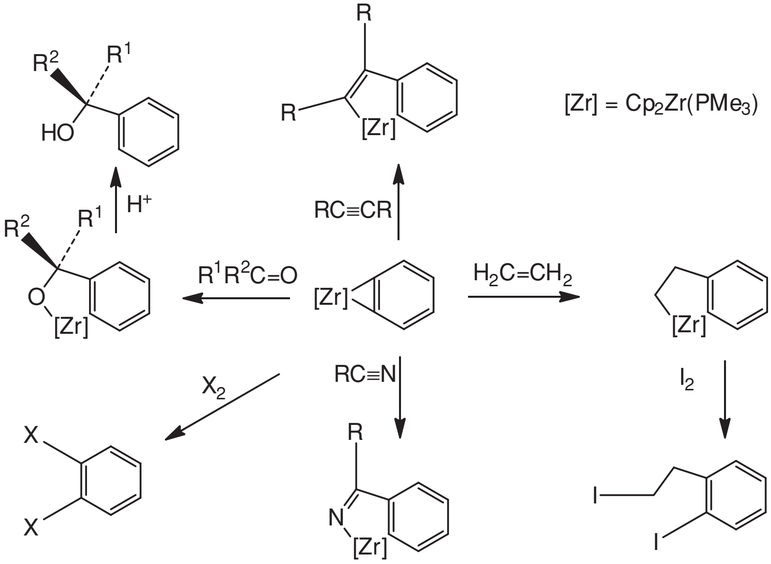
Zirconium combines two features that explain its special role in stoichiometric organic synthesis. It is the most electropositive metal among the transition elements (1.33) at the same level as magnesium (1.31). Its d^0 configuration in its normal +4 oxidation state provides a good kinetic stability to the zirconium–carbon bond by disfavoring the β-H elimination. The Zr–C bond is classically obtained by hydrozirconation of alkenes. The zirconium hydride used is generally the easily accessible Schwartz reagent whose synthesis has been mentioned in the section on hydrides. When using a mixture of internal and terminal alkenes, only the linear alkylzirconium species are obtained, zirconium preferring the terminal position for steric and electronic reasons. With alkynes, the addition of Zr–H is *cis* and zirconium occupies the less hindered position. With conjugated dienes, only the 1,2 addition is observed. The zirconium–carbon bond easily inserts carbon monoxide and isonitriles but does not react with alkyl halides. The cleavage is easily obtained by reaction with acids (formation of RH), bromine, iodine, *N*-chlororosuccinimide (formation of RX) and hydrogen peroxide (formation of ROH). Zirconium can be replaced by another metal using the reaction with metal halides derived from less electropositive metals (Al, Cu, Ni).



Another reagent of choice for the synthesis of the zirconium–carbon bond is the transient zirconocene [$ZrCp_2$] obtained by reaction of butyllithium with the stable zirconocene dichloride Cp_2ZrCl_2. The intermediate Cp_2ZrBu_2 loses butane and yields the η^2 complex of zirconocene with butene. This zirconocene reacts with two molecules of alkynes to give a zirconacyclopentadiene. In turn, this zirconacyclopentadiene can serve to prepare boroles, stannoles, siloles, phospholes, arsoles, etc. by metathesis with the appropriate dihalides.



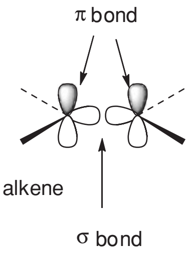
Another topic of interest concerns the stabilization of benzyne. This species has been transiently generated by various techniques in organic synthesis. It gives a stable η^2 complex with zirconocene which is obtained by thermolysis of Cp_2ZrPh_2 at 70 °C (loss of PhH) and further stabilized by complexation with Me_3P. This complex is, in fact, a zirconacyclopropene derived from Zr(+4). The complexed CC bond has the typical length of a C=C double bond (1.36 Å). It displays a rich chemistry as shown below.

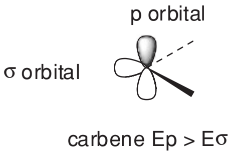


2.5 Metal Carbenes

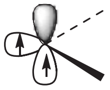
Metal carbene complexes are schematically divided into two classes, the so-called Fischer carbenes, discovered by Fischer in 1964, and the Schrock carbenes discovered 10 years later by Schrock. The Fischer carbenes are characterized by an electrophilic carbon, whereas the Schrock carbenes are nucleophilic. Both types are conventionally represented as having an M=C double bond but this representation is misleading. In fact, the best representation of the Fischer carbenes would display a single dative bond $R_2C \rightarrow M$, the Schrock carbenes being the only ones with a genuine $R_2C{=}M$ double bond. In the first case, the carbene acts as an L ligand and the oxidation state of the metal is 0, whereas in the second case, the carbene is equivalent to X_2 and the oxidation state of the metal is +2.

Before discussing the electronic structures of Fischer and Schrock carbenes, it is necessary to discuss the electronic structure of free carbenes themselves. These 6e species display two frontier orbitals (σ and p) which are shown in the scheme and correspond to the σ and π bond of an alkene which results from the combination of two carbenes.

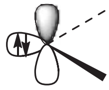




The two electrons of carbon that are not involved in its bonds can occupy the lower σ orbital to give a singlet. Alternatively, each electron can occupy a different orbital to give a triplet. The energies of these two orbitals are close, so the Hund's rule applies (see the section on ML_6 complexes) and states that the triplet is more stable than the singlet because it minimizes the interelectronic coulombic repulsion.

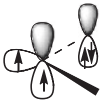


triplet carbene

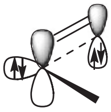


singlet carbene

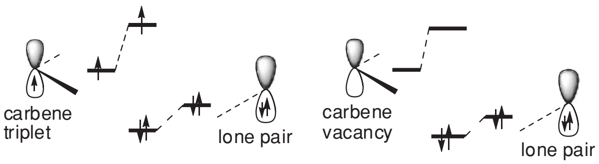
In fact, the triplet state of $[CH_2]$ is more stable than the singlet state by ca. 10 kcal mol^{-1}. The situation changes completely if one (or two) hydrogen is replaced by a lone pair substituent like oxygen or nitrogen. The singlet is strongly stabilized by interaction between the lone pair of the substituent and the vacant p orbital of the carbene whereas no sizeable stabilization occurs in the triplet (one electron is in a destabilized orbital). As a result, the singlet becomes the ground state.



