1-Metalla-1,3,5-hexatrienes and Related Compounds

Rudolf Aumann[a]

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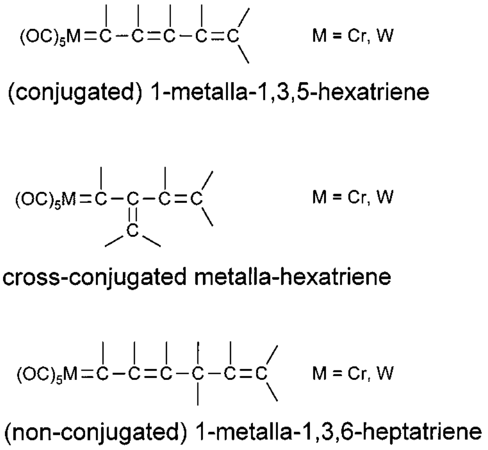
The term 1-metalla-1,3,5-hexatriene applies to a huge number of transition metal carbene complexes which contain a 1,3-butadien-1-yl side chain attached to the carbene carbon atom. Compounds of this type were found to play a crucial role as key intermediates and have also been utilized as stoichiometric reagents in a number of high-yielding transformations, which may successfully be applied to organic syntheses. Typical reaction pathways, structural features, and preparations of such compounds (with focus on M = Cr and W) have been summarized.

1 What is a “Metallahexatriene”?

The denotation “metallahexatriene”[1] does not rest safely on the terminology of IUPAC nomenclature, but is most efficiently used for the classification of an apparently huge and as yet not systematically investigated group of (1,3-butadien-1-yl)carbene complexes (= 1-metalla-1,3,5-hexatriene) and related compounds, whose structures are exemplified in Scheme 1. The chemistry of metallatrienes, as far as has been unraveled, is varied and comprises several unprecedented high-yielding transformations, which might be successfully applied to organic syntheses.

The group of metallatrienes includes conjugated, cross-conjugated, and nonconjugated compounds (Scheme 1), and may also be extended to compounds with cumulated double bonds (e. g. 1-metalla-1,2,3-butatrienes) as well as hetero-analogous compounds (e.g. 3-aza-1-metalla-1,3,5-hexatrienes, 5-oxo-1-metalla-1,3,6-heptatrienes etc.).



Scheme 1. Basic nomenclature of some metallatrienes

The basic structures of carbonyl-1-chroma-1,3,5-hexatrienes cover open-chain $(CO)_5Cr$- as well as cyclic $(CO)_4Cr$

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[a] Organisch-Chemisches Institut der Universität Münster,
Corrensstraße 40, D-48149 Münster, Germany
Fax: (internat.) + 49 (0)251/833 6502
E-mail: aumannr@uni-muenster.de

Aumann, Rudolf, born 1940; Dr. rer. nat. 1967 (TU München, E. O. Fischer); Postdoctoral Research 1967−1969 (UCLA, S. Winstein); Habilitation 1972 (Münster); Award 1974 Dozenten-Stipendium des Fonds der Chemischen Industrie; Visiting Professor 1976 (UW Madison) and 1980 (TU München); Universitätsprofessor 1983 (Univ. Münster); Organometallic Chemistry, synthethic aspects.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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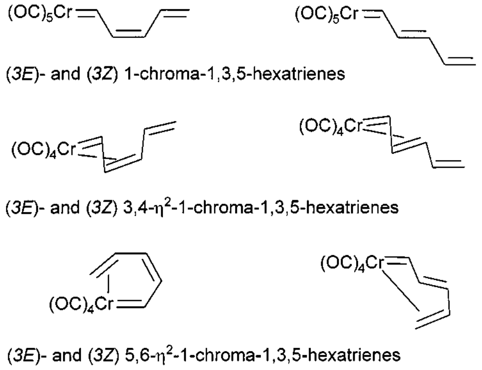


Scheme 2. Structures of conjugated 1-chroma-1,3,5-hexatrienes

complexes (Scheme 2). The latter are further distinguished by their coordination mode, 3,4-η^2 (= proximo) and 5,6-η^2 (= termino), respectively, which was found to have a strong influence on the reactivity of such compounds.[2][3]

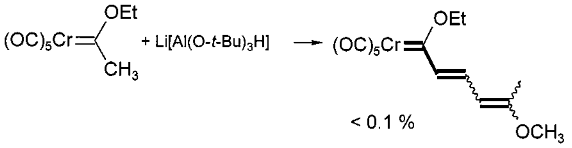
The main focus of this review is directed towards an application of 1-metalla-1,3,5-hexatrienes containing $M(CO)_5$ units (M = Cr, W) and various electron-donating amino as well as alkoxy substituents at C2, C4, and C6 of the ligand backbone as building-blocks for organic syntheses.

2 Routes to (Conjugated) 1-Metalla-1,3,5-hexatrienes

The scope of the "metallatriene concept" can be explored from a compilation of known approaches to the formation of open-chain 1-metalla-1,3,5-hexatrienes (Schemes 3−17), by which we want to stress that a wide variety of reactions can be channeled via 1-metalla-1,3,5-hexatriene intermediates.

2.1 1-Metalla-1,3,5-hexatrienes from $M{=}C{-}CH_2$ Precursors

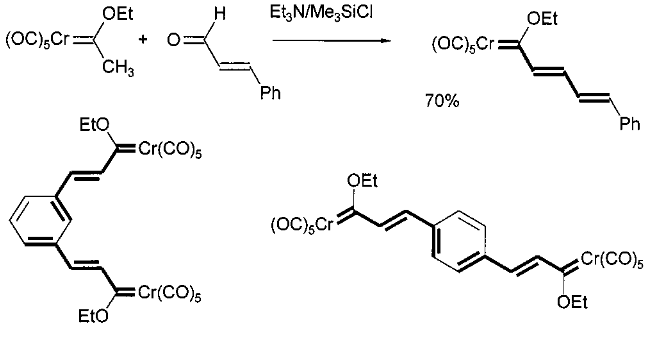
(Methyl)carbene complexes $(CO)_5M{=}C(OEt)CH_3$ (M = Cr, W) provide a convenient starting material for a variety of 1-metalla-1,3,5-hexatrienes.



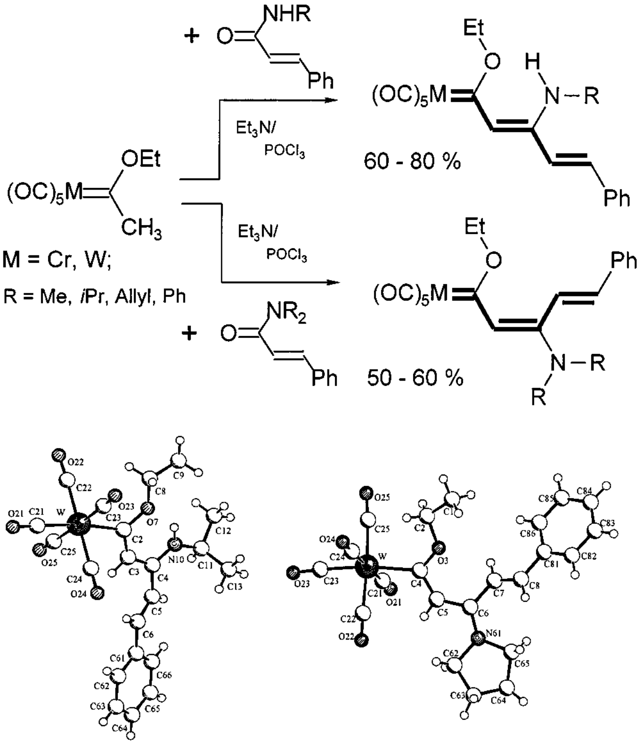
Scheme 3. The first 1-metalla-1,3,5-hexatriene

Many structures and reactions of carbene complexes can be traced back to the work of E.O. Fischer and his coworkers, who generated the first 1-metalla-1,3,5-hexatriene in 1971 (Scheme 3). Little attention had originally been paid to this compound, particularly since its chemical yield of 0.1% was not encouraging and the route of formation remained quite puzzling.[4]

The first rational synthesis of a 1-chroma-1,3,5-hexatriene was achieved, after 16 years of a shadow-like existence, by straightforward condensation of (methyl)carbene chromium complexes with mono- and dialdehydes in the presence of Et_3N/Me_3SiCl (Scheme 4).[1] Many dinuclear compounds of similar type and also other polyene-bridged carbene complexes with π-conjugated hydrocarbon bridges[5] have been generated in a similar manner since then, and have gained interest, e.g. for an eventual application in material science (metal−metal communication, nonlinear optics, etc).

