Transition metal catalyzed [6 + 2] cycloadditions

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The [6 + 2] cycloaddition reactions are one of the important synthetic transformations to construct eight membered carbo-/heterocyclic systems. The present review is an attempt to update readers on transition metal catalyzed [6 + 2] cycloaddition reactions of various 6π-contributing substrates such as cycloheptatrienes (CHT), cyclooctatetrenes (COTT), allenals, vinylcyclobutanes, fulvene etc. employing rhodium, cobalt, titanium, copper, platinum, ruthenium, merrifield and diphenylprolinol-silyl ethers etc. as catalysts. The transition metal catalyzed [6 + 2] cycloaddition reactions with a variety of functionalized substrates provide straightforward access to eight membered cyclic and/or 5/8, 6/8 etc. condensed carbo-/heterocyclic molecules in moderate to good yields.

Introduction

Cycloaddition reactions are considered to be one of the most powerful methods for the construction of cyclic skeletons with atom economy. There are ample reports on different variants of [4 + 2] and [3 + 2] cycloadditions which provide an easy access to a variety of five or six membered carbo-/heterocycles. However, the parallel methodologies such as [5 + 2], [6 + 2], [8 + 2] etc. for the synthesis of seven, eight or ten membered carbo-/heterocycles are still uncommon in the literature. Eight-membered rings are found in a wide variety of natural products and are useful ring systems available in variety of drugs, drug leads, or biological probes. Taxol, the well-known natural product in this family, is now among the most potent anticancer drug in clinical use. In 2008, another member of this family, pleuromutilin was approved for use as an antibiotic by Food and Drug Administration (FDA) (Fig. 1). Several methods including ring-closing metathesis and Cope rearrangement have been reported for the synthesis of eight-membered carbocycles. However, the intolerance to substrate substituent in conventional procedures along with complexities observed in natural products make these techniques ineffective and instigated the development of alternate protocols. Recent years have seen a significant upsurge in this direction with relatively few reports appearing on the synthesis of eight membered carbocycles using [6 + 2] and [4 + 2 + 2] cycloaddition reactions. Concerted [6 + 2] cycloaddition reactions are forbidden thermally as per Woodward–Hoffmann rules, when the two reacting π-systems add in a suprafacial fashion. However, transition metal-catalyzed [6 + 2] cycloadditions constitute one such protocol for the synthesis of monocyclic or condensed functionalized cyclooctadienes. The present review summarizes various reports on the transition metal catalyzed inter- and intra-molecular [6 + 2] cycloaddition reactions appeared in literature since 2000.

Rhodium catalyzed [6 + 2] cycloadditions

Rhodium complexes plays a pivotal role in organic synthesis as major catalytic contributors to C–C bond formation reactions. A number of carbo-/heterocyclic systems have been generated employing rhodium complexes as efficient catalyst in a variety of cycloaddition/cyclization reaction. Literature rationale suggests an inspiring advancement in this field and many research groups are extensively using rhodium complexes to efficiently conceive these reactions. Considering the importance of rhodium catalysed cycloadditions, there should have been a number of reports on generation of eight membered carbo-/heterocycles engaging rhodium complexes in [6 + 2] cycloadditions, however only a few reports are available which successfully comprehends [6 + 2] cycloadditions. Till now, different substrates such as cycloheptatriene, 2-vinylcyclobutane, allenals, allencyclobutanones, cyclooctatetraenes etc. have been reported as 6π-components in Rh(i) catalysed [6 + 2]...
Rh(\textit{i}) catalysed [6 + 2] cycloadditions of 2-vinylcyclobutanones

One of the earliest reports on Rh(\textit{i}) catalyzed [6 + 2] cycloadditions of 2-vinylcyclobutanones as 6π-components is reported by Wender \textit{et al.} It involves intramolecular [6 + 2] reactions of 2-vinylcyclobutanones 1\textit{a}-h with tethered alkenes for the construction of eight-membered-ring systems 2\textit{a}-h.\textsuperscript{18} The [6 + 2] reactions have diverse substrate compatibility and proceed for a variety of different tethers to produce \textit{cis}-fused condensed cyclooctatrienes 2\textit{a}-h in excellent yields (Scheme 1).

The [6 + 2] cycloadditions involve initial formation of a five-membered metallacycle \textit{A}, which undergoes ring expansion to nine-membered metallacycle \textit{B}, demetallation of \textit{B} affords eight-membered condensed carbocycles \textit{via} reductive eliminations (Fig. 2).