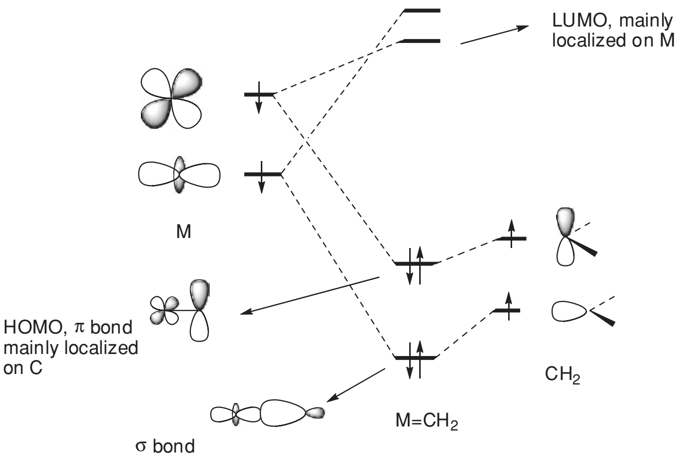
triplet carbene
no stabilization (3e)



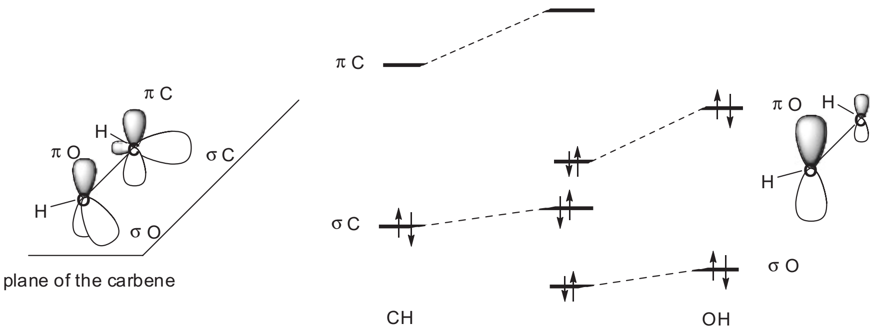
singlet carbene
stabilized (2e)



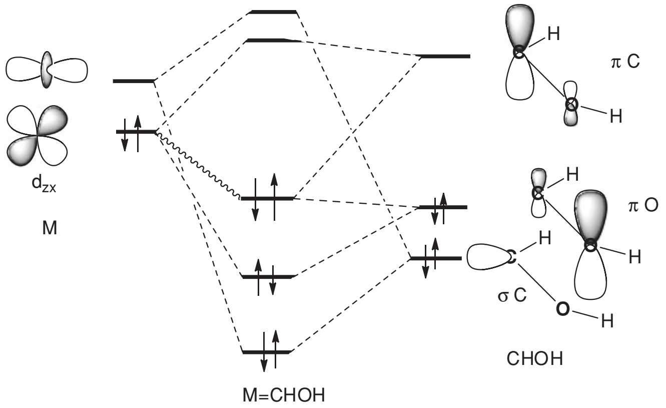
The Schrock carbenes correspond to the combination of a triplet carbene with a triplet metallic moiety as shown. The z axis is the axis of the double bond and the p orbital of the carbene is in the xz plane. The σ orbital of the carbene overlaps with the d_{z^2} of the metal to create a σ bond whereas the p orbital of the carbene overlaps with the d_{xz} orbital of the metal to create a π bond. The HOMO is centered on the carbon which is nucleophilic whereas the LUMO is centered on the metal. The π bond creates a barrier to the rotation around the M=C bond.



The situation is more complex with singlet heteroatom-substituted carbenes. Since the lone pair on the heteroatom is involved, four electrons must be taken into account. The case of [CHOH] is illustrated below. The singlet is more stable than the triplet by 17 kcal mol^{-1}. From an orbital standpoint, water and carbene are similar but the oxygen has two lone pairs, one σ and one π. Since C is less electronegative than O, its frontier orbitals are higher in energy e similar orbitals of O and, thus, are destabilized. The overlap between the two σ lone pairs at C and O is minimal for geometrical reasons. On the contrary, the two π orbitals at C and O strongly interact since they are parallel.

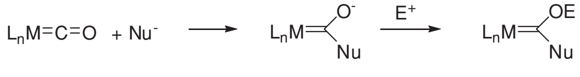


The Fischer carbenes typically involve the combination of a singlet carbene like [CHOH] with a singlet metal moiety. Since σ O is too low in energy to significantly interact with the metal orbitals, it suffices to consider σ C, π O, and π C when building M=CHOH.



σ C is stabilized by interaction with d_{z^2}. This orbital corresponds to the dative bond M ← C. The d_{zx} orbital is stabilized by the interaction with π C and slightly destabilized (poor overlap) by interaction with π O. This HOMO is mainly centered on the metal and corresponds to some backbonding M → C. The LUMO is mainly centered on carbon which is electrophilic. The rotation barrier (backbonding) is weak. These orbital schemes depict some limit cases of nucleophilic and electrophilic carbene complex. In practice, a continuum exits between these two limits and the reality is not so clear-cut. As a general rule, Schrock carbenes are derived from high oxidation state metals (Nb(+5), Ta(+5), W(+6)), the M=C double bond is shorter than the M–C single bond by ca. 10 % and the rotation barriers are in the range 10–15 kcal mol^{-1}. The Fischer carbenes are derived from low oxidation state metals (Cr(0), Mo(0), W(0), Fe(0)), the M–C bond is essentially a single bond and the rotation barriers are very low, ca. 0.5 kcal mol^{-1}.

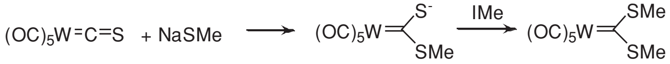
The synthesis of Fischer carbenes supports their theoretical description. The initial synthesis relied on the reaction of organolithium derivatives with metal carbonyls:



$$L_nM{=}C{=}O + Nu^- \longrightarrow L_nM{=}C(O^-)(Nu) \xrightarrow{E^+} L_nM{=}C(OE)(Nu)$$

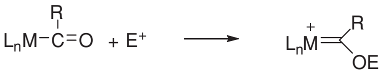
for example: $L_nM = W(CO)_5$, $Nu^- = RLi$ and $E^+ = Me^+ (Me_3O^+)$

Since all the chemistry takes place at carbon, the metal must keep its (0) oxidation state. The intermediate acyl anion has a delocalized negative charge between O (hard) and M (soft), thus a hard alkylation reagent is needed like a trialkyloxonium salt. This chemistry can be transposed to thiocarbonyl derivatives as shown in an example:

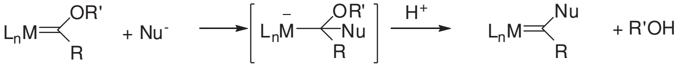


$$(OC)_5W{=}C{=}S + NaSMe \longrightarrow (OC)_5W{=}C(S^-)(SMe) \xrightarrow{IMe} (OC)_5W{=}C(SMe)(SMe)$$

Acyl derivatives can also be used as shown:

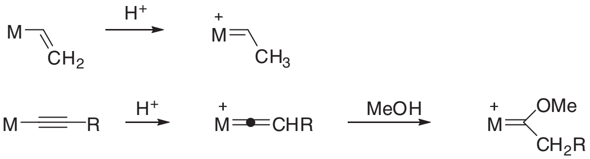


Since the carbon of Fischer carbenes is electrophilic, it can be attacked by nucleophiles. Using this feature, it is possible to exchange the carbene heterosubstituents:



$Nu^- = H^-, R^-, RS^-, R_2N^-$

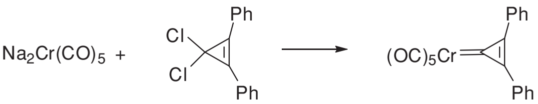
It must be noticed that the resulting carbene complex is, in some cases, neither a typical Fischer, nor a typical Schrock carbene complex. These ‘hybrid’ carbenes have a low stability. The attack of vinyl or alkynyl metal complexes by electrophiles is another route to carbene complexes:



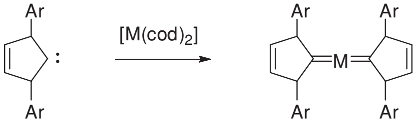
Still another possibility is the electrophilic abstraction of X$^-$:

$M = Fe(CO)(PPh_3)Cp$

In a very limited number of cases, the reaction of a gem-dihalide with a metal dianion can also afford a carbene complex. In the example shown, it is obviously the 2π aromaticity of the cyclopropenylium cation which drives the formation of the carbene complex which is of the Fischer type (electrophilic) even though it has no heteroatom substituent.

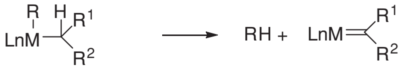


The final solution is to use stable free singlet carbenes. Most of them derive from the imidazole ring and are 6π aromatic systems [3]:



M = Ni, Pt
cod = cyclooctadiene
Ar = 2,4,6-$Me_3C_6H_2$

The Schrock carbene complexes are less accessible than the Fischer type. Their main synthesis relies on the α-H elimination:



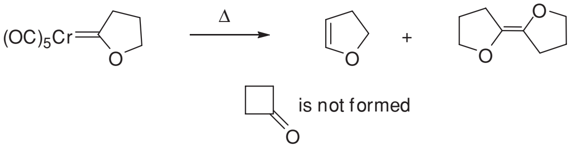
Since the β-H is easier than the α-H elimination, the carbon substituent must be devoid of β-H. R and CH must be cis. The reaction is favored by steric congestion on the metal since it leads to decompression. This is an intramolecular, first-order reaction. The first step involves a 1,2 migration of H from C to M, followed by a reductive elimination of RH, hence M must be electron deficient. The following example is representative.

$$\underset{14e}{Cl_2CpTa(CH_2CMe_3)_2} \rightarrow Cl_2CpTa{=}CHCMe_3 + CMe_4$$

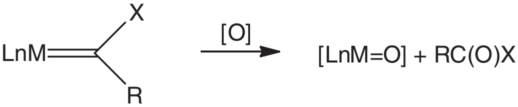
The elimination of CMe_4 is preferred to the elimination of HCl for thermodynamic reasons. The Ta–Cl bond is much stronger than the Ta–C bond.

The best detection tool for carbene complexes is ^{13}C NMR spectroscopy. The Fischer carbenes are found in the range 270–400 ppm (vs. tetramethylsilane), whereas the Schrock carbenes are in the range 225–300 ppm. There is no correlation between the charge at C and the chemical shift.

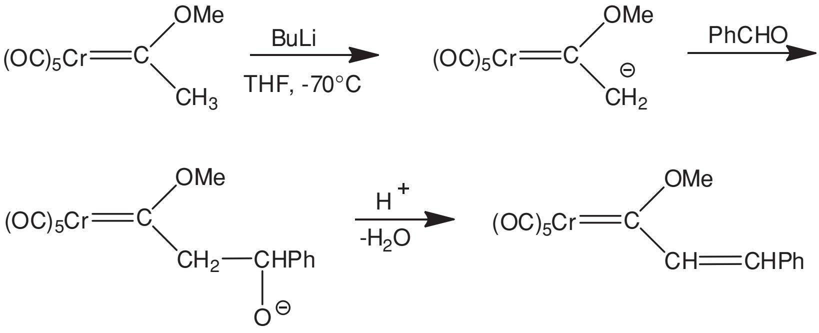
The thermal decomposition of Fischer carbenes yields a mixture of alkenes.



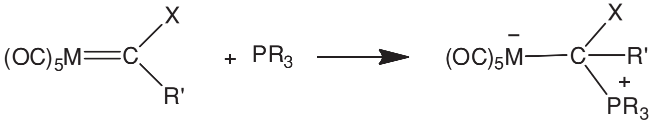
The reaction does not proceed via a free carbene. In the example shown, the free carbene would yield some oxetanone by ring contraction. Mild oxidation (air, Ce(+4), Me_2SO, etc.) yields the corresponding carbonyl derivatives:



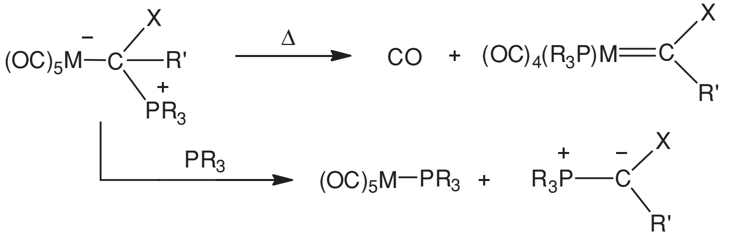
Organolithium derivatives can perform the exchange of the carbenic heteroatomic substituent as shown earlier. They also can act as a base and abstract a proton located in α position to the carbenic carbon. This reaction is favored over the substitution at low temperature.



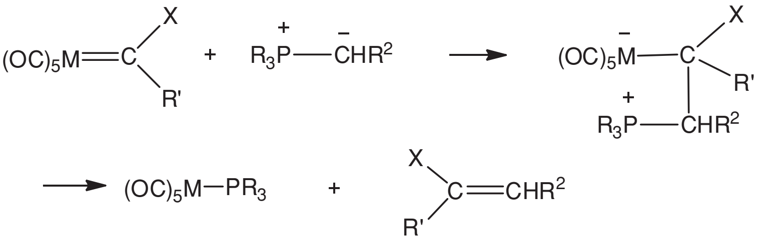
The reaction with phosphines can follow different pathways. The initial attack takes place at the electrophilic carbenic carbon as expected:



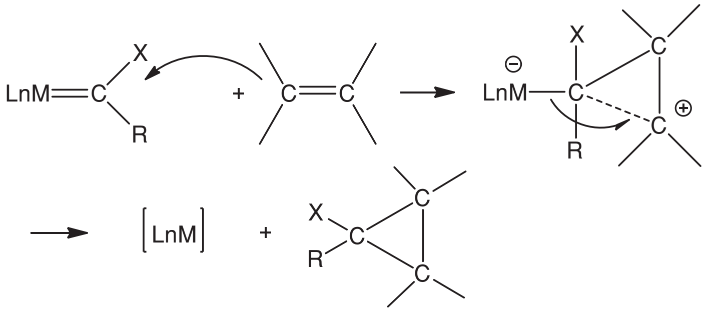
Then, either the phosphine migrates onto the metal or a second equivalent of phosphine displaces the Wittig ylide from the metal:



Wittig ylides can be viewed as a source of nucleophilic carbenes. As such, they can be coupled with electrophilic Fischer carbenes to give alkenes:

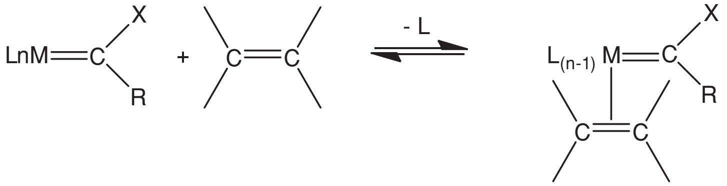


The reaction with alkenes is very sensitive to the substitution schemes of both reagents. In some cases, the alkene reacts as a nucleophile. The attack takes place at the carbenic carbon and the final product is a cyclopropane. The reaction is stoichiometric.

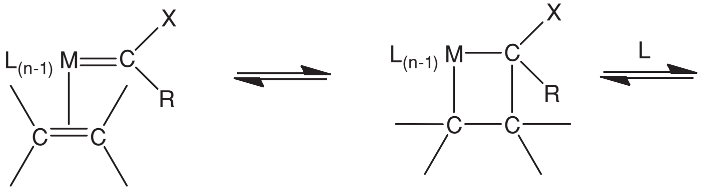


In some other cases, a metathesis is observed, leading to a new carbene complex and a new alkene. The reaction starts by the complexation of the alkene at the metal and is catalytic.

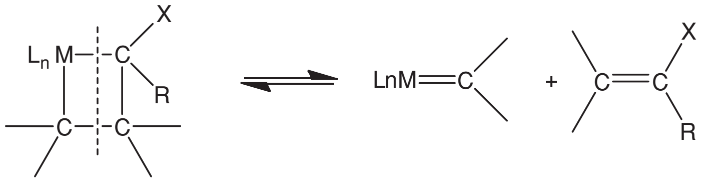
Complexation at the metal



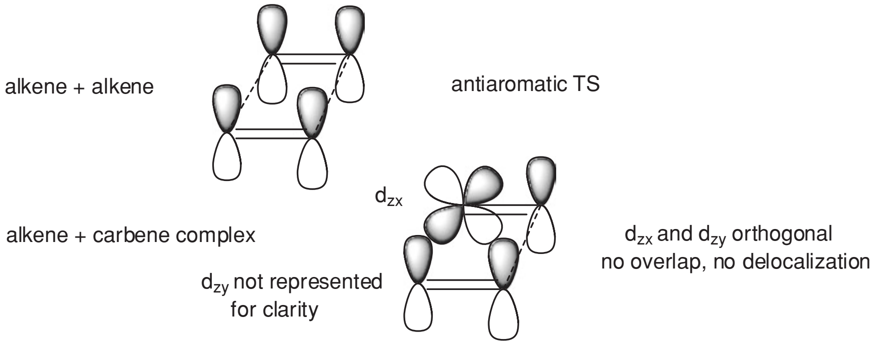
Formation of a metallacyclobutane



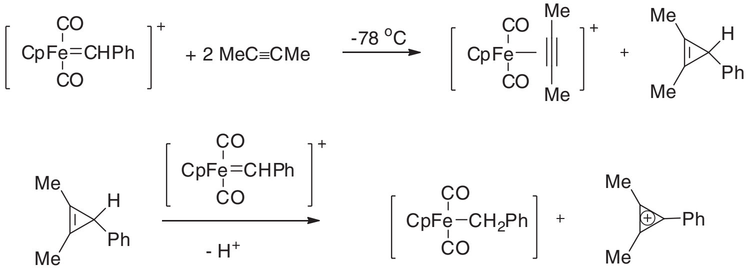
Cycloreversion



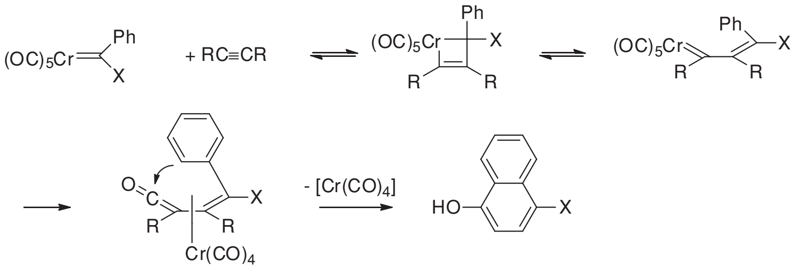
The [2 + 2] concerted cycloadditions are forbidden by the Woodward–Hoffmann rules, so the question which arises is why it becomes possible with a transition metal. The answer is that the interdiction results from the 4π antiaromaticity of the transition state in the alkene + alkene case. The transition metal switches off the delocalization in the transition state which is not antiaromatic anymore. Thus, the [2 + 2] cycloaddition becomes possible.



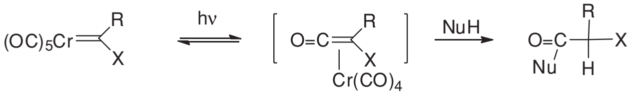
The reaction with alkynes can also lead to a three-membered ring, especially when the initially formed cyclopropene can aromatize to give a 2π cyclopropenylium ion. The cationic iron–carbene complex shown below is so powerful a reagent that it is used in organic synthesis.



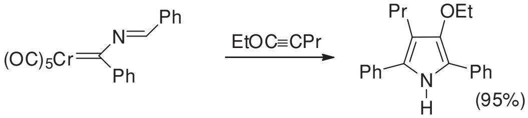
As with alkenes, the other possibility is the formation of a four-membered ring. The metallacyclobutene can evolve by ring opening to give a metallabutadiene. With a phenyl substituent on the carbene, the final product is a naphthol.



