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PENTADIENYLMETAL COMPOUNDS. STRUCTURAL ANALYSES AND APPLICATIONS IN ORGANIC SYNTHESIS

HAJIME YASUDA* and AKIRA NAKAMURA*
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

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Summary

This article reviews the recent advances in the chemistry of 2,4-pentadienylmetal compounds. The geometries of pentadienylmetals of the main Groups IA–IVB were found to be delicately controlled by a combination of the media and the identity of the metal and/or alkyl substituents. Thus pentadienylpotassium assumes the U-shaped (Z,Z)-structure in THF while that in hexane and pentadienyllithium prefer the W-shaped (E,E)-structure. The covalency at the metal–pentadienyl bond in $(C_5H_7)_2M$ (M = Mg, Zn, Be), C_5H_7M (M = $B(OR)_2$, Cu) or their alkyl derivatives increases the preference for the terminally σ-bonded W- or U-shape. The Groups IVA–VIII transition metal complexes with pentadienyl ligands exhibit unique geometries. This paper also describes the fascinating applications of pentadienylmetal compounds to a variety of organic transformations including alkylation, trimethylsilylation, reactions with carbonyl compounds, etc. Factors controling the regio- and stereo-selectivity in these reactions are described in fair detail.

Introduction

As the carbanion chemistry extends from simple alkyl, alkenyl to allyl anions, conjugation and hyperconjugation together with the size of counter-cations become the major controlling factors determining the (E)- or (Z)-structure and reactivity. When the conjugation is extended further to pentadienyl systems, three geometries must be considered; i.e., the horseshoe-like, "U"-shaped (Z,Z)-; the zigzag-like, "W"-shaped (E,E)-; and the sickle-like, "S"-shaped (Z,E)-structures. Experimental evidence and theoretical treatments with a sufficient accuracy are required to reveal the key factors which change the energetics of the geometrical isomers.

The scope of pentadienylmetals has now extended considerably, covering the Main Groups IA–IVB together with the Group IVA–VIII transition metals. These compounds serve as versatile reagents for the pentadienylation of various electrophiles. Consequently, a wide variety of regio- and stereo-selective reactions are now available by choosing metal/organic combinations appropriately. This paper deals

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(Z)

(E)

"U" (Z,Z)

"W" (E,E)

"S" (Z,E)

with some recent advances in the chemistry of pentadienylmetal compounds, including the preparative methods, configurational analysis, and the applications in organic synthesis. The geometries of the pentadienylmetal compounds will be described in some detail because structural elucidation is indispensable in designing the course or stereochemistry of the new reactions using pentadienylmetal compounds. An excellent masterly monograph written by Bates and Ogle should be consulted for the whole scope of carbanion chemistry [1].

Preparation of 2,4-pentadienylmetal compounds

A variety of 2,4-pentadienylmetal compounds containing Main Group elements have been synthesized according to the procedures given below, and most of them are isolated in a pure form:

(1) Metalation of 1,4-dienes with alkyllithium [2].

(2) Metalation of 1,4-dienes with MNH_2 (M = Na, K) in liquid NH_3 [3].

(3) Metalation of 1,3- and/or 1,4-dienes with alkali metals (M = Li, Na, K, Rb, Cs) in the presence of a tertiary amine [4].

(4) Cleavage of alkyl-2,4-pentadienyl ethers by alkyllithium [5].

(5) Oxidative addition of 2,4-pentadienyl halides to metals [5].

(6) Metal exchange reaction between pentadienylalkali-metals and metal halides or metal alkoxides (e.g., KO-t-Bu [6], $BeCl_2$ [7], $MgCl_2$ [8], $ZnCl_2$ [7], R_3SiCl [9], R_3SnCl [10], R_2BCl [11], BX_3 [6], etc.).

Procedures 1–4 are useful for the preparation of alkali metal compounds and procedures 5 and 6 are for other metal compounds. The syntheses of transition metal complexes with pentadienyl ligands are described later in this paper. Until the discovery of process 3, the utility of 1,3-dienes as a precursor of pentadienyl anions was neglected because most 1,3-dienes except cyclic ones undergo polymerization or dimerization immediately when treated with alkali metals or alkylalkali metal compounds under normal reaction conditions [12]. With the arrival of the effective and economical route 3, a series of alkyl-substituted pentadienyl anions with Li, Na, K, Rb or Cs cations can be conveniently prepared and isolated as orange crystals, starting from commercially readily available 1,3-pentadiene or its alkyl derivatives. Research on the chemistry of 1,3-pentadienylmetal compounds is omitted in this article (see refs. 13 and 14 for examples).