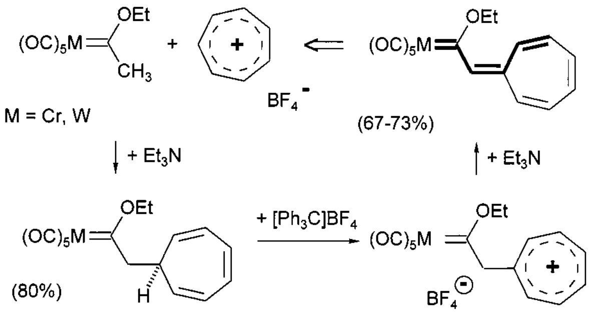


Scheme 4. 2-Ethoxy-1-chroma-1,3,5-hexatrienes by condensation of (methyl)carbene chromium complexes with aldehydes



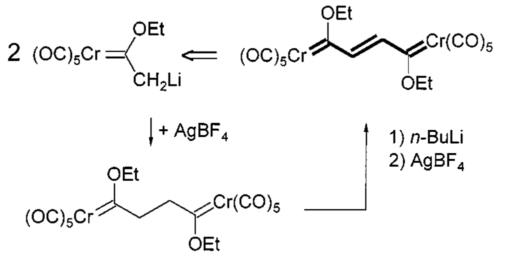
Scheme 5. 4-Amino-2-ethoxy-1-metalla-1,3,5-hexatrienes by condensation of (methyl)carbene complexes with acid amides

Not only aldehydes, but also acid amides were found to undergo condensation with (methyl)carbene complexes.[6] It thus became possible to selectively generate (3*Z*)-4-(*NH*-amino)-2-alkoxy-1-metalla-1,3,5-hexatrienes with "closed configuration" [the (3*Z*) configuration of which is stabilized by a N−H···O hydrogen bond][7] and (3*E*)-4-(dialkyamino)-2-alkoxy-1-metalla-1,3,5-hexatrienes with "open configuration" (Scheme 5).[8] 6-Amino-2-alkoxy-1-metalla-1,3,5-hexatrienes have been obtained accordingly by condensation of (methyl)carbene complexes with 1,3-diamino-1,3-butadienes.[9]



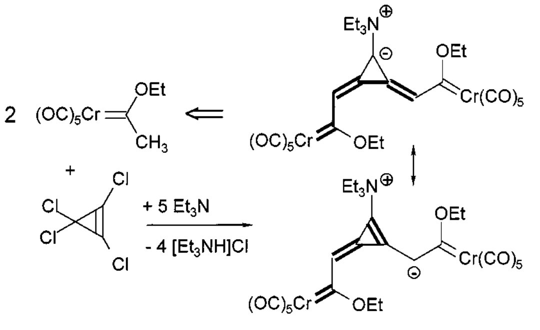
Scheme 6. 2-Ethoxy-1-metalla-1,3,5-hexatrienes by H^{-}/H^{+} abstraction

(Methyl)carbene complexes were found to yield 1-metalla-1,3,5-hexatrienes by condensation with a variety of electrophiles. For example, (heptafulvenyl)carbene complexes containing a conformationally rigid 2-alkoxy-1-metalla-1,3,5-hexatriene unit could be obtained by reaction of (methyl)carbene complexes with tropylium tetrafluoroborate and subsequent oxidation of the central C−C single bond of the product by H^{-}/H^{+} abstraction with (1) Ph_3CBF_4 and (2) Et_3N (Scheme 6).[10]



Scheme 7. 2,5-Diethoxy-1,6-dimetalla-1,3,5-hexatrienes by oxidative coupling of (methyl)carbene complexes

Dinuclear dimetallahexatrienes, e.g. 2,5-diethoxy-1,6-dimetalla-1,3,5-hexatrienes have been produced by oxidative coupling of two molecules of (methyl)carbene complexes with $AgBF_4$ and oxidation of the resulting C−C single bond in "reversed order" to that applied in Scheme 6, namely by H^{+}/H^{-} abstraction with (1) *n*BuLi and (2) $AgBF_4$ (Scheme 7).[11]

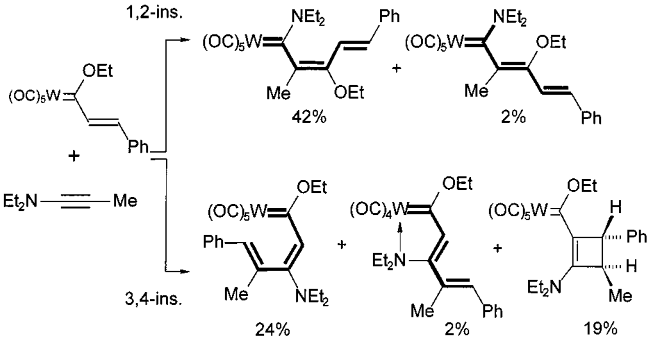


Scheme 8. 2,7-Diethoxy-1,8-dichroma-1,3,5,7-octatetraenes by bisalkenylation of (methyl)carbene chromium complexes

Formation of a dinuclear (triafulvenyl)carbene complex containing a 1,8-dichroma-1,3,5,7-octatetraene unit was achieved by bisalkenylation of (methyl)carbene complexes with tetrachlorocyclopropene in the presence of Et_3N (Scheme 8).[12]

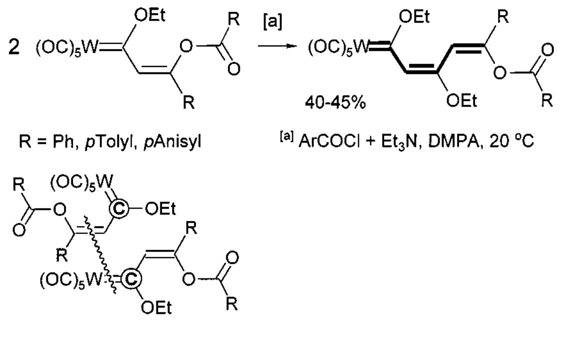
2.2 1-Metalla-1,3,5-hexatrienes from M=CC=C Precursors

An approach to 1-tungsta-1,3,5-hexatrienes involves chain extension of the W=C−C=C unit of 1-tungsta-1,3-butadienes[13][14] by two carbon atoms by insertion of a 1-aminoalkyne into the W=C and C=C bonds. The regioselectivity of this reaction was found to be surprisingly low, and 2-amino-4-ethoxy- and 4-amino-2-ethoxy-1-tungsta-1,3,5-hexatrienes were generated in similar amounts (Scheme 9).[13]



Scheme 9. 1-Tungsta-1,3,5-hexatrienes by chain extension involving an alkyne insertion

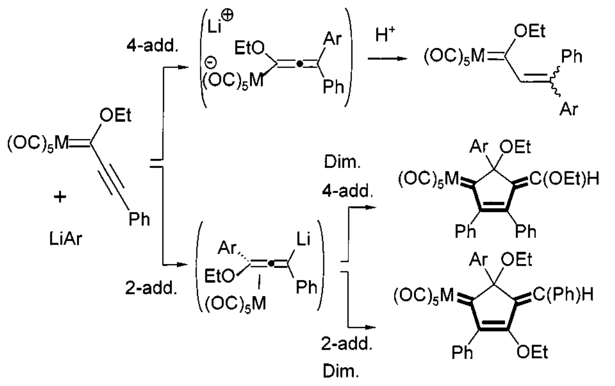
Metathesis was found to be a further means for chain-extension of a M=C−C=C unit. For example, metathesis of 4-acyloxy-1-tungsta-1,3-butadienes was found to afford 6-acyloxy-2,4-diethoxy-1-tungsta-1,3,5-hexatrienes (Scheme 10).[15]



Scheme 10. 2,4-Diethoxy-1-tungsta-1,3,5-hexatrienes by metathesis

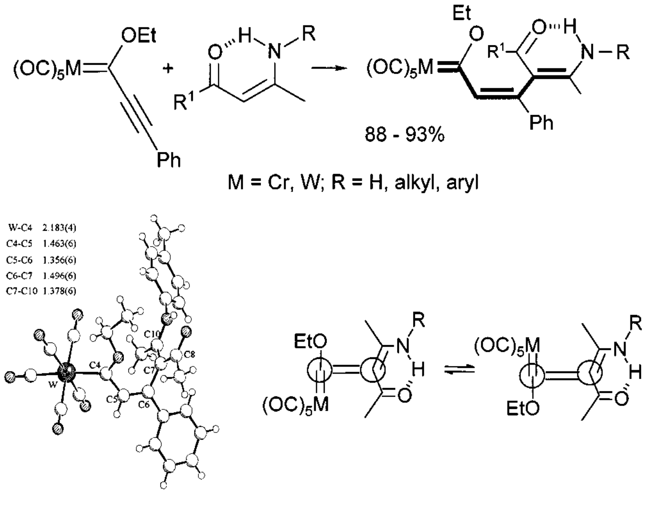
2.3 1-Metalla-1,3,5-hexatrienes from M=C−C≡C Precursors

The MC_3 unit of (1-alkynyl)carbene complexes[16] could be transformed into 1-metalla-1,3,5-hexatrienes by dimerisation of the ligand, as well as by addition of an alkene unit to the C≡C unit.



Scheme 11. 1-Metalla-1,3,5-hexatrienes by ligand-dimerization

Addition of aryl lithium compounds to a (1-alkynyl)carbene complex (M = Cr, W) yields Michael-adducts and cyclopentenylidene complexes containing a rigid 1-metalla-1,3,5-hexatriene unit, which is generated by ligand dimerization in a [3+2] fashion (Scheme 11).[17][18]

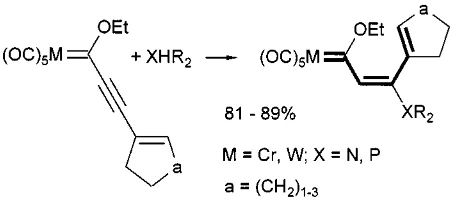


Scheme 12. 6-Amino-2-ethoxy-1-metalla-1,3,5-hexatrienes from (1-alkynyl)carbene complexes and *NH* enaminones

A very efficient entry to the formation of 1-metalla-1,3,5-hexatrienes is based on the addition of an electron-rich alkene to the terminal carbon atom of a M=C−C≡C moiety. For example, a variety of (3*Z*)-2-alkoxy-6-amino-1-metalla-1,3,5-hexatrienes could be obtained by addition of *NH*-enaminones to (1-alkynyl)carbene complexes (M = Cr, W). A structural feature most characteristic of such compounds is their "trough-shaped" geometry (Scheme 12), which is supposedly stabilized by dipole effects resulting from strong charge delocalization. In line with expectations, the "troughs" form diastereomers which were found to interconvert rapidly on the NMR time-scale.[19]

2.4 1-Metalla-1,3,5-hexatrienes from M=C−C≡C−C=C Precursors

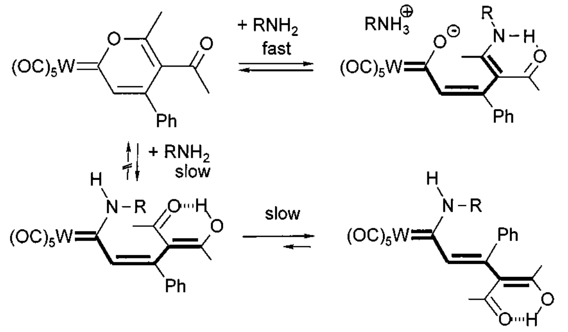
Formation of 1-metalla-1,3,5-hexatrienes could be triggered by addition of protic nucleophiles to the C≡C bond of the M=C−C≡C−C=C backbone of a 1-metalla-1,5-hexadien-3-yne (readily accessible by the Fischer route). This reaction was performed under mild conditions and was applied to the generation of, e.g. very thermolabile 2-alkoxy-4-amino-1-metalla-1,3,5-hexatrienes (M = Cr, W) (Scheme 13).[20]



Scheme 13. 4-Amino-2-ethoxy-1-metalla-1,3,5-hexatrienes from 1-metalla-1,5-hexadien-3-ynes

2.5 1-Metalla-1,3,5-hexatrienes from Ring Precursors

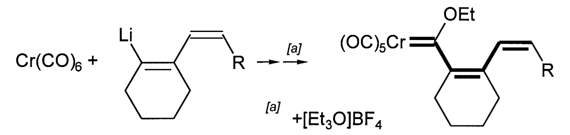
An approach to (3*Z*)-2-amino-6-hydroxy-1-metalla-1,3,5-trienes involves the ring-opening of pyranylidene complexes, e.g. by aminolysis (Scheme 14).[19d] Apart from the case observed with 2-alkoxy-1-metalla-1,3,5-trienes (Scheme 12), an "open" *s-trans,s-trans* (*E*)-configuration of *2-amino*-1-metalla-1,3,5-trienes is energetically favored over a "closed" ("trough-shaped") *s-trans,s-cis* (*Z*)-configuration, probably due to steric congestion resulting from the N−R bond *trans* to the metal unit.



