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Organometallic Manganese Compounds in Organic Synthesis

Alina A. Grineva[1,2], Noël Lugan[1], and Dmitry A. Valyaev[1]

[1] *LCC-CNRS, Université de Toulouse, CNRS, 31077 Toulouse cedex 4, France*
[2] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky Pr., Moscow, 119991 Russia*

1.1 Introduction

Organometallic manganese chemistry emerged in 1937 with the *in situ* generation of the first Mn(II) species, PhMnI[1], followed by the preparation of two other emblematic Mn(0) and Mn(I) derivatives, $Mn_2(CO)_{10}$ [2] and $CpMn(CO)_3$ [3] in 1949 and 1954, respectively. Despite a long history, this research field remained for many years a purely fundamental area with only sporadic applications in organic synthesis [4, 5] and homogeneous catalysis [6]. The situation started to change rapidly in the late 1970s, and Mn(II) σ-complexes soon became valuable tools for organic synthesis acting as soft and chemoselective nucleophilic reagents. Recent excellent reviews by Gérard Cahiez, one of the pioneers and key players in the field, are available on this topic [7], and therefore it will not be covered in our contribution. Even if the chemistry of Mn(I) complexes directed to organic synthesis is much less developed, some interesting results have been obtained during the last 30 years, but they have never been systematically reviewed. The main goal of this chapter is to provide an overview of the multiple facets of manganese organometallic chemistry, from the information on various metallic precursors and basic reactivity patterns to the design of Mn-containing chiral ligands and application of Mn(I)-mediated processes in organic synthesis.

1.2 Basic Manganese Precursors Relevant to Organometallic Chemistry

Unlike more electropositive alkaline and alkaline earth metals, commercial manganese powder undergoes the insertion across C—halogen bond to form organometallic RMnX species uniquely for highly activated allylhalides and α-halogenated esters under Barbier conditions [8]. Still, the reduction of Mn(II)

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salts MnX_2 or manganates $MnX_2 \times 2LiX$ (X = Cl, Br, I) with metallic Mg [9], Li/naphthalene [10] or Li/2-phenylpyridine [11] systems, and potassium graphite KC_8 [12] was shown to generate *in situ* a very reactive form of metallic manganese, capable of activating a variety of alkenyl-, aryl-, and heteroarylhalide substrates under mild conditions.

Commercially available anhydrous manganese salts MnX_2 represent the simplest manganese-containing starting materials. While $MnCl_2$ and $MnBr_2$ are very stable, MnI_2 is light sensitive, and its commercial form is often considered as too impure for given synthetic applications [7]. Fortunately, this compound can be easily prepared on demand upon reaction of Mn powder with iodine in ether [13]. The solubility of MnX_2 salts in ethereal solvents is markedly different and strongly decreases in $MnI_2 > MnBr_2 \gg MnCl_2$ order. Yet, when necessary, $MnCl_2$ can be easily transformed by refluxing in tetrahydrofurane (THF) into the pink solvated complex $MnCl_2 \times 2THF$ [14], which can be used for the synthesis of Mn(II) complexes, even in toluene [15].

Reactions of MnX_2 with organolithium RLi or Grignard RMgX reagents remain the most convenient route to organometallic Mn(II) complexes. In particular, mixed RMnX, homoleptic R_2Mn, and even manganate $[R_3Mn]^-$ or $[R_4Mn]^{2-}$ species can be obtained, depending on the reagents stoichiometry [7]. In general, their thermal stability follows the trend $[R_4Mn]^{2-} \approx [R_3Mn]^- > RMnX \gg R_2Mn$, and the less stable dialkylmanganese compounds typically decompose by a β-elimination process. However, some stable homoleptic Mn(II) σ-complexes such as $Mn_3(Mes)_6$ [16], (Mes – 2,4,6-trimethylphenyl), or $Mn_4(CH_2tBu)_8$ [17] can be conveniently produced on a multi-gram scale. In contrast to ubiquitous ferrocene, manganocene Cp_2Mn [18] (Cp = η^5-C_5H_5 herein and throughout the chapter) is not stable under ambient conditions due to the strongly ionic character of the Mn–Cp bond and thus has found quite a limited use in synthetic chemistry [19]. We can also mention the highly sensitive complex $[Mn_2(N(SiMe_3)_2)_4]$, yet accessible on a large scale [14], which has been applied recently to the preparation of some Mn(II) amidinate complexes [20] and well-defined clusters [21] using the ability of amide ligands to serve as internal base.

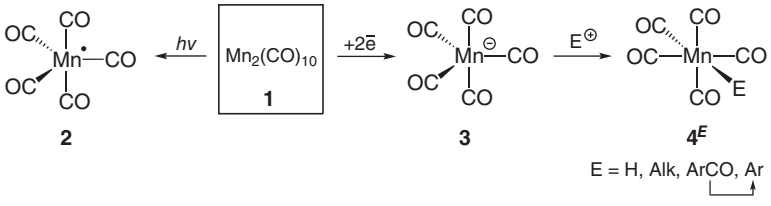
Manganese carbonyl $Mn_2(CO)_{10}$ is the foremost accessible Mn(0) compound, which can be easily transformed into Mn(I) halide complexes $Mn(CO)_5X$ (X = Cl, Br, I) upon the oxidation with the corresponding free halogen [22]. To date, commercially available air-stable $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ remain the most popular manganese precursors, which could be either directly used in catalysis [6, 23] or exploited for the synthesis of various Mn(I) precatalysts [24]. The chemistry of $Mn(CO)_5Cl$ and $Mn(CO)_5I$ is much less developed because of more difficult preparations and lower stability of these compounds. Half-sandwich Mn(I) complex $CpMn(CO)_3$, also known as cymantrene, and its methylated analogue $Cp'Mn(CO)_3$ (Cp′ = η^5-C_5H_4Me), belongs to a few examples of quite sophisticated transition metal organometallic compounds produced industrially at a scale of hundred tons per year as anti-knock gasoline additives. Although their use in such application is currently declining in many countries, technical grade $CpMn(CO)_3$ or $Cp'Mn(CO)_3$ are actually available at a cost 20–30 USD per kilogram from chosen suppliers, analytically pure samples suitable for laboratory use being eventually prepared upon

recrystallization from hexane [25] or vacuum distillation, respectively. The availability and rich reactivity of these organometallic complexes discussed in Sections 1.4 and 1.5 make them attractive candidates for application in organic synthesis.

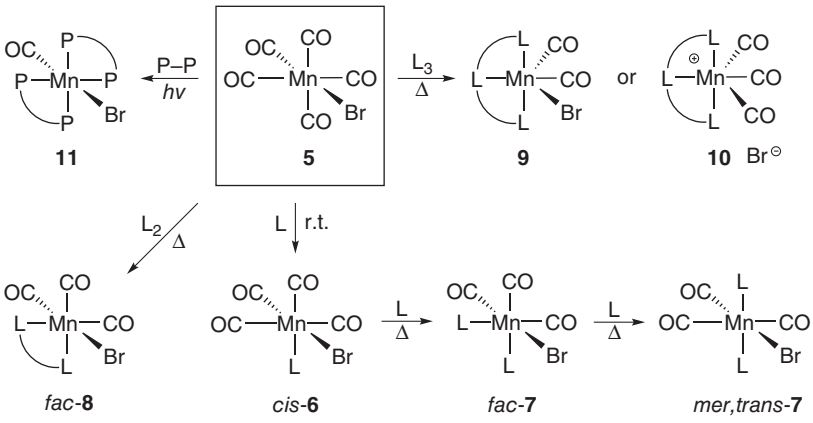
1.3 Overview of the Synthetic Chemistry for Main Classes of Mn(I) Complexes

Besides thermal CO ligand(s) substitution, the most important reactivity pattern of $Mn_2(CO)_{10}$ (**1**) deals with different types of activation of the metal–metal bond (Scheme 1.1). In particular, under UV (350 nm) or visible light (430 nm) irradiation, a smooth generation of the metal-centered radical **2** is achieved; this transformation has recently found numerous applications in photo-induced polymerization processes [26]. In addition to the oxidative Mn–Mn bond cleavage in **1**, induced by halogens already mentioned in Section 1.2, the reduction of this compound with sodium amalgam [27], Na/K alloy [28], or commercial trialkylborohydrides $M[BR_3H]$ [29] (M = Li, K) leads to the formation of anionic metallocarbonylate species **3**. Reactions of the latter with various electrophiles constitute a powerful approach to the synthesis of Mn(I) σ-complexes $Mn(CO)_5E$ ($\mathbf{4^E}$). Upon protonation of **3** with aqueous H_3PO_4, the hydride complex $\mathbf{4^H}$ can be isolated as a volatile liquid [30]. However, due to its extreme air sensitivity and toxicity, $\mathbf{4^H}$ is preferably generated and used *in situ* [31]. Substitution of one or two CO groups in $\mathbf{4^H}$ by P-donor ligands strongly improves the stability of the resulting hydrides $Mn(CO)_{5-n}(L)_nH$ [31, 32]. The alkylation of **3** with MeI proceeds easily to form air-stable $\mathbf{4^{Me}}$, which has been recently applied for expedient preparation of 16-electron Mn(I) complexes of bifunctional pincer ligands [28]. Similarly, the acylation affords isolable σ-acyl derivatives $\mathbf{4^{COAr}}$, which upon heating undergo selective CO deinsertion, providing a viable route to Mn(I) aryl complexes $\mathbf{4^{Ar}}$ [33].

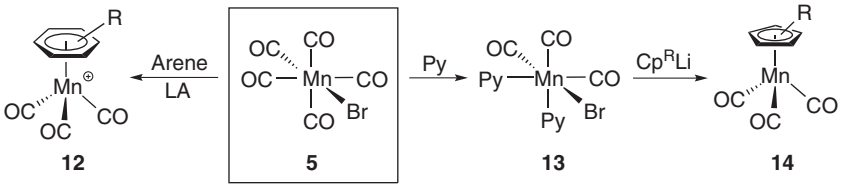
Carbonyl ligand substitution plays a central role in the chemistry of $Mn(CO)_5Br$ (**5**) in the context of the synthesis of various Mn(I) precatalysts (Scheme 1.2) [24]. While the first CO ligand can be easily replaced at room temperature by a donor ligand L to form *cis*-$Mn(CO)_4(L)Br$ (**6**) [34], heating at 50–60 °C is often required to remove the second CO group. For some monodentate ligands, besides the kinetically controlled formation of *fac*-**7** species, formation of more thermodynamically stable *mer,trans*-**7** products can eventually be observed at higher temperatures [35]. Chelating ligands necessarily lead to *fac*-isomers of complexes **8**. The thermal reaction of **5**



Scheme 1.1 Photo-induced and reductive cleavage of Mn—Mn bond in $Mn_2(CO)_{10}$ and the associated reactivity with electrophiles.



Scheme 1.2 Substitution of CO groups in $Mn(CO)_5Br$ with various donor ligands. Source: Garbe et al. [24a]; Mukherjee et al. [24b].

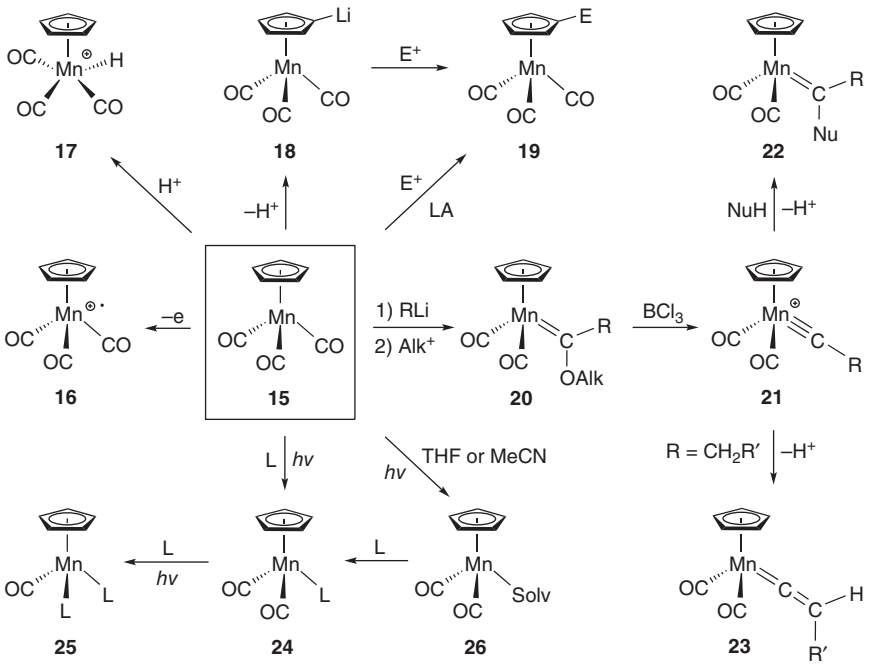


Scheme 1.3 Synthesis of half-sandwich Mn(I) complexes from $Mn(CO)_5Br$

with L_3 pincer-type systems can afford either the neutral dicarbonyl $Mn(CO)_2(L_3)Br$ (**9**) or the cationic tricarbonyl $[Mn(CO)_3(L_3)]Br$ (**10**) complexes upon substitution of three CO or two CO and Br^- ligand combinations, respectively [24]. However, the formation of monocarbonyl Mn(I) species *trans*-$Mn(P{-}P)_2(CO)Br$ (**11**) from **5** and chelating diphosphines involving the substitution of four CO ligands can be achieved only under UV irradiation [36].