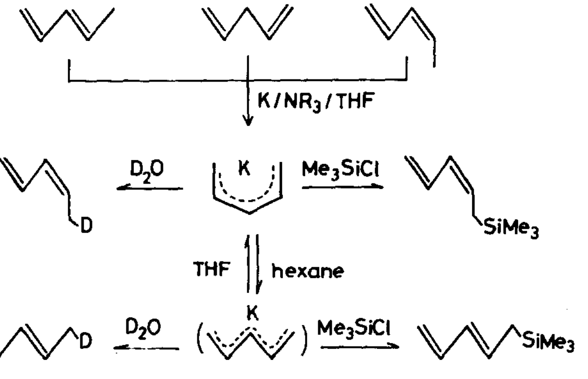
Geometries of pentadienylmetal compounds

(a) Structural elucidation by chemical derivation

It is fundamentally important to clarify the geometry and charge distribution of pentadienyl anions in order to understand and even predict the mode of characteristic C–C bond forming reactions. For the parent pentadienyl anions, three geometries (U, W and S) are conceivable, as described above. Chemical derivation of the carbanions provides reliable information on the structures. The U-shaped structure has been suggested for pentadienyl-potassium, -rubidium and -cesium in an ethereal solution such as THF [4], 1,3-dioxane and diglyme [15] on the basis of the hydrolysis which gives rise to (*Z*)-1,3-pentadiene exclusively (99%). Chemical derivation by trimethylsilylation [9] or by the dialkoxyboration-oxidation procedure [6] also confirmed the (*Z*)-geometry of pentadienylpotassium, 2-methylpentadienylpotassium, 2,4-dimethylpentadienylpotassium and 2,4-dimethylpentadienyllithium. On the other hand, pentadienyllithium has been proposed to exist as the W-shaped, single torsional isomer in an ethereal solution by the similar chemical trapping experiments [6,9]. Thus, the geometry of the pentadienyl anions varies on changing the counter cation from K to Li. If the above compounds assume the S-shape, hydrolysis should give rise to a mixture of (*Z*)- and (*E*)-isomers.

In chemical derivation, particular attention should be paid to the handling of the reagents because these carbanions often show a quite unique medium effect. When trimethylsilylation of pentadienylpotassium was carried out with $(CH_3)_3SiCl$ in a non-polar solvent such as hexane or octane, where the anion is insoluble and precipitates as a yellow powder, the product comprised only the (*E*)-isomer (99%), in contrast to the exclusive formation of the (*Z*)-isomer (99%) as observed in the reaction with a homogeneous THF solution [4,9]. Such a marked medium effect has also been observed even when the THF solution was cooled to −78°C, in which case 80–90% of pentadienylpotassium precipitated. Trimethylsilylation of the precipiate gave (*E*)-2,4-pentadienyltrimethylsilane in ca. 80% selectivity even in the presence of THF.

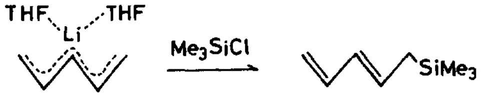
Attempts to elucidate the X-ray structures of pentadienylpotassium and pentadienylrubidium have failed because the number of observed reflections was insufficient to establish the exact molecular structure. Although the geometry of the pentadienyl anion in the solid state has not yet been unambiguously solved, the marked geometrical change due to the medium effect is extremely useful for selective interconversion of (*E*)-, (*Z*)-1,3-pentadiene or 1,4-pentadiene into (*E*)- or (*Z*)-1,3-pentadiene-d_1 [4] or silylated derivatives [9] as shown in eq. 1.



(1)

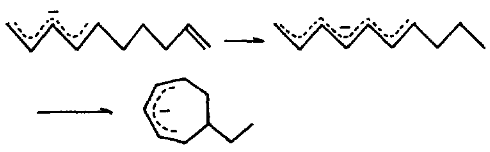
In contrast, pentadienyllithium does not show such a medium effect, presumably because of the strong solvation by THF or amines. The THF coordinated to C_5H_7Li

was not liberated even at 120°C in vacuo, while the analogous K, Rb and Cs compounds readily release the coordinated THF under vacuum at 60°C and even when washed with hexane. Accordingly, pentadienyllithium always gives the (*E*)-isomer on trimethylsilylation, ignoring the medium effect. On this basis, the "W" form



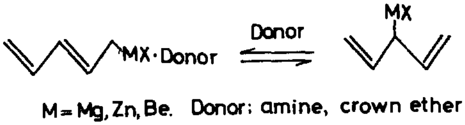
(2)

is proposed for solvated pentadienyllithium, which should exist as a solvent-separated ion pair. Potassium and cesium analogues should be present as a contact ion pair even in ethereal solutions. In the experiments dealing with these compounds, great care is necessary, especially in the case of alkyl, allyl or heteroatom-substituted pentadienyl anions, because electrocyclic and/or sigmatropic rearrangement occasionally occur even at room temperature [16]. A typical example is shown in eq. 3.