Rh(\textit{i})-catalyzed formal [6 + 2] cycloadditions of allene

Sato \textit{et al.} have developed an efficient methodology for the synthesis of fused bicyclic ketones 4. It involves the Rh(\textit{i})-catalyzed intramolecular [6 + 2] cycloadditions of alkyne/allene tethered allenal 3\textit{a}-\textit{j} using Rh(\textit{i})-complex as catalyst. [Rh(\textit{I-Mes})(\textit{cod})]ClO\textsubscript{4} is an effective catalyst in these [6 + 2] cycloadditions.\textsuperscript{19} The use of other Rh(\textit{i}) complexes as catalyst such as [Rh(\textit{IPr})(\textit{cod})]ClO\textsubscript{4}, [Rh(\textit{IPr})(\textit{cod})]ClO\textsubscript{4} and [Rh(\textit{IMes})(\textit{cod})]ClO\textsubscript{4} afford bicyclic ketones in lower yields and [Rh(dppe)]ClO\textsubscript{4} is completely ineffective in conceiving [6 + 2] reactions. The [6 + 2] cycloadditions using RhCl([PPh\textsubscript{3}])\textsubscript{3} afford bicyclic ketone 4 in relatively good yield (72%) but with longer time. The cyclizations of 3\textit{a} and 3\textit{b} having phenyl and TMS groups on the allene moiety provide 4\textit{a} and 4\textit{b} in 71% and 90% yields respectively. Substrate 3\textit{d-f} containing a heteroatom in the chain afforded corresponding heterocycles 4\textit{d-f} in good to excellent yields. Elongation of the tether between the allenyne and allene moieties by one carbon is well tolerated in the [6 + 2] cycloaddition reaction and afford 6/8 fused bicyclic ketone 4\textit{g} in 70% yield as evident by the conversion of 3\textit{g} to 4\textit{g}. The cyclizations of substrates 3\textit{h-i} having an tethered allene also afford bicyclic ketones 4\textit{h-i} in a stereoselectively (Scheme 2).

The [6 + 2] cycloaddition of enantiomerically enriched (S)-5 (94% ee) yields cyclic ketone (S)-6 in high yields with reasonable transfer of chirality (86% ee) as shown in Scheme 3.*

The possible mechanism for the formation of 6 involves the oxidative addition of Rh(\textit{i}) complex to the C–H bond of the aldehyde 5 followed by insertion of the C=C bond of the allene to give oxo-rhodacycle 6 which undergoes isomerization to oxo-rhodacycle 6 via \textit{π}-allylrhodium intermediate F. Insertion of an alkyne or allene into the Rh–C bond followed by reductive elimination yields bicyclic ketone 4/6 (Fig. 3).

Sato \textit{et al.} have also explored the intermolecular [6 + 2] cycloadditions of 4-allenal 7 and allyne 8, for the synthesis of functionalised monocyclic cyclooctane derivatives 9.\textsuperscript{20} The intermolecular [6 + 2] cycloadditions suffer from unfavorable entropy disadvantage which resulted in decreased yield of the [6 + 2] cycloadducts with the isolation of side products 10 through hydroacylation of allene 7\textsuperscript{25} and formation of 11 by trimerization of allyne 8 (Scheme 4).

The [Rh(SiMes)(cod)]ClO\textsubscript{4} have been found to be efficient in conceiving intermolecular reactions with the selective formation of eight-membered carbocycle 9 (68%). The [Rh(IMes)(cod)]ClO\textsubscript{4} as catalyst is non selective and afford mixture of eight
membered carbocycle 9 (61%) and six-membered carbocycle 12 (19%). Other tested catalysts such as [RhCl(PPh₃)₃] and [Rh(dppe)]ClO₄ do not promote the intermolecular [6 + 2] cycloaddition reactions (Scheme 5).

The intermolecular [6 + 2] cycloadditions of 7a with various terminal alkynes possessing benzyloxy 8b–c, benzoate 8d and sulphonamide moiety 8e have also been reported to proceed in a stereoselective manner affording eight membered carbocycles 9b–e in high yields. The propargyl tethered alkyn moiety 8f, however, provide regiomeric cyclooctadienone 9f and 9f' in yields of 64% and 10% respectively. Employing 1-hexyne have yielded a mixture of isomeric eight-membered rings 9g/9g' in 68% and 5% yields along with six-membered carbocycles as side product 12g (11%). Electron-withdrawing carboxylate functionality on alkyne nucleus 8h have led to the regioemic cyclooctadienones 9h/9h' in comparatively lower yields (56% & 22% respectively). 4-Allenal substituted with benzyloxy 7a–b, benzyl 7c, sulphonamide 7d and TMS 7e afford regioselective octacyclic compounds 9a, i–l in yields of 69%, 81%, 72% and 82% respectively. Phenyl substitution on allene however, retards the reaction rate and regioselectivity resulting in isolation of 9m/9m' in 51% and 23% respectively.

The allenal 7g–h possessing alkyl substitution between allene and aldehyde have resulted in increased formation of hydroacylation product 12n–o in 28% and 17% yields along with intramolecular [6 + 2] cycloadducts 9n–o in 37% and 44% yields respectively (Scheme 6).
Rh(I) catalysed [6 + 2] cycloaddition reactions of allenylecyclobutanes

Mukai et al. have devised a cycloisomerisation methodology using rhodium(I) catalysed alkyne-allenyl unfunctionalised cyclopropane/butane 13 to afford bicyclic and compounds 15 and 14 through [5 + 2]21 and [6 + 2]22 cycloaddition respectively. The un-functionalized simple cyclobutane ring in [6 + 2] cycloadditions behaves as 6p-component and afford an easy construction of the bicyclo[6.3.0]undecatrienes 14 in good yields (Scheme 7).

