

NOVEL π SYSTEMS POSSESSING CYCLOPROPENYLIDENE MOIETY

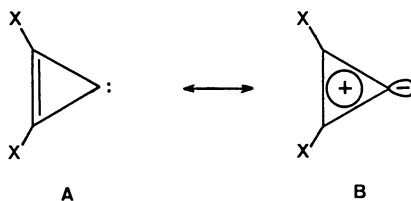
Zen-ichi Yoshida

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto, 606, Japan

Abstract — As one of the most attractive π systems cyclopropenylidene metal complexes are prepared and their structure, especially carbene carbon-metal bonding is examined. In the lithium complex, this bonding is substantially ionic, on the other hand, in the transition metal complexes the carbene carbon-metal bond is shown to have double bond character by the π back donation. The σ donating and π accepting powers of cyclopropenylidenes change dramatically with presence or absence of amino substituent. Novel triafulvenes, triafulvalenes and related π system are taken up. The simplest triafulvenes and triafulvalenes possessing conjugate π systems are synthesized. Triafulvalenes (3-5, 3-7, 3-9 systems) are also prepared. The structural features of these triafulvenes and triafulvalenes are discussed based on the spectral data. The parent compound of "cyclic dicalicene" which have peripheral 16π and central 8π structures is synthesized. The X ray analysis indicates that this novel system has planar (D_{2h}) structure. Its π electron configuration is determined by ^1H - and ^{13}C -NMR spectra and MINDO/3 investigation.

INTRODUCTION

The novel π systems which possess highly strained ring moiety should be the synthetic target to be challenged because of the synthetic difficulty, the structural interest and the possibility of peculiar properties. Among such sort of highly strained systems, cyclopropenylidene is particularly interesting from the following reason:



This carbene has the largest $S_0 - T_1$ gap (Ref. 1) due to 2π aromaticity (canonical form B) of the C_3 ring in addition to the highly strained σ framework (bent σ bond and non-equivalency in hybridization of the ring carbon σ orbitals). The present paper deals with the novel π systems which should be considered to be formally formed by the combination of substituted cyclopropenylidene with metal (ion) or another carbene having conjugate π structure. In the former case the bonding nature (i.e. ionicity or covalency of σ bond, and double bonding character) of the carbene carbon-metal bond should be the most interesting problem. In the latter case the π electron delocalization in whole molecule should be the most important problem to be discussed. Novel triafulvenes and triafulvalenes as examples of such sort of π systems will be discussed. A success in synthesis of novel π system "cyclic dicalicene" having peripheral 16π and central 8π structure should give an extremely interesting problem to discuss the π electron delocalization.

CYCLOPROPENYLIDENE METAL COMPLEXES

Since our first finding (Ref. 2) of diaminocyclopropenylidene formation in solution, we have investigated the synthesis and structural feature of substituted cyclopropenylidene metal complexes. The extended Hückel HOMO-LUMO gap (a measure of the stability) for free cyclopropenylidenes increases with increase of electron donating power of substituent X as is shown in Table 1. The greatest energy gap for diaminocyclopropenylidene suggests dominant contribution of canonical form B.

As shown in Table 2, remarkably much amounts of negative charge is at carbene carbon of diaminocyclopropenylidene, either from extended Hückel or MINDO/3 MO calculations.

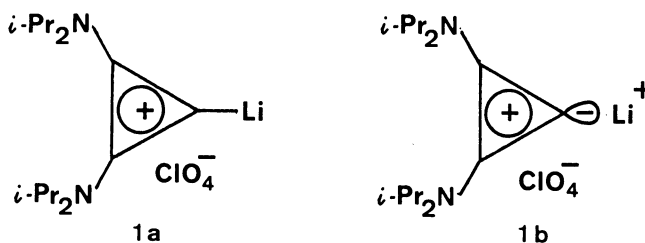
Table 1 HOMO-LUMO gap, ΔE (eV) on several cyclopropenylienes, X_2C_3 : by extended Hückel MO calculations

X	H	Me	Ph	HS	H ₂ N
ΔE	3.034	3.021	2.199	3.137	3.334

Table 2 Total charge density at carbene carbon on X_2C_3 estimated by extended Hückel and MINDO/3 MO calculations

X	H	Me	Ph	HS	H ₂ N
Extended Hückel	-0.703	-0.865	-0.815	-0.990	-1.000
MINDO/3	-0.162	-0.159	-0.208	-0.211	-0.276

This result coupled with the fact that introduction of two amino groups greatly stabilizes the cyclopropenium system means that diaminocyclopropenyliene should have a character close to that of carbanions. One of the most interesting problems in the lithiocarbene (bis(diisopropylamino)cyclopropenyliene lithium complex, 1) as an example of cyclopropenyliene-typical metal complexes is the nature of the carbene carbon-lithium bond.



In order to determine whether this C-Li bond is covalent (1a), ionic (1b) or mixed one of the both natures, ⁷Li-NMR spectra of lithio-complex (1) generated by our method (Ref. 2) have been examined by the measurement of ⁷Li chemical shifts and rate of Li-Li exchange reaction between representative organolithium compound (n-BuLi, PhLi, PhC≡CLi and 1) and LiClO₄. Since ⁷Li chemical shifts are highly affected by solvation of lithium compounds in polar solvents and their aggregation states (Ref. 3), the ⁷Li chemical shift values at high dilution with ether/hexane were measured. These values are shown in Table 3.

Table 3 ⁷Li Chemical shifts from 0.082 M LiCl (in DMSO-d₆) and Lamor frequencies for organolithium compounds and LiClO₄ (in ether/hexane 10:1 solution)

Compd.	Lamor frequencies at 21,100 Gauss (34.8 MHz+, KHz)	Chemical shifts from LiCl (ppm)
n-BuLi	23.6806	2.40
PhLi	23.6625	1.88
PhC≡CLi	23.6398	1.23
(1)	23.6269	0.86
LiClO ₄	23.5883	-0.25

These chemical shifts are in the range of -0.3 - 2.5 ppm, where the most cationic Li atom (LiClO₄) is most shielded and the reverse is true (n-BuLi). The most shielding for the most cationic Li atom should be attributable to diffusion of the positive charge on Li atoms as a result of the most effective solvation by ether. It is noteworthy that there is considerable correlation between ⁷Li chemical shifts and hybridization of the α -carbon

atoms. The ^7Li nuclei are shielded in the order of $\text{sp}_3 > \text{sp}_2 > \text{sp}$. Hybridizations of the α -carbons are surely correlated with the polarization of Li-C bonds and hence should be correlated with the chemical shifts of ^7Li . Effect of ring current on ^7Li chemical shifts of PhLi seems to be little in comparison with those observed in ^1H -NMR spectra of aromatic compounds. Chemical shift of **1** is closest to that of $\text{PhC}\equiv\text{CLi}$. This fact suggests the carbene carbon of **1** is almost sp hybridization on bonding with Li atom. Furthermore the fact that Li nucleus of **1** is 0.37 ppm more shielded than that of $\text{PhC}\equiv\text{CLi}$ indicates more ionicity of the C-Li bond of **1**. This finding is supported from the Li-Li exchange experiments. The values of free energy activation (ΔG^\ddagger) for Li-Li exchange reaction are summarized in Table 4, in which k_c is the rate constant for Li-Li exchange at coalescence temperature and k_o is that at 0°C . ΔG^\ddagger values decreased in the order of $n\text{-BuLi}$, PhLi, $\text{PhC}\equiv\text{CLi}$ and **1**. Even if taking account of aggregation of these compounds at those temperatures, the above ΔG^\ddagger values should fairly reflect the degree of ionic character of Li-C