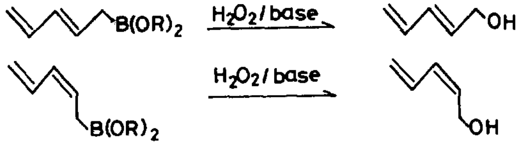
(3)

The geometries of pentadienyl compounds of the Main Groups IIA–IVB metals cannot usually be elucidated by chemical derivation because these compounds are rather inert towards Me_3SiCl, RX and $BF(OR)_2$. However, the hydrolysis of bis(pentadienyl)metal compounds of Mg [8], Zn and Be [7] proved that they exist as equilibrium mixtures. The ratio of (*E*)-, (*Z*)-1,3-pentadiene and 1,4-pentadiene is 65/14/21, 60/8/32 and 14/1/85, respectively. The amount of (*Z*)-1,3-pentadiene formed is remarkably small, indicating that the 1,3-rearrangement takes place retaining the W-form. The equilibrium shifts far to the left when an equivalent of a strong donor such as pyrrolidine, piperidine, tetramethylcyclam, or 15-crown-5 is



(4)

added to the magnesium or zinc compound (eq. 4). The yield of (*E*)-1,3-pentadiene was greater than 95% when hydrolysis was carried out after the addition of such donors. Pentadienylboron compounds have not yet been isolated due to their great thermal instability. However, the oxidation of these compounds at −78°C gave pure 2,4-pentadien-1-ol in good yield. Since the $C_5H_7B(OR)_2$ type pentadienylboron compound derived from (*E*)-pentadienyllithium or (*Z*)-pentadienylpotassium gave



(5)

(E)- or (Z)-2,4-pentadien-1-ol, respectively, in quantitative yields, the interconversion between the two boron isomers seems to be effectively suppressed at low temperature [6]. Among the pentadienylmetal compounds, pentadienylsilanes are the most stable thermally and they are inert towards air and moisture under ordinary conditions. Therefore, their structures are readily analyzed directly by spectroscopic methods after the geometrical isomers have been separated into individuals on a preparative gas chromatograph.

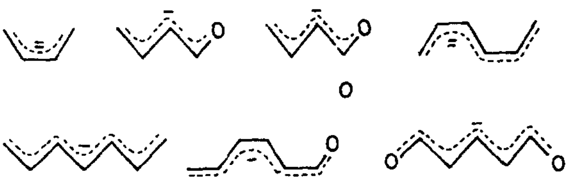
(b) NMR studies

The U-shaped structure predicted for pentadienylmetals (K, Rb, Cs) was finally confirmed by ^{1}H NMR studies using 1,1,5,5-tetradeuterated pentadienylalkali metals dissolved in THF-d_8 at −70°C [9]. The coupling constant J_{23}, 8.7 Hz for K, Rb and Cs analogues is very close to the value for cyclooctadienylpotassium (7.8 Hz) and cycloheptadienylpotassium (7.8 Hz) of U-shaped configuration. The S-shaped structure can be ruled out because of the symmetrical spectral patterns observed. In contrast to the above, pentadienyllithium, hexadienyllithium in THF [2] and pentadienylpotassium, hexadienylpotassium in liquid NH_3 exist in the W-shaped form as demonstrated by the coupling constant J_{23} (11.5-16.5 Hz) [3]. Although the S-shaped structure is observed for methylidene-2-cyclohexenyllithium with a cyclic carbon skeleton [2c] and is postulated for the 1,5-dioxapentadienyl anion based on MO calculation [7], the linear S-shaped pentadienyl had not been reported until the discovery of 1,3,5-tris(trimethylsilyl)pentadienyllithium [27]. The geometry of allylic anions also changes depending on the counter-cation; i.e., butenylpotassium favors the Z (*endo*) structure [19] while butenyllithium assumes the E (*exo*) structure [20].

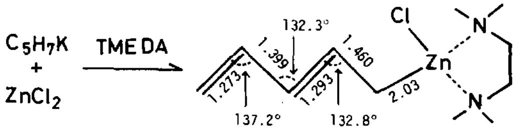
endo-C_4H_7K

exo-C_4H_7Li

For related carbanions including highly conjugated systems or hetero-atom substituted pentadienyl anions, the following geometries are suggested on the basis of NMR studies [21–26].