The [6 + 2] cycloaddition reactions are conceived by heating a solution of 13 in 1,2-dichloroethane at 80 °C in the presence of 10 mol% [RhCl(CO)2] as catalyst to afford the desired bicyclo[6.4.0]dodecatriene 14 in 40% yield along with monocyclic side product 16 (52%). Replacement of catalyst to [RhCl(CO)dppp]2 in toluene have witnessed a marked increase in yield of 6/8 bicyclic product 14 (80%). Other rhodium carbonyl catalysts are less effective in conceiving these [6 + 2] cycloadditions. Best results for [6 + 2] cycloaddition reactions are observed employing [RhCl(dppe)]2 as catalyst without carbon monoxide as ligand. A decrease in catalyst loading to 5 mol% has observed a lowering in reaction yield of 14, however, using 5 mol% [RhCl(dppe)]2 in 0.1 M dioxane solvent at 80 °C have led to the formation of bicyclo[6.4.0]dodecatrienes 14 (87%) (Scheme 8).

The proposed mechanism involves the coordination of 13 with Rh(i) complex through allenal double bond, C-C bond of the strained cyclobutane ring and alkyne to produce intermediate G, which opens up immediately to rhodabicyclo[4.3.0]nonadiene intermediate H followed by π-carbon elimination of the strained cyclobutane ring of H leading to the formation of nine membered intermediate I, which undergoes reductive elimination leading to bicyclo[6.4.0]dodecatrienes 14. However, π-hydride elimination instead of π-carbon elimination of I generates intermediate J which on reductive elimination yields monocyclic adduct 16. Alternatively, rhodacycle intermediate K23–25 produced from ring opening of strained cyclobutane ring intermediate G, undergoes insertion of C–RhIII bond into the triple bond leading to the production of intermediate P23 (Fig. 4).

Rh(I) catalysed [6 + 2] cycloadditions of cyclooctatrienes

Conjugated cyclic trienes viz. cycloheptatrienes (CHT), cyclooctatrienes (COTT) etc. are excellent participants in [6 + 2] cycloadditions as the embedded trienes in the favored cisoid conformations acts as 6p-components with different alkenes, alkynes and dienes acting as 2p-component. The use of metal catalysts in these cycloaddition reactions have found an extensive place in literature. Metal catalysts such as titanium,36 ruthenium,27 molybdenum,28 cobalt,29 chromium30 and iron31 complexes have been widely used to perceive such reactions.
Mach et al. have engaged Ziegler catalyst (TiCl_4/Et_2AlCl) in achieving these [6 + 2] cycloadditions.\textsuperscript{23} Rigby et al. have employed carboxylchromium(0) complex bearing labile ligand to effectively achieve [6 + 2] cycloadditions.\textsuperscript{10a–d} Buono et al. have recently established [6 + 2] cycloadditions of CHT with terminal alkynes.\textsuperscript{33} Also, cobalt(i) catalysed protocol has been applied to [6 + 2] cycloadditions of COTT and internal and terminal alkynes\textsuperscript{14} and CHT to substituted alkenes.\textsuperscript{35}

Wang et al. have explored [6 + 2] cycloadditions of cycloheptatriene with internal alkynes employing different rhodium(i) catalysts. The [6 + 2] cycloadditions do not occur using PPh_3RhCl as catalyst at 60 °C.\textsuperscript{36} The [6 + 2] cycloadditions at elevated temperature (120 °C) witness the formation of cycloadduct (64%). Further increase in reaction temperature causes decrease in yield of 20 (53%). Introducing additives such as CuI (10 mol%) which acts as phosphine cleavage reagent\textsuperscript{37} have increased the yield of 20 (75%). Exchanging the catalyst to [Rh(COD)Cl]_2 steers the reaction to better results (71%). Best results for [6 + 2] cycloadditions (88%) are witnessed using [Rh(COD)Cl]_2 as catalyst along with PPh_3 (10 mol%) and CuI (10 mol%) at 120 °C. A number of terminal alkynes have been tried by Wang et al. The electron donating groups at para position of phenyl acetylene such as 19a, 19c, 19d and 19f have afforded better yields of [6 + 2] cycloadducts (88%, 85%, 87% and 88% respectively). Conversely, electron withdrawing substituents on alkyne such as 19g–h, 19i, 19j, 19k resulted in lowering of reaction yields to 70%, 73%, 70%, 72% and 67% respectively demonstrating the importance of electron donating substituents. No substitution on alkyne nucleus 19b have led to 81% isolation of 20b. Introducing bulky groups as in 19l–n have resulted in poor isolation of 20l–n in 48%, 40% and 30% yields owing to the strong detrimental steric effect played by these groups (Scheme 9).

The mechanism for [6 + 2] cycloadditions involves the initial conversion of catalytic precursor [Rh(COD)Cl]_2 to (Ph_3P)_2Rh(COD)Cl N, followed by exchange of COD ligand with CHT generating intermediate O. Replacement of PPh_3 with alkyne in the presence of CuI leads to intermediate P which immediately undergoes oxidative cyclometalation to intermediate Q. Addition of alkyne to Q produces π,π-allyl complex R which undergoes reductive elimination through transition state S to intermediate T. Ligand exchange of T with CHT delivers cycloadduct 20 and regenerates rhodium complex P to renter the catalytic cycle. DFT calculations employing M06 function taking Rh(I) model as catalyst also confirms the proposed reaction mechanism with the observation of strong additive effect for the CuI in these [6 + 2] reactions (Fig. 5).