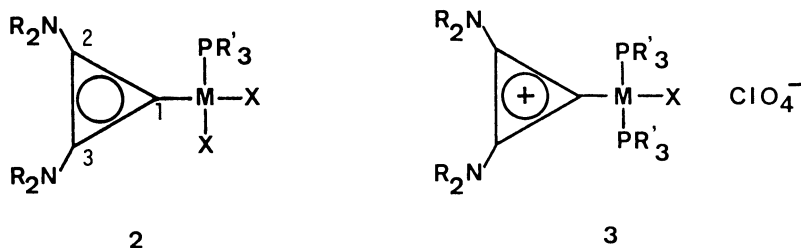
Table 4 Kinetic parameters for Li-Li exchange between organolithium and LiClO_4

Compd.	T_c (K)	k_c	k_o	ΔG_c^\ddagger (Kcal/mol)
$n\text{-BuLi}$	261	3.8×10^2	1.2×10^3	12.1
PhLi	235	1.8×10^2	5.8×10^3	11.2
$\text{PhC}\equiv\text{CLi}$	233	2.3×10^2	8.8×10^3	11.0
1	<184	$<1.7 \times 10^2$	3.1×10^4	8.7*

($E_a = 8.6$ Kcal/mol,
 $\log A = 14.6$)

*) Average value between -79 and -89°C .

bonds of these compounds. In addition, the order of ΔG^\ddagger is in good agreement with the order of ^7Li chemical shifts. These results also indicate appreciable ionic C-Li bonding of **1**. It is therefore, concluded that **1** possesses a character considerably close to that of diaminocyclopropenylidene itself (**1b**). The research on cyclopropenylidene transition metal complexes should provide us valuable informations for the nature and structure of cyclopropenylidene itself. Although, the first example of such sort of complexes was reported by Öfele about diphenylcyclopropenylidene Pd(II) and Cr(0) complexes (Ref. 4, 5), the subsequent structural study (Ref. 6) for these compounds is of no sufficient accuracy to clarify the nature of these cyclopropenylidene complexes. In the present paper, the structural problems of various transition metal complexes of cyclopropenylidenes will be discussed based on the spectral data.



The square planar type transition metal complexes (neutral complex **2**, cationic complex **3**, M: Pd, Pt, Ph, X: halogen) have been synthesized by either oxidative addition of diaminohalocyclopropenium halide to zerovalent metal or direct metal exchange reaction of diaminocyclopropenylidene lithium (**1**) with transition metal complexes as shown in scheme 1, where R: Me_2N , Et_2N , $i\text{-Pr}_2\text{N}$, L: PR'_3 , L': Cl, CO, X: Cl. These complexes are very stable in air at room temperature. The cis-coordination of halogen in the neutral complex **2** and trans-coordination of PR'_3 in the cationic complex **3** have been determined by IR and ^{13}C -NMR (coupling constant $^2J_{\text{C}_1\text{-Pd-P}}$) spectra. Physical properties and ^{13}C -NMR spectra (^{13}C -chemical shifts and coupling constants of C_1 with P of PR'_3) for the complexes **2** and **3** are shown in Table 5. It appears that the structure of diaminocyclopropenylidene moiety in the neutral complexes (**2**) is similar to that of the cationic complexes (**3**). The stretching band for the $\text{C}_2\text{-N}$ (or $\text{C}_3\text{-N}$) bond appears at lower frequencies in comparison with that of corresponding diaminocyclopropenium cation (**4**). This lower shifts should be attributed to the decreasing of π interaction between nitrogen lone pair and C_3 ring system. These trend in infrared spectra are consistent with the free energy of activation

Scheme 1

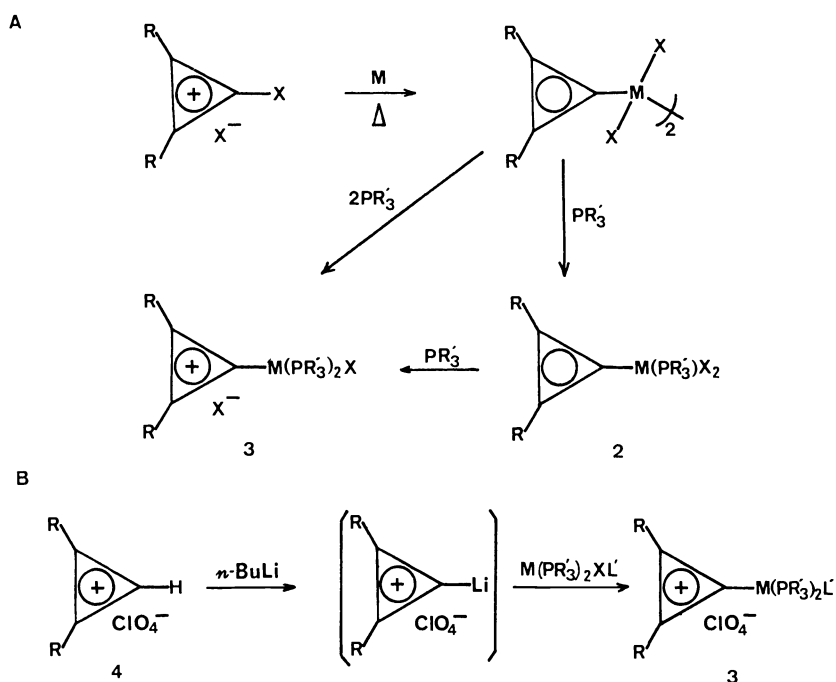


Table 5 Properties and ^{13}C -NMR (CDCl_3) for complexes 2 and 3
where PR'_3 is $n\text{-Bu}_3\text{P}$

2 or 3	R_2N	M	X(L')	mp ($^\circ\text{C}$)	Color*	$\delta(\text{C}_2)$	$\delta(\text{C}_1)$	$^2\text{J}_{\text{C}_1\text{-P}}$ (Hz)
2a	Me_2N	Pd	Cl	172	W	150.6	125.0 d	6.1
2b	Et_2N	Pd	Cl	142	W	149.5	125.6 d	5.9
2c	$i\text{-Pr}_2\text{N}$	Pd	Cl	208	W	147.4	128.4 d	4.9
3a	Me_2N	Pd	Cl	129	W	151.6	122.0 t	10.5
3b	Et_2N	Pd	Cl	78	W			
3c	$i\text{-Pr}_2\text{N}$	Pd	Cl	120	W	147.8	125.6 t	11.3
3d	$i\text{-Pr}_2\text{N}$	Pt	Cl	154	PY			
3e	$i\text{-Pr}_2\text{N}$	Rh	CO	195	Y	149.9	147.8 t**	18.3

* W: white, PY: pale yellow, Y: yellow

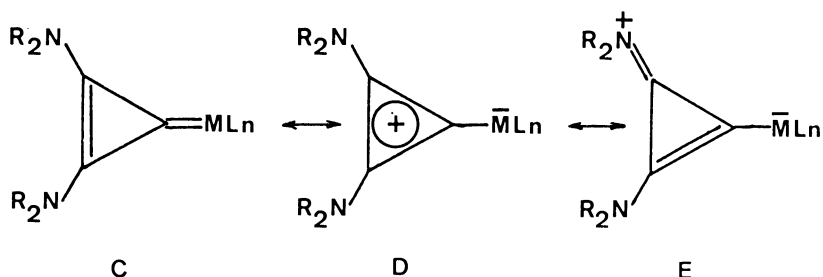
** pair of triplet, $\text{J}_{\text{C}_1\text{-Rh}} = 43.0$ Hz