Complex **5** is also a useful precursor for the synthesis of half-sandwich Mn(I) complexes (Scheme 1.3). Cationic π-arene complexes $(\eta^6\text{-}RC_6H_5)Mn(CO)_3^+$ (**12**) are easily obtained upon heating **5** with the corresponding aromatic compound in the presence of Lewis acids as bromide scavengers [37]. While for simple arenes, cheap $AlCl_3$ can be typically applied for the generation of "$[(CO)_5Mn^+]$" intermediate, the use of silver salts is essential for a better functional group tolerance [38]. Alternatively, the $[Mn(CO)_5]^+$ synthon can be prepared by the oxidation of $Mn_2(CO)_{10}$ with strong acids under heating in $(CF_3CO)_2O$ [37]. Direct reaction of **5** with cyclopentadienide salts led mostly to its reduction to $Mn_2(CO)_{10}$, but the use of its easily available bis-pyridine-substituted derivative **13** [39] allowed the efficient preparation of substituted cymantrene derivatives **14**, for example, $Cp^*Mn(CO)_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) [40].

Cymantrene **15** can undergo reversible one-electron oxidation at +0.92 V vs. Fc/Fc^+ in a CH_2Cl_2 medium, but the resulting radical cation **16** is much less stable than ferrocenium and therefore has been isolated only recently, using non-nucleophilic $B(C_6F_5)_4^-$ anion (Scheme 1.4) [41]. As expected, the incorporation



Scheme 1.4 General overview of reactivity for cymantrene $CpMn(CO)_3$. Source: Based on Laws et al. [41].

of more donating ligands into the cymantrene moiety decreased the oxidation potentials [42], which can reach −0.3 V vs. Fc/Fc^+ in CH_2Cl_2 for $Cp(CO)_2Mn(NHC)$ derivatives [43], and increased the stability of the resulting 17-electron radical cations.

Reversible protonation of **15** to form the cationic hydride **17** can be achieved only at −100 °C in HSO_3F/CH_2Cl_2 mixture [44]. For more basic analogues such as CpMn(CO)(P−P) bearing chelating diphosphine ligands, even the strength of CF_3COOH (added in excess) is sufficient for the spectroscopic detection of the corresponding hydride species at room temperature [45]. In line with this trend, hydride complex $[CpMn(PMe_3)_3H]BF_4$ obtained by protonation of the corresponding triphosphine precursor could effectively be isolated [46]. Deprotonation of the Cp ligand in **15** upon treatment with alkyllithium reagents and subsequent reaction of the lithiated derivative **18** with various electrophiles represent the main strategy for the modification of the Cp ring in cymantrene [47]. The selectivity in the reaction strongly depends on the choice of base, solvent, and reaction temperature, providing under optimized conditions (*n*BuLi, THF, −80 °C, 1.5–2 hours [48a] or *t*BuLi, THF, −80 °C to −50 °C, 30 minutes [48b]), the Cp-substituted derivatives **19** in 80–90% yield. An alternative approach for the **15** → **19** transformation consists in the use of Friedel–Crafts electrophilic substitution processes. While this method is synthetically valuable for preparation of cymantrenyl (Cym) ketones [49], it generally suffers from a low regioselectivity [50].

Reactions of **15** with organolithium reagents *at room temperature* in ether lead to the selective nucleophilic attack of a carbonyl ligand to form acyl derivatives, the alkylation of which affords Fischer carbenes **20** in good yield [51]. The alkoxy group in the latter can be smoothly removed by the treatment with excess of BCl_3 at low temperature to form cationic carbyne complexes **21** [52]. While complexes $[Cp^{(\prime)}(CO)_2Mn{\equiv}C{-}R]BCl_4$ typically start decomposing above −20 °C and are extremely sensitive to air and moisture, replacing the BCl_4^- counteranion by non-nucleophilic BPh_4^- considerably improves the stability of the resulting salts, allowing, for instance, the isolation of $[Cp^{(\prime)}(CO)_2Mn{\equiv}C{-}Ar]BPh_4$ on *ca.* 10 g scale as a solid, perfectly stable under ambient conditions [53]. Complexes $[\mathbf{21}]^+$ are highly electrophilic species reacting in solution with a wide variety of nucleophiles to form the corresponding Fischer carbenes **22** (see Section 1.5.3 for some examples). Deprotonation of alkyl-substituted derivatives **21** with Et_3N leads to the quantitative *in situ* formation of the manganese vinylidene complexes **23** [52b].

In contrast to $Mn(CO)_5Br$, the substitution of CO ligand in $CpMn(CO)_3$ for two-electron donors requires a photochemical activation ($\lambda < 400$ nm). Again, the replacement of the first CO ligand to get monosubstituted derivatives **24** proceeds easily in aliphatic or aromatic solvents, whereas the formation of the disubstituted species **25** is much less common and can be achieved only with a few phosphines or arsines. The direct substitution of *all* CO ligands in **15** is known uniquely for the molecules having significant π-acidity such as PF_3 [54] or isocyanides [55], whereas carbonyl-free half-sandwich Mn(I) complexes bearing donor phosphorous ligands can be alternatively prepared from Cp_2Mn or $CpMn(\eta^6\text{-}C_7H_8)$ by thermal substitution of the π-ligand [56]. Whether the resulting dicarbonyl products **24** are unstable under irradiation conditions or the reaction proceeds with low selectivity between **24** and **25**, an alternative approach consisting in the preparation of solvate complexes **26** can be employed. In most cases, thermally unstable $Cp(CO)_2Mn(THF)$ is generated *in situ* under UV irradiation at low temperature to provide the best conversion of the starting material, and then the easily dissociating THF ligand in **26** is replaced upon warming to room temperature by the given incoming ligand L. Alternatively, it is possible to use the acetonitrile complex $Cp(CO)_2Mn(NCMe)$, which is isolable on 10 g scale and air-stable in the solid state [57]. While the MeCN ligand substitution can be performed simply under heating, in some cases this reaction may advantageously be carried out instantaneously at room temperature in the presence of a small amount of the oxidant ($Cp_2^{Ac}FeBF_4$) [57] via a redox catalytic process [42b].

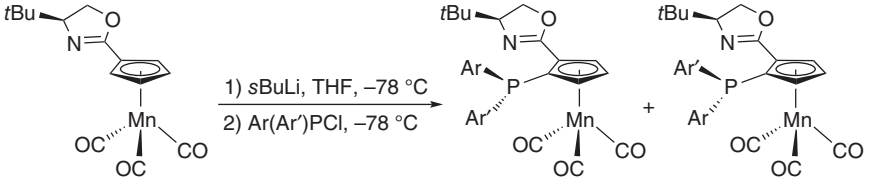
Thanks to a persistent interest of many researchers to fundamental organometallic chemistry since 1960s, now a complete toolbox for "on demand" synthesis of various Mn(I) complexes is available. However, it should be pointed out that this chemistry is sometimes quite delicate and often requires a rigorous purification of the target Mn(I) products in order to obtain NMR data of good quality. Indeed, trace amounts of paramagnetic Mn(II) decomposition products lead to a significant line broadening (sometimes with singlet signal half-width up to 200–300 Hz) in ^1H spectra, thus precluding reliable NMR characterization.

1.4 Planar Chiral Ligands Based on Cymantrene Scaffold

Though the overwhelming majority of bidentate ligands having planar chirality elements are based on ferrocene [58], some interesting results were also obtained from cymantrene scaffold. In 1998, looking for efficient chiral ligands for Pd-catalyzed allylic substitution with cyclic substrates, Helmchen et al. designed the phosphine–oxazoline ligands **28** (Scheme 1.5). Diastereoselective C–H lithiation of the oxazoline-substituted cymantrene **27**, available in two steps from CymCOCl and (*S*)-*tert*-leucenol in *ca*. 70% overall yield, followed by quenching the organolithium intermediate with chlorophosphines afforded the mixture of epimeric P-chirogenic phosphines **28** and **28′**, which were separated by crystallization and column chromatography [59].

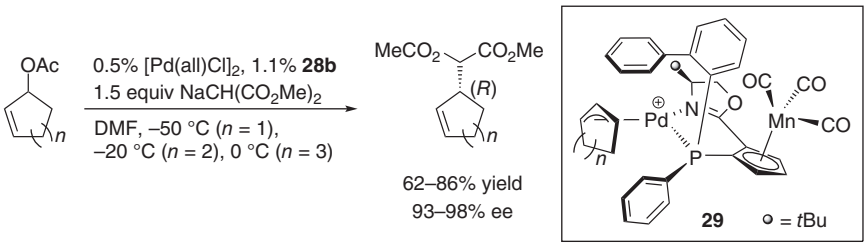
The configuration of the phosphorous atom in these ligands emerged as a crucial factor for the chirality induction in Pd-catalyzed allylic substitution of cyclic substrates. While the use of **28b′** led to only 30% enantiomeric excess (ee), comparable to a similar system showing a benzene spacer between phosphine and oxazoline moieties [60], the catalytic system based on **28b** provided excellent results with 98% ee (Scheme 1.6). Further increase of the steric hindrance (**28a**, 44% ee) or variation of the electronic properties of the aryl substituents (**28c**, 87% ee; **28d**, 92% ee) resulted in a lower asymmetric induction. The outstanding efficiency of the ligand **28b** was rationalized by the stabilization of its specific conformation in the cationic complexes **29** (Scheme 1.6), in which the bulky [$Mn(CO)_3$] fragment forces the 2-biphenylyl group to point toward the π-allyl ligand. The ligand **28b** was then successfully used in the allylic substitution with non-stabilized enolates [61] and for the preparation of building blocks for natural product synthesis [62].

More recently, Kamikawa et al. reported a series of chiral phosphine–alkene ligands **36** (Scheme 1.7) [63]. Starting from optically active acetal **30**, easily available from CymCHO and (*S*)-1,2,4-butantriol [64], the aldehyde (*S*)-**32** was obtained in more than 99.9% enantiomeric purity by a sequence of metallation, bromination, and deprotection steps. The subsequent Wittig olefination, photochemical CO

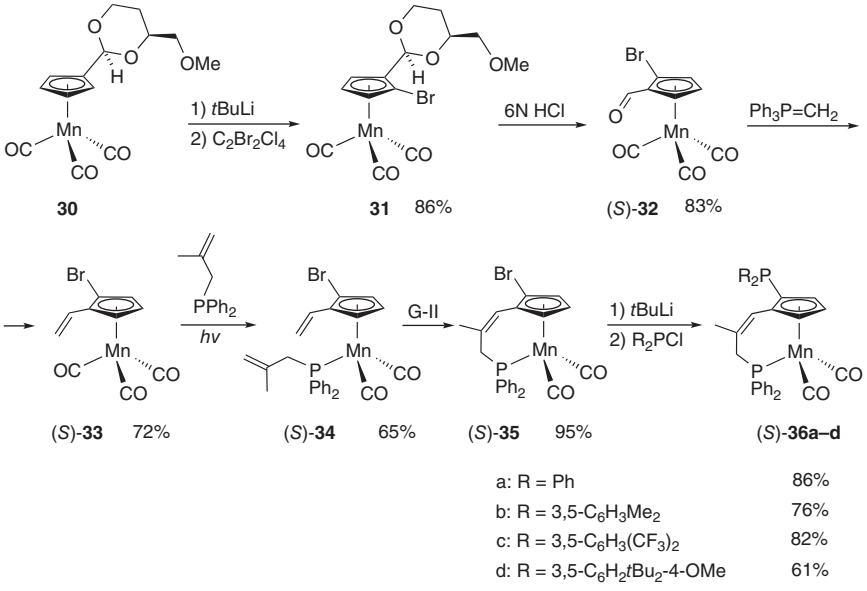


27	28a–d′	28a–d
a: Ar = Ar′ = 2-C_6H_4Ph	–	28%
b: Ar = Ph; Ar′ = 2-C_6H_4Ph	31%	26%
c: Ar = Ph; Ar′ = 3,5-$C_6H_3Me_2$	n.r.	32%
d: Ar = Ph; Ar′ = 3,5-$C_6H_3(CF_3)_2$	n.r.	31%

Scheme 1.5 Synthesis of planar chiral phosphine-oxazoline ligands **28** based on cymantrene scaffold.



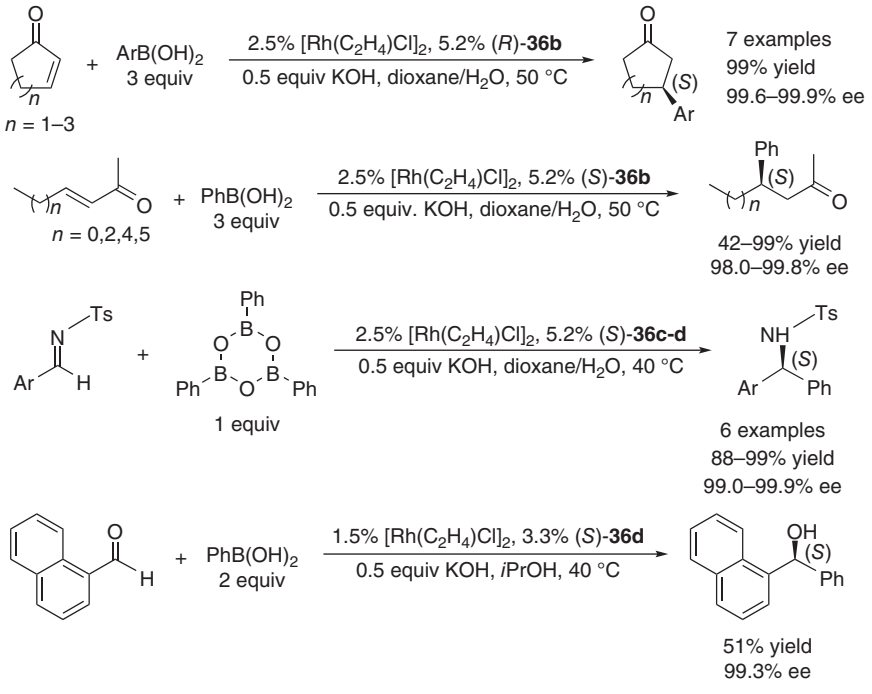
Scheme 1.6 Asymmetric allylic substitution catalyzed by Pd(II) complex bearing cymantrene-based chiral phosphine-oxazoline ligand **28b**.