Scheme 14. 2-Amino-6-hydroxy-1-metalla-1,3,5-hexatrienes from pyranylidene complexes

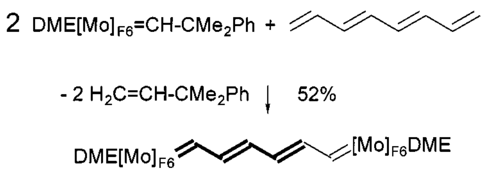
2.6 1-Metalla-1,3,5-hexatrienes from M=C Precursors

Generation of 2-alkoxy-1-chroma-1,3,5-hexatrienes could also be achieved by the Fischer route, involving addition of a 1-butadienyl lithium compound to a Cr=C=O bond of $Cr(CO)_6$. The application of this reaction is somewhat limited by the availability of the corresponding lithium compounds (Scheme 15).[21]



Scheme 15. 2-Ethoxy-1-chroma-1,3,5-hexatrienes by the Fischer route

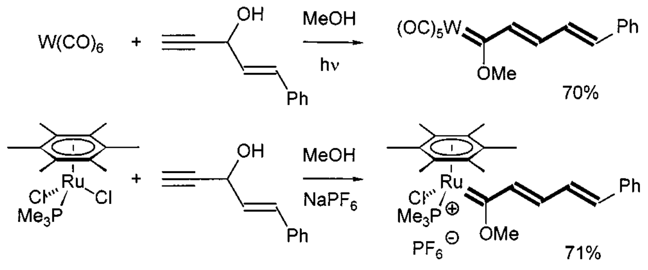
Metathesis of neopentyl-type molybdenum complexes with terminal bisalkenes has been utilized for the preparation of 1,8-dimolybdena-1,3,5,7-octatetraenes (Scheme 16) in ROMP and Wittig-type reactions.[22]



Scheme 16. 1,8-Dimetalla-1,3,5,7-octatetraenes by metathesis of terminal bisalkenes

2.7 1-Metalla-1,3,5-hexatrienes from L*n*M Precursors

A further approach to the generation of 1-metalla-1,3,5-hexatrienes is based on the direct attachment of a C_5-chain to a metal center. This route has been exemplified by the preparation of several 2-alkoxy-1-metalla-1,3,5-hexatrienes (M = W, Ru) from 1-propyn-3-ols and $W(CO)_6$ or (π-aryl)Ru complexes in the presence of MeOH (Scheme 17).[23]



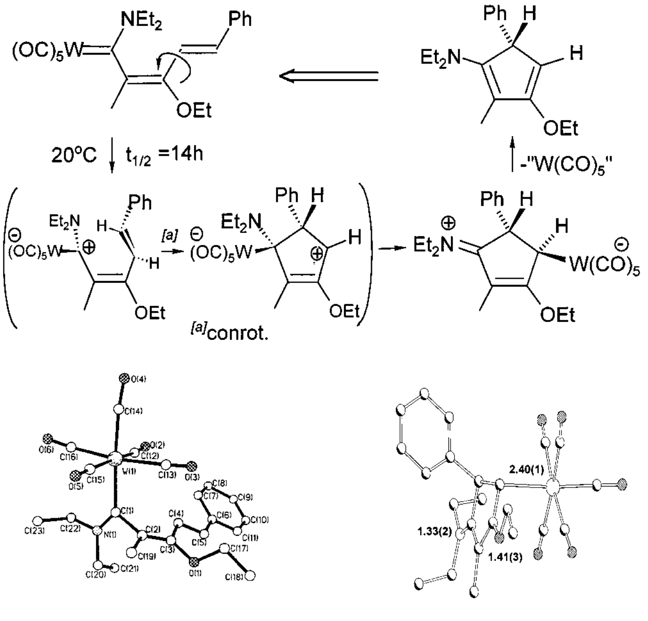
Scheme 17. 1-Metalla-1,3,5-hexatrienes from 1-propyn-3-ols

3 Typical Reactions of Conjugated 1-Metalla-1,3,5-hexatrienes

Our attention was drawn to the reactivity of 1-metalla-1,3,5-hexatrienes, when we discovered in 1991 that cyclopentadienes could be generated by π-cyclization reactions of 1,1,1,1,1-pentacarbonyl-1-tungsta-1,3,5-hexatrienes (Scheme 18).

3.1 Cyclopentadienes by π-Cyclization of 1-Metalla-1,3,5-hexatrienes

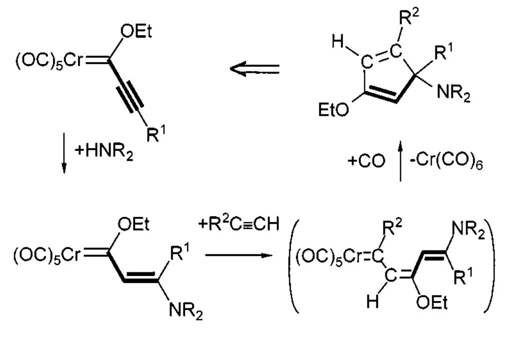
The (3*Z*)-2-amino-4-ethoxy-1-tungsta-1,3,5-hexatriene depicted in Scheme 18 was found to undergo smooth ring closure in solution without loss of carbon monoxide to give a cyclopentadiene $W(CO)_5$ complex, even at 20 °C.[13] The crystal structure analysis of the latter compound revealed an unprecedented η^1-coordination mode of the cyclopentadiene to a $W(CO)_5$ unit. Based on the long W−C bond length of 2.40(1) Å and the short C=N bond length of 1.33(2) Å, the compound is best considered a (zwitterionic) carbiminium carbonylmetallate.[24]



Scheme 18. Amino cyclopentadienes by π-cyclization of 2-amino-1-metalla-1,3,5-hexatrienes

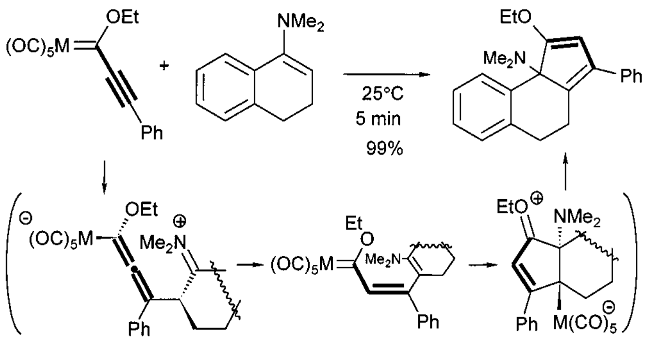
The stereochemistry of the ring-closure was startling because it involves addition of the terminal C=C bond to the W=C bond of the 1-tungsta-1,3,5-triene in an *anti* fashion.[20] Assuming that orbital control is predominant, the *anti* addition might be explained as a result of conrotatory electrocyclic ring-closure (Scheme 18), somewhat reminiscent of the Nazarov cyclization.[25] The *torquo* selectivity rests on the assumption that the (open-chain) 1-tungsta-1,3,5-hexatriene would acquire the conformation depicted in Scheme 18 under the influence of a supposedly strong 1,3-allylic strain.[13] The experimental proof of an *anti* addition (which could recently be confirmed with cyclic systems, vide infra) is in marked contrast to the conventional assumption that 5,6-η^2-1-tungstahexa-1,3,5-trienes and 1-tungstacyclohexa-2,4-dienes, might be formed as direct precursors to cyclopentadienes, since such structures would necessarily result in *syn* addition of the terminal C=C bond. The reaction sequence outlined in Schemes 9 and 18 provides an intriguing means for the generation of cyclopentadienes in an overall [3+2] cycloaddition, which has subsequently been developed for synthetic application (vide infra).