Cobalt catalyzed [6 + 2] cycloadditions

Co(i) complexes have been observed an excellent catalyst for [6 + 2] cycloadditions of cycloheptatrienes, cyclooctatetraenes, dicobalt acetylene complexes as 6π-components with alkyne, allene enol silyl ethers as 2p-components to yield variety of monocyclic or condensed eight membered carbocycles. All the reported studies involve the intermolecular [6 + 2] variants of these cycloadditions and Co(i) catalysed intramolecular [6 + 2] cycloadditions are scarcely available in literature.

[6 + 2] cycloadditions of cycloheptatriene (CHT) and alkynes

Buono et al. have reported the first cobalt(i) catalyzed [6 + 2] cycloadditions of cycloheptatriene (CHT) 18 with alkynes 21 to afford 7-alkyl-bicyclo[4.2.1]nona-2,4,7-trienes 22 (Scheme 10).\textsuperscript{18} Various cobalt(i) catalytic systems\textsuperscript{39} have been tested for [6 + 2]
cycloadditions. Best results are witnessed using cobalt(II)iodide/1,2-bis(diphenylphosphino)ethane (dppe) as catalyst, zinc metal as reducing agent, zinc iodide as a Lewis acid in 1 : 3 : 2 molar ratio in 1,2-dichloroethane as solvent. The catalytic combination of CoI$_2$(dppe)/Zn/ZnI$_2$ have also proven excellent tolerance to various functional groups such as nitrile, alcohol, imide, sulfone, ketone, ester, ketal or ethers substituted alkyne 21a–m in their [6 + 2] cycloaddition reactions with CHT 18. Alkynes having remotely substituted functional groups to the triple bond such as 21f, 21j, 21m afford cycloadducts 22f, 22j and 22m in excellent yields. The alkynes have substitution propargylic carbon 21d, 21k provide low yield of [6 + 2] cycloadducts. Electron poor alkynes such as methyl propiolate 21g have afforded [6 + 2] cycloadduct 22g with poor yield (21%) due to the preferential coordination of cobalt with 21g initiating its cyclotrimerisation process. The efficacy of cobalt catalysed [6 + 2] cycloadditions are bettered using syringe pump controlled slow addition of the alkyne and lowering the catalyst loading (2.5 mol%) (Scheme 10).

A plausible mechanism involves the ZnI$_2$ reduction of CoL$_2$I$_2$ by zinc metal to cationic [Co(I)L$_2$]$^+$ complex which coordinates with alkyne 21 and CHT 18 followed by oxidative cyclometalation to produce cobalta-cyclopentene intermediate U. 1,5-migration of the C(sp$^3$)–Co bond of U through consecutive π,π-allyl complexes V and W leads to bicyclo cobalta-cycle X which on reductive elimination generates cycloadduct 22 and regenerates cationic intermediate [Co(I)L$_2$]$^+$ to return to the catalytic cycle (Fig. 6).

An enantioselective version of the [6 + 2] reactions has also been explored using phosphoramidite ligand as chirality inductors with improved yields and good enantioselectivity.

[6 + 2] cycloadditions of cycloheptatriene (CHT) and allene
Buono et al. have also reported cobalt catalyzed [6 + 2] cycloadditions of cycloheptatriene (CHT) 18 with variety of allenes 23 to afford bicyclic 7-bicyclo[4.2.1]nona-2,4-dienes 24 with an improved yield, enhanced regio- and geometrical selectivity (Scheme 11). The treatment of CHT 18 with phenylallene 23a under CoI$_2$(dppe)/Zn powder/ZnI$_2$ as catalytic system have resulted in an exclusive formation of $E$-isomer of 7-benzylidenebicyclo[4.2.1]nona-2,4-diene 24a without the isolation of even traces of the other geometrical or regioisomer 25. Zinc metal plays a pivotal role in these cycloaddition reactions, absence of which leads to non-isolation of [6 + 2] cycloadduct. Also, ligand plays an equally important role as bis(diphenylphosphino)methane (dpdm) and 1,3 bis(diphenylphosphino)propane (dppp) were ineffective in conceiving these reactions. Optimal reaction conditions leading to best results in terms of yield of 24 is witnessed using CoI$_2$(dppe) catalytic system with Zn/ZnI$_2$ reducing agent in 1,2-dichloroethane as solvent. 40

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**Scheme 10** Cobalt(II) catalyzed [6 + 2] cycloaddition reactions of CHT with terminal alkynes.

**Scheme 11** Cobalt catalysed [6 + 2] reactions of CHT with substituted allenes.
The \([6 + 2]\) cycloaddition reactions of monosubstituted allenes 23 are also studied using Co(II) complexed as catalysts. The methoxy or methyl substitution at ortho- or para- position of phenylallene 23a–d, is well accepted and lead to the exclusive formation of \(E\)-isomers 24a–d in good yields. \([6 + 2]\) cycloadditions of benzylallene 23f with CHT 18 also leads to the exclusive formation of \(E\)-7-benzylidenecyclo[4.2.1]nona-2,4-diene 24f in 82% yield. \(\alpha\)-allenol 23g and \(\beta\)-allenol 23h are non reactive under these reaction conditions. With tetrahydropropyl and benzoate protected \(\alpha\)-allenes 23i and 23e, excellent yields of 93% and 94% are achieved for cycloadducts 24i and 24e respectively. Conversely, tert-butyl dimethylsilyl protected \(\alpha\)-allenes 23j leads to relatively low yields of \([6 + 2]\) cycloadducts 24j (54%) due to the degradation of allene during the catalytic cycle. The \([6 + 2]\) cycloadditions of disubstituted allenes, require high temperature and greater reaction time to manage similar results both in terms of yield and selectivity48 (Scheme 11).