Scheme 1.7 Synthesis of planar chiral phosphine-alkene ligands **36** based on cymantrene scaffold. Source: Based on Kamikawa et al. [63].

substitution for (methallyl)PPh_2, and ring closing metathesis afforded the key intermediate (*S*)-**35**, which was finally transformed into the target ligands (*S*)-**36** using Grubbs-II (G-II) catalyst bearing different substituents at the phosphorous atom. The corresponding enantiomers (*R*)-**36** were prepared either in the same way starting from (*R*)-**30**, or through the separation of racemic **35** by chiral preparative HPLC.

Phosphine–alkene ligands **36** have appeared extremely efficient in a variety of Rh-catalyzed arylation processes (Scheme 1.8) [63]. In particular, the $[Rh(C_2H_4)Cl]_2$/**36b** rhodium system catalyzes the 1,4-arylation of both cyclic and acyclic enones with arylboronic acids in very high yields and typically more than 99% ee, whereas the use of less bulky **36a** or very crowded **36d** ligands provided only modest enantioselectivity (30–60% ee). In contrast, 1,2-arylation of arylimines using phenylboroxine can be more efficiently performed using ligands **36c** and **36d**. Finally, in the highly challenging 1,2-arylation of aromatic aldehydes, the bulkiest ligand **36d** was the most efficient, providing the best induction level reported to date.

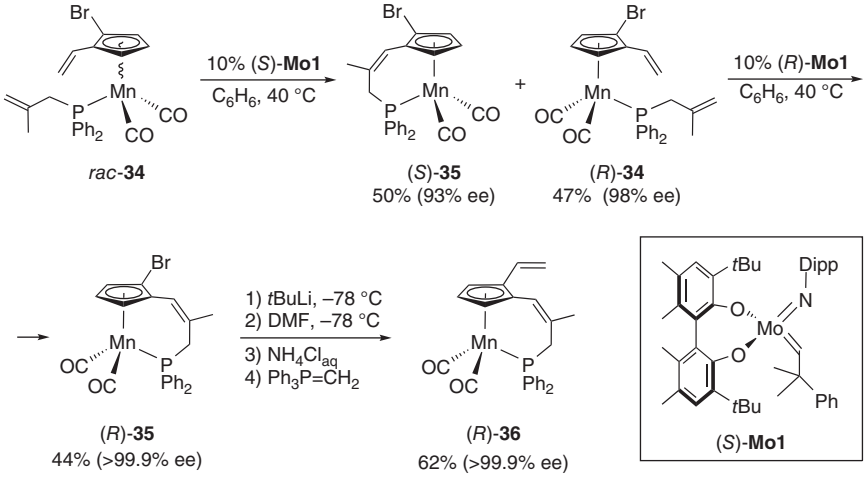


Scheme 1.8 Asymmetric arylation of enones, imines and aldehydes catalyzed by Rh(I) complexes bearing cymantrene-based chiral phosphine-alkene ligands **36**. Source: Based on Kamikawa et al. [63].

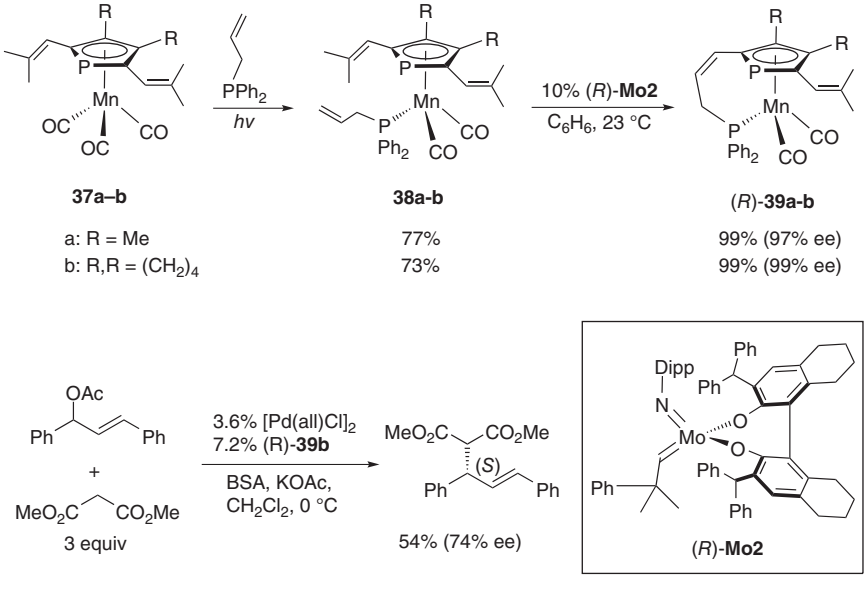
Later on, the same group published an alternative strategy for the preparation of enantiopure alkene-bromide derivatives **35** using kinetic resolution of the racemic complex **34** with optically active Schrock metathesis catalysts (Scheme 1.9) [65]. The catalyst (*S*)-**Mo1** was highly discriminant, cyclizing mainly (*S*)-**34** at the expense of the other enantiomer (selectivity factor $k_{rel} = 127$). The cyclization of the recovered (*R*)-**34** (98% ee) using antipodal (*R*)-**Mo1** catalyst afforded the analogous complex (*R*)-**35** (44% yield from *rac*-**34**, >99.9% ee), which was used for the preparation of planar chiral diene ligand (*R*)-**36** similarly as it was described earlier. Contrary to the previous family of ligands, (*R*)-**36** was much less efficient in Rh-catalyzed 1,4-arylation of cyclohexenone under the same conditions (Scheme 1.8), both in terms of activity (23% yield) and enantioselectivity (52% ee).

Chiral molybdenum alkylidene complex (*R*)-**Mo2** was used for the desymmetrization of C_s-symmetric phosphacyclopentadienyl manganese complexes **38** to give quantitatively the corresponding cyclized products (*R*)-**39** with excellent optical purity (Scheme 1.10) [66]. The preliminary tests for these alkene-phospha Cp ligands in Pd-catalyzed allylic substitution demonstrated the potential utility of these new class of ligands in asymmetric catalysis.

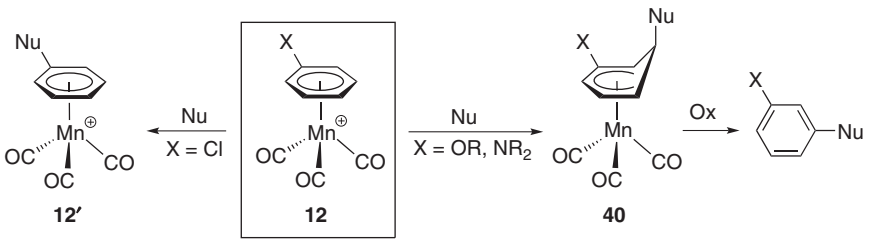
Although ferrocene and cymantrene virtually display the same synthetic chemistry at the Cp ligand, the design of cymantrene-based chiral ligands and their application in homogeneous catalysis still are in their infancy. Yet, cymantrene-derived ligands can have a significant potential of their own due to an easy modulation of the steric bulk of the metal moiety by CO substitution and the possibility to create additional chirality at the metal atom.



Scheme 1.9 Synthesis of planar chiral diene ligands 36 using kinetic resolution with Mo-based ofefin metathesis catalyst as a key step Source: Based on Ogasawara et al. [65].



Scheme 1.10 Synthesis of planar chiral phosphacyclopentadienyl-alkene ligands **39** and their evaluation in Pd(II)-catalyzed asymmetric allylic substitution.



Scheme 1.11 Reactions of cationic Mn(I) π-arene complexes with nucleophiles.

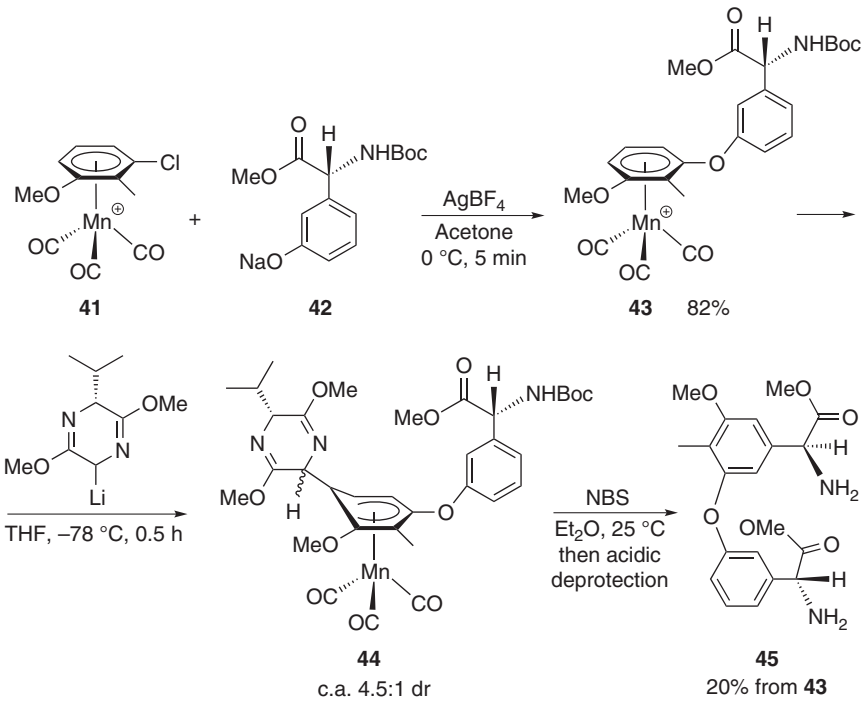
1.5 Mn(I)-Mediated Transformations in Organic Synthesis

1.5.1 Ring-Centered Reactivity in Half-Sandwich Mn(I) π-Complexes

In addition to the S_NAr substitution (Scheme 1.11, left), nucleophilic *C*-attack on π-coordinated arene ligands in complexes **12** to form selectively *exo*-η^5-cyclohexadienyl products **40** is of primary importance for these compounds from a practical point of view (Scheme 1.11, right) [67]. Noteworthy, due to their overall positive charge, Mn(I) complexes **12** are much more electrophilic than the more studied (π-arene)$Cr(CO)_3$ species, which lead to an acceleration of S_NAr processes [68] and allow the use of weaker nucleophiles (Grignard reagents, enolates, etc.) in the preparation of **40** [69]. While in the latter process, the directing effect of a simple carbon or halogen substituents is rather small, highly selective *meta*-addition that is a characteristic of phenol and aniline-based π-ligands [69], provided interesting applications in organic synthesis [70, 71]. The resulting functionalized arenes can be easily displaced from neutral complexes **40** by oxidation either with Jones reagent [69], 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [70], or *N*-bromosuccinimide (NBS) [71] under mild conditions, the latter procedure being compatible with some sensitive functional groups.

The representative application of this methodology to the synthesis of deoxyristomycinic acid derivative **45**, a structural motif presented in Ristocetin antibiotics family, is illustrated in Scheme 1.12 [71a, b]. The reaction of complex **41** with phenoxide **42** in the presence of silver salt as chloride scavenger afforded in good yield the diarylether derivative **43**, which was treated with Schöllkopf's nucleophile to form the η^5-cyclohexadienyl product **44**. Separation of the diastereomers, followed by the oxidative decomplexation and deprotection of Boc group, led to the enantiomerically pure compound **45**. This approach was later used for the preparation of even more elaborated polysubstituted aromatic structures containing sensitive functional groups [71c, e].