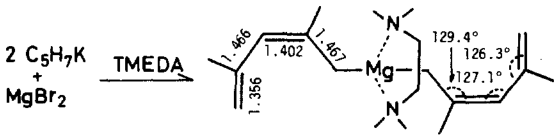


The geometry of the 2,4-pentadienyl group in $(C_5H_7)_2M$ and C_5H_7MX (M = Mg, Zn, Be) is estimated to be essentially the (E)-form on the basis of the magnitude of J_{23} (12.5–15.3 Hz), although the compound is in equilibrium with other isomers at room temperature [7,8]. The value is consistent with that found for (E)-butenylmagnesium bromide. At −70°C in THF, $(C_5H_7)_2Zn \cdot (THF)_2$, $(C_5H_7)_2Zn \cdot$ TMEDA, $(C_5H_7)_2Be \cdot$ TMEDA and $(C_5H_7)_2Mg \cdot$ 15-crown-5 showed the limiting s-*trans*-(E)-2,4-pentadienylmetal structure. X-Ray analysis of $C_5H_7ZnCl \cdot$ TMEDA supports the above conclusion [7]. The coordination geometry around the zinc atom is found to be essentially tetrahedral and the (E)-2,4-pentadienyl group is bonded to the metal at the terminal C(1) atom. The derivatives of the bis(pentadienyl)metals



(6)

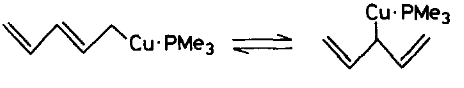
(Be, Mg, Zn) substituted with an alkyl group at the C(2) or C(4) atom also prefer the s-*trans*-(*E*)-pentadienyl structure, as indicated by the ^{1}H NMR spectrum. However, alkyl substitution at both C(2) and C(4) atoms brings about the s-*cis*-(*Z*)-2,4-pentadienyl structure, as confirmed by X-ray analysis of bis(2,4-dimethylpentadienyl)magnesium · TMEDA [8]. The 2,4-pentadienyl group is σ-bonded to the metal at C(1) and the two double bonds show a clear bond alteration as shown in eq. 7. The C(2)–C(3) and C(4)–C(5) bonds are not coplanar and the dihedral angle



(7)

between the C(1)–C(2)–C(3) and C(3)–C(4)–C(5) planes is 22.6°. The observed geometry corresponds well to the out-of-plane U-shaped structure suggested for 2,4-dimethylpentadienyl-potassium and -lithium. Thus the geometry of 2,4-dimethylpentadienyl anions remains intact even when they are converted to a magnesium analogue with terminal M–C σ-bonding. A similar trend is also observed between hexadienylpotassium [4] and bis(hexadienyl)magnesium [8], both of which prefer the (*E*,*Z*)-structure and upon hydrolysis gave (*E*,*Z*)-2,4-hexadiene in good yield.

Alkyl- or allyl-coppers are generally thermally unstable and consequently NMR studies are less prevalent. On the other hand, pentadienylcopper ($C_5H_7Cu \cdot PBu_3$) and 1,5-bis(trimethylsilyl)pentadienylcopper ($C_5H_5(SiMe_3)_2Cu \cdot PBu_3$) possess a relatively high thermal stability due to the stabilization of conjugation and hence measurement of the spectrum is successful even at room temperature [27]. The spectral pattern is very similar to that of pentadienylmagnesium compounds in a wide temperature range (– 70 to 40°C). The coupling constant J_{23} (12.5–14.5 Hz) for the equilibrating copper compounds suggests that they prefer the s-*trans*-(*E*)-2,4-pentadienyl structure.

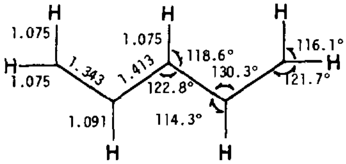


(8)

(c) *MO studies*

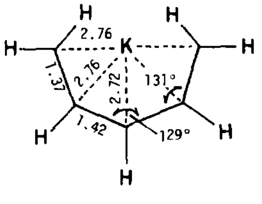
The conformational preference and relative stability of pentadienyl anions (free carbanion) were first calculated by Hoffmann and Olofson on the basis of the orbital symmetry [28]. Since the non-bonding pentadienyl π-orbital is 1,5-bonding, net stabilization of pentadienyl anions should result if centers 1 and 5 approach close enough for a significant $2p_z$ orbital overlap. If this geometry could be attained, the resulting U-shaped form would be the most stable. A CNDO/2 calculation by

Bushby and Patterson predicted that the planar U- and planar S-shaped anions are slightly more stable than the W-form [29]. More recently, an MO calculation of high quality has been reported by Dewar et al., using the MNDO procedure [30]. The result does not agree with the above. The calculated heat of formation (ΔH_f) shows that the planar W-shaped geometry is more stable than the planar U- or the planar S-shape by 3.7 and 1.0 kcal/mol, respectively. Although ab initio studies with the STO-3G basis set have also been presented by Bongini et al. and W-shaped geometry is computed to be more stable than the U- and the S-shaped structures by 160 and 5 kcal/mol, respectively, the value for the U-form seems to be too positive [31]. These authors also stated that the non-planar spiral U-isomer of the covalent lithium derivative is lower in energy than the planar W-isomer by 12 kcal/mol. A more refined treatment is necessary to obtain reliable data. We have reinvestigated the isomer stability using the geometry-optimized STO-3G atomic orbital calculation [32]. Our major interest lay in determining whether the planar form is more stable than the non-planar geometry in the presence and absence of interaction with metals. The results of our calculations on the free pentadienyl carbanions differ significantly from the results of Bongini et al. [31]. The planar W-shaped structure was computed to be only slightly more stable than the planar U- and planar S-forms by 4.9 and 1.7 kcal/mol, respectively, the relative values being consistent with Dewar's prediction and parallel to the experimental evidence obtained from pentadienyllithium. The final calculated values for C_5H_7 (free carbanion) are given below.