It was shown by de Meijere et al. in independent studies that reactions of alkynes RC≡CH with (2-amino-1-alkenyl)-carbene chromium complexes (= 4-amino-1-chroma-1,3-butadienes) $(CO)_5Cr{=}C(OEt)CH{=}C(NR_2)R^1$ led to the generation of cyclopentadienes (Scheme 19) instead of Dötz products. It was hypothesized that 6-amino-1-chroma-1,3,5-



Scheme 19. Cyclopentadienes from 4-amino-1-chroma-1,3-dienes and alkynes

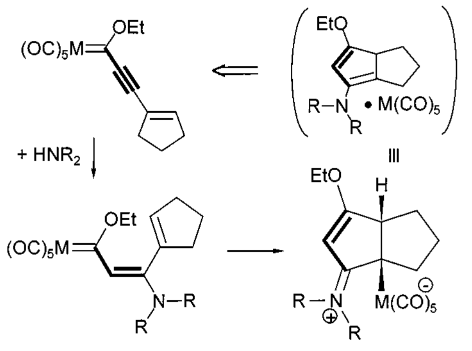
hexatrienes were generated as key intermediates, though experimental proof has not been provided in this case. Reactions of alkynes with (amino)arylcarbene chromium complexes $(CO)_5Cr{=}C(NR_2)Ar$ were previously reported by Dötz et al.[27] and also by Yamashita[28] to produce amino indenes, supposedly by a mechanism similar to that outlined above. In related reactions, phosphanyl indenes were obtained by thermally-induced cyclization of (2-phosphanyl-1-alkenyl)carbene chromium complexes $(CO)_5Cr{=}C(OEt)CH{=}C(PR_2)Ph$.[36b]



Scheme 20. Cyclopentadienes via 6-(dimethylamino)-2-ethoxy-1-metalla-1,3,5-hexatrienes from (1-alkynyl)carbene complexes and cycloalkenyl amines

Whilst pursuing our studies, 6-(dimethylamino)-2-ethoxy-1-metalla-1,3,5-hexatrienes $(CO)_5M{=}C(OEt)CH{=}C(Ph)C({\sim}){=}C({\sim})(NR_2)$ (M = W, Cr) could be obtained by addition of cycloalkenyl amines $({\sim})CH{=}C({\sim})NMe_2$ to (1-alkynyl)carbene complexes[16] and could be smoothly transformed into cyclopentadienes (Scheme 20).[19c,19g] It should be noted that this "alkene route to cyclopentadienes" (Scheme 20) is complementary to the "alkyne route to cyclopentadienes" (Schemes 18 and 19) with respect to its connectivity of building-blocks in the 1-metalla-1,3,5-hexatrienes as well as in the cyclopentadiene derivatives.

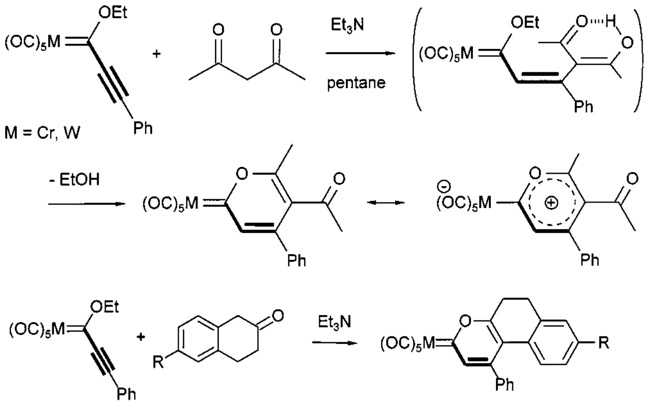
A strong driving force for the π-cyclization of 1-metalla-1,3,5-hexatrienes to cyclopentadienes seemed to be provided by amino substituents. 6-Amino substituents especially, (Scheme 19 and 20) but also 2-amino substituents (Scheme 18) were found to enhance this reaction. Our studies were thus extended to investigate the influence of 4-amino substituents on the cyclization step. (3*E*)-4-Amino-1-metalla-1,3,5-hexatrienes could be obtained by addition of secondary amines to [2-(1-cyclopentenyl)ethynyl]carbene complexes (M = W, Cr). These compounds are stable in solid state, but (as expected), underwent ring-closure in solution at ambient temperature to give zwitterionic η^1-cyclopentadiene complexes (Scheme 21).[20]



Scheme 21. Cyclopentadienes via 4-(dialkylamino)-2-ethoxy-1-metalla-1,3,5-hexatrienes

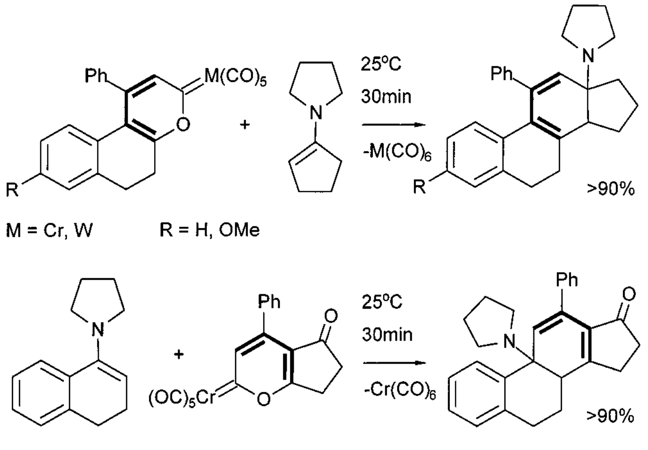
3.2 Cyclocondensation Reactions Involving Oxygen Substituents

Whilst π-cyclization reactions to cyclopentadiene complexes are typically observed with 2-, 4-, or 6-(dialkylamino)-1-metalla-1,3,5-hexatrienes, intramolecular condensations were found to be prevalent for 6-hydroxy- as well as 6-(*NH*-amino) derivatives, and led to pyranylidene complexes (= pyrylium carbonylmetallates) and dihydropyridinylidene complexes (= pyridinium carbonylmetallates), respectively.



Scheme 22. Pyrylium carbonylmetallates via 6-hydroxy-1-metalla-1,3,5-hexatrienes

6-Hydroxy-1-metalla-1,3,5-hexatrienes could readily be generated by base-catalyzed *C*-addition of enolizable organic carbonyl compounds to (1-alkynyl)carbene complexes (Scheme 22).[19d,29,30] These compounds did not afford cyclopentadienes by π-cyclization, but instead gave pyranylidene complexes by base-catalyzed intramolecular condensation. Pyranylidene complexes provide an excellent starting material for the generation of 2-amino-1-metalla-1,3,5-hexatrienes (Scheme 14) and were also found to undergo condensation with enamines to give cyclohexa-1,3-diene annelation products under very mild conditions at 20°C (Scheme 23).[29][30]

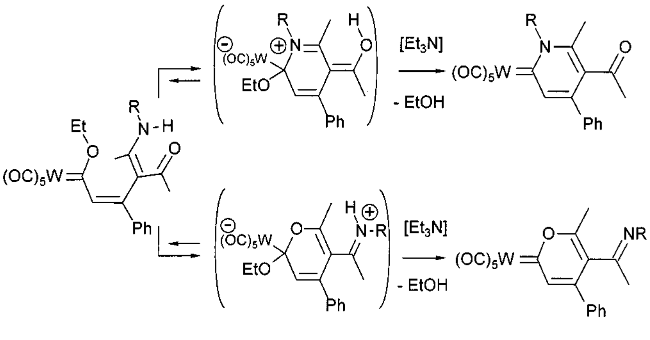


Scheme 23. Cyclohexadiene annelation to cycloalkenyl amines by condensation of pyranylidene complexes

A cyclohexadiene annelation to a cycloalkenyl amine is achieved in two steps already at 20°C involving: a) condensation of a (1-alkynyl)carbene complex $(CO)_5M=C(OEt)C\equiv CPh$ (M = Cr, W) with an enolizable carbonyl compound (e.g. 2,4-pentanedione, 3-oxo-butyric acid ester, 2-tetralones, and 1,3-cyclopentandione) to give a pyran-2-ylidene complex (Scheme 22); and b) formation of a [4+2] cycloadduct of the pyran-2-ylidene complex with a cycloalkenyl amine, from which a 5-amino 1,3-cyclohexadiene is generated by a spontaneous Retro-Fischer reaction [= elimination of $M(CO)_6$]. Bicyclic ring skeletons, steroid-like molecules, as well as other tetracyclic compounds could thus be obtained with high regioselectivity and mostly in good chemical yields (Scheme 23).[29][30]

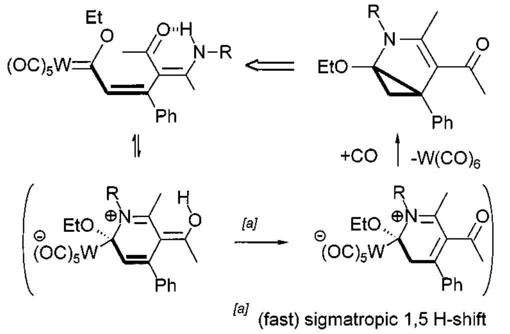
3.3 Cyclocondensation Reactions Involving Nitrogen Substituents

Other than the cyclization of 6-hydroxy-2-ethoxy-1-metalla-1,3,5-hexatrienes described above, cyclization of the corresponding 6-(*NH*-amino) derivatives could be directed in different directions, depending on whether the reaction was induced thermally, under essentially neutral conditions, or under the influence of a base catalyst.



Scheme 24. Base-catalyzed cyclization of 6-(*NH*-amino)-2-ethoxy-1-tungsta-1,3,5-hexatrienes to pyranylidene- and dihydropyridinylidene complexes, respectively

6-(*NH*-Amino)-2-alkoxy-1-tungsta-1,3,5-hexatrienes are stable in solid state, but in solution form mixtures of 1,2-dihydropyridin-2-ylidene- and pyranylidene complexes, if triethylamine is added to the reaction mixture (Scheme 24).[19b] The base is required in the final step of the reaction sequence, involving 1,6-elimination of ethanol from the zwitterionic intermediate. If no base is present, the zwitterionic iminium carbonylmetallate intermediate was found to generate 2,3-homopyrroles (Scheme 25).