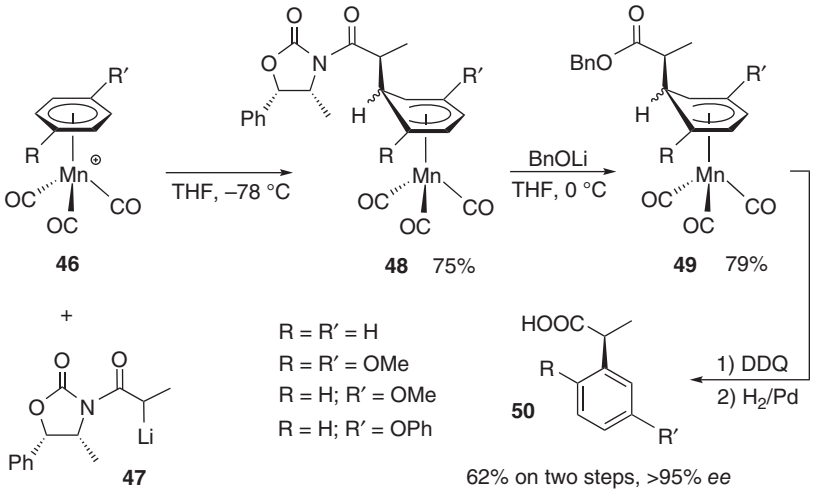
Treatment of the π-arene complex **46** (R = R′ = H) with the Evans's enolate **47** afforded complex **48** in a 9 : 1 dr, the major diastereomer being isolated in 75% yield (Scheme 1.13) [70]. The cleavage of the chiral auxiliary in the latter, followed by demetallation and Bn group removal, afforded 2-phenylpropionic acid **50** in more



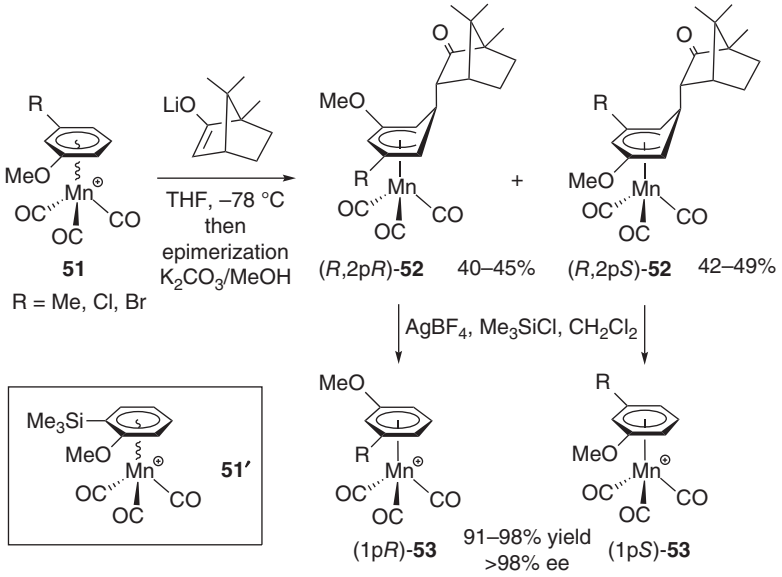
Scheme 1.12 Synthesis of deoxyristomycinic acid derivative **45** from Mn(I) π-arene complex **41**. Source: Based on Pearson et al. [71].

than 95% ee. Lower diastereoselectivity level observed for η^5-cyclohexadienyl complexes **48**, derived from substituted π-arene precursors, actually did not affect the overall synthesis of analogous acids **50**, isolated in similar yield and optical purity, as the destruction of the second chiral center occurred during the oxidative decomplexation of **49**.

Besides oxidative decomplexation to release free arenes, Mn(I) η^5-cyclohexadienyl complexes can be selectively transformed back into π-arene derivatives, typically using *exo*-hydride abstraction by the Ph_3C^+ cation [68, 72]. Noticeably, Rose and coworkers applied the combination of nucleophilic addition and rearomatization to design an elegant route to enantiomerically pure manganese π-arene complexes (Scheme 1.14) [73]. The reaction of complexes **51** based on 1,3-substituted arenes with the enolate obtained from natural *D*-camphor led to the formation of four diastereomers **52** resulting from the presence of central and planar chirality elements. Controlled epimerization allowed an enrichment of the mixture in the two *endo*-isomers (*R*,2p*R*)-**52** and (*R*,2p*S*)-**52** (for the stereochemistry definition of these molecules, see Ref. [74]), which were isolated in pure form with >98% de after column chromatography and crystallization. The treatment of the latter species with a mixture of $AgBF_4$ and Me_3SiCl, or simple protonation with $HBF_4 \times OMe_2$, induced a smooth elimination of the enolate to form the desired optically active π-arene products **53** with a perfect retention of planar chirality. This "round-trip" approach



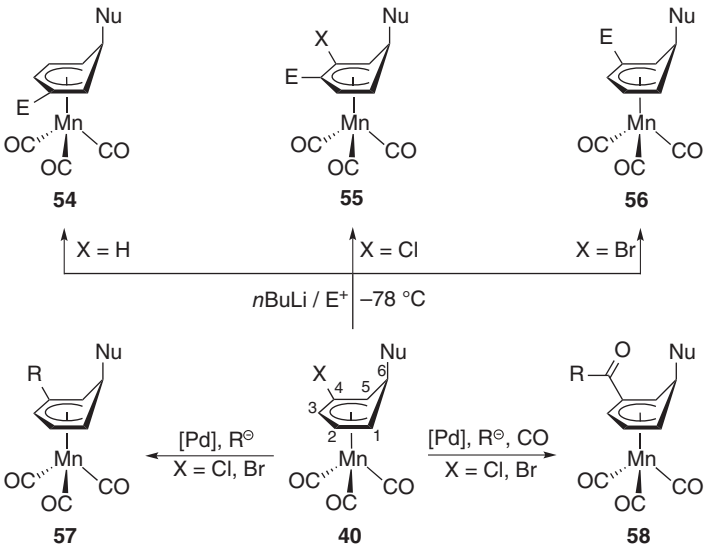
Scheme 1.13 Asymmetric synthesis of 2-arylpropionic acids using cationic Mn(I) π-arene complexes **46**. Source: Based on Miles et al. [70].



Scheme 1.14 Synthesis of enantiomerically pure planar chiral Mn(I) π-arene complexes.

was quite general and could be applied for the resolution of the 1,2-disubstituted π-arene complex **51′** as well (Scheme 1.14).

Besides the nucleophilic attack on cationic π-arene precursors described earlier, direct η^5-cyclohexadienyl ligand functionalization appeared as a viable complementary strategy to access more structurally elaborated Mn(I) species. The first approach dealt with a C–H bond deprotonation in complexes **40** with *n*BuLi/TMEDA at −78 °C and quenching the resulting lithiated species with

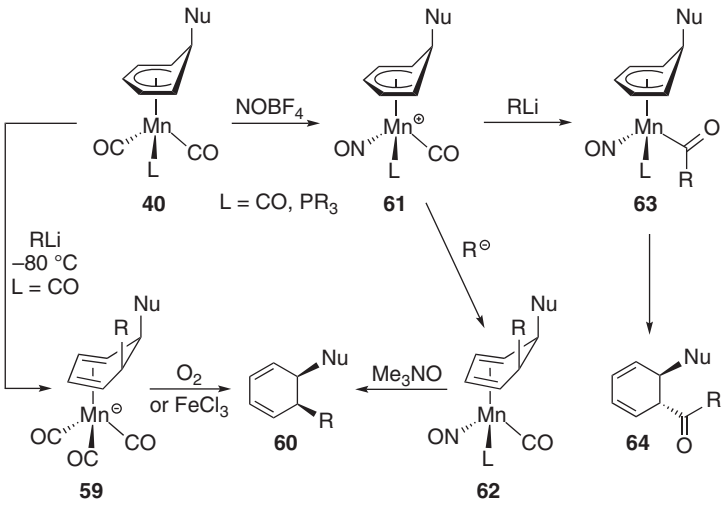


Scheme 1.15 Various strategies for the functionalization of η^5-cyclohexadienyl manganese complexes.

various electrophiles to form the substituted η^5-cyclohexadienyl products **54–56** in moderate to high yield (Scheme 1.15) [75]. Direct use of acyl chloride as electrophile led to a significant degradation of the organolithium intermediates, but the yield of the targeted products could be strongly improved by applying transmetallation with $Li_2[MnCl_4]$, followed by the acylation of the organomanganese derivatives, catalyzed with $Fe(acac)_3$ [75e]. While for non-substituted derivatives, the deprotonation occurred mostly at the C2 carbon atom, a perfect regioselectivity for the *ortho*-position relative to the chloride, ether, or amine directing groups were observed with a net preference for the C3 carbon to form complexes **55**. Similar initial treatment of the bromo-substituted **40** with *n*BuLi led to the selective metal/halogen exchange to form *in fine* complexes **56** [77]. Interestingly, for the η^5–1,2,4,5-tetramethyl-6-phenylcyclohexadienyl substituted version of complex **40**, deprotonation took place exclusively at the benzylic (C2)C–H bond, leaving intact the usual aromatic C3 position [76].

The second powerful strategy, largely exploited for the functionalization of halogen-containing η^5-cyclohexadienyl complexes, was based on Pd-catalyzed cross-coupling processes including Suzuki-Miyaura [78], Sonogashira [72b, 72d, 79b], Stille [72a–c, 80], and Negishi [72b] reactions as well as the efficient installation of O-, S-, N-, and P-nucleophiles to form a variety of products **57** [72b]. Importantly, the majority of these processes could be performed with a simple $Pd_2(dba)_3/AsPh_3$ catalytic system and worked well under CO atmosphere to afford the corresponding carbonylated products **58** in good yield [72b, 72d, 80c].

The formation of 1,3-cyclohexadienes with good stereoselectivity upon nucleophilic addition onto the Mn(I) η^5-cyclohexadienyl complexes **40** represents the most important synthetic application of these compounds (Scheme 1.16). The reaction of tricarbonyl species **40** with strong nucleophiles led to the formation of

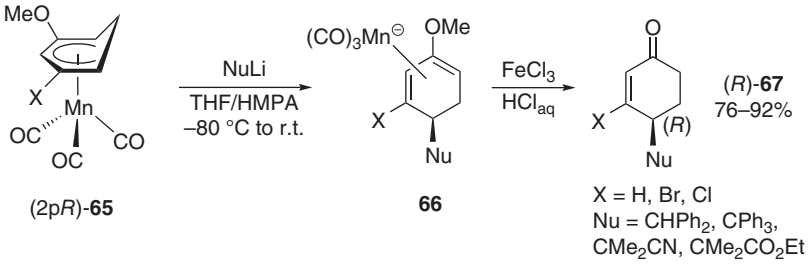


Scheme 1.16 Synthesis of 1,3-cyclohexadienes using the reactions of Mn(I) η^5-cyclohexadienyl complexes with nucleophiles.

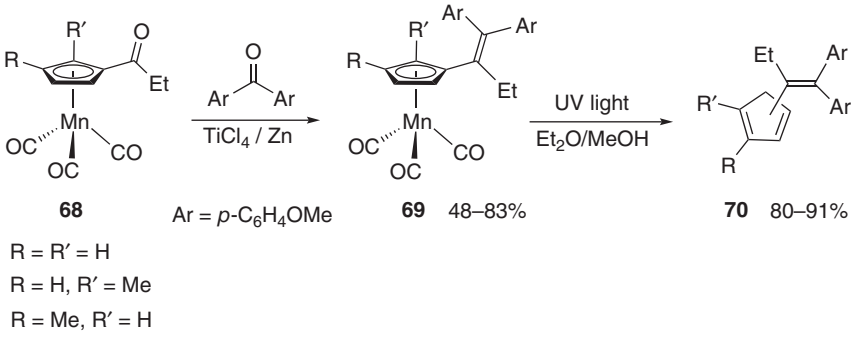
anionic η^4-diene intermediates **59** that release the corresponding dienes **60** upon oxidation with $FeCl_3$ [73] or upon simple exposure to air [81]. The substitution of one CO ligand in **40** for NO led to the cationic species **61**, capable of readily accommodating a variety of weaker nucleophiles to yield the neutral η^4-diene products **62** in moderate to good yield [82]. The latter reactions were more efficient for phosphine-containing complexes **61** due to the suppression of side electron transfer processes, resulting in 10–20% higher yield [82b]. Neutral diene complexes **62** have been more stable than their anionic analogues **59** and typically required Me_3NO for the demetallation step. Interestingly, the treatment of complexes **61** with MeLi or PhLi led *in fine* to the selective formation of dienes **64** incorporating an acyl group in *trans*-arrangement relative to Nu. This unexpected selectivity was rationalized by the occurrence of the initial nucleophilic attack at the carbonyl ligand, followed by reductive elimination in the resulting σ-acyl intermediates **63** [83].

A representative application of η^5-cyclohexadienyl complexes to the enantioselective synthesis of 2-cyclohexenones is shown on Scheme 1.17 [73]. The reaction of complexes (2p*R*)-**65** obtained from optically pure π-arene precursors (1p*R*)-**53** (see Scheme 1.14) with a variety of C-nucleophiles proceeded with complete stereoselectivity to afford the target enones (*R*)-**67** in excellent yield after the demetallation of the anionic diene intermediates **66** with $FeCl_3$ and acid hydrolysis. Interestingly, the stereoselective reduction of a selected cationic η^5-cyclohexadienyl Mn(I) complex was used by Miles et al. as one of the key steps for the formal total synthesis of (+)-Juvabione [84].

It is important to mention that η^5-cyclopentadienyl ligands in cymantrene derivatives can be also efficiently transformed into the corresponding conjugated dienes upon UV irradiation in a 2 : 1 Et_2O/MeOH mixture acting as a proton source [85]. This reaction was applied by Top, Jaouen et al. as a key step for the preparation of substituted cyclopentadiene derivatives (Scheme 1.18) [85a, b]. As



Scheme 1.17 Enantioselective synthesis of 2-cyclohexenones from optically pure Mn(I) η5-cyclohexadienyl complexes (2p*R*)-**65**. Source: Eloi et al. [73].

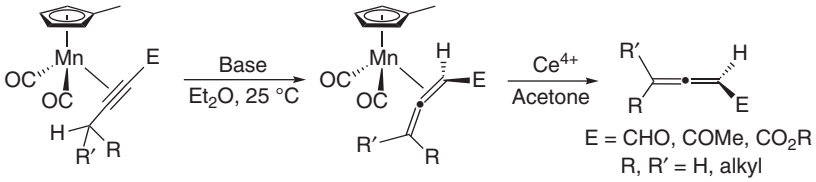


Scheme 1.18 Synthesis of substituted cyclopentadienes by McMurry reaction of cymantrenyl ketones followed by photochemical demetallation. Source: Jaouen and coworkers [85].