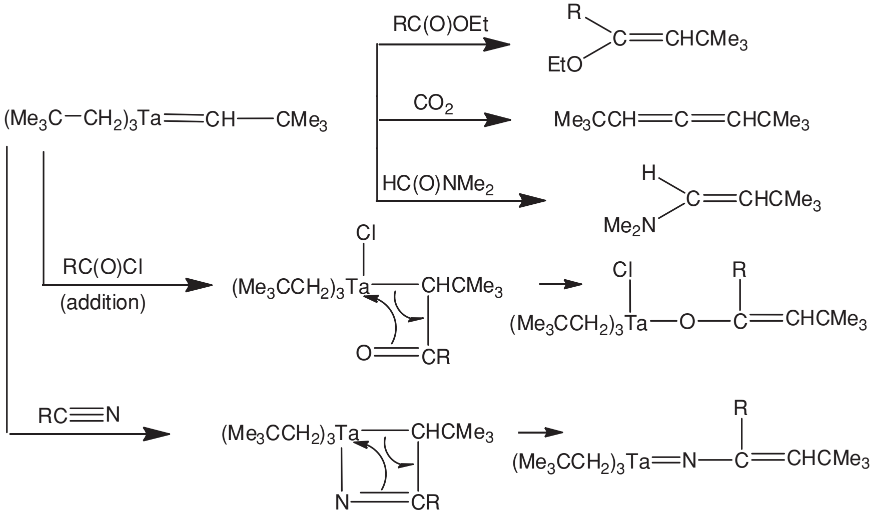
The intermediate ketene complex can be trapped by a nucleophile.



With an imino substituent on the carbene, a pyrrole can be obtained in good yield through a formal [3 + 2] cycloaddition.

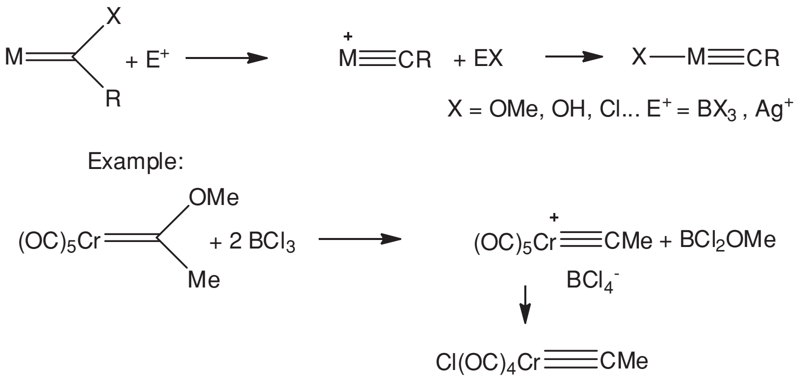


Numerous other synthetic applications of Fischer carbenes are known. Such is not the case for Schrock carbenes which are more difficult to prepare and for which the variety of substituents is more limited. Their widest application is as catalysts for the metathesis of alkenes. This point will be discussed later. Apart from that, they behave as super Wittig ylides. The driving force of the Wittig reaction is the formation of the strong P=O bond (ca. 130 kcal mol^{-1}). With Schrock carbenes, the driving force is much higher: M=O ca. 170–180 kcal mol^{-1}. The examples given hereafter have no equivalents with Wittig ylides. In practice, only the Tebbe's reagent, a stabilized form of [CP$_2$ Ti=CH$_2$], has found some use in organic synthesis.



2.6 Metal Carbynes

Metal carbyne complexes can be obtained from Fischer carbene complexes by electrophilic abstraction:



X = OMe, OH, Cl... $E^+ = BX_3$, Ag^+

Example:

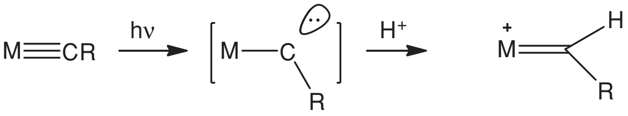
Another, less versatile method, relies on a double α-H elimination promoted by a very high steric congestion on the metal:

$$WCl_6 + 6LiCH_2SiMe_3 \rightarrow (Me_3SiCH_2)_3W{\equiv}CSiMe_3 + 2Me_4Si$$

Other possibilities are the metathesis between M≡M and C≡C triple bonds and the deprotonation of some carbene complexes M=CHR.

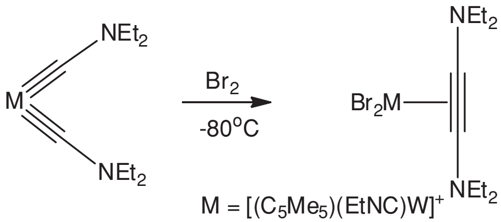
From a theoretical standpoint, a free carbyne [RC] has three frontier orbitals, one σ orbital on the z axis and two degenerate orthogonal p orbitals p_x and p_y of slightly higher energy. Two main electronic configurations are possible. Each of the three available electrons can occupy a different orbital. This configuration behaves as an X_3 ligand (OS + 3, see the tungsten example before). In the second configuration, two electrons occupy the σ orbital and one a degenerate p orbital. The carbyne behaves as an LX ligand (OS + 1). In practice, the difference between the two types of carbyne complexes is minimal.

The chemistry of carbyne complexes is less developed than the chemistry of carbene complexes. The UV irradiation leads to a transient 1e carbyne complex that can be protonated:



Cycloaddition onto the M≡C triple bond is observed with sulfur, SO_2 and $[PtL_2]$. Metathesis of alkynes is possible and is now used in organic synthesis. The coupling of two carbynes within a single coordination sphere to give an alkyne has been demonstrated. The deprotonation of a methylidyne complex to give a carbon complex has been achieved.

$$\mathrm{Cl_3(Et_3PO)W{\equiv}C^tBu + PhC{\equiv}CPh \xrightarrow{70\ ^\circ C} Cl_3(Et_3PO)W{\equiv}CPh + PhC{\equiv}C^tBu}$$



M = $[(C_5Me_5)(EtNC)W]^+$

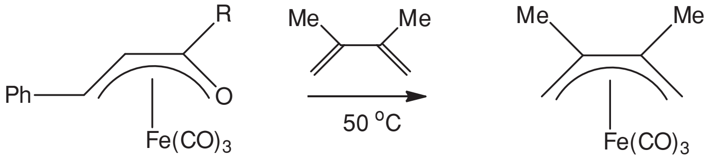
$$\mathrm{(R_2N)_3Mo{\equiv}CH \xrightarrow[THF]{PhCH_2K} [(R_2N)_3Mo{\equiv}C]^-}$$

2.7 Some Representative π Complexes

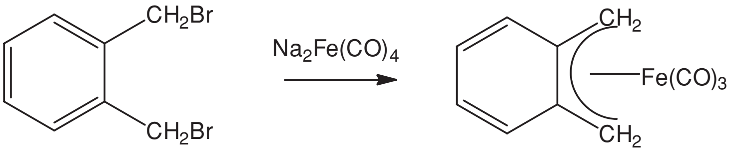
The field of π complexes is so enormous that it is impossible to cover it in any detail within the restricted size of this book. A few representative complexes have been chosen for which some applications in organic chemistry have been developed.