Scheme 25. 2,3-Homopyrroles by cyclization of 6-(*NH*-amino)-2-ethoxy-1-tungsta-1,3,5-hexatrienes under neutral conditions

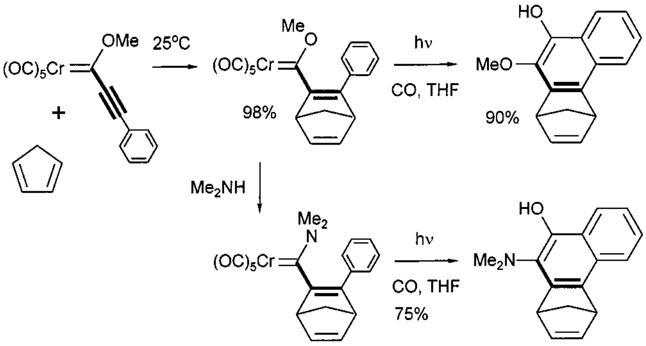
6-(*NH*-Amino)-2-ethoxy-1-tungsta-1,3,5-hexatrienes underwent a smooth fragmentation to 2,3-homopyrroles and $W(CO)_6$ in the *absence* of base (Scheme 25). This quite unexpected transformation is explained on the basis that due to the lack of a base, the elimination of ethanol becomes slower than a 1,5-sigmatropic hydrogen migration of the 1,3-pentadien-5-ol unit of the iminium carbonylmetallate, which is generated in the initial cyclization step (Scheme 25).[19b] 2,3-Homopyrroles could be obtained in 65−90% yield, also in a one-pot procedure by condensation of 4-(*NH*)-amino-pent-3-en-2-ones MeC(NHR)=C(H)COMe (R = C_6H_5, *p*-Me−C_6H_4, *p*-MeO−C_6H_4, *p*-HO−C_6H_4, CH_3, *i*-C_3H_7, *n*-C_4H_9) with the (1-alkynyl)carbene complex $(CO)_5W=C(OEt)C\equiv CPh$ (Scheme 12).

3.4 Cyclization Reactions Involving Chain Extension by a C_1 Unit

Carbocyclic six-membered ring compounds could be derived from open-chain 1-metalla-1,3,5-hexatrienes by insertion of carbon monoxide or isocyanides into the M=C bond.

3.4.1 Insertion of Carbon Monoxide into the M=C Bond

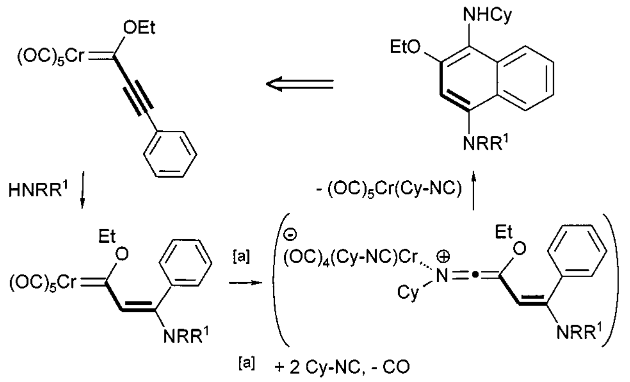
Photocyclization of a 1-chroma-1,3,5-hexatriene moiety was previously found to afford 1,2-dioxy naphthalene derivatives (Scheme 26).[31] The photocyclization of 1-chroma-1,3,5-hexatrienes leading to 1,2-dioxy naphthalenes is complementary to the formation of 1,4-dioxy naphthalenes from (chelated) 2-alkoxy-3,4-η^2-1-chroma-1,3,5-hexatrienes in the Dötz reaction.[2] Photocyclization of an aminocarbene complex leads to the production of a 2-amino-1-oxy naphthalene derivative.[31b,32]



Scheme 26. 1,2-Dioxo- and 2-amino-1-oxo photocyclization

3.4.2 Insertion of an Isocyanide into the M=C Bond

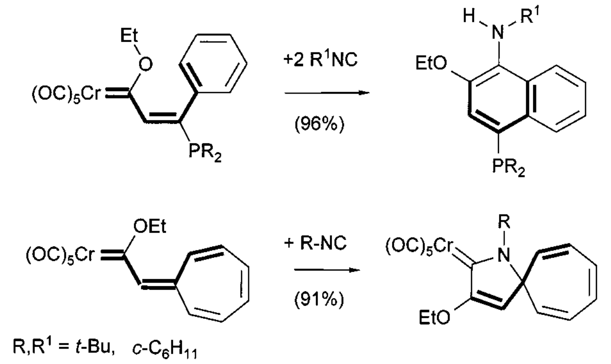
Insertion of an isocyanide into a M=C bond yields ketenimine complexes, from which a variety of different organic products has been derived.[33] It was shown, for example, that 1,4-diamino-2-ethoxy naphthalenes are obtained in 72−85% yields under mild conditions from dienyl ketenimine precursors generated by addition of cyclohexyl isocyanide to 4-amino-1-chroma-1,3-dienes (Scheme 27).[34][35]



Scheme 27. 1,4-Diaminonaphthalenes via ketenimine complexes

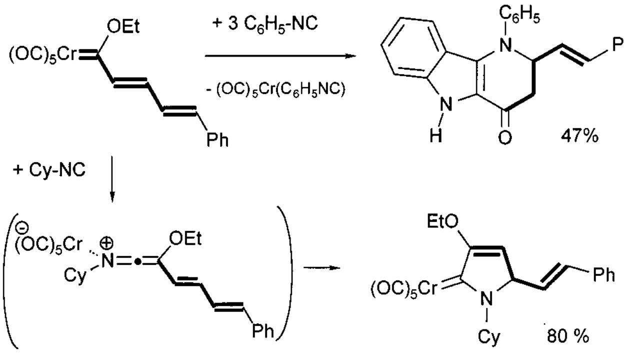
The insertion of an isocyanide into the M=C bond of a 1-metalla-1,3,5-hexatriene unit may result in cyclization by "end-on" addition (leading to, e.g. a naphthalene derivative) or by "side-on" addition of the isocyanide unit (leading to *spiro* compounds), depending on the configuration of the corresponding 1-metalla-1,3,5-hexatriene (Scheme 28).[36]

Reaction of a (3*E*)-1-ethoxy-1-chroma-1,3,5-hexatriene with phenyl isocyanide affords δ-carbolines. Reaction with cyclohexyl isocyanide yields a dihydropyrrol-2-ylidene complex.[33][37] Common to both reaction paths is the formation of ketenimine complexes as key intermediates (Scheme 29).



Scheme 28. Influence of configurational rigidity on cyclization mode of 1-metalla-1,3,5-hexatriene

3.5 Miscellaneous Cylization Reactions

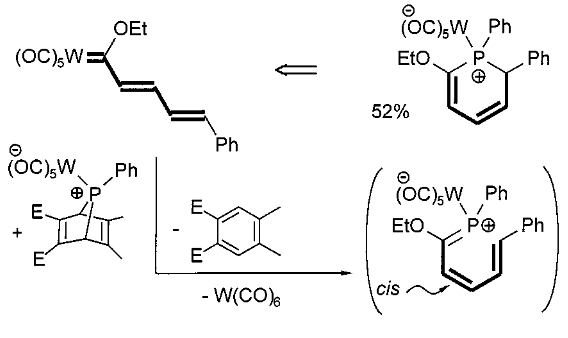


Scheme 29. Formation of δ-carbolines and 2,5-dihydropyrrol-2-ylidene complexes

A wide range of chain-extension reactions of 1-metalla-1,3,5-hexatrienes can be anticipated to yield ring compounds. The few examples which have been investigated so far comprise: a) the insertion of a phosphene; b) the successive insertion of an alkyne and carbon monoxide; and c) the insertion of an alkene.

3.5.1 Insertion of a Phosphene into the M=C Bond

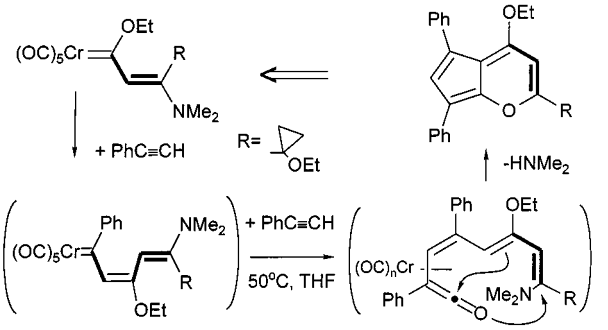
Generation of a stable 1,2-dihydrophosphabenzene tungsten complex was achieved by insertion of a phosphene unit into the W=C bond of a 2-alkoxy-1-chroma-1,3,5-hexatriene (Scheme 30).[38]



Scheme 30. 1,2-Dihydrophosphinines from 1-tungsta-1,3,5-hexatrienes

3.5.2 Successive Insertion of an Alkyne and Carbon Monoxide into the M=C Bond

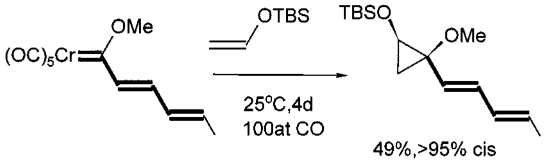
The insertion of alkynes into a Cr=C bond leads to vinylogous carbene complexes, which are prone to undergo further insertion reactions into the newly-generated Cr=C bond. It was reported, for example, that 4-amino-2-ethoxy-1-chroma-1,3-dienes would undergo successive insertion of two molecules of a terminal alkyne and carbon monoxide to finally produce cyclopenta[*b*]pyrans (Scheme 31).[26f]



Scheme 31. Cyclopenta[*b*]pyrans by successive insertion of two alkyne units and carbon monoxide into a Cr=C bond

3.5.3 Insertion of an Alkene into the M=C Bond

An insertion of alkenes into a M=C bond provides a means for the generation of a cyclopropane ring. The insertion of alkenes into the Cr=C bond of 2-methoxy-1-chroma-1,3,5-trienes was studied, e.g. in connection with model reactions for the generation of prostaglandin derivatives (Scheme 32).[39]

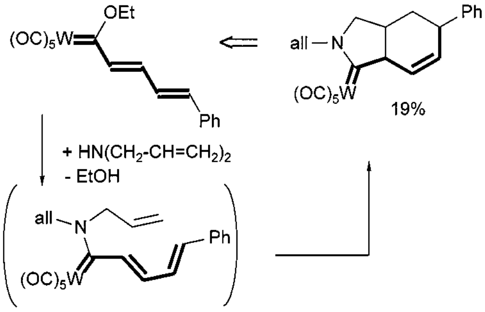


Scheme 32. Cyclopropanation of an alkene

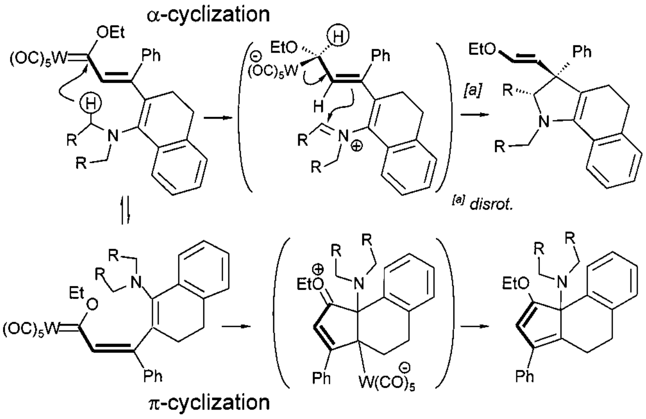
3.6 Cyclization Reactions Involving a Side Chain