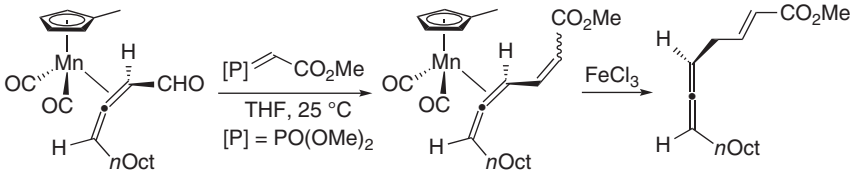
an example, the cymantrenyl ketones **68**, easily obtained upon Friedel–Crafts acylation, were first engaged into the McMurry reaction with substituted benzophenone to produce **69**, from which the target alkenyl-substituted cyclopentadienes **70** were obtained as a mixture of regioisomers upon such a demetallation. This procedure was further applied to the synthesis of rather elaborated molecules, including ethynylestradiol-substituted cyclopentadiene [85a, b].

1.5.2 Preparation of Allenes Using [Cp′(CO)$_2$Mn] Auxiliary

In 1979, Franck-Neumann et al. reported the isomerization of the Mn(I) η^2-alkyne complexes **71** bearing electron-withdrawing substituents into the corresponding η^2-allene products **72** in the presence of basic alumina (Scheme 1.19) [86a]. The manganese moiety in complexes **72** was always coordinated to more electron-poor double bond. While under these conditions, a mixture of *exo*- and *endo*-isomers, differing by the relative positions of the metal fragment and the larger allene substituent R or R′, was typically produced; the use of stoichiometric amounts of stronger base such as DBU or *t*BuOK both accelerated the reaction rate and afforded preferentially the *exo*-**72** derivative [86b]. These species were generally air-stable and could be purified by chromatography on silica, while the corresponding allenes **73** were readily released upon oxidation with Fe(III) or Ce(IV) salts (Scheme 1.19) [86].



Scheme 1.19 Synthesis of allenes by base-catalyzed isomerization of Mn(I) π-alkyne complexes and oxidative dematallation. Source: Based on Franck-Neumann et al. [86].

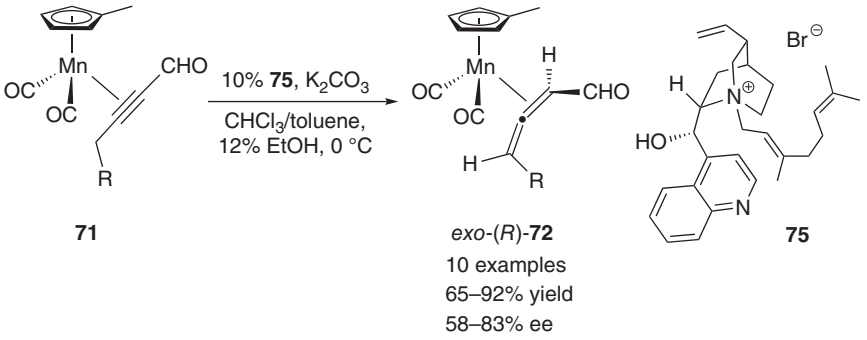


Scheme 1.20 Asymmetric synthesis of bee pheromone using Mn(I) η^2-allene complex *exo-(R)*-**72**. Source: Based on Franck-Neumann et al. [86].

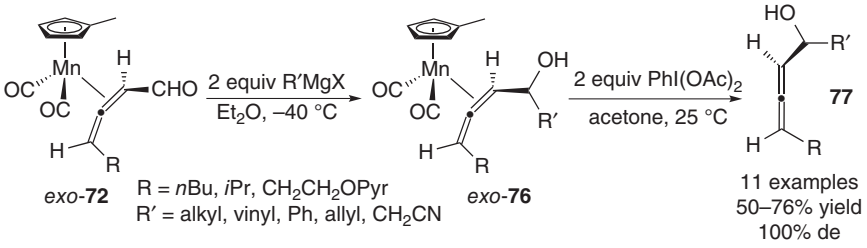
Allenylcarbaldehyde complexes *exo*-**72** (E = CHO, R = H, R′ = *n*Hex, *n*Oct) can be resolved using (*S*)-5-(α-phenylethyl)semioxamazide chiral auxiliary to afford both optically pure products in *ca*. 35% yield each [86c]. These optically pure species were used for the efficient asymmetric synthesis of bee pheromone (Scheme 1.20) [86c]. Horner–Evans olefination of *exo*-(*R*)-**72** (R = *n*Oct) led to the clean formation of the corresponding alkene derivatives *exo*-(*R*)-**73** as a mixture of *E/Z* isomers, from which the desired *E*-compound could be obtained in 79% yield providing the target molecule upon oxidative decomplexation. Importantly, the olefination of free allenyl aldehyde led to lower yield (41%) and significant racemization.

Later, Lepore and coworkers showed that the enantioenriched Mn(I) complexes *exo*-(*R*)-**72** can be prepared under biphasic conditions using a specially designed chiral phase-transfer catalyst **75** based on cinchonidinium scaffold (Scheme 1.21) [87]. Though the ee values were not very high, this method represents the first catalytic route to protected allenyl aldehydes from readily available alkynyl aldehydes. While the optical purity of *exo*-(*R*)-**72** was not improved by crystallization due to their oily aggregation state, the replacement of Cp′ for Cp, which typically facilitates crystallization, could be a possible solution for this problem in light of further applications in organic synthesis.

The reaction of *exo*-**72** with Grignard reagents led to a 1,2-addition onto the carbonyl group of the coordinated allenyl aldehyde with complete diastereoselectivity, to form the Mn(I) complexes *exo*-**76**, from which the corresponding allenols **77** are easily displaced upon oxidation with $PhI(OAc)_2$ (Scheme 1.22) [86c, 88]. Organolithium and organozinc nucleophiles gave similar results; no ee erosion was detected for optically pure substrates *exo*-**72** [86c]. This approach was also applied for disubstituted allene precursors, providing reasonable dr ratios in **77** even for small alkyl groups (5 : 1 for Me/Et). The presence of the coordinated $[Cp'(CO)_2Mn]$



Scheme 1.21 Synthesis of enantio enriched Mn(I) η^2-allene complexes *exo-(R)*-**72** using cinchonidinium-based phase-transfer catalyst **75**. Source: Based on Roy et al. [87].



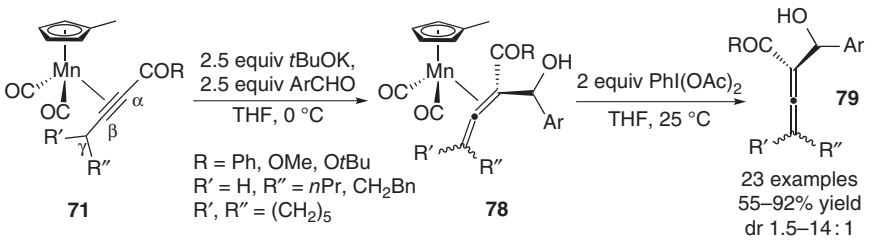
Scheme 1.22 Synthesis of allenols using the reaction of Mn(I) η^2-allene complexes with nucleophiles. Franck-Neumann et al. [86]; Roy et al. [88].

fragment plays a crucial role in this process, controlling both the discrimination between the remote allene substituents in the γ-position and the preferred side of the nucleophilic attack. Noteworthy, for free allenals, a reasonably high level of diastereoselectivity was achieved only with substrates containing the very bulky Ph_2tBuSi group. The sequence of enantioselective preparation of complex *exo*-(*R*)-**72** (R = *n*Bu) and its diastereoselective reaction with $NCCH_2MgX$ was used as a basis of one of the most concise asymmetric total syntheses of Hagen's gland lactone [87].

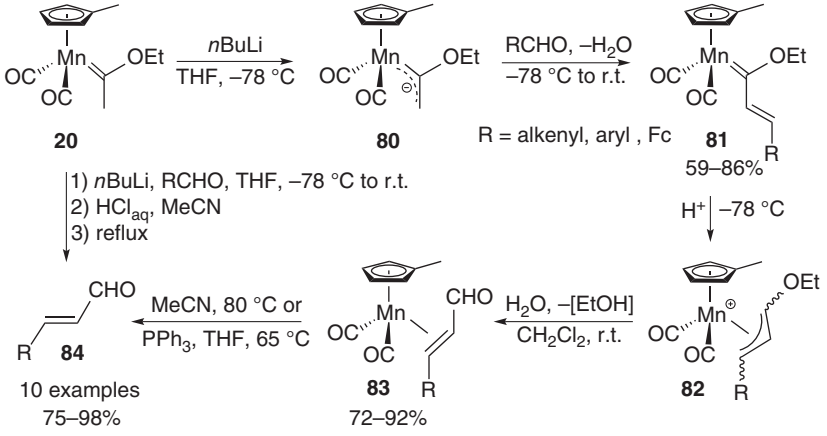
The reactions of anionic cumulenolate derivatives, obtained *in situ* upon treatment of the π-alkyne complexes **71** by an excess of strong base with arylaldehydes, followed by oxidative demetallation, were found to proceed exclusively at the α-position, to afford aldol products **79** in moderate to excellent yields (Scheme 1.23) [89]. While the diastereoselectivity for ester substrates was rather low (dr 1.5–2 : 1), alkynyl ketones ensured much better results (dr 9–14 : 1). Importantly, the aldol-type processes in the case of free alkynyl ketones and esters produced the addition products uniquely at the γ-position and with rather poor yields.

1.5.3 Synthetic Applications of Mn(I) Fischer Carbenes

Stoichiometric reactions of group 6 Fischer carbenes have found numerous applications in organic synthesis [90]. Despite the related manganese complexes have attracted much less attention, in some cases the reactivity of these species was remarkably different from their chromium and tungsten analogues leading to



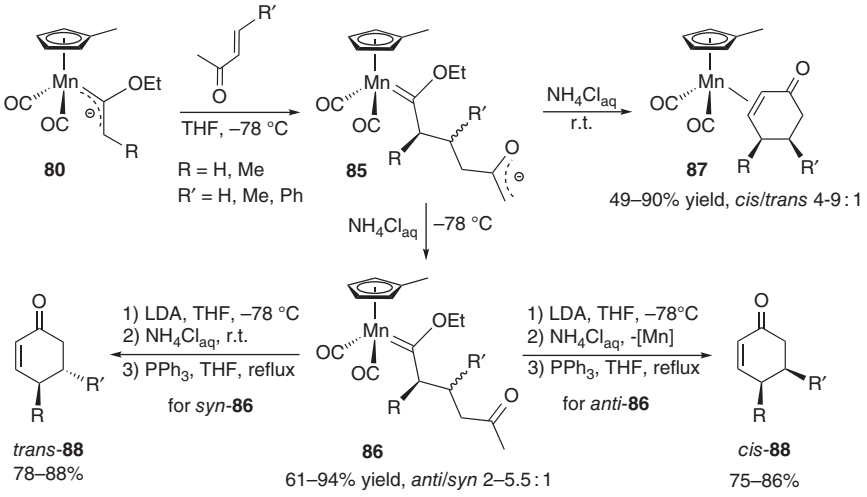
Scheme 1.23 Synthesis of functionalized allenes by aldol-type reaction of Mn(I) π-alkyne complexes followed by oxidative dematallation. Source: Based on Bhowmick et al. [89].



Scheme 1.24 Vinylogation of aldehydes using Mn(I) alkoxycarbene complexes. Source: Yi et al. [91]; Mongin et al. [91].

some valuable results. The less electrophilic character of the $[Cp(CO)_2Mn]$ moiety, compared with $[(CO)_5M]$ (M = Cr, W) resulted in a much higher nucleophilicity of the carbene enolates derivatives. As a representative example of such behavior, condensation of the carbene enolate **80** with a variety of aldehydes readily afforded alkenylcarbenes **81** (Scheme 1.24) [91]. Protonation of the latter species at low temperature, followed by treatment with water, afforded complexes **83** via the intermediacy of the cationic π-allyl intermediates **82**. The α,β-unsaturated aldehyde ligands in **83** were easily released upon thermal substitution for PPh_3 or MeCN. The overall process, which could eventually be performed in "one pot" turned as an efficient aldehyde vinylogation procedure with synthetically useful yields.