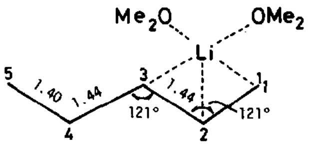
Charge distribution	
C(1)(C(5))	−0.274
C(2)(C(4))	−0.044
C(3)	−0.242

We have also calculated the isomer stability of pentadienylpotassium using the geometry-optimized STO-3G procedure [32]. The 1–5-η-coordinated U-shaped pentadienylpotassium is 10.0 and 9.4 kcal/mol more stable than the 1–4-η-coordinated S- and 1–3-η-coordinated W-shaped planar pentadienylpotassium, respectively. The calculated bond distances, bond angles and charge distribution for the U-shaped pentadienylpotassium are given below. The respective values are consistent with the experimental observations (chemical derivation and NMR studies). All the carbon



Charge distribution	
C(1)	−0.242
C(2)	−0.037
C(3)	−0.218
C(4)	−0.036
C(5)	−0.243

atoms (C(1)–C(5)) are nearly coplanar, and the angle between the C(1)–C(2) and C(4)–C(5) bond is 31° due to steric repulsion between C(1) and C(5) atoms. The geometry of solvated pentadienyllithium has been calculated by Sebastian et al., using $C_5H_7Li(CH_3OCH_3)_2$ as a model [33]. The result of the geometry-optimized CNDO/2 calculation agrees well with the NMR data for C_5H_7Li in ethereal solution. The STO-3G calculations mentioned above revealed another important



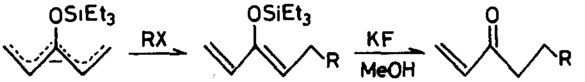
Charge distribution	
C(1)	−0.187
C(2)	+0.142
C(3)	−0.172
C(4)	+0.083
C(5)	−0.187

point: that the planar geometry is always more stable than the non-planar geometry regardless of the presence of alkali-metal cations and the shape of the geometries (U, W and S).

Alkylation of pentadienyl anions

The alkylation or acylation of pentadienylmetal compounds is a fundamentally important procedure in organic synthesis. However, direct alkylation of pentadienylmetals as well as allylic metal compounds is not as useful because they do not react regioselectively, e.g. at the α-carbon atoms [34,35]. Some ingenious contrivances are necessary to improve the selectivity. One effective method to circumvent this difficulty is to change the medium. For example, allylation of pentadienylpotassium in THF, diglyme or 1,3-dioxane with allyl bromide occurs in > 85% regioselectivity at the terminal carbon while the corresponding reaction in hexane (solid-state reaction) gives 3-allyl-1,4-pentadiene in 99% selectivity [15]. This type of reaction was successfully applied to the preparation of $CH_2{=}CHOCH_2CH_2CH(CH{=}CH_2)_2$, which is a useful starting material for semiconducting organometallic polymers containing $Fe(CO)_3$ or $Ru(CO)_3$ fragments [36]. An alternative method to control the regioselectivity is to introduce an electron-withdrawing substituent onto the pentadienyl group. When the Et_3SiO group is introduced onto the C(3) atom of pentadienyllithium, the succeeding alkylation with CH_3I or $(CH_3)_2C{=}CHCH_2Br$ takes place selectively at the terminal carbon of the carbanion [37]. Removal of Et_3SiOMe from the product with KF/MeOH gives a synthetically useful vinyl ketone. Substitution with a trimethylsilyl group is also an effective way to bring about regioselective alkylation [18]. Alkylation of 1-(trimethylsilyl)pentadienyllithium or 1,5-disilylated pentadienyllithium with RX (R = t-Bu, i-Bu, s-Bu, $PhCH_2$) occurred at the central carbon atom in > 95% selectivity. The CuCl-catalyzed

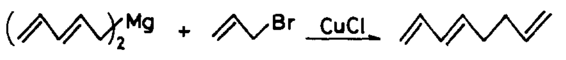
(9)



(10)

(11)

allylation of pentadienylmagnesium also occurs regioselectively to give a terminally bonded product [8]. The CuCl-mediated coupling reaction with pentadienylpotassium gave pure 1,3,7,9-decatetraene while thermal degradation of $(C_5H_7)_2Zn$ gave a