\([6 + 2]\)-cycloadditions of cyclooctatetraene and terminal allenes

D’yakonov et al. have accomplished the Co(II) catalyzed \([6 + 2]\)-cycloadditions of 1,3,5,7-cyclooctatetraene 26 (COTT) with functionalized terminal allenes 27a–e in the presence of \(\text{CoI}_2/\text{dppe/Zn/ZnI}_2\) catalytic system using 1,2-dichloroethane as solvent at 60 °C to afford \(\{E\}\)-bicyclo[4.2.2]deca-2,4,7,9-tetraenes 28a–e in good yields (78–85%; Scheme 12).48 The reactions are gauged using varied reaction and catalytic system. It is observed that \(\text{CoI}_2\) or \(\text{ZnI}_2\) alone do not conceive the reactions even at elevated temperature (100 °C).

The \([6 + 2]\) cycloadditions of COTT 26 with 1,2-cyclooctanadiene 27f under similar reaction conditions afford tricyclo[9.4.2.0]heptadeca-2,12,14,16-tetraene 28f in 65% yield. Interestingly, the reactions also proceed further to produce regioand stereomeric bis-adduct mixture 29a and 29b in total yield of 30%48 (Scheme 13).

\([6 + 2]\) cycloadditions of cyclooctatetraene with alkynes

Buono et al. have also explored the cobalt-catalyzed \([6 + 2]\) cycloaddictions of cyclooctatetraene 26 with alkynes 30a–j for the synthesis of monosubstituted bicyclo[4.2.2]deca-2,4,7,9-tetraenes 31a–j in fair to good yields (56–94%). The reaction of phenylethyne 30a with COTT 26 using \(\text{CoI}_2/\text{dppe}\) as catalyst/ligand and \(\text{ZnI}_2/\text{Zn}\) as Lewis acid/reducing agent couple in 1,2-

dichloroethane at 40 °C have resulted in the isolation of 7-phenylbicyclo[4.2.2]deca-2,4,7,9-tetraene 31a in 70% yield. Alternatively employing \(\text{CoI}_2/\text{dppe}, \text{Bu}_4\text{NBH}_4/\text{ZnI}_2\) catalytic system have led to the isolation of 31a in 66% yield. The reaction protocol had proven to be of wide spread applicability as various functionalities on alkyne nucleus viz. ester, amide, nitrile, sulphonate, ketone, sulphones and trimethylsilyl are very well accepted as evident from moderate to good yields of \([6 + 2]\) cycloadducts 31a–j (56–94%; Scheme 14).48

The \([6 + 2]\) cycloadditions encountered similar success when COTT 26 is made to react with symmetrical alkynes 30k–l for synthesis of cycloadducts 31k–l in yields of 78% and 77% respectively. The \([6 + 2]\) cycloadditions however have failed for diphenylethene or 3-hexyne (Scheme 15).42

The cobalt-catalyzed cycloaddictions of cyclooctatrienes (COTT) 32 with various alkynes 30a–e afford a mixture of desired \([6 + 2]\) cycloadducts 33a–e and tricyclic adduct 34a–e. The absence of cycloadducts of type 35 and 36 from the product range rules out the possible \([4 + 2]\) cycloaddition pathway for COTT 26 and COTT 32 (Scheme 16).

The COTT 32/COTT 26 can exist in two isomeric forms namely monocyclic form X and 6π bicyclic isomeric electrolyte Y. The \([6 + 2]\) cycloaddition of terminal alkyne 30 to isomeric form X have resulted in the formation of desired cycloadduct 33, whereas, \([4 + 2]\) cycloaddition of 30 to bicyclic isomeric form Y have led to the isolation of cycloadduct 34. The direct non participation of X in \([4 + 2]\) cycloaddition with terminal alkyne 30 have resulted in non isolation of hypothetical products 35 and 36 (Fig. 7).
Mechanistically, the reaction is expected to proceed through two pathways. Oxidative cyclometallation of I followed by its coordination to alkyne 30 generates cobaltacycle VI in the first path. Alkyne insertion to Co–C bond leads to cobaltabicycle V, which on reductive elimination of cobalt affords cycloadduct 31/33 and regenerates active [CoL2]+ to reenter the catalytic cycle. In the second path, oxidative cyclometallation of II leads to complex III which on 1,3-migration of Co–C(sp^3) bond through σ-π-allyl complex forms cobaltabicycle adduct V. Formation of [4 + 2] cycloadduct proceeds via sequential oxidative cyclometallation, alkyne insertion and reductive elimination of intermediate VII and VIII leading to product 34 (Fig. 8).  

Tanino et al. have developed methodology for the stereoselective synthesis of cyclooctanones 40 by formal [6 + 2] cycloadditions of a hexa carbonyl dicobalt acetylene complex 38 (6σ component) with several enol silyl ethers 2π component 37 under the influence of EtAlCl2.

The methodology holds special importance as no side product arising from intramolecular cyclisation/homo coupling of the cobalt complex is noticed which allowed equivalent mixing of reactants without employing high dilution synthesis (Scheme 17).  