The outcome of the Michael addition of the enolate **80** to α,β-unsaturated ketones was dramatically dependent on the hydrolysis temperature (Scheme 1.25) [92]. The acidic quenching of the conjugated addition product **85** led to the formation of carbene complexes **86** as a mixture of *cis* and *trans*-isomers, eventually separated by column chromatography. In contrast, room temperature evolution of **85**, followed by protonation, gave the cyclohexenone complexes **87** as *cis* and *trans*-isomers through a sequence of intramolecular nucleophilic attack of the remote enolate to the carbene atom, with concomitant elimination of EtO^- group, protonation, and carbene-to-alkene isomerization. Noteworthy, for chromium Fischer carbenes, the



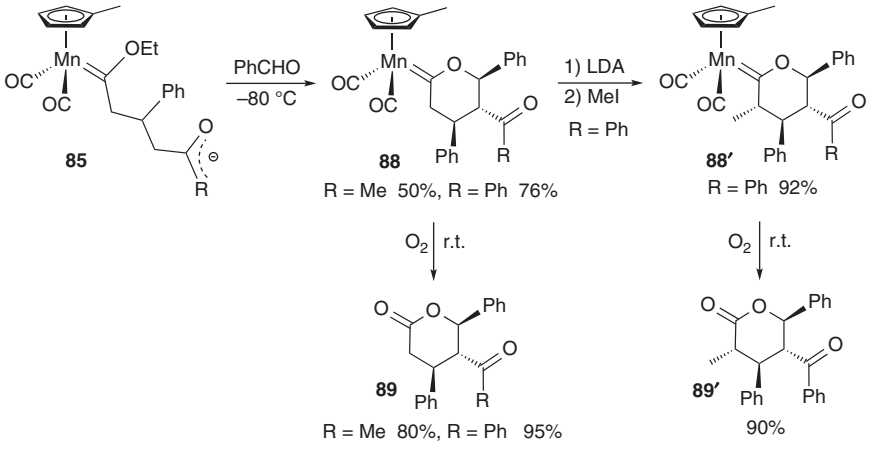
Scheme 1.25 Stereoselective synthesis of 4,5-disubstituted cyclohexenones from enolates of Mn(I) alkoxycarbene complexes. Source: Based on Mongin et al. [92].

remote enolates similar to **85** typically undergo the proton transfer from α-carbene position due to its higher C–H acidity, to form stable carbene enolate isomer, thus precluding the further cyclization. Diastereoselective high yield formation of *cis*- and *trans*-4,5-disubstituted cyclohexenones **87** was achieved from pure stereoisomers of **86** upon a sequence of low temperature deprotonation, room temperature protonation, and finally demetallation upon heating with PPh_3 in refluxing THF (Scheme 1.25).

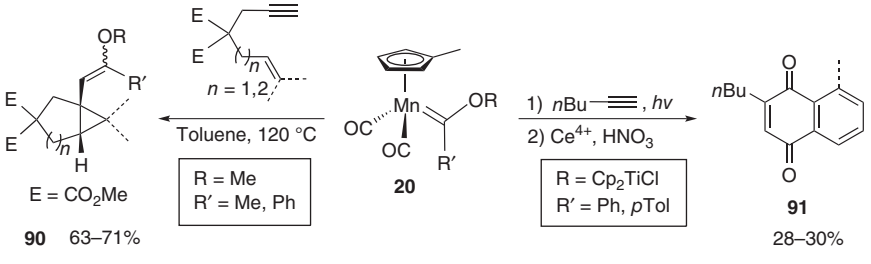
The reaction of the enolates **85** with benzaldehyde led to the diastereoselective formation of six-membered cyclic Fischer carbenes **88** in good yield (Scheme 1.26) [93]. Further methylation of the α-position relative to the carbene atom occurred in totally stereoselective manner, providing complex **88′** showing four contiguous stereogenic carbon centers. The corresponding lactones were conveniently released upon decomposition of the complexes under air atmosphere. This reaction represents an illustrative example of highly stereoselective assembly of polysubstituted cyclic molecules from simple Fischer carbenes, enone, and aldehyde, proceeding as tandem Michael addition/aldol condensation/transesterification process.

The reactivity of manganese Fischer carbenes with alkynes has been scarcely explored. Thermal reaction of complexes **20** with enynes leads to the formation of bicyclic vinylcyclopropanes **90** (Scheme 1.27, left equation) [94]. The only example of Dötz benzannulation for manganese complexes bearing acceptor $Cp_2Ti(Cl)O$ carbene substituent was achieved under UV irradiation to form, after oxidation in acidic medium, quinones **91** in moderate yield (Scheme 1.27, right equation) [95]. Notably, regular alkoxycarbene **20** (R = Me) was completely unreactive showing that the increased electrophilicity of carbene ligand was a crucial factor enabling this reactivity.

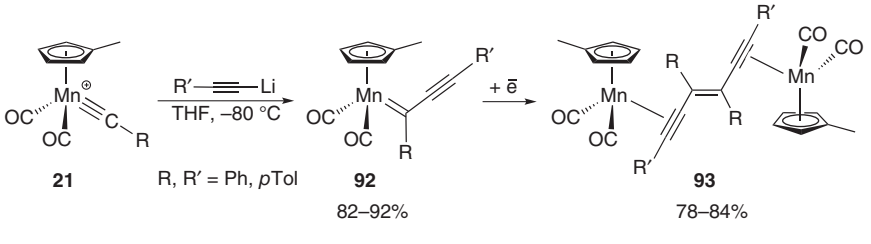
The Mn(I) alkynylcarbene complexes **92**, easily available from carbyne precursors **21** and alkynyllithium derivatives [53a, 96, 98a], can undergo coupling of the remote



Scheme 1.26 Stereoselective synthesis of polysubstituted lactones using enolates of Mn(I) alkoxycarbene complexes. Source: Based on Mongin et al. [93].



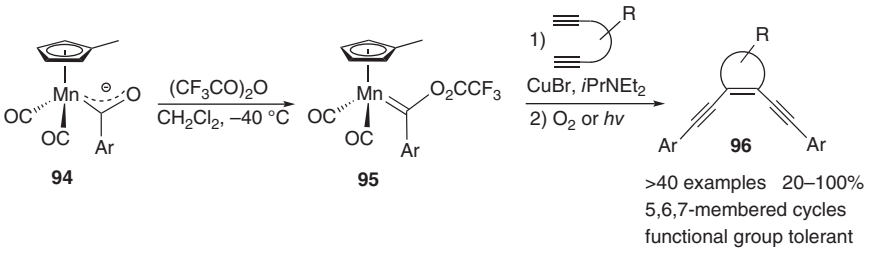
Scheme 1.27 Cyclization reactions of Mn(I) alkoxycarbene complexes with terminal alkynes and enynes. Source: Based on Hoye et al. [94].



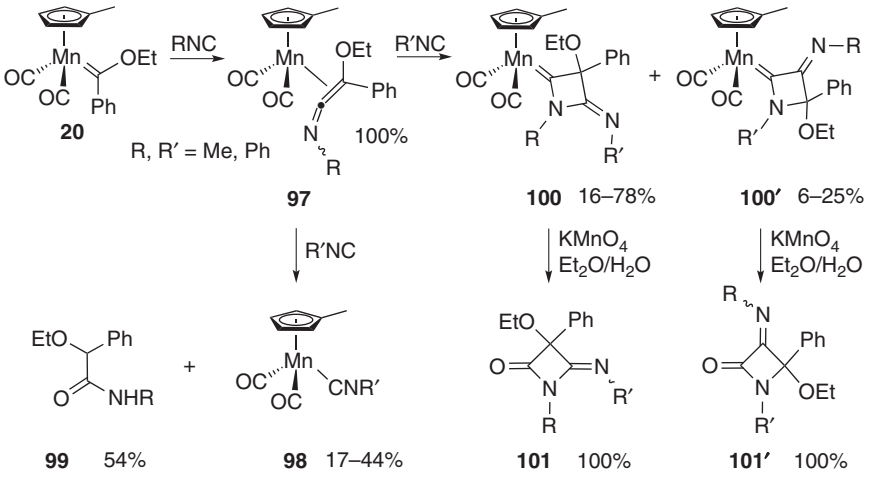
Scheme 1.28 Synthesis and reductive dimerization of Mn(I) alkynylcarbene complexes.

alkynyl carbon atoms, to give binuclear ene-diyne products **93** (Scheme 1.28). While the thermal reaction was shown to proceed with low *E/Z* selectivity and was accompanied by partial R/R′ scrambling [96], under electrocatalytic reduction conditions, the *E*-isomers of **93** were formed exclusively in excellent yield [97].

The intramolecular version of this dimerization process constitutes a highly efficient route to cyclic ene-diynes **96**, starting from readily available terminal dialkynes (Scheme 1.29) [98]. Under optimized conditions, binuclear alkynylcarbenes could be generated *in situ* by copper-mediated alkyne addition to trifluoroacetylcarbenes



Scheme 1.29 Synthesis of cyclic endiynes by the dimerization of Mn(I) alkynylcarbene complexes. Source: Casey et al. [98].

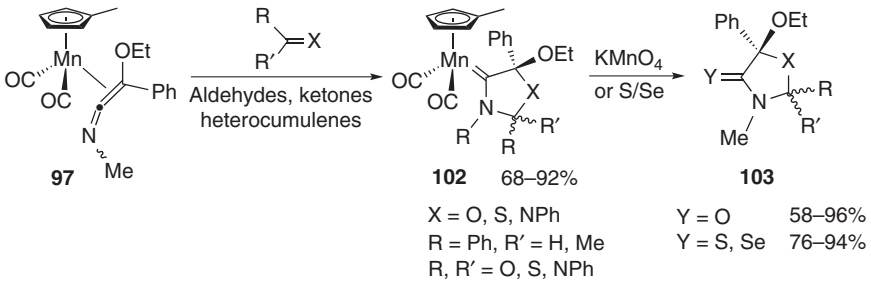


Scheme 1.30 Reactions of Mn(I) alkoxycarbene complexes with isonitriles. Source: Based on Aumann et al. [99].

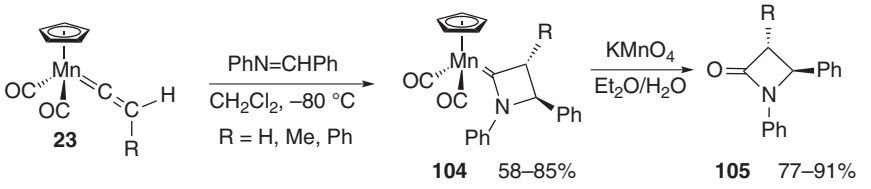
95 acting as carbyne surrogates upon the partial dissociation of CF_3COO^- anion. The demetallation of the resulting products was achieved either by Cu(II)-catalyzed O_2 oxidation [98a] or by visible light irradiation in CH_2Cl_2/THF solution [98b]. This approach showed an ample scope, tolerated numerous functional groups, and could even be applied for the preparation of non-symmetric ene-diynes **96** in 18–40% yields, starting from an equimolar mixture of σ-acyl complexes **94** [98b].

The insertion of isocyanides across Mn=C bond in complexes **20** afforded quantitatively the η^2-keteneimine products **97** (Scheme 1.30) [99]. The thermal reaction of the latter with a second equivalent of isocyanide led to three competitive processes of keteneimine liberation (selective for R = cyclohexyl (Cy) to form the amide **99** after hydrolysis), and the formation of two isomeric four-membered cyclic aminocarbenes **100** and **100′** via [3+1] and [2+2] cycloadditions, respectively. The oxidation of these complexes with $KMnO_4$ under biphasic conditions efficiently produced the corresponding 4-imino- (**100**) and 3-imino-2-azetidinones (**100′**), respectively.

The reactions of **97** with a variety of substrates having polar C=X bonds efficiently produced the five-membered cyclic aminocarbenes **102** (Scheme 1.31) [100]. While the diastereoselectivity in reactions with aldehydes and ketones was modest, these



Scheme 1.31 [3+2] cycloaddition of Mn(I) η^2-keteneimine complexes with the substrates containing polar double bonds. Source: Based on Aumann et al. [100].



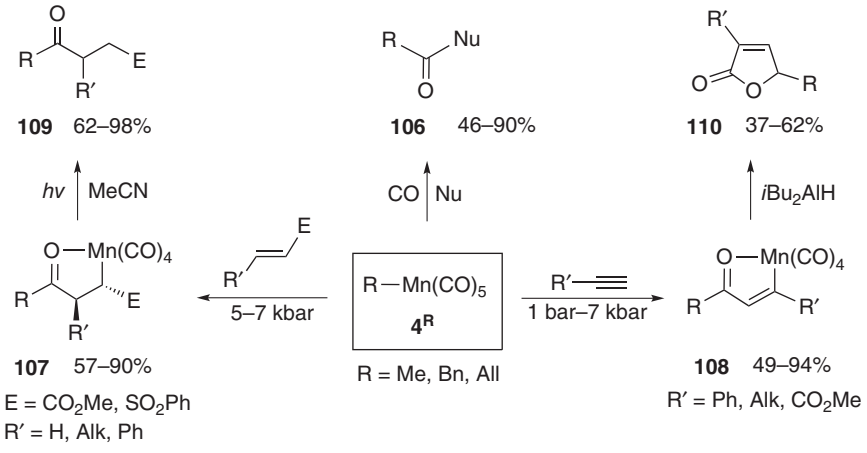
Scheme 1.32 Stereoselectively synthesis of β-lactams from Mn(I) vinylidene complexes. Source: Based on Terry et al. [52].

reactions were especially efficient for different heterocumulenes. Besides oxidation, the cleavage of Mn=C bond could be readily achieved by the treatment with elemental sulfur or selenium.

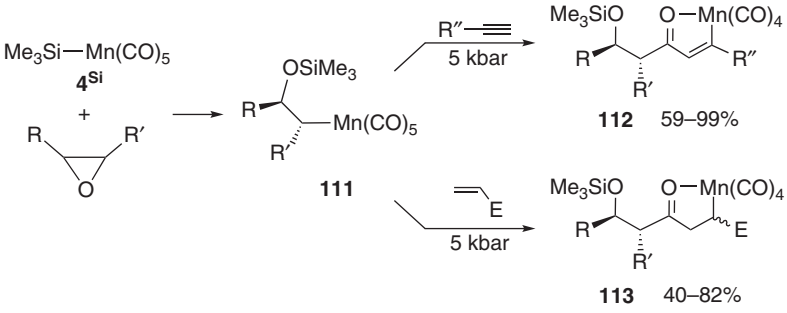
The reaction of the vinylidene complexes **23** with imines was found to proceed as a formal [2+2] cycloaddition to form stereoselectively aminocarbene complexes **104** (Scheme 1.32) [52b]. The latter products could be readily transformed to the corresponding β-lactams **105** in good yield.