(ΔG_c) to rotation about $\text{C}_{\text{ring}}\text{-N}$ bond as shown in Table 6. As is seen in Table 6, $\text{C}_{\text{ring}}\text{-N}$ stretching bands of 2c, and 3c, appear at still lower frequencies than that of 2a, b and 3a, b. Moreover, difference in frequencies between 2c, and 4c, is clearly larger than that between 2a, b and 4a, b. Presumably nonbonding interactions between bulky alkylamino groups or between these groups and metal ligands destroy the $\text{C}_{\text{ring}}\text{-N}$ planarity and induce more decreased multiple bonding character of the $\text{C}_{\text{ring}}\text{-N}$ bond. In spite of these spectroscopic observations the stability of complexes 2c and 3c is compared favorably with that of the other bisaminocyclopropenyliene complexes. Bulkiness of this substituent may

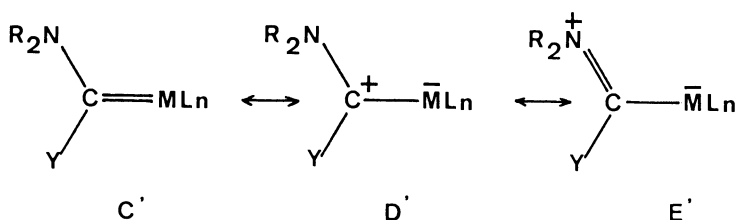
Table 6 The ring deformation (ν_{Δ}) and $C_{\text{ring}}-\text{N}$ stretching ($\nu_{C-\text{N}}$) absorption bands, and G_c to rotation about the $C_{\text{ring}}-\text{N}$ bonds for 2, 3 and 4

	ν_{Δ} (cm^{-1})	$\nu_{C-\text{N}}$ (cm^{-1})	ΔG_c (Kcal/mol)
2a	1903	1557	15.4
2b	1886	1526	15.5
2c	1860	1490	≤ 8.4
3a	1903	1567	≤ 8.4
3b	1886	1523	
3c	1854	1494	≤ 9.7
3d	1860	1497	≤ 9.7
3e	1858	1485	
4a	1915	1616	19.1
4b	1091	1591	
4c	1884	1572	17.8

affect advantageously the stabilization of the complexes. Following canonical forms can be written to present formal bondings in diaminocyclopropenylidene transition metal complexes:



Decreased multiple bonding character of $C_{\text{ring}}-\text{N}$ bond generally observed for diaminocyclopropenylidene palladium complexes suggests that participation of metal d orbital in the π -back bonding from central metal atom to the C_3 ring system (form C) is comparable in its magnitude to that of amino groups (form E). This is interesting in view of the generally accepted dominant contribution of form E' for Wanzlic carbene complexes as shown below (Ref. 7).



To gain insight into the molecular (electronic) structure of diaminocyclopropenylidene-transition metal complexes the precise X ray analysis has been carried for diaminocyclopropenylidene palladium (Ref. 8). The X ray structure (a perspective view of the inner coordination sphere) of $\text{cis-PdCl}_2[\text{C}_3(\text{NMe}_2)_2](n\text{-Bu}_3\text{P})$ is shown in Figure 1. It is to note that the plane of the C_3 ring is nearly perpendicular to the square-plane of the metal. The bond distance 1.963(3) Å for Pd-C(1) is somewhat shorter for ordinary Pd-C single bond length, even though hybridization is taken into account. For example Pd-C(sp^2) distances of the metal σ -vinyl bonds in $\text{cis-bis}[1,2\text{-bis}(\text{trifluoromethyl})\text{-3-acetyl-4-oxo-pent-1-enyl-O,C}]\text{palladium(II)}$ are 1.993 Å in average (Ref. 9). The nitrogen atoms which are sp^2 hybridized and co-planar with the C_3 ring are bonded at a 1.320(4) Å distance from the ring carbon atoms. This distance is markedly shorter than C-N single bond distance of 1.475(5) Å observed for CH_3NH_2 . Judging from the high symmetry of the C_3 ring, with uniform bond distribution, the π -back donation from the Pd atom seems to be comparable in its magnitude to the electron releasing from the dimethylamino groups. This is in good agreement with the results obtained from infrared and ^{13}C -NMR structural studies. There are considerable differences in the average $C_{\text{ring}}-\text{C}_{\text{ring}}$ and $C_{\text{ring}}-\text{N}$ bond distances between the aromatic tris(dimethylamino)cyclopropenium cation [$C_{\text{ring}}-\text{C}_{\text{ring}}$ 1.363(7), $C_{\text{ring}}-\text{N}$ 1.333(7) Å] (Ref.10) and the present case [$C_{\text{ring}}-\text{C}_{\text{ring}}$ 1.383(2), $C_{\text{ring}}-\text{N}$ 1.320(4) Å], though N-Me distances are

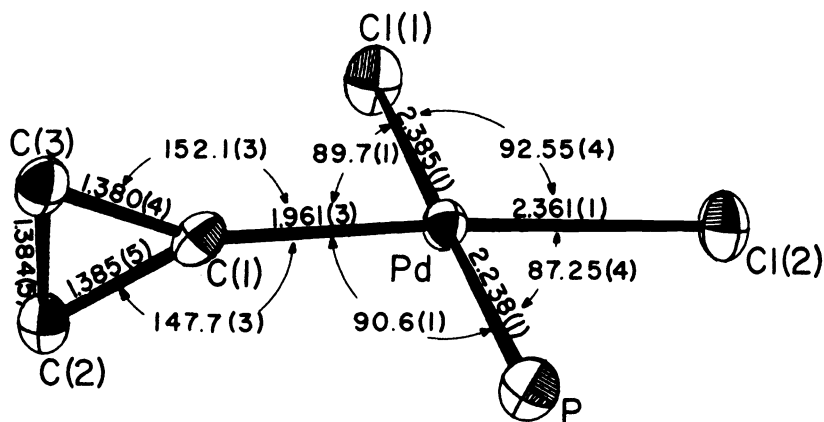


Fig. 1 X-ray structure of the inner coordination sphere of *cis*-PdCl₂[C(Me₂NC)₂](P-*n*-Bu₃)

the same in both cases. As for the preferred canonical form no simple description of the present structure appears possible in terms of canonical forms C₃VE. Form C is favored by short Pd-C bond and suitable arrangement of the C₃ ring relative to the metal-ligands plane. However, shorter C-N bond lengths and planarity of the ring-nitrogen part of the complex favor form E. Equality of the three bond lengths within C₃ ring suggests comparable contribution of the two forms C and E. This also supports the conclusion obtained from spectral data. The MINDO/3 calculation accounts for the expansion of the C₃ ring and the enhanced back π bonding from Pd to the C₃ ring due to the efficient interaction of ψ₁₅ orbital (π*) of diaminocyclopropenylidene with 4d_{xz} orbital (filled) of Pd. Dialkyl- and diphenylcyclopropenylidene Pd complexes (neutral complexes, 5 and cationic complexes, 6) have also been synthesized according to the method A in scheme 1 starting from dialkyl or diphenyldichlorocyclopropene instead of dialkylaminohalocyclopropenium ion.

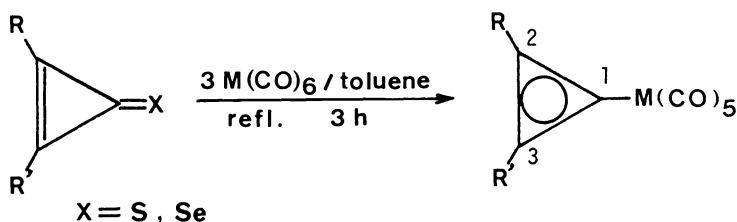


The Ir and the ¹³C-NMR spectra of complexes 5 and 6 are summarized in Table 7.