The reaction proceeds with the stereoselective formation of dicobalt acetylene complex 39 in good yields. Acyclic enol silyl ethers 37c, 37d, 37e produce cycloadducts 39c, 39d and 39e in 73% (88 : 12), 68% (cis) and 83% (86 : 14) yields respectively with the major product having cis arrangement of alkyl and silyloxy group. However, trans fused cyclooctanone 39f is obtained as a single cycloadduct (81%) by employing cyclic enol silyl ether 37f.

The [6 + 2] cycloadditions can be utilized to generate a model compound of taxane diterpenoid. The B–C ring system of taxane is constructed by employing [6 + 2] cycloaddition reaction of diacetylene dicobalt complex 38 with cyclic enol silyl ether 37f.

Titanium(II) catalyzed [6 + 2] cycloadditions

Titanium complexes has successfully tested in [6 + 2] cycloadditions of variety of cycloheptatrienes, cyclooctatetraenes,
bis(1,3,5-cycloheptatriene-7-yl)alkanes as 6π-components with alkyne, 1,2-dienes, as 2π-components to yield variety of monocyclic or condensed eight-membered carbocycles. All the reported studies involve only intermolecular variants of [6 + 2] cycloadditions.

Titanium(II) catalyzed [6 + 2] cycloadditions of cycloheptatrienes with alkynes

D'yakonov et al. have explored the [6 + 2] cycloadditions of 7-alkyl(allyl,phenyl)-1,3,5-cycloheptatrienes 41 with alkynes 42 catalyzed by the two-component Ti(acac)2Cl2–Et2AlCl system, resulting in the formation of substituted bicyclo[4.2.1]nona-2,4,7-trienes 43/44 in excellent yields (up to 90%). The addition of alkyne 42 to the cycloheptatriene 41 (1:1) occurs in a stereoselective manner to afford predominantly syn-isomer. The [6 + 2] cycloadditions using alkyne 42 having ethyl-, butyl-, phenyl-, and allyl-substituted cycloheptatrienes 41b, 41c, 41d and 41e lead to cycloadducts 43c–j syn-specificity (Scheme 18). Symmetrical alkynes such as hex-3-yne, oct-4-yne and dec-5-yne are incompetent 2π-components in [6 + 2] cycloadditions and have shown competitive homo-cyclotrimerization. The [6 + 2] reactions afford bicyclic systems 43/44 using (i-PrO)2TiCl2 and (t-BuO)2TiCl2 or TiCl4 as catalysts. The [6 + 2] reactions of 7-alkyl(allyl,phenyl)-1,3,5-cycloheptatrienes 41 with Si-containing alkynes 45 catalyzed by the Ti(acac)2Cl2/Et2AlCl system, furnish substituted bicyclo[4.2.1]nona-2,4,7-trienes 46 in good yields (79–88%; Scheme 19).

[6 + 2] cycloadditions of cycloheptatrienes with 1,2-dienes

D'yakonov et al. have also envisaged [6 + 2] cycloadditions of functionalized cycloheptatrienes 41 with allenes(1,2-dienes) 27 using Ti(acac)2Cl2–Et2AlCl system as catalyst to generate predominantly endobicyclo[4.2.1]-nona-2,4-dienes 47a–f in good yields. The enhanced syn selectivity is largely attributed to the steric bulk at 7-position of CHT nucleus (Scheme 20).

D'yakonov et al. have also studied [6 + 2] cycloadditions reactions using functionalized cycloheptatrienes 41 and 1,2-cyclononadiene 27f to yield a mixture of syn and anti of isomeric triylocycle[9,4,1,0]-hexadeca-2,12,14-trienes 48a–d (78–85%; Scheme 21).

[6 + 2] cycloadditions of bis(1,3,5-cycloheptatriene-7-yl)alkanes

D'yakonov et al. have explored [6 + 2] cycloadditions of Si-containing alkynes 45 and bis(1,3,5-cycloheptatriene-7-yl)alkanes 49 using Ti(acac)2Cl2–Et2AlCl as catalytic system, leading to selective formation of mono- and bis-adducts [9-[4-(2,4,6-cycloheptatrienyl)alkyl]-8-alkyl(phenyl)bicyclo[4.2.1]nona-2,4,7-triene-7-yl][trimethylsilanes 50a–f and bis(7-trimethylsilyl-8-alkyl(phenyl)bicyclo[4.2.1]nona-2,4,7-triene-7-yl)alkanes 51a–f in 78–88% yields respectively. The cycloaddition reactions of alkynes 45 and bis(1,3,5-cycloheptatriene-7-yl)alkanes 49 are stereoselective, resulting in the isolation of syn-isomer. The high

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**Scheme 17** [6 + 2] cycloadditions of various enol silyl ether with dicobalt acetylene complex.

**Scheme 18** Ti-catalyzed [6 + 2] cycloadditions of alkynes to 7-substituted 1,3,5-cycloheptatrienes.

**Scheme 19** Ti-catalyzed [6 + 2] cycloadditions of silicon containing alkynes to 7-substituted 1,3,5-cycloheptatrienes (CHT).

**Scheme 20** Ti-catalyzed [6 + 2] cycloadditions of 1,2-dienes to 7-substituted 1,3,5-cycloheptatrienes (CHT).
stereoselectivity is presumably attributable to steric factors associated with the bulky substituent at the bridging carbon atom in the initial bis{1,3,5-cycloheptatriene-7-yl}alkane 49 (Scheme 22).