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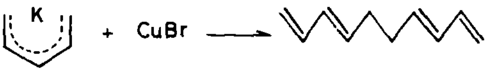
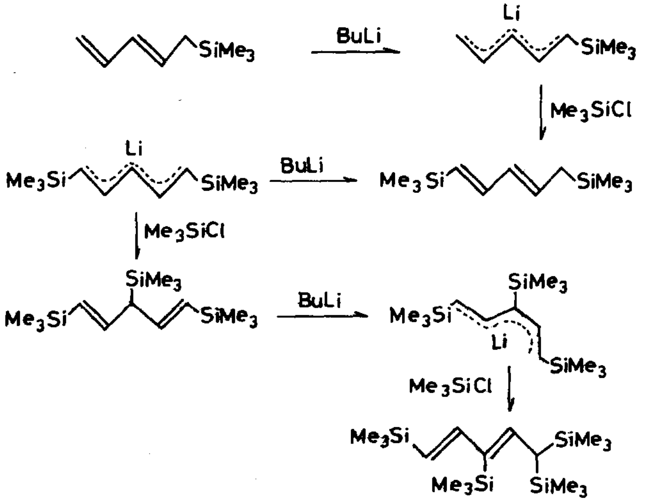


(13)

mixture of $C_{10}H_{14}$ through pentadienyl radicals [7]. These coupling products are useful ligands for organometallic compounds [38]. Such a transition metal mediated or catalyzed reaction seems worthy of further study.

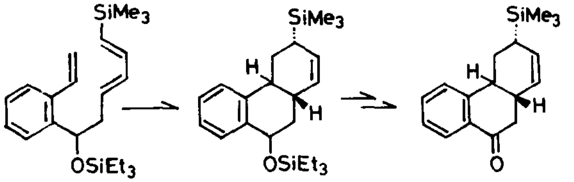
Stereoselective multiple silylation

Multiple silylation of the pentadienyl anion is a synthetically useful procedure because it gives the product with high regio- and stereo-selectivity [18]. 2,4-Pentadienyltrimethylsilane derived from pentadienyl anions easily underwent metalation on treatment with butyllithium in THF to give a W-shaped silylated pentadienyl anion, and the successive trimethylsilylation afforded the (*E*,*E*)-1,5-disilylated 1,3-pentadiene in good yield (eq. 14). The repeated metalation with BuLi in THF gave a 1,5-bis(trimethylsilyl)pentadienyl anion of the (*E*,*E*,*E*,*E*)-configuration, as confirmed by the NMR studies. Thus metalation occurs readily when a silyl group is attached to the carbanion excluding the alkyllithium-catalyzed polymerization. The mode of trimethylsilylation with a 1,5-disilylated pentadienyllithium is different from the above. The silylation occurrred preferentially at the central C(3) atom and gave (*E*,*E*)-1,3,5-bis(trimethylsilyl)-1,4-pentadiene. Quadruple silylation of 1,3-pentadiene has also been achieved by repeated lithiation-trimethylsilylation sequences.



(14)

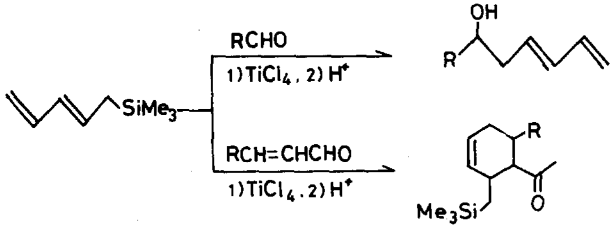
The resulting silylated pentadienes act as good dienophiles and a variety of 6-membered ring compounds have been prepared by the Diels–Alder reaction [10b].



(15)

Regioselective pentadienylation of carbonyl compounds

Regioselective pentadienylation of carbonyl compounds has been achieved by two different methods. One is the Lewis acid ($TiCl_4$, BF_3, $AlCl_3$) induced reaction between pentadienylsilanes and carbonyl compounds or acetals via carbocation intermediates [39]. The other is nucleophilic attack of pentadienylmetal compounds to carbonyl compounds (via a carbanion) [27]. A representative reaction of the former is shown below. Addition of electrophiles occurs selectively at the terminal carbon atom and gives, upon hydrolysis, (*E*)-3,5-hexadien-1-ol and its alkyl derivatives. When an α,β-unsaturated ketone or aldehyde is used, the reaction gives a cyclic product (Diels–Alder product). This type of reaction is already familiar in allylsilane chemistry [40].