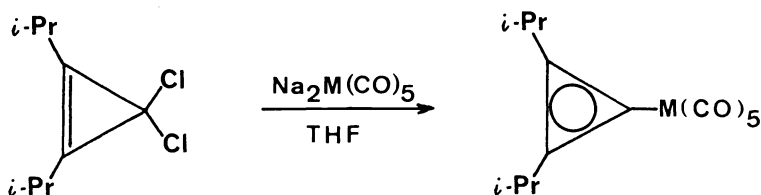
Table 7 The ring deformation band (ν_Δ), ¹³C-chemical shifts and the coupling constants of C₁-P (CDCl₃) for 5 and 6

compd.	R	ν _Δ (cm ⁻¹)	δ(C ₂)	δ(C ₁)	² J _{C₁-P} (Hz)
5a	<i>i</i> -Pr	1797	195.1	205.7 d	≤ 1.2
5b	<i>t</i> -Bu	1780	196.5	205.2 d	≤ 1.2
5c	Ph	1794	175.2	195.3 d	2.9
6a	<i>i</i> -Pr	1788	198.7	205.4 t	9.8
6b	<i>t</i> -Bu	1774	199.7	205.8 t	9.8
6c	Ph		176.0	195.2 t	10.7
2a	Me ₂ N	1903	150.6	120.5 d	6.1
3a	Me ₂ N	1903	151.6	122.0 t	10.5

These spectral data suggest that the canonical forms C and D should be predominant with dialkyl- and diphenylcyclopropenylidene palladium complexes, while forms C and E are dominant with diaminocyclopropenylidene palladium complexes. The structural problems in the square planar complexes of group VIII element (mainly Pd) with cyclopropenylidenes were discussed above. In order to get the further information on unique properties of cyclopropenylidenes, for example σ -donating and π -accepting ability of cyclopropenylidenes, the octahedral complexes of group VIa element with cyclopropenylidenes, $(RR'C_3)M(CO)_5$ ($R=Me_2N, i-Pr_2N, t-BuS, Ph$; $R'=Me_2N, i-Pr_2N, t-BuS, Ph$; $M=Cr, Mo, W$) have been synthesized by desulfurization and deselenization reactions of cyclopropenethiones and cyclopropeneselones with $M(CO)_6$. This new synthetic method shown below has a merit to be applicable for cyclopropenylidene ligand possessing many kind of substituents.



Dialkylcyclopropenylidene pentacarbonyl complexes are synthesized by the following reaction. This reaction, however has the limitation for disubstituted dichlorocyclopropene as the reactant. For example, aminodichlorocyclopropene does not give such sort of complex.



From the analyses of infrared absorption bands for carbonyl stretching vibration of these complexes, it is possible to estimate bonding situation between carbene carbon and metal center. In hexane solution, these complexes exhibit three absorption bands characteristic to C_4v pentacarbonyl complexes (Ref. 11). An example is shown in Figure 2. The strongest

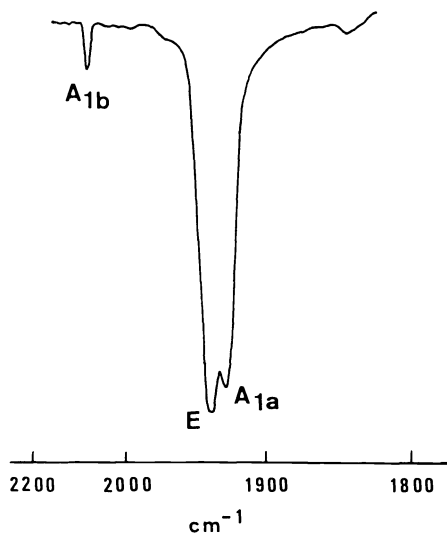


Fig. 2 Infrared spectrum of $[(i-Pr_2N)_2C_3]Mo(CO)_5$ in hexane

absorption one is assigned to the carbonyl stretching of E mode and two medium absorption bands are to that of two A_1 modes. The stronger (A_{1a}) of the two A_1 bands is derived from the vibration of the single carbonyl group at a trans position to cyclopropenylidene ligand. The frequency of this band increases with decrease of electron donating power of substituents (R, R') in the complexes $(RR'C_3)M(CO)_5$. This trend can be interpreted in terms of the relative σ charge-donating power of these ligands. Because of the directional

nature of the hybrid metallic bonding orbital, the carbonyl group trans to the cyclopropenylidene ligand should receive the largest part of the charge from the metal through bond formation. Such an accumulation of charge on the trans CO can produce a greater mixing of π - and π^* -orbitals of this group than in the case of four cis CO which receive relatively little of the charge. Therefore a ligand which possesses greater charge-donating ability should lower the carbon-oxygen bond order of the trans CO and, consequently, the frequency of A_{1a} . The σ charge-donating ability of cyclopropenylidene ligand can be correlated with the net σ charge density at the carbene carbon (C_1). There are fair correlation between the MINDO/3 σ net charge densities at carbene carbons of substituted cyclopropenylidenes (Table 1) and frequencies of A_{1a} bands of the corresponding $(R_2C_3)M(CO)_5$ complexes. On the other hand the strongest band E which is assigned to the degenerated stretching vibration of four cis carbonyl groups can be affected by the charge acceptability of the cyclopropenylidene ligand. When the ligand has greater acceptability for the metallic charge, there exists possibility that the more charge may be withdrawn from the four cis carbonyl groups. This causes higher frequency of E. In Fig. 3 frequencies of A_{1a} are plotted vs. those of E with two series of chromium and molybdenum complexes discussed here. The complexes $(RR'C_3)M(CO)_5$ in Fig. 3 are as follows: 7, $R=R'=\text{Me}_2\text{N}$, 8, $R=R'=\text{t-BuS}$, 9, $R=R'=\text{Ph}$, 10, $R=R'=i\text{-Pr}$, 11, $R=\text{Me}_2\text{N}$, $R'=\text{t-BuS}$, 12, $R=i\text{-Pr}_2\text{N}$, $R'=\text{Ph}$, a, $M=\text{Cr}$, b, $M=\text{Mo}$. In these series bis-

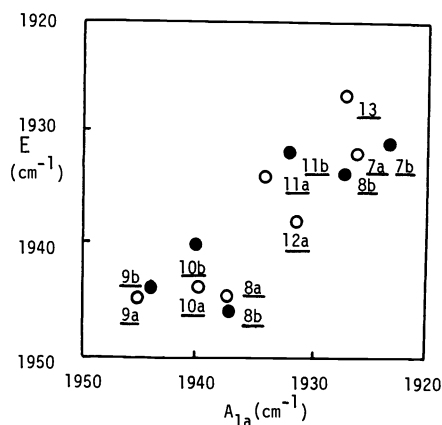
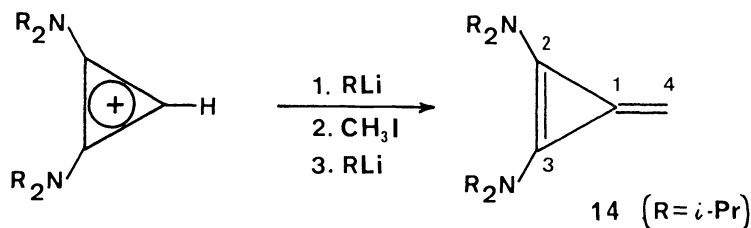


Fig. 3 Plots of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands for Cr complexes (○) and Mo complexes (●)