1.5.4 Carbonyl-Containing Manganese σ-Complexes in Organic Synthesis

Synthetic application of Mn(I) complexes $(CO)_5MnR$ was extensively developed by group of DeShong in the late 1980s (Scheme 1.33) [101]. Beyond the classic migratory CO insertion leading to σ-acyl complexes being trapped with nucleophiles (Reppe carbonylation) to form the corresponding carbonyl derivatives **106**, highly selective sequential insertion of CO and unsaturated C—C bonds can be achieved at room temperature to form cyclometallated species **107** and **108**. Though the most reactive $(CO)_5MnMe$ can readily insert several terminal alkynes (R′ = Ph, CO_2Et) [101d], in all other cases these transformations were performed only using solution high-pressure techniques, allowing a better stabilization of the $(CO)_4$(substrate)MnCOR intermediates. While the substrate scope was restricted to strained cyclic systems like norbornene and disubstituted olefins bearing electron-withdrawing groups, both terminal and internal alkynes could be engaged, albeit with modest regioselectivity in the latter case. Photolysis of complexes **107** in MeCN afforded ketones **109** in good yield [101b]. Protonation of complexes **108**



Scheme 1.33 Synthesis of various carbonyl derivatives from Mn(I) σ-complexes $(CO)_5MnR$ under high-pressure conditions. Source: DeShong et al. [101].

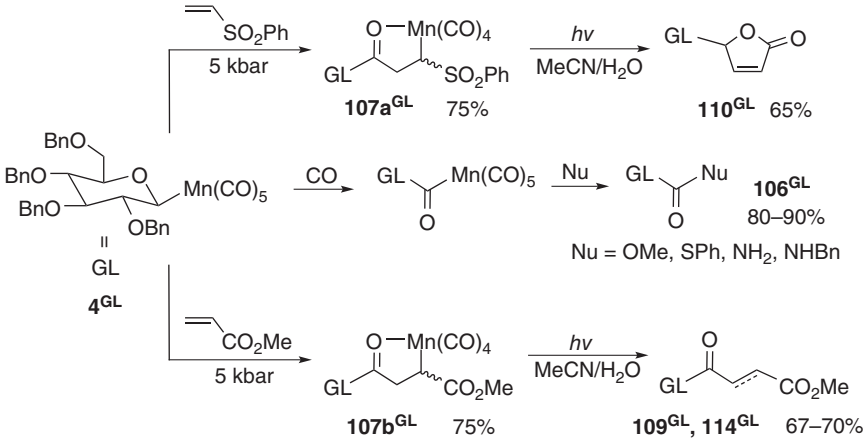


Scheme 1.34 Three-component reaction between Mn(I) complex $(CO)_5MnSiMe_3$, epoxides and organic substrates containing unsaturated C-C bonds. Source: Based on DeShong et al. [102].

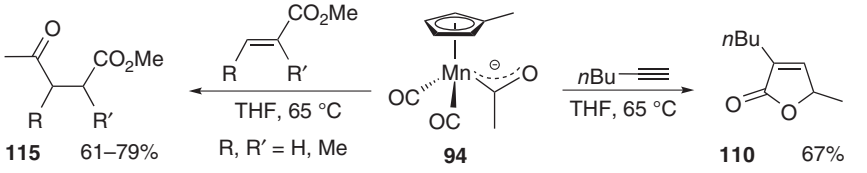
induced the Mn—C bond cleavage, liberating the corresponding enones, whereas their reduction with iBu$_2$AlH gave butenolide products **110** in moderate yield [101c].

Trimethylsilyl-substituted manganese σ-complex $\mathbf{4^{Si}}$ could be applied even to a three-component synthesis of metallacyclic products **112–113** from epoxides to unsaturated hydrocarbons (Scheme 1.34) [102]. Thermodynamically favorable epoxide insertion into the Mn—Si bond to form σ-alkyl species **111**, having *anti*-configuration, seems to be the key feature allowing the excellent level of selectivity observed in this reaction.

The most important practical application of this methodology dealt with the synthesis of glucoside derivatives (Scheme 1.35) [103]. The representative insertion reactions of the β-anomer $\mathbf{4^{GL}}$, available in a nearly quantitative yield from α-glucopyranosyl bromide and $(CO)_5MnK$, always proceeded with a complete retention of the configuration for the reacting carbon center. Reppe carbonylation of complex $\mathbf{4^{GL}}$ in the presence of various O-, N-, and S-nucleophiles led to a highly efficient formation of the corresponding carbonyl derivatives $\mathbf{106^{GL}}$, suitable for



Scheme 1.35 Application of Mn(I) σ-complexes for synthesis of glucoside derivatives. Source: DeShong et al. [103].



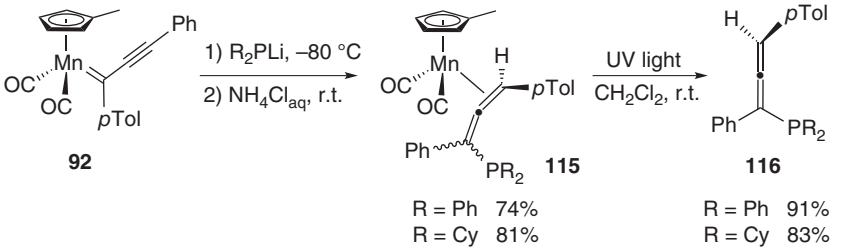
Scheme 1.36 Carbonylation of alkenes and terminal alkyne with anionic Mn(I) σ-acyl complex under atmospheric pressure. Source: Based on Hoye et al. [94].

further derivatization [103d]. UV irradiation of sulfonylated compound **107a**^{GL} in aqueous acetonitrile afforded butenolide **110**^{GL} in good yield. Interestingly, the outcome of the photochemical demetallation in the case of acrylate insertion product **107b**^{GL} can be easily switched by the presence of oxygen, selectively affording either the enone **114**^{GL} or its saturated analogue **109**^{GL} for air-saturated or degassed MeCN/H_2O solutions, respectively [103d].

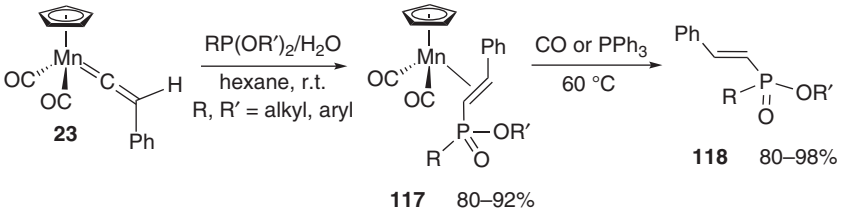
Similar transformations can also be performed in one step under atmospheric pressure for the anionic half-sandwich σ-acyl manganese complex **94**, to afford the butenolide **110** and the γ-ketoester **115** derivatives (Scheme 1.36) [94]. Despite the availability of cymantrene-derived σ-acyl complexes and a convenient reaction setup, this approach was not extended to more elaborated substrates.

1.5.5 Mn-Mediated Synthesis of Organophosphorous Compounds

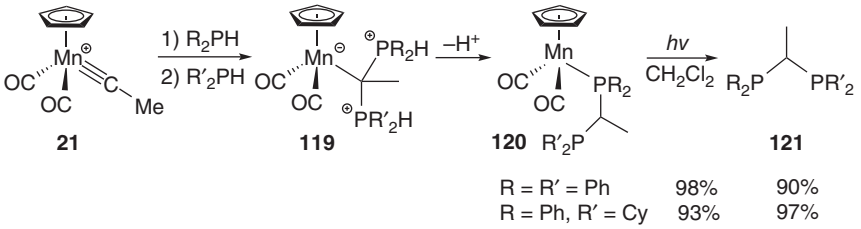
The manganese alkynylcarbene complex **92** reacts at low temperature with lithium phosphides to afford after protonation *syn/anti* mixtures of the η^2-allene complexes **115**, resulting from a nucleophilic attack of the phosphide on the remote γ-carbon atom (Scheme 1.37) [104]. Photochemical decomposition of the resulting Mn(I) species under UV irradiation in CH_2Cl_2 solution readily released the corresponding phosphinoallenes **116** in good yield.



Scheme 1.37 Synthesis of allenylphosphines from Mn(I) alkynylcarbene complexes. Source: Based on Sentets et al. [104].



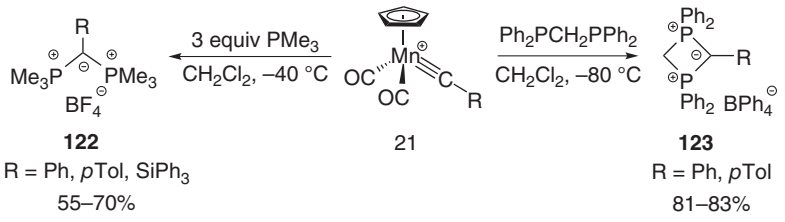
Scheme 1.38 Synthesis of styrylphosphonates from Mn(I) vinylidene complexes and phosphites. Source: Antonova et al. [105].



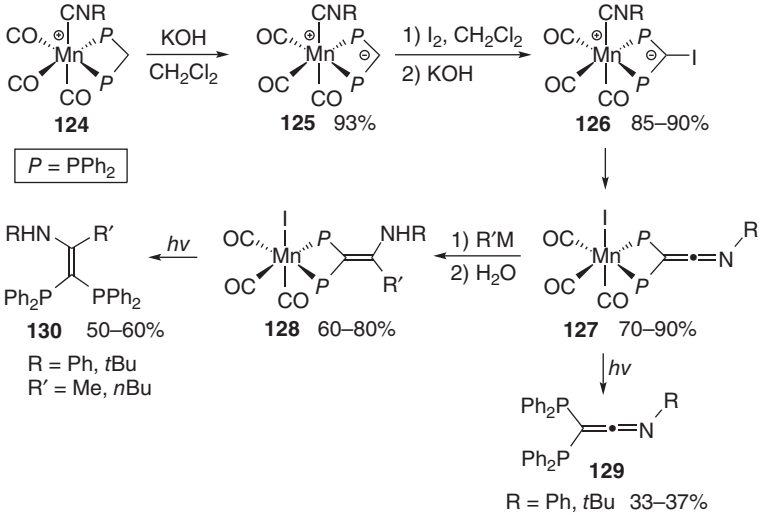
Scheme 1.39 Synthesis of diphosphinomethane derivatives by the coupling of Mn(I) carbyne complex with secondary phosphines. Source: Based on Valyaev et al. [107].

The reaction of vinylidene complex **23** with phosphites readily afforded η^2-styrylphosphonate complexes **117**, to yield free alkenes upon substitution with CO or P-ligands (Scheme 1.38) [105]. The key step of this reaction includes the hydrolysis of zwitterionic phosphite adducts $Cp(CO)_2Mn^--C(RP^+(OR')_2=C(H)Ph$ with elimination of R′OH [106].

Some of us have recently shown that the cationic carbyne complex **21** is able to accommodate two molecules of secondary phosphines, the same or different, to afford zwitterionic intermediates **119**, which are prone to undergo a 1,2-proton shift from more acidic phosphonium site to the adjacent carbon atom, to form *in fine* the Mn(I) complexes **120** bearing κ^1-coordinated bridge-substituted diphosphinomethane ligands (Scheme 1.39) [107]. The resulting organophosphorous products **121** can be quantitatively obtained upon visible light irradiation of **120** in CH_2Cl_2 solution, provided the pendant phosphine moiety is blocked from potential coordination by complexation with borane or protonation with strong acid such as $HBF_4 \times OEt_2$ [107].



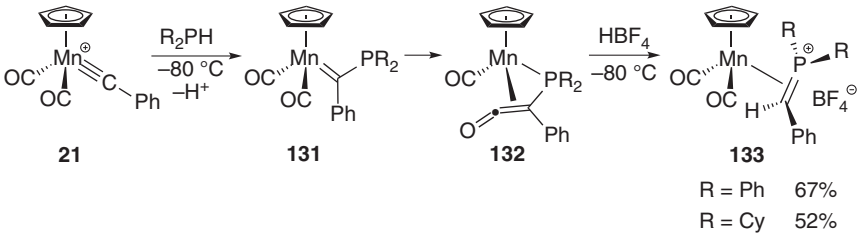
Scheme 1.40 Synthesis of phosphorus semi-ylides by the reaction of Mn(I) carbyne complex with two tertiary phosphines. Source: Valyaev et al. [107].



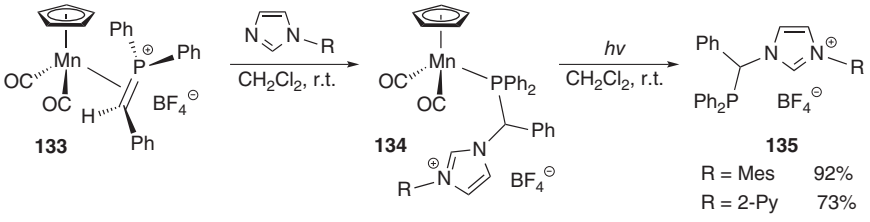
Scheme 1.41 Bridge modification of dppm ligand in manganese coordination sphere. Source: Ruiz et al. [109].