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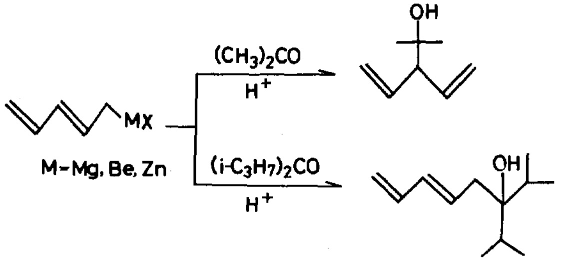
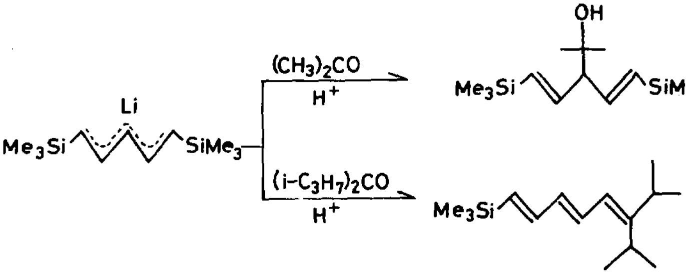
Direct pentadienylation of carbonyl compounds with pentadienyl alkali metals has less utility in organic synthesis because it gives a mixture of products through the competitive addition at the α- and γ-positions of the pentadienyl group [34,41]. However, the regioselectivity can be improved by replacing the counter-cation (Li^+, Na^+, K^+) by less positive Mg [8], Zn [7], Be [7] or B [11]. The resulting metal compounds of the type $(C_5H_7)_2M$, C_5H_7MX or its alkyl derivatives readily react with a variety of carbonyl compounds selectively at the C(3) atom of the pentadienyl



(17)

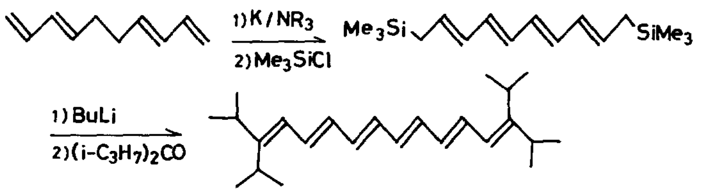
group. Thus, the present reaction fills the deficiency of the Lewis acid induced pentadienylation which gives only terminally-bonded products. When bulky ketones were used in reactions with $(C_5H_7)_2Mg$ or $(C_5H_7)_2Zn$, pentadienylation occurred at the terminal carbon selectively (eq. 17).

Allyl anions and their alkyl derivatives usually show a low regioselectivity like pentadienyl anions do in reaction with carbonyl compounds. Much effort has been made to improve the selectivity, and the mode of the reaction has been modified by introducing an SR, OR, X or SiR_3 group onto the α-carbon [35]. From this point of view, we considered the utility of the silylated pentadienyl anions again as reagents [27]. Actually, 1,5-bis(trimethylsilyl)pentadienyllithium reacts with simple ketones



(18)

and aldehydes selectively at the C(3) atom of the carbanion while bulky ketones react at the terminal atom of the pentadienyl group to give conjugated trienes. The present triene synthesis can be successfully applied to sterically less hindered ketones and aldehydes by treating them with 1,3,5-tris(trimethylsilyl)pentadienyllithium [27]. The reaction proceeds through Peterson elimination. This type of reaction was further extended to the preparation of highly conjugated polyenes under mild conditions (eq. 19). When the 1,5-disilylated pentadienyllithium is treated with



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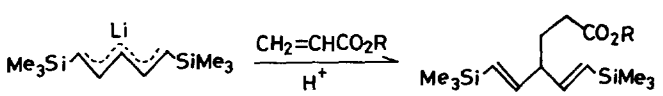
α,β-unsaturated ketones or esters, 1,4-addition occurs predominantly at the C(3) atom of the pentadienyl group. The selectivity is sufficiently high.



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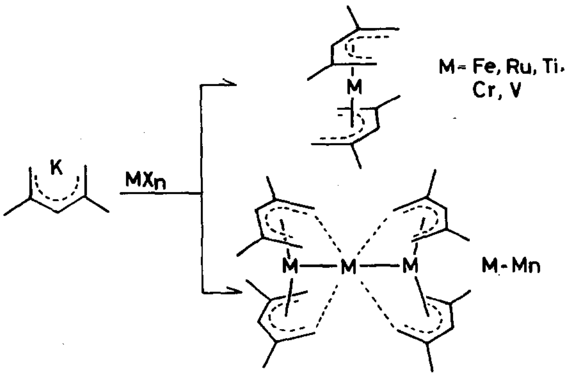
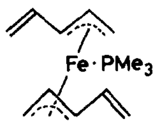
Transition metal complexes containing pentadienyl or pentadiene ligands