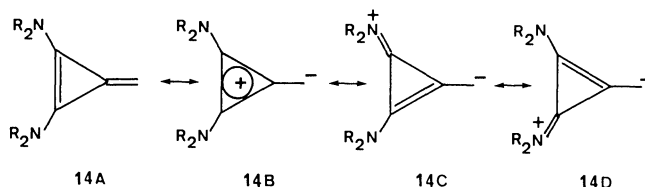
aminocyclopropenylidene is expected to possess the strongest σ -charge donating ability and the least π -charge acceptability, while the reverse could be true with bisphenyl- and bis(*i*-propyl)cyclopropenylidenes. The frequencies of A_{1a} and E of Wanzlic type carbene complex, pentacarbonyl(*N,N'*-dimethylimidazoline-2-ylidene)chromium 13 (Ref. 12) are also plotted in Fig. 3. Compared to 13, the cyclopropenylidene complexes (except 7a and b) show higher frequencies of A_{1a} and E. This suggests that the cyclopropenylidene ligands have less charge donating power through the hybrid metallic bond (except 7a and b) and more charge acceptability for back donation from the metal through $d-\pi^*$ interaction than is the case of such a Wanzlic type carbene, i.e., 1,3-dimethyl-4-imidazolin-2-ylidene ligand. The trend observed with CO stretching vibration are also seen with ^{17}O -chemical shifts of carbonyl ligands. Thus cyclopropenylidene ligands in Fig. 3 can be classified into three groups. They are (1) bisaminocyclopropenylidenes, (2) monoaminocyclopropenylidenes, and (3) the other cyclopropenylidenes. Bisaminocyclopropenylidene has the greatest charge (σ) donating power and the least back π charge acceptability, and cyclopropenylidene which possesses no amino substituent has the least σ charge donating power and the highest back π charge acceptability in the series of cyclopropenylidene complexes discussed here.

TRIAFULVENES, TRIAFLVALENES AND RELATED SYSTEMS

In spite of the special interest as a valence isomer of C_4H_4 (eg. cyclobutadiene, tetrahedrane), triafulvene as parent member of the simplest cross conjugated systems has not been isolated yet. So far reported triafulvenes have the polar (electron withdrawing) group on the exomethylene carbon. Recently triafulvenes which have alkyl groups on both the C_3 ring and the exomethylene carbon have been reported (Ref. 13, 14). However, triafulvenes possessing no substituent on the exomethylene carbon have been unknown. We succeeded in synthesizing diaminofulvene (14) by the following reaction starting from diaminocyclopropenium ion. Diaminotriafulvene (14), being obtained as colorless crystals by cooling the reaction mixture to $-20^\circ \sim -30^\circ$, is thermally unstable and gradually



decomposes even at room temperature under inert atmosphere. The $^1\text{H-NMR}$ spectrum of 14 in tetrahydrofuran- d_8 shows signals at 4.20 (4H, $-\text{CH}(\text{CH}_3)_2$), 2.50 (2H, exo-CH_2-), 1.41 (24H, $-\text{CH}(\text{CH}_3)_2$). The significantly large upfield shift of the exo-CH_2 protons should be due to a large contribution of dipolar form (14B) to the resonance hybrid. Also contribution of immonium forms (14C and 14D) should be considered. The HMO calculation (π electron densities and π bond orders shown in Fig. 4) supports the important contribution of the polar canonical forms (14B-14D).



Reaction indices (superdelocalizabilities, S_E , localization energy L_E as well as the charge densities q_r) suggest the large reactivity of C_4 towards electrophiles.

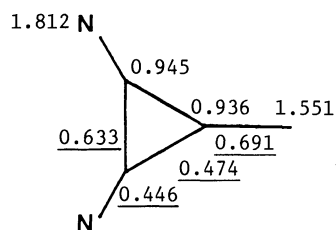
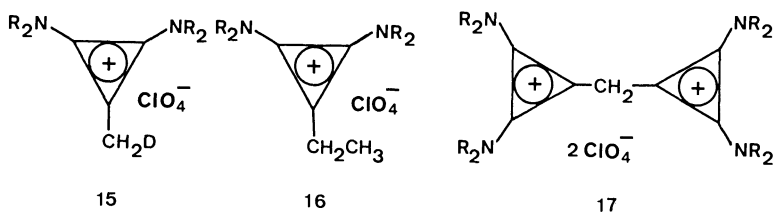
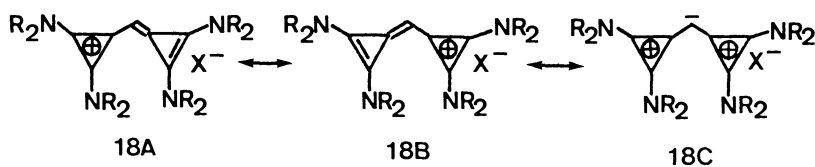


Figure 4. Charge Density and π Bond Order for 14

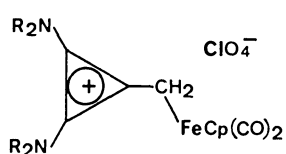
In accord with this expectation, the electrophilic attack occurs on the C_4 in regioselective manner. For example, the reaction with $\text{CF}_3\text{CO}_2\text{D}$, CH_3I and diaminomethoxycyclopropenium ion give 15, 16 and 17, respectively.



The methylene-bridged dication (17) is readily deprotonated by aqueous potassium hydroxide to afford the interesting mesomeric salt (18). The $^1\text{H-NMR}$ spectrum of the olefinic proton of 18 appears at δ 4.00. This value is in higher magnetic field than that (δ 6.52) of the corresponding tetraphenyl derivative (Ref. 15), indicating the importance of the tripolar canonical form (18c)



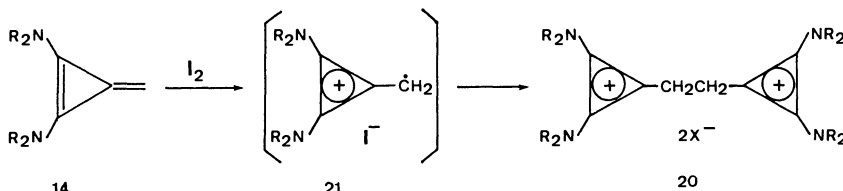
Diaminotriafulvalene (14) reacts with cyclopentadienyl iron dicarbonyl iodide to give the first triafulvene iron complex (19) as yellow plates. This iron complex is stable in crystalline form but considerably sensitive to air in solution. $^1\text{H-NMR}$ (δ for CH_2 , 2.20),



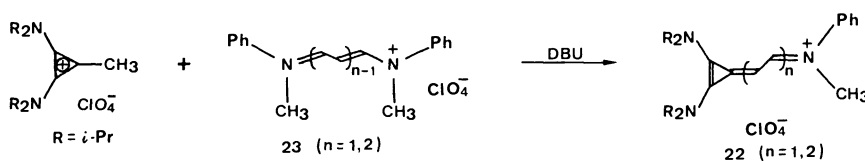
19

^{13}C -NMR (δ for CH_2 , -18.8) and IR spectra indicate that the structure of this complex can be expressed by the σ complex (19). The oxidation of 14 with iodine give the ethylene-bridged dication (20). This reaction should proceed the cation radical (21) intermediate, because of extremely low ionization potential value (calculated one ~ 7.1 eV) of 14. By the extension of cross conjugated double bond having immonium group at its chain end in diaminotriafulvene, triafulvene immonium salt (22) is given.

Such sort of compounds is of interest not only as a model to examine π electron delocalization but also as nonbenzenoid analog of cyanine dyes. The immonium salts (22, $n=1,2$) are



synthesized by the reaction of 1,2-bis(diisopropylamino)-3-methylcyclopropenium perchlorate and polymethinium perchlorates (23, $n=1,2$) in the presence of diazabicycloundecene (DBU). The products (22, $n=1,2$) are isolated as stable crystalline solid: 23 ($n=1$), pale yellow prisms: 22 ($n=2$), brilliant yellow plates.