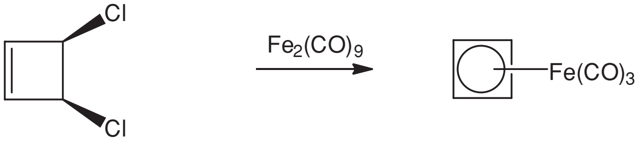
2.7.1 *η⁴-Diene-Irontricarbonyls*

The first complex of this class was discovered in 1930. The preparation is quite simple. It suffices to heat a free diene with an iron carbonyl. The more reactive $[Fe_2(CO)_9]$ is preferred to the rather inert $[Fe(CO)_5]$. It is possible to exchange a complexed diene with a more reactive free diene:



It is also possible to prepare complexes deriving from dienes that are unstable in the free state using *inter alia* the reaction of sodium tetracarbonylferrate with the appropriate dihalides:

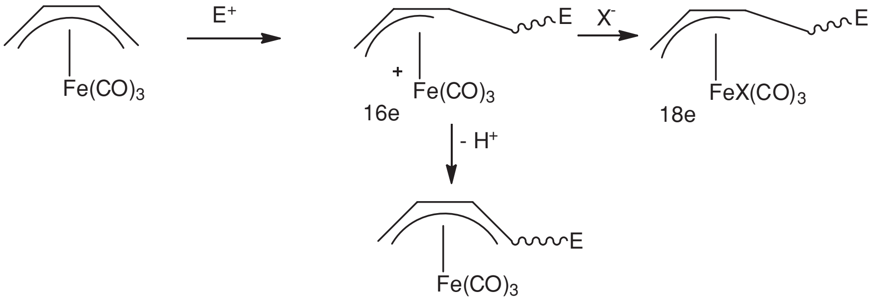




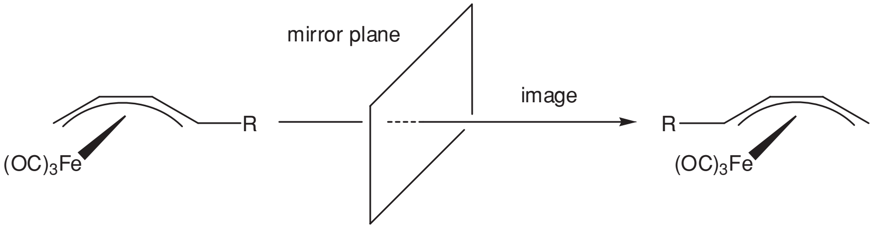
Contrary to the antiaromatic and unstable free cyclobutadiene, its irontricarbonyl complex is stable and aromatic: it formally derives from the 6π aromatic cyclobutadiene dianion. Its discovery in 1958 was a highlight of transition metal chemistry. Its decomplexation by mild oxidation (Ce(+4)) has served to generate free transient cyclobutadiene and develop its chemistry.

In the butadiene complex, the diene is planar and the iron atom is located on an axis perpendicular to this plane at ca. 1.64 Å. The C–C bonds of the diene are equal at ca. 1.40–1.42 Å. The strength of the iron–diene bond is average at ca. 48 kcal mol^{-1}. The NMR data are quite striking. The terminal CH_2 protons are found at 0.22 (*endo*) and 1.90 (*exo*) ppm and the carbon at 41.6 ppm. This huge shielding effect is quite characteristic of the π complexation.

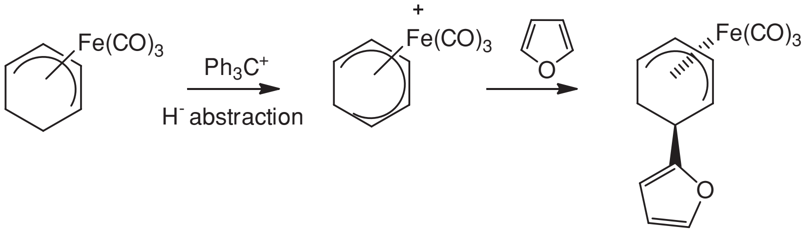
The most significant chemistry is the reactivity toward electrophiles. Two pathways are possible, leading either to η^3-allyl or to functional η^4-diene complexes.



The reaction gives the η^3-allyl complex when X^- has a good coordinating ability (Cl^-) and the diene complex when X^- is not a ligand ($AlCl_4^-$). The acetylation (EX=MeC(O) $AlCl_4$) of butadiene-irontricarbonyl is 3,850 times faster than the acetylation of benzene. The formylation (E=CHO) by HC(O)N(Me)Ph + $P(O)Cl_3$ is also possible. Another point of interest is that, since the two faces of the diene are nonequivalent in these complexes, the terminal carbon atoms become chiral when they are substituted. The complex is, indeed, different from its image as shown. Hence, the possibility to develop some applications in enantioselective synthesis has been explored.

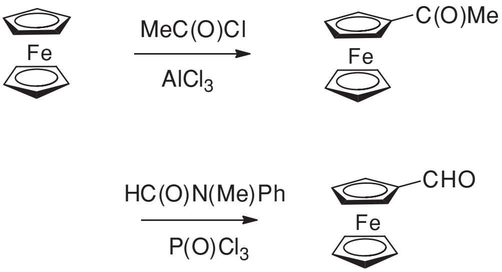


Finally, the easily formed η^5-coordinated α-carbocations can serve to perform electrophilic substitutions on electron-rich arenes.

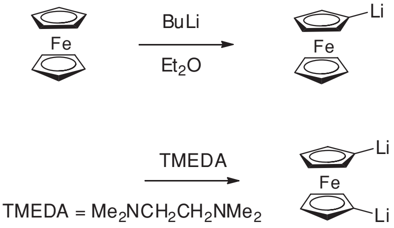


2.7.2 Ferrocene

The discovery of ferrocene in 1951 was a major turning point of transition metal chemistry. This stable orange solid is easily obtained by reacting [CpM] (M = Li, Na, MgBr…) with $FeCl_2$. All the Fe–C bonds are equal at 2.06 Å. The two parallel Cp rings rotate almost freely (barrier ca. 3.8 kJ mol^{-1}). The NMR data shows the characteristic shielding associated with π complexation: δ(H) 4.04, δ(C) 68.2 ppm (in $CDCl_3$). The system is highly aromatic. Both electrophilic acylation and formylation are possible. In fact, the acetylation by MeC(O)Cl + Al Cl_3 is 3×10^6 times faster than that of benzene.



The 1,1′-diacylation on the two rings is also possible but the 1,1′-diformylation is not. The protonation with strong acids takes place at iron as shown by NMR: δ(H)—12 ppm. Mono- and dilithiations are feasible:



Aminomethyl substituents direct the metalation toward the α position by chelation of lithium. Oxidation produces the 17e ferricinium ion. The oxidation is reversible with a midpoint potential $E_{1/2}$ of 0.34 V versus SCE. The α-ferrocenylcarbocations display a very high stability due to a through-space interaction between iron and the cationic carbon. Finally, a ferrocene with two substituents on the same ring is chiral; this is what is called planar chirality. The combination of a very high stability with a very rich functionalization chemistry explains why ferrocene is such a popular building block for the synthesis of a wide variety of polyfunctional ligands used in homogeneous catalysis.