Cyclization reactions of 1-metalla-1,3,5-hexatrienes involving a side chain have been verified: a) by intramolecular $4\pi+2\pi$ cycloadditions of π-bonds of the side-chain of a 1-metalla-1,3,5-hexatriene (Scheme 33); and b) by an insertion of the carbene carbon atom into an α-HC(N) bond of a side-chain (Scheme 34).[40]

A drastic change of the cyclization mode of 6-amino-2-ethoxy-1-tungsta-1,3,5-hexatrienes can be induced by variation of the substituents R of the $(RCH_2)_2N$ group. Whilst the dimethylamino derivative (R = H) underwent π-cyclization to a cyclopentadiene in 80% yield (Scheme 20 and Scheme 34, R = H),[19c,19g] increasing amounts of dihydropyrrole derivatives were formed by α-cyclization involving insertion of the carbene carbon atom into the α-HC(N) bond of the tertiary amino unit, for bulkier substituents R = Me, Et (Scheme 34).[41][42] The "molecular switch" of this reaction is based on changes in the (3*E*/3*Z*) molecular orientation of the highly congested 6-amino-2-ethoxy-1-tungsta-1,3,5-hexatrienes by the bulk of substituents R.[41]



Scheme 33. Intramolecular $4\pi+2\pi$ cycloaddition of a 1-metalla-1,3,5-hexatriene



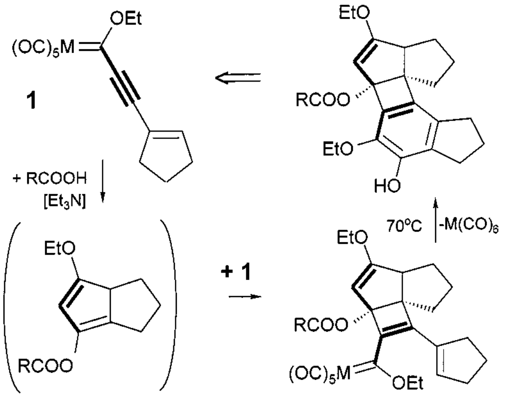
Scheme 34. π-Cyclization vs. α-cyclization of 6-amino-1-metalla-1,3,5-hexatrienes

3.7 Cascade Cyclizations

Addition of oxygen nucleophiles (CH_3COOH, PhCOOH, PhOH, EtOH) to 1-metalla-1,5-hexadien-3-ynes (M = W, Cr) results in the formation of cyclopentadienes, which spontaneously add to another molecule of the starting component in a [2+2] fashion and thus form a 1-metalla-1,3,5-hexatriene system. Thermally-induced fragmentation of the latter compounds quite unexpectedly leads to annelation of a six-membered ring by insertion of carbon monoxide into the W=C bond (Scheme 35).[43]

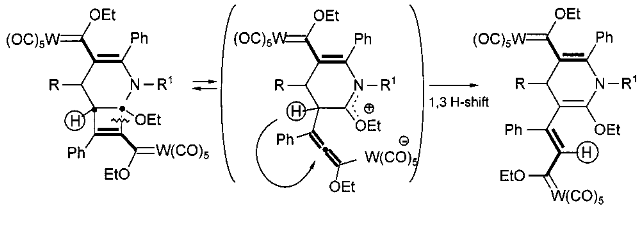
4 Non-Conjugated 1-Metalla-1,3,6-heptatrienes

Reactions between (1-alkynyl)carbene complexes and *NH*-enaminones or cyclic enamines were shown to provide a good entry into the generation of conjugated 1-metalla-1,3,5-hexatrienes (Schemes 12 and 20). Whilst pursuing these studies, a crucial influence of the structure of the en-



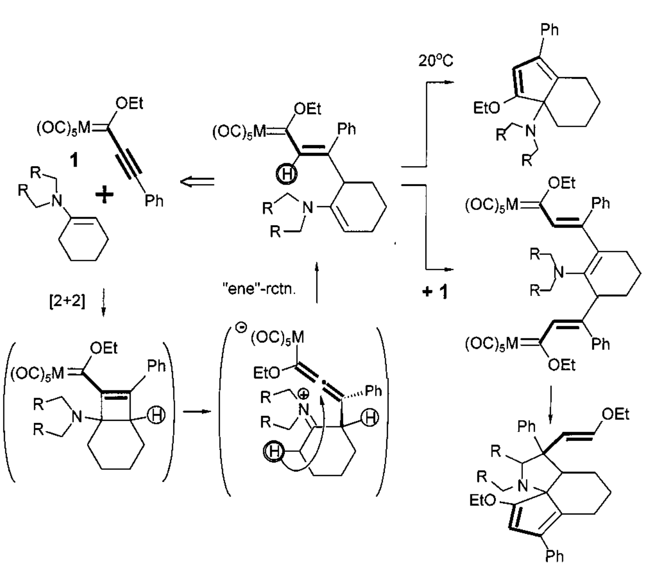
Scheme 35. Cascade cyclization of 4-acyl-1-metalla-1,3,5-hexatrienes

amine on the reaction courses was found. Even though it appears that all of these reactions are initiated by the formation of (4-aminocyclobutenyl)carbene complexes, three different types of ring-opening reactions of the (4-aminocyclobutenyl)carbene complexes can be envisaged for the next step to occur. They may involve: a) ring-opening of the C(1)−C(4) bond and transfer of the hydrogen atom 3-H to give a conjugated 1-metalla-1,3,5-hexatriene (Scheme 36, path *a*); b) ring-opening of the C(1)−C(4) bond and transfer of an α-hydrogen atom to give a nonconjugated 1-metalla-1,3,6-heptatriene (Scheme 37, path *b*); and c) ring-opening of the C(3)−C(4) bond leading to cross-conjugated metallatrienes (Scheme 44 and 45, path *c*).



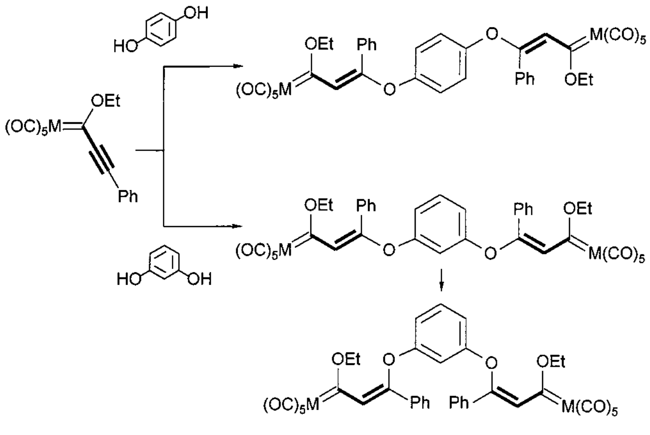
Scheme 36. Ring-opening path *a*: formation of conjugated 6-amino-1-tungsta-1,3,5-hexatrienes from (4-aminocyclobutenyl)carbene tungsten complexes

Ring-opening of the C(1)−C(4) bond of a (4-aminocyclobutenyl)carbene complex and a subsequent transfer of the hydrogen atom 3-H to give a (conjugated) 1-metalla-1,3,5-hexatriene could be studied by model reactions, in which the (4-aminocyclobutenyl)carbene tungsten complex depicted in Scheme 36 (characterized by a crystal structure analysis) was shown by NMR spectra to smoothly rearrange in solution into a 6-amino-1-tungsta-1,3,5-hexatriene (characterized by a crystal structure analysis).[44] This rearrangement is assumed to proceed through a zwitterionic intermediate as indicated,[45] and is considered to be the key-reaction for the formation of 1-metalla-1,3,5-hexatrienes from enamines and (1-alkynyl)carbene complexes. Two further modes, paths *b* and *c*, for the opening of the (4-aminocyclobutenyl)carbene moiety are shown in Scheme 37 and Scheme 45, respectively.



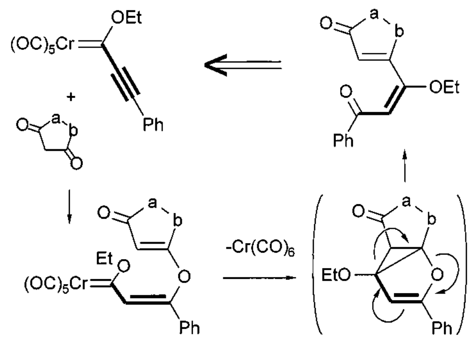
Scheme 37. Ring-opening path *b*: formation of nonconjugated 1-metalla-1,3,6-heptatrienes from (4-aminocyclobutenyl)carbene complexes and cascade reactions resulting thereof

If an α-hydrogen atom $CH_2C(NR_2)=C$ is present in an enamine unit, the formation of a nonconjugated 1-metalla-1,3,6-heptatriene unit by an "ene"-type reaction (Scheme 37) becomes favored over formation of conjugated 1-metalla-1,3,5-hexatrienes (Scheme 36).[41] These compounds underwent π-cyclization at 20°C to form cyclopentadiene derivatives, but on exposure to an excess of (1-alkynyl)carbene complex, gave binuclear compounds, which subsequently were transformed into *spiro*-tetrahydropyrroles by thermally-induced α-cyclization.