From the vicinal coupling constants for cross conjugated double bond of 22, the transoid conformation and considerable π electron delocalization of the side chain are indicated. For example, the vicinal coupling constants for 22 ($n=2$) are $J_{1,2}=15.0$, $J_{2,3}=11.0$ and $J_{3,4}=12.8$ (No. of side chain proton or carbon: see Fig. 5). The ^{13}C -NMR chemical shifts of 22 are summarized in Fig. 5. The π electron densities at cross conjugated double bond

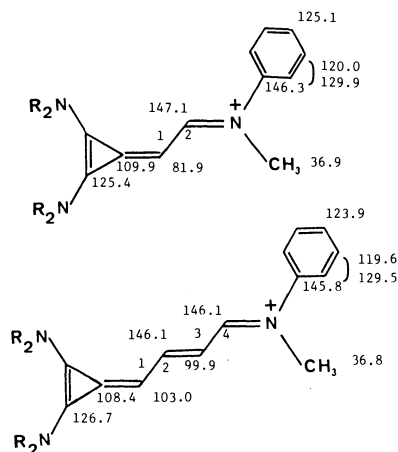
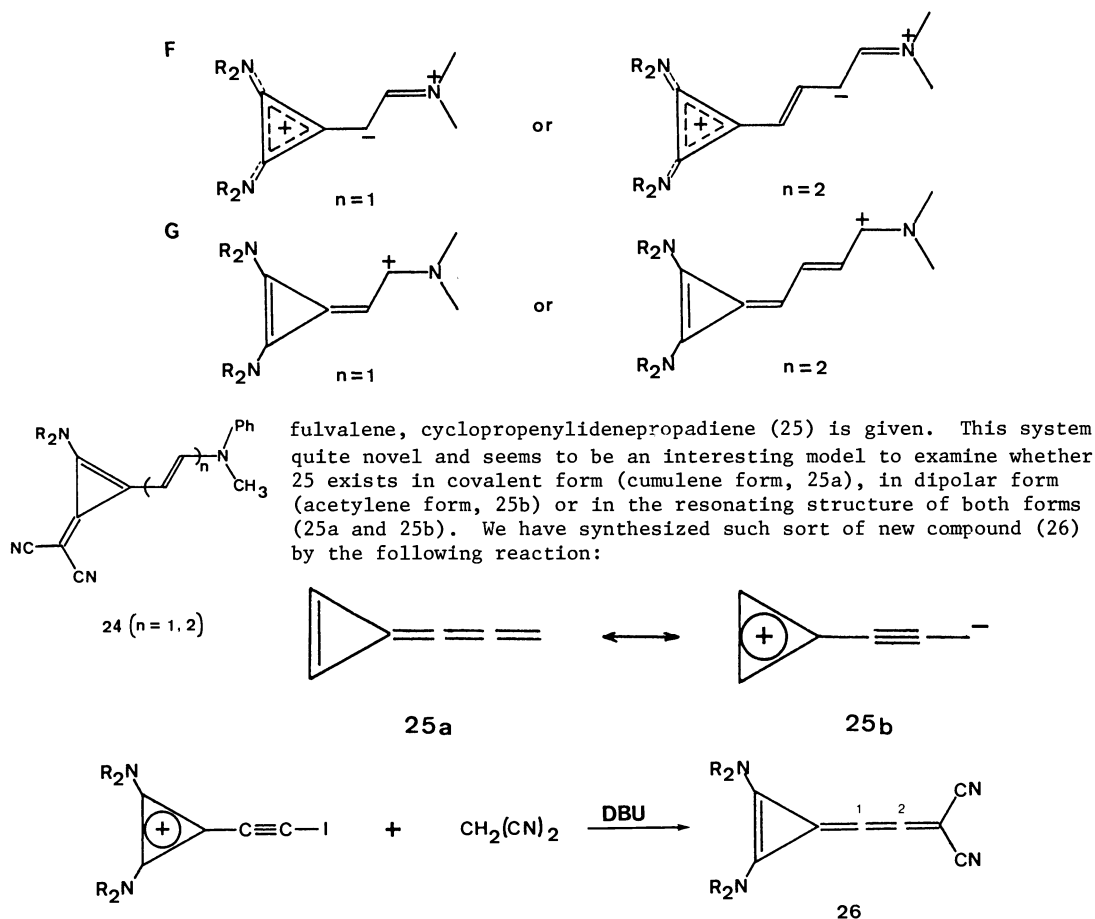


Figure 5. ^{13}C -NMR Chemical Shifts (in CDCl_3) of 22 ($n=1$) (top) and 22 ($n=2$) (bottom)

carbon atoms estimated from ^{13}C chemical shift suggest the contribution of both forms, F and G to the ground state of 22. The immonium salts 23 ($n=1,2$) has two absorptions in which the longer absorption band shows big bathochromic shifts (ca. $50\sim 60$ nm per vinyl group) with extension of polymethine chain. The absorption spectra (λ_{max} , $\log \epsilon$) of 23 ($n=0,1,2$) in CH_3OH are following: 230 (4.8), 279 (4.45) for $n=0$, 234 (3.85), 342 (4.18) for $n=1$, and 264 (3.52), 392 (4.09) for $n=2$. Interestingly, nucleophilic attack of the conjugate base of malononitrile toward 22 occurs at the three membered carbon atom and not at the side chain carbon. This reaction leads to the formation of the product 24. If two sp carbon atoms are inserted between the ring carbon and the exomethylene carbon of tria-



The product (26) is pale yellow crystals and stable to oxygen. The IR spectra (2135 cm^{-1}) for C_1 and C_2 of 26 are in the region of acetylene band ($2260\sim 2100\text{ cm}^{-1}$) rather than that of cumulene band ($2000\sim 1900\text{ cm}^{-1}$). The ^{13}C -chemical shift for C_1 and C_2 of 26 (see Fig. 6) are clearly in the region ($\delta 65\sim 90$) of acetylene ^{13}C -chemical shifts (Ref. 16, 17) and

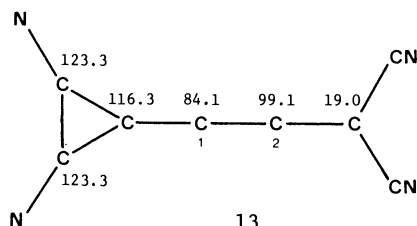
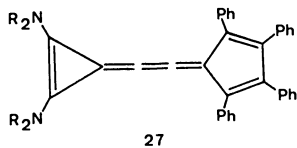
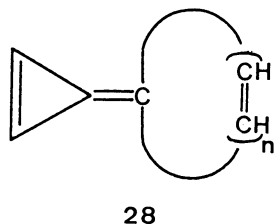


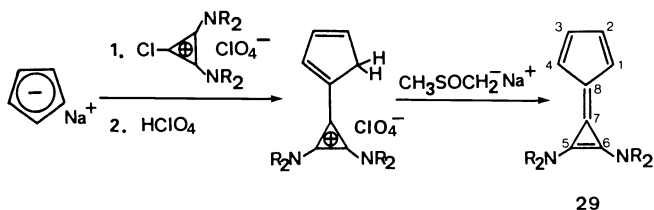
Figure 6. ^{13}C -chemical shift for 26

quite different than the ^{13}C -chemical shifts ($\delta 149\sim 182$) of cumulenes (Ref. 17). It is therefore concluded that 25 exists in the dipolar form (25b) when substituted with NR_2 at the C_3 ring and with CN at the side chain end. The similar compound (27), which has no strong electron withdrawing group, has also been shown to exist in the dipolar form from its spectral data. Although cross conjugated system 27 is a kind of triafulvalene, the typical triafulvalenes are expressed by formula 28. The CNDO/2 investigation for triafulvalene (calicene, 28, $n=2$) and vinylfulvene indicates that σ electron shift is found from the five membered ring to the three membered ring, and the σ moment in calicene is opposite to the π moment in its direction. Even in triaheptafulvalene (28, $n=3$) the similar trend is found. Such sort of electron shift is considered to be a feature of triafulvalenes. It is to note that triafulvalenes except calicenes have not been reported so far. Also the simple derivatives of calicene without any substituents on the five membered ring have never