A similar reaction of **21** with tertiary phosphines led to the formation of the semi-ylides **122**–**123** in good yield (Scheme 1.40) [107, 108]. While for the reactions with PMe_3 the semi-ylide **112** was released upon reaction with the excess of phosphine to form $Cp(CO)_2Mn(PMe_3)$ as a by-product [108a], the intermediate cyclic four-membered derivatives similar to **119** obtained from bis[diphenylphosphino]methane (dppm) underwent spontaneous loss of the $[Cp(CO)_2Mn]$ moiety upon simple warming to room temperature affording **123** [107, 108b].

An interesting modification of the bridge in dppm ligand in manganese coordination sphere was reported by Ruiz and coworkers (Scheme 1.41) [109]. The readily available zwitterionic complexes **126**, bearing iodo-substituted κ^2-diphosphinomethanide ligand, undergo a metal-to-carbon migration of the coordinated isocyanide ligand to form neutral species **127** exhibiting an aza-allene dppm scaffold. The cumulene fragment in the latter complexes can be further modified by adding organolithium or Grignard reagents, followed by hydrolysis to



Scheme 1.42 Synthesis of Mn(I) methylenephosphonium complexes from carbyne precursor and secondary phosphine. Source: Based on Valyaev et al. [110].



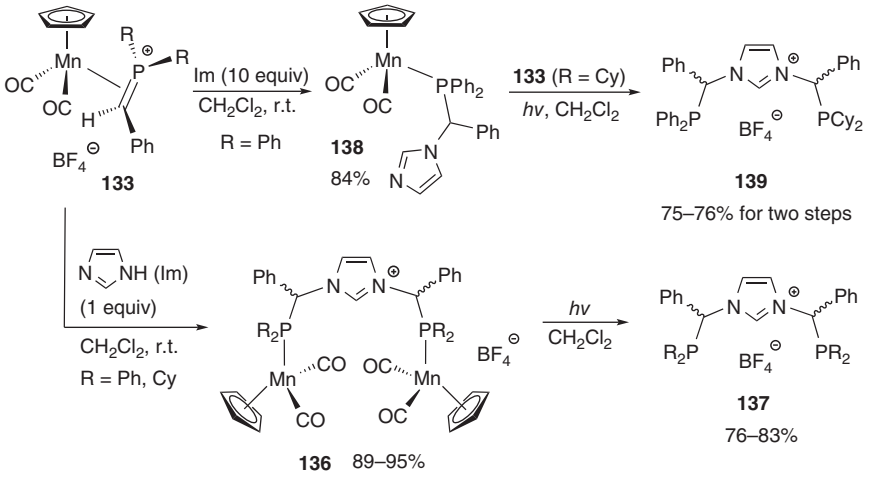
Scheme 1.43 Synthesis of phosphine-imidazolium salts from Mn(I) methylenephosphonium complexes. Source: Valyaev et al. [110].

complexes **128**. Photochemical decomposition of manganese products **127** or **128** affords the corresponding diphosphines **129**–**130** in moderate yields.

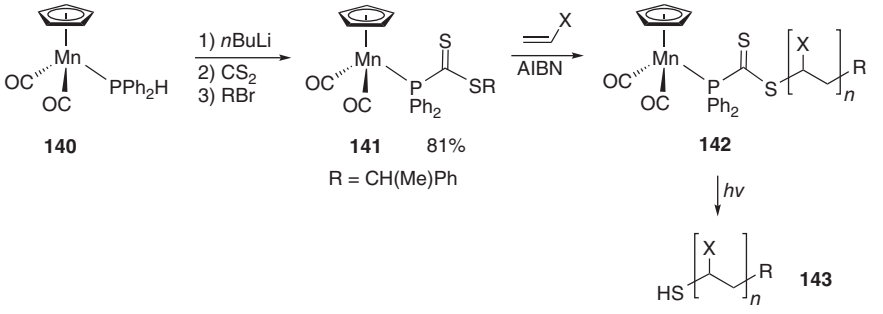
Other important organophosphorous synthons, the cationic half-sandwich Mn(I) complexes **133**, bearing η^2-methylenephosphonium ligands, have been prepared recently by some of us via a sequence of intramolecular migratory CO insertion in Fischer-type phosphinocarbenes **131**, followed by protonation-induced CO-deinsertion in the resulting η^3-phosphinoketene products **132** (Scheme 1.42) [110a]. The overall transformation sequence of **21** into **133** can be performed in one pot on a 20 mmol scale, the final synthons **133** being stable in the solid state under ambient conditions.

In contrast to iminium salts, the chemistry of their phosphorous analogues, methylenephosphonium species, has been barely developed, likely because of their relative instability. Yet, their reactivity was characterized by their propensity to react with nucleophiles at the phosphorous atom, giving the corresponding phosphonium salts [111]. Beyond stabilizing methylenephosphonium cations, the metal moiety in complexes **133** totally inverted the regioselectivity of the eventual nucleophilic addition, thus opening new synthetic perspectives. As a representative example, reaction of **133** with easily available substituted imidazoles instantaneously afforded the phosphine complexes **134**, featuring a pendant imidazolium moiety (Scheme 1.43) [110]. Direct irradiation of crude **134** with visible light affords the corresponding phosphine–imidazolium salts **135**, precursors of bi- and tridentate (for R = 2-Py) N-heterocyclic carbene (NHC)-phosphine ligands, in good yield.

The reaction of **133** with 1 equiv of imidazole afforded an equimolar mixture of binuclear meso- and racemic phosphine complexes **136** (Scheme 1.44) [110a]. These air-stable complexes can be readily separated by column chromatography, to provide (after photochemical demetallation) the imidazolium salts **137**,



Scheme 1.44 Synthesis of precursors of chiral pincer-type phosphine-NHC-phosphine ligands from Mn(I) methylenephosphonium complexes. Source: Based on Valyaev et al. [110a].

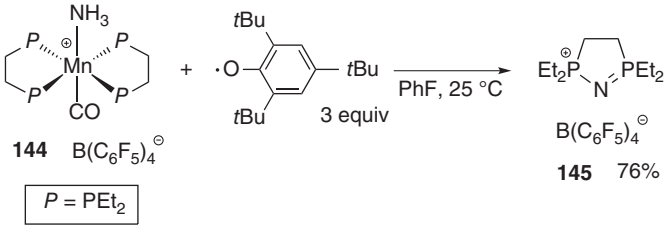


Scheme 1.45 Synthesis of Mn-based agent for RAFT polymerization and its photochemical decomposition. Source: Based on Kulai et al. [57].

precursors of pincer-type phosphine-NHC-phosphine ligands, in good yields. Notably, non-symmetric version of these pre-ligands, **139**, can be readily prepared upon reaction of **133** with an excess of imidazole, followed by the treatment of the resulting complex **138** with a different methylenephosphonium complex, separation of diastereoisomers, and release of the corresponding organophosphorous products **139**.

Novel phosphorous-containing agent **141** for Reversible Addition Fragmentation chain Transfer (RAFT) polymerization for styrene and acrylate monomers was recently prepared from cymantrene-derived diphenylphosphine complex **140** using a classic approach (Scheme 1.45) [57]. Interestingly, unlike all previously reported examples in this section, visible light irradiation of the resulting polymers **142** proceeded with complete destruction of the Ph_2PCS_2 fragment, allowing the efficient preparation of thiol-terminated polymers **143** under mild conditions.

Very recently, Bullock and coworkers showed that triple hydrogen atom abstraction from the ammonia manganese complex **144** with stable



Scheme 1.46 Synthesis of cyclic phosphazenium salt by hydrogen atoms abstraction in Mn(I) ammonia complex. Source: Based on Cook et al. [112].

2,4,6-tri-*tert*-butylphenoxyl radical leads to the formation of the rare cyclic phosphazenium salt **145** in good yield (Scheme 1.46) [112].

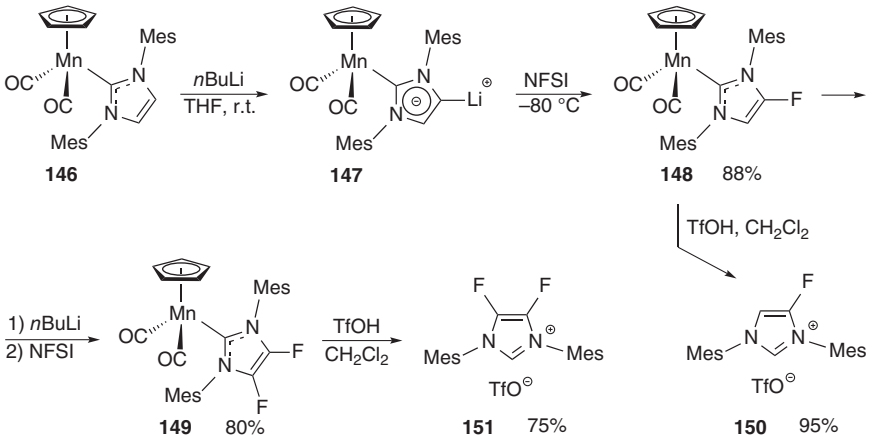
1.5.6 Backbone Modification of N-heterocyclic Carbenes in Mn(I) Coordination Sphere

We have recently shown that deprotonation of the half-sandwich manganese complex **146**, readily available from cymantrene and free carbene on 10 g scale [43a], with *n*BuLi at room temperature selectively proceeds at the backbone position of the NHC ligand to form bimetallic complex **147**, bearing an anionic imidazol-2,4-diylidene ligand (Scheme 1.47) [25]. In contrast to other complexes of this type, the $[Cp(CO)_2Mn]$ transition metal fragment did not migrate from the "normal" to the "abnormal" carbene position, thus permitting to exploit the highly nucleophilic character of the latter. In particular, this approach was used for the stepwise electrophilic fluorination with *N*-fluorobenzenesulfonimide (NFSI) to form complexes **148** and **149**, bearing unprecedented $IMes^F$ and $IMes^{F2}$ ligands, respectively (Scheme 1.47) [113]. Very importantly, simple treatment of complexes **148** and **149** with triflic acid in CH_2Cl_2 solution led to the quantitative release of the corresponding imidazolium salts **150** and **151**. This reaction, which likely involves protonation at the manganese center, followed by elimination of the imidazolium for the resulting cationic hydride intermediates $[Cp(CO)_2(NHC)MnH]^+$, appears to be quite general for $Cp(CO)_2Mn(NHC)$ complexes.

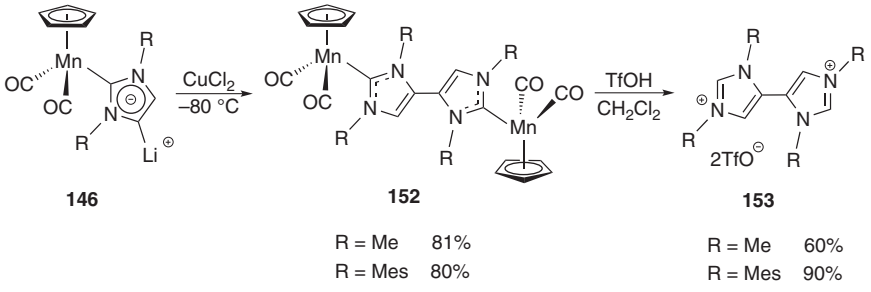
Synthetic potential of the anionic imidazol-2,4-diylidene manganese complexes **146** can be further illustrated by their oxidative coupling, mediated by $CuCl_2$, leading to bimetallic complexes **152** exhibiting new Janus-type bis(carbene) ligands, in which two imidazol-2-ylidene moieties are connected by a simple C—C bond (Scheme 1.48) [43a]. As in the previous case, the corresponding bis(imidazolium) salts **153** are readily released from **152** upon protonation.

1.6 Summary and Conclusions

The information systematically collected in this chapter illustrates a significant potential of various classes of organometallic Mn(I) complexes in organic synthesis. In this chapter, we deliberately selected reactions leading to effective formation of organic compounds, whereas many other relevant transformations existing in



Scheme 1.47 Synthesis of backbone fluorinated imidazolium salts in Mn(I) coordination sphere. Source: Based on Grineva et al. [113].



Scheme 1.48 Synthesis of bis-imidazolium salts by oxidative coupling of abnormal carbenes in Mn(I) NHC complex **146**. Source: Based on Grineva et al. [113].

the literature were not covered. The role of the most common Mn(I) fragments ($Cp(CO)_2Mn$, $(CO)_5Mn$, $(CO)_3Mn$) in these processes can vary from simple action as a protecting group for allene, phosphine, and NHC moieties to the direct influence on the ligand-centered reactivity in the case of η^5-cyclohexadienyl, carbene, and methylenephosphonium complexes. It is particularly important to point out that numerous demetallation protocols including oxidation, ligand substitution, protonation, and photochemical destruction have been already developed for different types of Mn(I) complexes, thus ensuring this crucial step for metal-mediated synthesis. While catalysis undoubtedly remains the privileged way for the design of highly selective and atom economical processes, stoichiometric reactivity of complexes based on cheap and non-toxic 3d metals may sometimes provide a valuable alternative. Considering a tremendous progress in homogeneous catalysis with organometallic manganese complexes over the last few years, and existing solid background in synthetic chemistry of Mn(I) species, we expect that Mn-mediated organic synthesis will attract continuously growing attention of the research community in the near future.

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