Scheme 38. Non-conjugated 5-oxa-1-metalla-1,3,6-heptatrienes

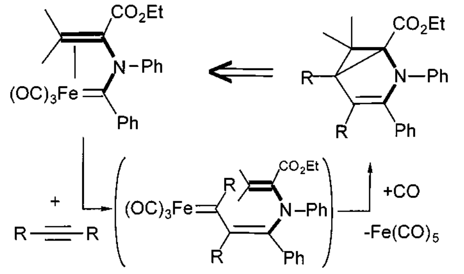
A variety of nonconjugated 1-metalla-1,3,6-heptatrienes containing a heteroatom are obtained, e.g., by addition of phenol derivatives to an (1-alkynyl)carbene complex (M = Cr, W) (Scheme 38).[45] Some reactions of (nonconjugated) hetero-1-metalla-1,3,6-heptatrienes, which may be of inter-



Scheme 39. 2,4-Heptadien-1,7-diones by fragmentation of 5-oxa-1-chroma-1,3,6-heptatrienes

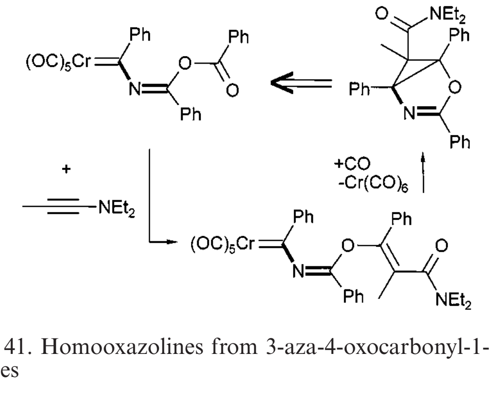
est for synthetic applications, are shown in Schemes 39−43.

Addition of enolizable 1,3-diones to (1-alkynyl)carbene chromium complexes affords *C*-, as well as *O*-addition products. Compounds of the latter type, e.g. the 5-oxa-1-chroma-1,3,6-heptatrienes shown in Scheme 39, undergo a thermally induced fragmentation to give a 2,4-heptadien-1,7-dione and $Cr(CO)_6$, probably by intermediate formation of a homofuran.[46]



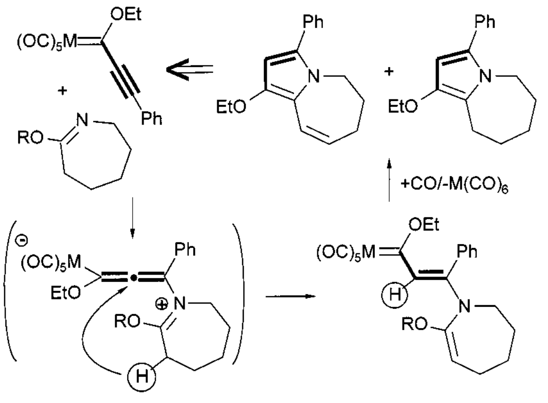
Scheme 40. 2,3-Homopyrroles from 5-aza-1-ferra-1,3,6-heptatrienes

5-Aza-1-ferra-1,3,6-heptatrienes obtained from insertion of an alkyne into the Fe=C bond of a 3-aza-1-ferra-1,4-pentadiene yield homopyrroles by a thermally-induced intramolecular cyclopropanation (Scheme 40).[47]



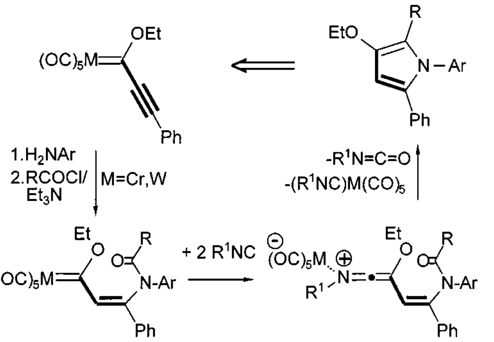
Scheme 41. Homooxazolines from 3-aza-4-oxocarbonyl-1-chroma-1,3-dienes

The reaction principle outlined in Schemes 39 and 40 can easily be extended to many other 1-metalla-1,3,6-heptatrienes. For example, the 3-aza-5-oxa-1,3,6-heptatriene shown in Scheme 41 (obtained by insertion of an 1-aminoalkyne into the C=O bond of a 3-aza-4-oxocarbonyl-1-chroma-1,3-diene) was shown to form a stable homooxazoline (= 2-oxa-4-aza-bicyclo[3.1.0]hexene) on thermolysis.[48]



Scheme 42. Pyrrolo[1,2-*a*]azepines from 5-aza-1-metalla-1,3,6-heptatrienes

Addition of lactimes to (1-alkynyl)carbene complexes results in formation of 5-aza-1-metalla-1,3,6-heptatrienes. Pyrolysis of the tetrahydroazepine derivative shown in Scheme 42 affords a 1:1 mixture of dihydro- and tetrahydropyrrolo[1,2-*a*]azepines together with $W(CO)_6$.[49]



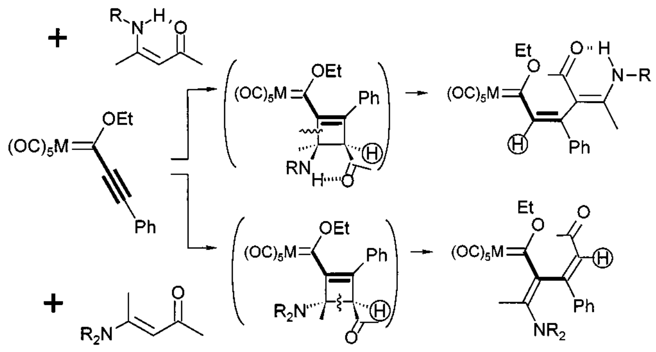
Scheme 43. Pyrroles from 5-aza-7-oxa-1-metalla-1,3,6-heptatrienes by ring-closing metathesis

5-Aza-7-oxa-1-metalla-1,3,6-heptatrienes {= [(acylamino)-ethenyl]carbene complexes} add isocyanides to give ketenimine complexes,[33] which were shown to undergo a spontaneous fragmentation to form pyrroles (Scheme 43).[50]

5 Cross-Conjugated Metallahexatrienes

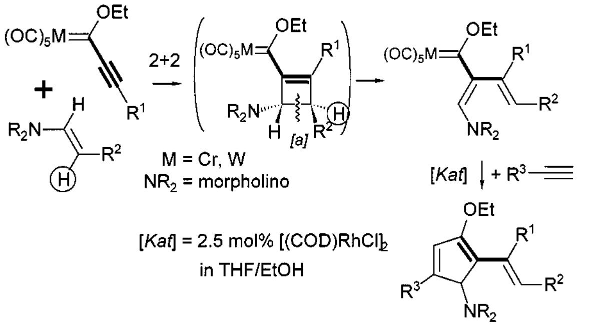
It was found in previous studies that addition of secondary enaminones[19a,b] to (1-alkynyl)carbene complexes led to conjugated 6-amino-1-metalla-1,3,5-hexatrienes (Scheme 12 and 44), whilst tertiary enaminones gave cross-conjugated amino metallahexatrienes by a different type of ring-opening of its (4-aminocyclobutenyl)carbene complex precursors (Scheme 44).[51][52]

Formation of conjugated 1-metalla-1,3,5-hexatrienes from secondary enaminones was tentatively attributed to the supposedly higher acidity of the α-hydrogen atom of the carbiminium carbonylmetallate [resulting from fission of the C(1)−C(4) bond of the 4-aminocyclobutene ring] due



Scheme 44. Different reaction modes of (1-alkynyl)carbene complexes (M = W, Cr) with secondary and tertiary enaminones

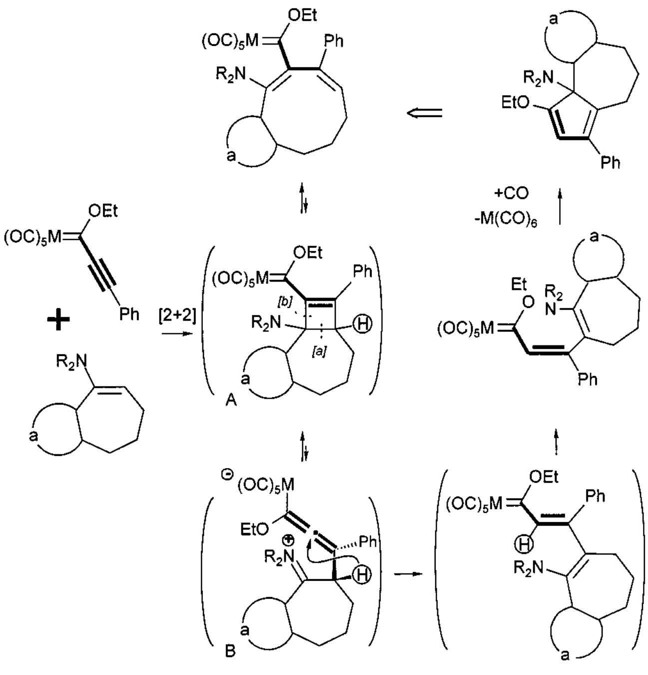
to stabilization of an almost planar ring configuration by a N−H···O hydrogen bond.[44]



Scheme 45. Rhodium-catalyzed formation of vinyl cyclopentadienes from (1-alkynyl)carbene complexes, enamines and alkynes

Cross-conjugated metallahexatrienes (= 1-amino-1,3-butadien-2-yl)carbene complexes were also generated by addition of open-chain enamines of the type (*E*)-$R_2NCH=CHR^2$ to (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)C{\equiv}CR^1$ **1** (M = Cr, W; R^1 = Ph, cyclohex-1-enyl) (Scheme 45). These compounds could be transformed into vinyl- and divinyl cyclopentadienes, under exceedingly mild conditions, even at 20°C, by reaction with alkynes $R^3C{\equiv}CH$ (R^3 = Ph, cyclohex-1-enyl, isopropenyl, methoxymethyl, 1-trimethylsiloxycyclohex-1-yl) in the presence of catalytic amounts of $[(COD)RhCl]_2$.[53] This is one of the rare examples in which a reaction of a Fischer carbene complex has been *catalyzed* by transmetallation with a different transition metal complex.[54]