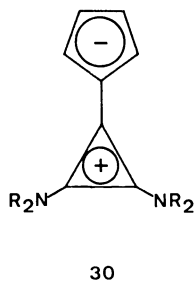




been reported. From this situation, we attempted to synthesize novel diaminotriafulvalenes. Diaminotriapentafulvalene (diaminocalicene, 29) has been prepared as below. Surprisingly 29 (colorless crystals) is fairly stable to oxygen in crystalline solid but rapidly oxidized with air in solution. Its ring protons resonate at δ 6.22 (H₂, H₃) and 6.62 (H₁, H₄). The vicinal proton coupling constants are 4.0 Hz for J_{1,2} and 2.8 Hz for J_{2,3}. The ¹³C-chemical shifts (C₈ 98.2, C₂, C₃ 112.7, C₁, C₄ 113.7) of the five membered ring are more close to that of cyclopentadienide



(102.1) rather than those of cyclopentadiene (132.3, 133.0). These NMR data indicate that the five membered ring of 29 is aromatic and the dipolar form (30) of 29 dominantly contributes to its ground state. The marked blue shift of UV spectra of 29 with increasing polarity of solvent supports this conclusion. This is a first example in which calicene is aromatic. So far reported calicene is olefinic and occurs the $8\pi + 2\pi$ type thermally allowed cycloaddition reaction with dienophile such as dimethylacetylene dicarboxylate and TCNE (Ref. 18, 19). However 29 does not undergo the cycloaddition reaction with dienophile but Michael type addition reaction. This behavior should be explained by the Fig. 7.



In alkyl substituted calicene, electron density at C₁ is so high as to make 8π (for calicene) + 2π (TCNE) type interaction easy. On the other hand in 29 such sort of interaction is difficult to occur because of no positive overlap between α , ω - position of 29 and olefinic carbons of TCNE. Fig. 7 suggests that electrophilic substitution is easy to occur at C₂ (or C₃) position, because of the larger value of frontier electron density at C₂ (or C₃). The experimental results (nitration etc) accord with this expectation.

Diaminocalicene (29) reacts with M(CO)₆ (M: Cr, Mo, W) and FeCl₂ to give the following organometallic compounds (30~33). The C_{ring}-N stretching (ν_{C-N} cm⁻¹) absorption bands (a measure for π electron delocalization) for these metal complexes are 1490 for 29, 1527 for

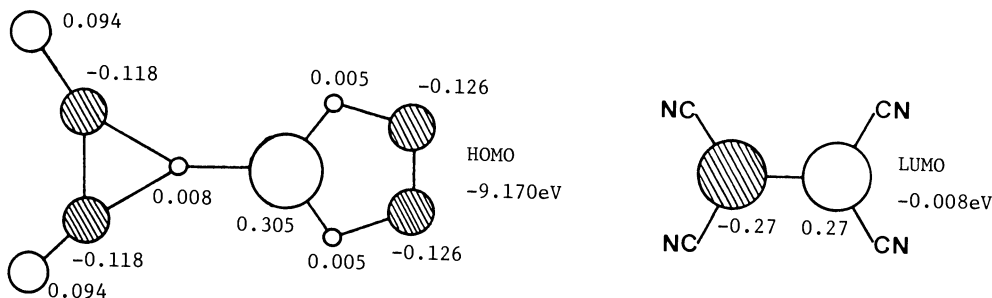
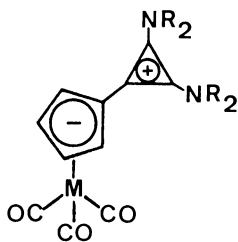
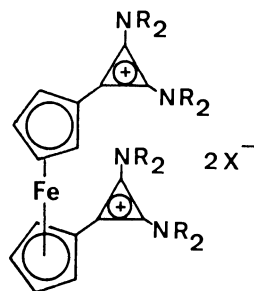


Figure 7. HOMO for diaminocalicene and LUMO for tetracyanoethylene (EHMO)



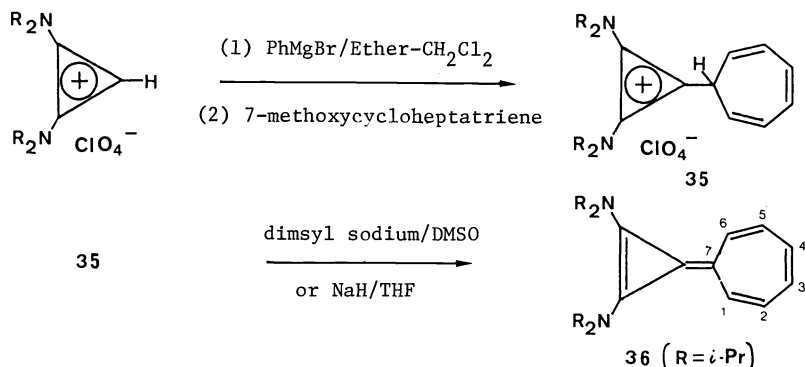
32 M=Mo

33 M=W

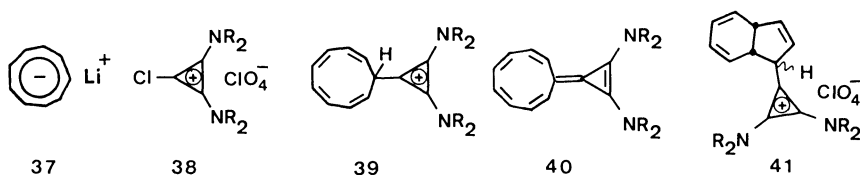


34

31, 1527 for 32, 1531 for 33 1548 for 34, indicating that the π electron delocalization (contribution of dipolar form 30) increases in the order of $34 > 33 > 32 > 31$ and become largest in the complex 34. This conclusion is supported by the ^{13}C -NMR chemical shifts for these complex. For example, ^{13}C -NMR chemical shifts of the five membered ring and the three membered ring in 34 are close to those of ferrocene and diaminophenylcyclopropenium ion, respectively. As the cyclic cross conjugated 10π system, diaminotriaheptafulvalene (36) has been prepared by the following method.



The treatment of 35 with dimethylsodium at room temperature immediately produced a dark blue solution. The ^1H -NMR spectra provides the direct evidence for the formation of 36, which shows a doublet at δ 4.77 (2H, $\text{H}_{1,6}$), a quartet at 4.26 (2H, $\text{H}_{3,4}$), and a multiplet at 3.68 (2H, $\text{H}_{2,5}$) as the ring proton resonance. These ring proton chemical shifts accord with the CNDO/2 charge distribution of seven-membered ring ($\text{C}_{1,6}$ +0.03, $\text{C}_{2,5}$ -0.05, $\text{C}_{3,4}$ 0.00, C_7 -0.11). The coupling constants ($J_{1,2}$ 11.0Hz, $J_{2,3}$ 4.4Hz) of 36 clearly indicates that the seven membered ring is not aromatic but polyolefinic. 36 slowly reacts with CH_3I to give the methyl substituted compound which has similar structure to 35. In spite of the various approaches to prepare trianonafulvalene, cyclic cross conjugated 12π system possessing highly strained cyclopropenylidene moiety, the work was not successful so far. We have tried to prepared diaminotrianonafulvalene (40) by the reaction of diaminochlorocyclopropenium salt (38) with two molar amount of lithium cyclononatetraenide (37) in THF at 0°C . In order to isolate the protonated diaminotrianonafulvalene (39), the reaction mixture was acidified with diluted perchloric acid. The product obtained was not expected one (39) but its electrocyclic ring closure compound (8,9-dihydroindene derivative, 41). Such sort of disrotatory process is reported to be easy to occur even at room temperature for cyclononatetraene derivatives (Ref. 20, 21). It was observed that 39 was deprotonated by the addition of 37 to yield 40 which was protonated with HClO_4 to reproduce 39 leading to the rapid formation 41. The main obstacle to preparation of 40 is that the extremely