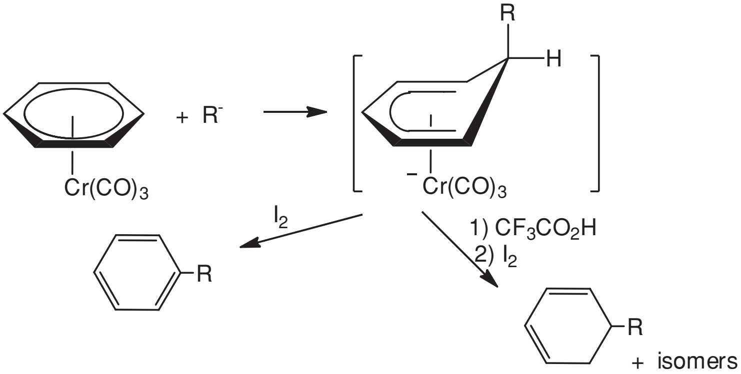
2.7.3 η^6-Arene-Chromiumtricarbonyls

These species are easily obtained by allowing a free arene to react with chromium hexacarbonyl. The reaction is favored by donor substituents and inhibited by acceptor substituents. In difficult cases, $Cr(CO)_6$ is replaced by $Cr(CO)_3L_3$ ($L = CH_3CN$, for example). The decreasing stability order is:

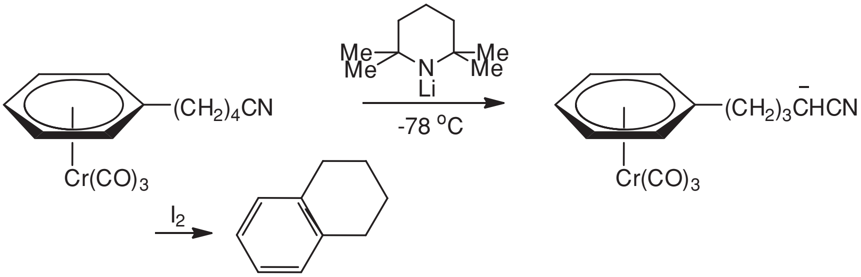
$$\begin{aligned} &Me_6C_6 > Me_3C_6H_3 > Me_2N{-}C_6H_5 > Me_2C_6H_4 > C_6H_6 > MeC(O)C_6H_5 \\ &\qquad > XC_6H_5\ (X = Cl,\ F) > C_{10}H_8 \end{aligned}$$

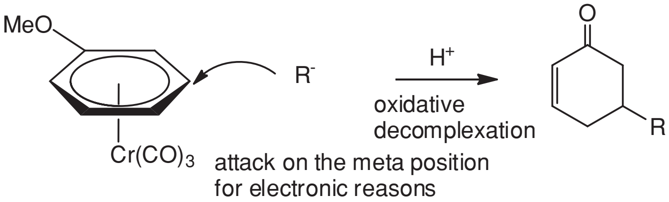
Naphthalene ($C_{10}H_8$) is the easiest arene to replace and this has synthetic applications. The complexes have the structure of a piano stool (Cr–benzene distance 1.73 Å) and can be characterized by IR spectroscopy. They give two bands, the band at low frequency is degenerate and is split when a bulky substituent on the arene breaks the C_{3v} symmetry, for example: $(C_6H_6)Cr(CO)_3$: ν(CO) 1987, 1917 cm^{-1}; $(Me_2N{-}C_6H_5)Cr(CO)_3$: ν(CO) 1969, 1895, 1889 cm^{-1}.

Since the $Cr(CO)_3$ group is strongly electron withdrawing, it activates the arene and its substituents toward the attack by nucleophiles.

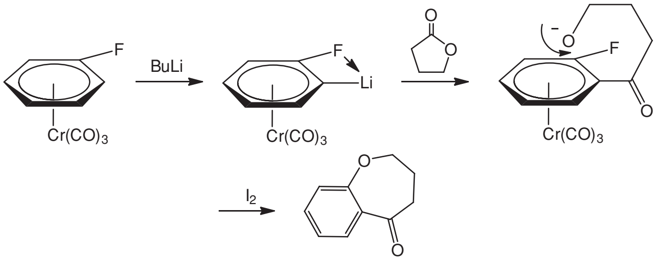


Decomplexation is achieved by mild oxidation. This scheme has numerous synthetic applications. Some of them are shown here.

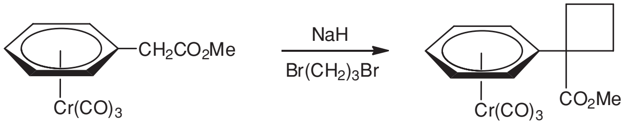




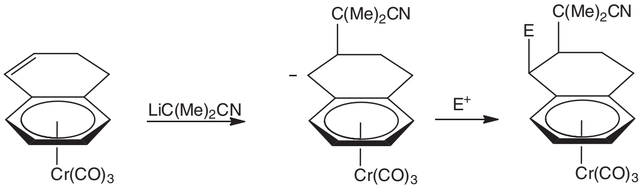
Lithiation needs a directing group in order to be regioselective.



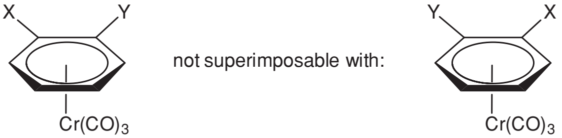
The $Cr(CO)_3$ complexing group also activates the benzylic positions, allowing a facile dimetalation:



The steric bulk of $Cr(CO)_3$ can also be used to control the stereochemistry of the reactions on the side chains:



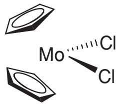
As in the case of ferrocene, an *ortho*-disubstituted derivative with two different substituents is chiral. Many applications of this planar chirality are possible, especially in enantioselective catalysis.



2.8 Problems

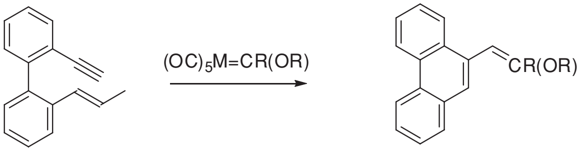
II.1

How would you synthesize $[Cp_2Mo(C_2H_4)Me]^+$ from Cp_2MoCl_2? There is no free rotation of ethylene around its bond with molybdenum. What does that mean? What is the orientation of ethylene with respect to the Mo–Me bond? (use arguments based on orbital interactions). How can you establish this orientation using a classical spectroscopic technique. You have to recall that Cp_2MoCl_2 has a bent metallocene structure.