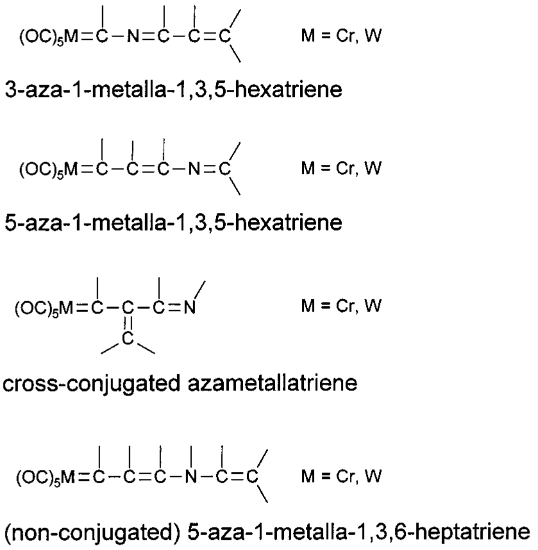
Experimental proof for the conversion of a cross-conjugated metallahexatriene (in this case, part of a nine-membered ring) into a conjugated metallahexatriene was provided by the reaction shown in Scheme 46. 2-Aminocyclonona-1,8-dienyl carbene complexes were generated in high yields by addition of cycloheptenylamines to (1-alkynyl)carbene complexes $(CO)_5M=C(OEt)C{\equiv}CPh$ (M = W, Cr) in pentane, in which these compounds are only slightly soluble (Scheme 46). The products are stable in solid state but in solution they undergo contraction of the nine-membered ring to form a (2-aminocycloheptenyl)alkenyl carbene complex. The latter compounds could be transformed into hexahydroazulenes by thermally induced fragmentation. The overall transformation rests on a hitherto unknown rearrangement of a (1,3-butadien-2-yl)carbene- into a (1,3-butadien-1-yl)carbene complex, which is assumed to proceed via a (4-aminocyclobutenyl)carbene complex (Scheme 46).[19h]



Scheme 46. Rearrangement of cross-conjugated into conjugated metallahexatrienes

6 (Conjugated) Aza-Metalla-1,3,5-hexatrienes

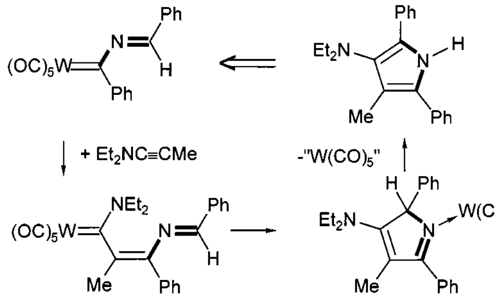
The systematic nomenclature suggested in Scheme 1 for metallatrienes was extended to the nitrogen analogues (Scheme 47).



Scheme 47. Some basic nomenclature of aza-metallatrienes

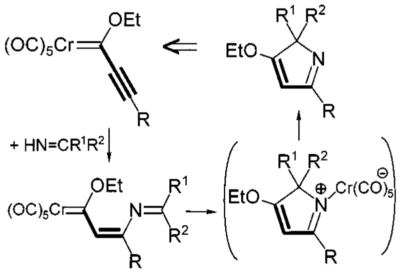
Reactions of nonconjugated aza-1-metalla-1,3,6-heptatriene unit have been described in Schemes 40−42 already.

Reactions of conjugated 5-aza-1-metalla-1,3,5-hexatrienes studied so far comprise the formation of dihydropyrroles by π-cyclization (Schemes 48−50). Reactions reported on cross-conjugated aza-metallatrienes involve an α-cyclization [addition of an α-CH(N) bond to the carbene carbon atom] (Scheme 51 and 52).



Scheme 48. 2*H*-Pyrroles from 5-aza-1-tungsta-1,3,5-hexatrienes generated from 3-aza-1-tungsta-1,3-butadienes and alkynes (= "alkyne route to pyrroles")

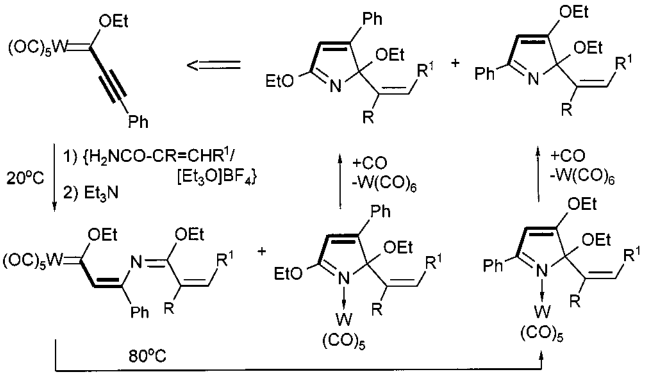
Generation of pyrroles by π-cyclization of (conjugated) 1-tungsta-5-aza-1,3,5-trienes has been achieved in two different ways, in which the 1-metalla-5-aza-1,3,5-triene precursor is generated either by insertion of an alkyne into the M=C bond (Scheme 48, "alkyne route to pyrroles") or by addition of an NH imino group to a (1-alkynyl)carbene complex (Scheme 49 and 50, "imine route to pyrroles"). The 1-tungsta-5-aza-1,3,5-hexatrienes afford 2*H*-pyrrole complexes (characterized by several crystal structure analyses), from which 1*H*-pyrroles could be obtained by disengagement of the metal unit (Scheme 48).[55c] Depending on the type of alkyne which is reacted with a 3-aza-1-tungsta-1,3-butadiene, cyclization was found to produce pyrroles together with dihydropyridones.[55a,55b,56]



Scheme 49. 2*H*-Pyrroles from conjugated 5-aza-1-chroma-1,3,5-trienes generated by addition of imines to (1-alkynyl)carbene chromium complexes (= "imine route to pyrroles")

Addition of ketimines $R^1R^2C=NH$ (R^1,R^2 = Ph, *p*-MeOC$_6$H$_4$, *c*Pr) to (1-alkynyl)carbene chromium complexes (R = *n*Pr, *c*Pr, *t*Bu) at 25°C affords 1-chroma-5-aza-1,3,5-trienes in 41−98%, which cyclize at 50−55°C to 2*H*-pyrroles (= "imine route to pyrroles") (Scheme 49).[57]

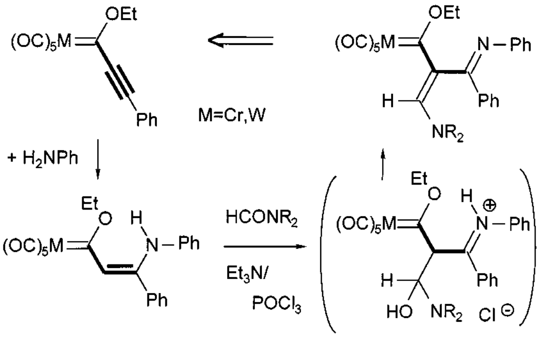
Addition of primary alkenyl imidates (generated in situ by alkylation of primary alkenyl amides $R^1CH=CR-CONH_2$ with $[Et_3O]BF_4$) to the (1-alkynyl)carbene tungsten complex $(CO)_5W=C(OEt)C\equiv CPh$ affords 5-aza-1-metalla-1,3,5,7-octatetraenes $(CO)_5W=C(OEt)CH=C(Ph)N=C(OEt)CR=CHR^1$ (R, R^1 = H, Me, Ph) in 60−80% yields, together with vinyl-2*H*-pyrrole complexes in 12−20%. The latter compounds were shown to be generated in a hitherto unknown manner by addition of the imidate to the carbene carbon atom of the (1-alkynyl)carbene complex. Cyclization of the 5-aza-1-metalla-1,3,5,7-octatetraenes results in the formation of vinyl-2*H*-pyrrole complexes of structures different from those generated by disengagement of the metal unit (Scheme 50).[58]



Scheme 50. Vinyl-2*H*-pyrroles from (1-alkynyl)carbene tungsten complexes and acid amides (= "imidate route to pyrroles")

7 Cross-Conjugated Aza-Metallahexatrienes

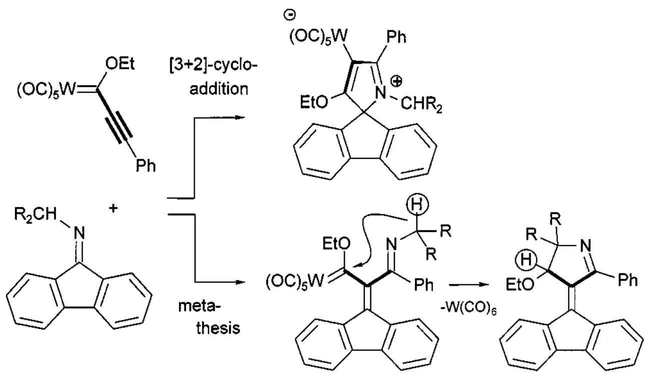
Generation of cross-conjugated aza-metallahexatrienes was achieved by an aminomethylenation (Scheme 51) as well as by a metathesis reaction of a C=N bond (Scheme 52).



Scheme 51. Cross-conjugated aza-metallahexatrienes by aminomethylenation of 4-*NH*-amino-1-metalla-1,3-butadienes

Aminomethylenation of 4-*NH*-amino-1-metalla-1,3-butadienes $(CO)_5M=C(OEt)-CH=C(NHR)Ph$ (M = Cr, W) with formamides $HCONR_2$ (NR_2 = NMe_2, pyrrolidine, morpholine) in the presence of $Et_3N/POCl_3$, affords cross-conjugated aza-metallahexatrienes $(CO)_5M=C(OEt)-C[C(Ph)=NPh]=CHNR_2$ in 61−83% yields (Scheme 51).[59]

Reaction of a (1-alkynyl)carbene complex with non-enolizable imines, like fluorenone imines yields two type compounds: a) novel pyrrolium complexes by [3+2] cycloaddition; and b) dihydropyrroles by metathesis (Scheme 52).



Scheme 52. Pyrrolium complexes and dihydropyrroles from (1-alkynyl)carbene complexes and imines

The dihydropyrroles were shown to be generated from cross-conjugated aza-metallahexatriene precursors.[60]

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