Only relatively few transition metal complexes with one or two pentadienyl ligands were known until the discovery of open metallocenes by Ernst and co-workers in 1980 [42]. This field will be critically reviewed from the inorganic point of view [42e]. The orientation of the pentadienyl groups and the M–C bond distances in the open metallocenes are similar to those of well-characterized sandwich-type metallocenes such as ferrocene, chromocene, etc. Open titanocene is especially interesting since the corresponding $(C_5H_5)_2Ti$ has not yet been isolated because of its thermal

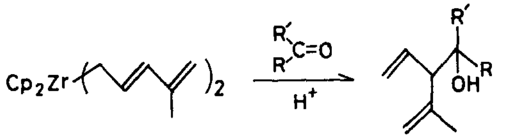


(21)

instability. X-Ray analysis of the 2,4-dimethylpentadienylmanganese complex revealed that it is an unusual trimetallic complex of formulation $Mn_3(C_6H_9)_4$ [43]. All of the 2,4-dimethylpentadienyl groups described in this section assume the η^5-U-shaped coordination. The η^3-s-*trans-(E)*-pentadienyliron complex shown below has recently been prepared starting from the parent pentadienyl anions in which alkyl substituents are absent [44]. A related nickel complex also favors the W-shape [45].



Thus the preferred W-geometry for pentadienyllithium and the U-geometry for 2,4-dimethylpentadienyl anions are reflected in some of the structures of transition metal complexes. Exceptional are the U-shape for $(C_5H_7)M(CO)_3$ (M = Mn, Re) [46a,b] and $CpNi(C_5H_7)$ [46c] and the S-shape for $(C_5H_7)Mn(CO)_3PMe_3$ [47]. Although the application of these complexes in organic synthesis has not yet been well developed, these complexes have a potential utility since the pentadienyl ligand has a great versatility and application in synthetic methodology compared to the cyclopentadienyl ligand. (*E*)-4-Methyl-2,4-pentadienylzirconium of linear geometry is an excellent reagent for organic synthesis [48]. The complex reacts with carbonyl compounds at its C(3) atom regioselectively. Since the corresponding (*E*)-2-

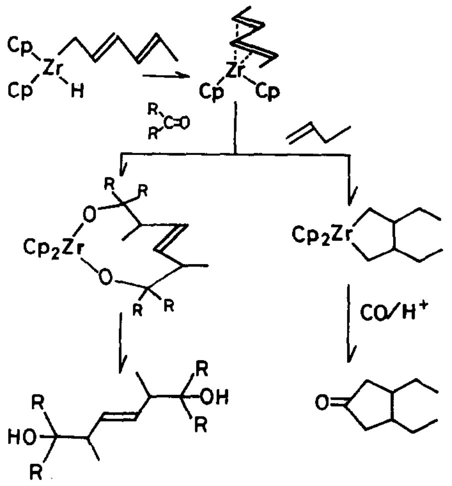


(22)

butenylzirconium complex is known to react with aldehyde *threo*-selectively [49], the alkyl-substituted pentadienylzirconium compounds are expected to undergo stereo- and regio-controlled addition reactions with aldehydes.

Another useful application of the pentadienyl anion is the preparation of pentadienezirconium complexes, e.g., Cp_2Zr(1,3-pentadiene) [48]. Here, pentadienylation of

Cp_2ZrHCl followed by thermal σ,π-rearrangement gave a novel η^4-pentadiene complex in s-*cis* and s-*trans* isomers. Starting from hexadienyl anions with Li or K counter-ions, the Cp_2Zr(2,4-hexadiene) complex was obtained (eq. 23). Unlike the pentadieneiron complexes, these complexes are highly reactive towards both carbonyl compounds and unsaturated hydrocarbons (olefins, dienes and alkynes). Their chemical behavior differs significantly from that of the corresponding isoprenezirconium complex [50]. For example, Cp_2Zr(2,4-hexadiene) reacts with two equivalents of aldehydes and/or ketones to give, upon hydrolysis, derivatives of 3-hexen-1,6-diols in good yield. When the complex was treated with 1-butene or 1,7-octadiene and then 1 atm of carbon monoxide, 2,3-diethylcyclopentanone or hydrindanone was obtained on hydrolysis of the product (eq. 23). Zirconium complexes of silylated pentadienes (shown below) are also prepared by a similar σ,π-rearrangement [48].



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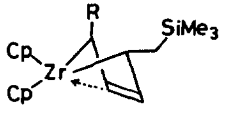

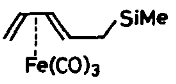

The above-mentioned transmetalation of pentadienyl anions leading to transition metal complexes will ensure the further development of the chemistry of pentadienylmetals. The direct complexation of the pentadienylmetals to transition metal fragments, e.g., $Fe(CO)_3(Me_3SiCH_2CH{=}CHCH{=}CH_2)$ shown above [13], is also an attractive research target since the metal complexes of functionalized dienes are known to serve as useful synthetic reagents and as electrical semiconducting materials after doping [38].

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