**Platinum(a) catalyzed intramolecular [6 + 2] cycloadditions**

Platinum(a) complexes has efficiently been explored in relatively less explored intramolecular variant of [6 + 2] cycloadditions to afford bicyclic cyclopentane fused bicyclo[4.2.1]nona-2,4,7-trienes. Tenaglia et al. have developed a facile, chemoselective and high yielding platinum-catalyzed (5 mol%) en route for intramolecular [6 + 2] cycloadditions of alkynes tethered to cycloheptatrienes 52a–k at room-temperature to afford cyclopentane fused bicyclo[4.2.1]nona-2,4,7-trienes 53a–k in good yields (66–99%). The cycloisomerizations of 52 with other metal complexes such as [RuCl2(CO)3]2 and AuCl3 provide satisfactory results, whereas rhodium complexes are poor in catalysing these reactions. The best results are obtained using PtCl2 (5 mol%) as catalysts. The reactions are also analyzed in different solvents, such as THF (85%), acetone (91%), toluene (94%) are observed most promising solvent and cycloadditions in methanol, acetonitrile and DMF are unsuccessful. The [6 + 2] cycloaddition can tolerate variety of substitutions at cycloheptatrienes such as CHT carrying acetal 52f, ether 52d–e, ester 52h–j, sulfonate 52b, cyclic carbonate 52g, halide 52k or nitrile substituents 52c afford [6 + 2] cycloadducts in good yields. However, lengthening the tether by an additional carbon unit in 52 has a detrimental effect and no [6 + 2] cycloadduct is realised (Scheme 23).

The CHT bearing internal alkynes 54a–e have been observed reluctant participants in intramolecular [6 + 2] cycloadditions even at elevated reaction temperature (110 °C; Scheme 24).

Alkyl 54a–b and phenyl 54c substituted trienynes are unreactive whereas, electron deficient 54d–e afford [6 + 2] adducts 55d–e albeit in low yields of 64% and 22% respectively.

The intramolecular [6 + 2] cycloisomerisations of trienynes 57a–g bearing heteroatom in the tether yield [6 + 2] cycloadducts 58 along with the formation of side products such as dihydropyranes or tetrahydropyranes 59 via 1,2-hydrogen or alkyl migration, along with other products 60, 61 and 62 as depicted in Scheme 25.

The proposed mechanism involves the exo cyclisations of 57 leading to pentadienyl cationic intermediate IX which through electronic redistribution affords [6 + 2] cycloadducts 58. With trienyne bearing an acyl functionality, carbonyl group trigger the cyclisation of 57, leading to dihydropyran 59. Endocyclisation of 57 through zwitter ion X and platinacarbene intermediate XI leads to product 59 presumably through a 1,2-hydrogen/alkyl shift followed by the elimination of metal ion. Formation of 60 is owed to the coordination of Pt2+ species to distant double bond of 59 followed by ring cleavage of the cyclopropane moiety. The tetrahydropyran ring opening of 58c/58e driven by HCl (generated from PtCl2) affords tertiary allylic carbocation yielding products 61 and 62 respectively (Fig. 9).

**Ruthenium(0) catalyzed [6 + 2] cycloadditions of cyclooctatetraene (COT) with alkynes**

Mitsudo et al. have envisaged [6 + 2]cycloaddition reactions of ruthenium(0) complex such as Ru(n4-cod)(n8-cot) 63 with
maleic anhydride \(64a\) or maleimides \(64b-e\) to generate a series of novel divalent ruthenacycles \(65a-e\). The reaction proceeds by employing equivalent amounts of both reactants in \(n\)-hexane as solvent for 2 h to afford ruthenacycles \(65a-e\) (Scheme 26).

Mitsudo \textit{et al.} have also studied electron deficient alkenes such as dimethyl fumarate and dimethyl maleate in \([6 + 2]\) cycloadditions to afford \(\text{Ru}[(\eta^5-\text{cot})(\eta^5-\text{dimethyl fumarate})]^{\delta}\). Employing p-benzoquinone in place of maleic anhydride produces an uncharacterizable mixture of products. \(N,N\)-Dimethylacrylamide and methyl vinyl ketone are ineffective in conceiving these reactions. Terminal alkynes on the other hand have afforded a zerovalent \(\eta^5,\eta^5\)-bicyclodecatriene product.\(^{32}\) The proposed mechanism for the production of ruthenacycles \(65\) involves the change of coordination mode of \(\text{COT}\) ligand of \(63\) from 1-6-\(\eta^6\) to 1-2:5-6-\(\eta^4\) or 1-4-\(\eta^4\) followed by \(64\) occupying its vacant coordination site to either produce intermediate \(\text{XIIa}\) or \(\text{XIIIa}\). The oxidative cyclisation of \(\text{COT}\) and \(64\) generates ruthenacycles intermediates \(\text{XIIb}\) and \(\text{XIIIb}\), which re-coordinates of the \(\text{C}=\text{C}\) bond affording desired ruthenacycles \(65\) (Fig. 10).\(^{30}\)