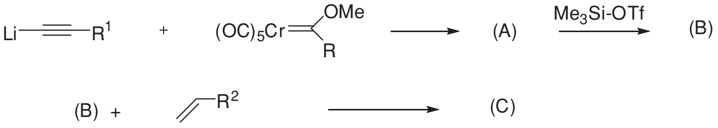
II.2

Propose a mechanism for:



II.3

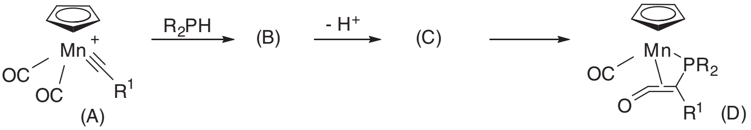
The following stoichiometric chemistry has been performed by Barluenga:



What are the formulas of the chromium complexes (A) and (B) (B does not contain silicon). What are the formula and the two possible stereochemistries of the cyclic organic product (C)

II.4

The reaction of the cationic carbyne complex (A) with a secondary phosphine in the presence of an amine gives the ketene complex (D) (Lugan, Organometallics 2011):



(1) Give the formula of the intermediates (B) and (C).
(2) Propose a mechanism for the last step. What analogy do you find in chromium Fischer carbene chemistry?

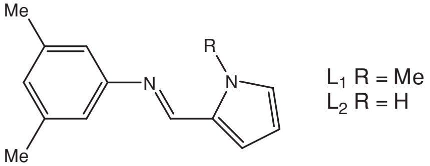
II.5

Cp* stands for η^5-C_5Me_5.

(a) Propose a structure for the complex $[IrCl_2Cp^*]_2$. Discuss the electron count.
(b) Upon reaction with NaOAc (OAc = acetate), $[IrCl_2Cp^*]_2$ gives a monomeric complex. Propose a structure for this monomer.

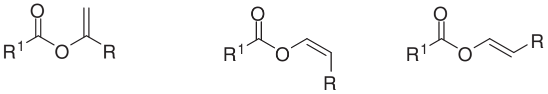
(c) $[IrCl_2Cp^*]_2$ + NaOAc reacts with L_1 to give a single complex A. The ^1H NMR spectrum of A shows two doublets at δ 6.41 and 6.78 ppm due to the pyrrole ring.
(d) The same iridium system reacts with L_2 to give complex B. The ^1H NMR spectrum of B shows three doublets at δ 6.38, 6.78 and 7.17 ppm due to the pyrrole protons. Give the structures of A and B and their mechanisms of formation.

Note: The complexes are mononuclear (one Ir), the oxidation state of Ir stays identical, the backbone of L is preserved.



II.6

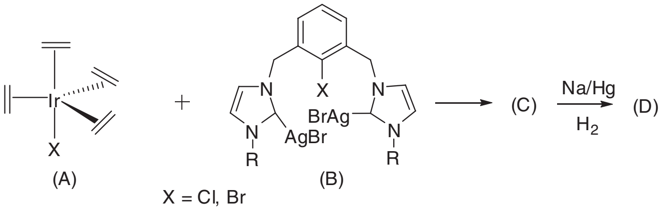
(1) A ruthenium catalyst represented by [Ru] gives two complexes with a primary alkyne R–CC–H. One is a carbene complex. Give the formula of these two complexes and explain the formation of the carbene complex.
(2) The reaction of these two complexes with the carboxylate anion $R^1CO_2^-$ yields three products after protonation and loss of [Ru]:



Explain the formation of these products

II.7 Heinekey et al. Organometallics (2011)

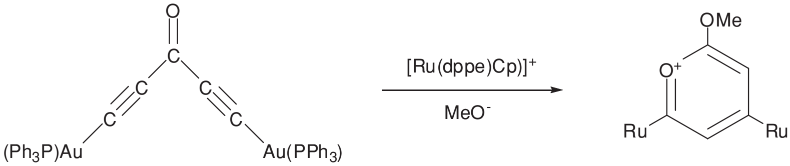
The reaction of the Ir(I) complex (A) with (B) gives a square pyramidal Ir(III) complex. What are the formula and the number of electrons of (C)?



Upon reaction with sodium under hydrogen, (C) gives the octahedral Ir(III) complex (D). This complex shows a single ^1H resonance at −9 ppm (4H). What is the formula and the number of electrons for (D)? Why is only one resonance observed for the hydride? The reaction of (D) with PMe_3 gives another complex (E) with two hydride resonances (1H + 1H), whereas the reaction with pyridine gives (F) with a single hydride resonance (2H). Why?

II.8

The synthesis of an organometallic pyrylium salt has been described (Bruce et al. Organometallics 2011):

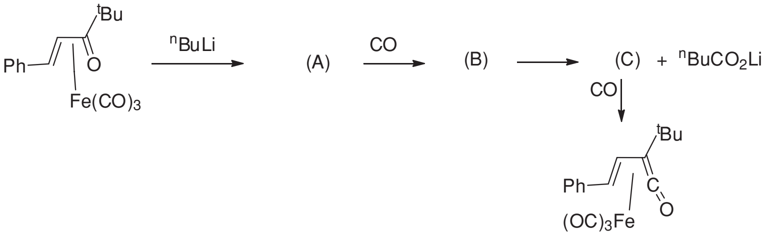


Ru = Ru(dppe)Cp
Cp = η^5–C_5H_5
dppe = Ph_2P-$CH_2CH_2PPh_2$

The proposed mechanism involves first a metal exchange to give (A), then a double protonation to give a biscarbene complex (B). The attack of this biscarbene by methylate anion gives a four-membered OC_3 ring (C) whose rearrangement gives the pyrylium salt. Give the structures of (A), (B), and (C) and comment on the various steps. What is the rearrangement that transforms (C) into the final product?

II.9

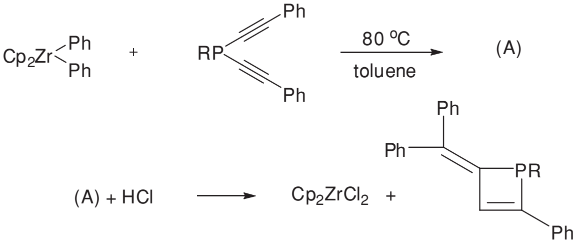
The following reaction sequence has been described (Alcock et al. Organometallics 1991, 10, 231):



(A), (B), and (C) are Fe–carbene complexes. Propose a formula for (A), (B) and (C) and discuss the mechanism for their formation. What reaction described in the book is reminiscent of this transformation?

II.10 Meunier, Majoral et al. Angewandte (1997)

The following reactions have been performed:



What is the formula of (A)? Propose a mechanism for the formation of (A). What is the actual zirconium derivative that reacts with the phosphine?

References

1. Jessop PG, Morris RH (1992) Reactions of transition metal dihydrogen complexes. Coord Chem Rev 121:155
2. Elian M, Hoffmann R (1058) Bonding capabilities of transition metal carbonyl fragments. Inorg Chem 1975:14
3. Crudden CM, Allen DP (2004) Stability and reactivity of N-heterocyclic carbene complexes. Coord Chem Rev 248:2247