The ruthenacycles \(65a-e\) react in a number of ways to create cyclooctyl complexes \(66-70\) respectively. The ruthenacycles \(65d\), for example, on hydrogenation at 1 atm pressure affords \(N\)-phenylecyclooctylsuccinimide \(66\) in overall yields of 56%. The treatment of \(65d\) with \(\text{HCl}\) in \(\text{Et}_2\text{O}\), however, have resulted in the formation of \(N\)-phenyl[3,5-cyclooctadien-1-yl]succinimide \(67\) in 62% yield using mild reaction conditions. The ruthenacycle \(65d\) undergoes ring closure via reductive elimination at high temperature to afford tricylic \([6 + 2]\) cycloadduct \(68\). Introduction additives such as PPh\(_3\) promotes the production of \(68\) from \(65d\), while 1,2-bis(diphenylphosphino)ethane (dppe) does not yield \(68\), instead stable ruthenacycle \(69\) is formed (71%) presumably via ligand displacement between COD and dppe. The reaction of \(65d\) with \(\text{CO}\) in \(\text{toluene}\) at 1 atm pressure for 3 h have resulted in the isolation of ticasryl ruthenacycle complex \(70\) in an overall yield of 76%. The reaction proceeds with full dissociation of COD ligand from \(65d\) followed with the insertion of three molecules of \(\text{CO}\) coordinated to Ru along with cycloheptadienyl hapicity change from the change \(\eta^1\) to \(\eta^3\). The theoretical studies have also been carried to support the experimental results (Scheme 27).\(^{39}\)

**Cu(II) catalysed \([6 + 2]\) cycloaddition reactions**

Dethe \textit{et al.} have recently studied highly regio- and diastereoselective facile, one pot Lewis acid catalysed \([6 + 2]\) cycloaddition reactions for the synthesis of highly substituted pyrrolo[1,2-\(j\)j]indoles having three contiguous stereocenters. The reactions of indole alcohol \(71a-d\) with conjugated indole ester \(72a-e\) in the presence of 5 mol\% \(\text{Cu(OTf)}_2\) afford pyrroloindoles \(73a-j\) and \(74a-j\) in excellent overall yields of 85–92% with outstanding regio- and diastereoselectivity\(^{33}\) (Scheme 28).

The ester moiety in case of \(72\) is crucial in controlling diastereoselectivity in these cycloadditions. Other Lewis acid catalysts such as \(\text{TiCl}_4\), \(\text{BF}_3\cdot\text{Et}_2\text{O}\), \(\text{FeCl}_3\), \(\text{AlCl}_3\), \(\text{Sn(OTf)}_2\) and \(\text{Fe(OTf)}_3\) have resulted in poor diastereoselectivity of \(11 : 1, 14 : 1, 4 : 1, 3 : 1, 7 : 1\) and \(6 : 1\) for products \(73/74\). The methodology has also been used for the construction of the fully functionalized tricyclic core of bioactive natural product yur-eremamine which has been isolated from the stem bark of...
Mimosa hostilis having hallucinogenic and psychoactive effects (Fig. 11).

Chromium catalysed [6 + 2] cycloaddition reactions

Chromium(0) complexes are also been tested in [6 + 2] cycloadditions and a single report on Cr(0) catalysed [6 + 2] cycloadditions is disclosed by Rigby et al. It involves the development of resin supported chromium(0) catalytic system and their use as catalyst in [6 + 2] cycloadditions of cycloheptatriene (CHT) with variety of alkenes. The resin based chromium catalyst prepared from chloromethylated polystyrene (PS-DVB) (Merri field resin, 2% cross linked) 75 (9 mol%) catalyses the [6 + 2] cycloadditions of CHT 18 with excess ethyl acrylate 76 to afford bicyclo[4.2.1]nona-2,4-diene 77 in 59% yield. However, the catalytic system has a serious drawback of recyclability owing to thermal denaturation of the catalytic systems (Scheme 29).

Replacing chromium coordination sphere to η^6-C_{6}H_{5} has marked effect on its multiple recyclability by simple filtration followed by washing with non polar solvents (Scheme 30). The catalyst 78 affords [6 + 2] cycloadditions in excellent yield (64–92%) in the reactions of CHT 18 with various electron rich trienophiles.

Conclusion

In conclusion, the present review summarises transition metal catalysed [6 + 2] cycloaddition reactions that have appeared in literature since 2000. Various inter and intramolecular versions have been explored employing various substrates contributing...
as $6\pi$ component promoted by different transition metal catalysts. The developed methodologies have provided a facile access to mono- and bicyclic carbo-/heterocyclic eight membered core structures which are otherwise difficult to achieve. Although, the developed protocols have provided an informal to functionalised ring systems, but, the true potential of $[6 + 2]$ cycloadditions still need to be scrutinized so as to access its regio and stereoselective versions under milder reaction conditions. Copper, ruthenium, chromium and platinum based complexes have made entry to the list of metals catalysed $[6 + 2]$ cycloadditions, but the detailed studies on such metals catalysed $[6 + 2]$ cycloaddition involving other prevalent substrates as $6\pi$ components still need to be explored. Moreover, the semicyclic variants of $6\pi$ components in transition metal catalysed still need to be studied. The studies on $[6 + 2]$ cycloadditions involving different heterodienophiles also need to be explored. Hence, $[6 + 2]$ cycloadditions have an enormous potential for the synthesis of eight membered monocyclic or fused heterocyclic systems.

The authors have tried to recapitulate most of the reports appearing within the stipulated time frame, nonetheless there will always be some experts missing for which we deeply apologize.

**Conflicts of interest**

There are no conflicts to declare.

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