high sensitivity of 40 to air (oxygen) and the facile rearrangement to 41. To avoid this problem, bridged cyclononatetraenide (Ref. 22, 23) instead of 37 was chosen. The reaction of 38 with excess lithium 1,5-methanocyclononatetraenide (42) in THF at room temperature followed by the treatment with dil. HClO_4 gave pale yellow crystals (43) which is quite stable in air at room temperature. Its structure was confirmed by the spectral data and microanalysis. Deprotonation of 43 with dimethylsulfinyl sodium in DMSO immediately gave an orange-red solution. The ^1H -nmr spectrum provides direct evidence for the formation of 1,6-methano-9,10-diaminotrianonafulvalene (44): 6.60 (m, 3H, olefin), 6.29 (m, 2H, olefin), 5.86 (m, 1H, olefin), 4.16 (sep, 4H, $-\text{CH}(\text{CH}_3)_2$), 1.27 (a pair of d, 24H, $-\text{CH}(\text{CH}_3)_2$), 1.14 (d, 1H, $-\text{CH}_2-$, $J=7.0$ Hz), -0.60 (d, 1H, $-\text{CH}_2-$, $J=7.0$ Hz). The increase in the *gem*-coupling constant from 3.5 for 43 to 7.0 Hz for 44 clearly indicates that the 44 exists in the cycloheptatriene form (44) and not the norcaradiene form (44') at room temperature, in quite contrast to the case of corresponding nonafulvene system (45, 45') (Ref. 24). In Table 8 are summarized the values of the chemical shifts and the *gem*-coupling constants of the bridgemethylene protons in the diaminotrianonafulvalene 44 and related compounds. Compared

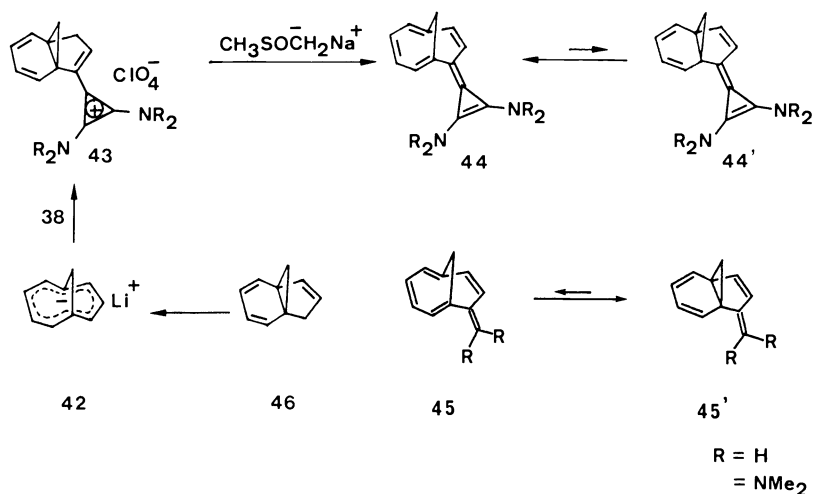
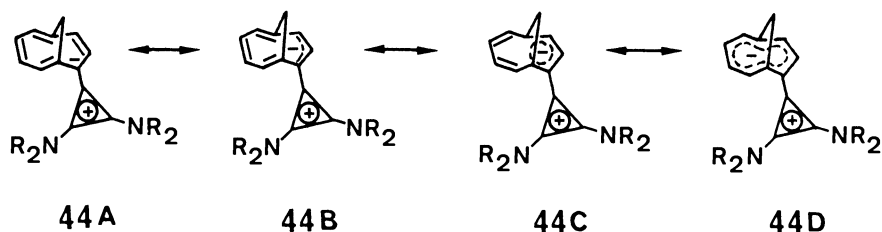


Table 8 Chemical shifts and coupling constants of the bridge-methylene protons

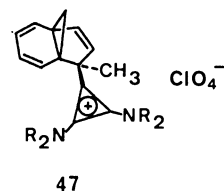
compound	δ ($-\text{CH}_2-$, ppm)	J_{gem} (Hz)
43	1.59, 0.22	1.37 3.5
46	1.47, 0.10	1.37 3.5
45 R = H	1.65, 0.19	1.46 2.5
N(CH ₃) ₂	1.71, 0.13	1.58 3.0
44	1.14, -0.60	1.74 7.0
42	-0.45, -0.95	0.50 7.5

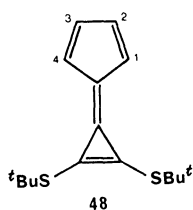
the chemical shifts of the bridge-methylene protons in 44 with those of the related norcaradiene compounds 43, 46 and 45, the protons in 44 are more shielded than those in 43, 46 and 45. This fact suggests the contribution of the polar canonical structures (44A-44D) to the ground state of 44. On the other hand, the bridge-methylene protons of the 10 π aromatic anion 42 resonate at higher magnetic field than those of 44, indicating that the contribution of the 10 π aromatic structure 44D is not dominant for 44. It is important to note



that the difference of the chemical shifts between the two bridge-methylene protons ($\Delta \delta$) in 44 (1.74 ppm) is very large comparing that in the aromatic anion 42 (0.50 ppm). If the 10 π aromatic structure 44D is important for the ground state of 44, the diamagnetic ring current on the nine-membered ring should shift the two bridge-methylene protons almost equally to higher field. Observed large value of $\Delta \delta$ in 44 suggests the contribution of the ionic structures (44A, 44B) as well as the 6 π homocyclopentadienide structure (44C) rather than the 10 π cyclononatetraenide structure (44D). The reaction of 44 with methyl iodide leads to the formation of methylated compound 47 in stereospecific manner.

As triafulvalene possessing thio substituent instead amino group, dialkylthioalcalicene (48) was synthesized by the reaction of bis-(*t*-butyl)dichlorocyclopropene with sodium cyclopentadienide in THF at -35°C . Dithioalcalicene (48) is very sensitive to air and gradually decomposes at room temperature. The vinylic coupling constant ($J_{1,2}$ 4.7, $J_{2,3}$ 2.7) suggests that 48 has intermediate nature between aromatic one (eg. dimethylsulfonium cyclopentadienylide $J_{1,2}$ 3.9, $J_{2,3}$ 2.8) and polyolefinic one (eg. dimethylfulvene $J_{1,2}$ 5.1, $J_{2,3}$ 1.9) in its ground state. By examining the reaction condition the formation of 7,15-di-*t*-butylthiocyclic dicalicene





(redish violet crystals) has been observed. After treating with tri-*n*-butyltin hydride in the presence of azoisobutyronitrile, silica gel treatment gave orange crystals (dec. 125-130°). This hydrocarbon was pentacyclo[8(3, 0^{1,5}), (1, 0^{6,8}), (3, 0^{9,13}), (1, 0^{14,16})]sexdeca-1,3,5,7,9,11,13,15-octaene (49, abbreviation: cyclic dicalicene), which has peripheral 16 π and central 8 π structures. 49 is considered to be extremely interesting system to examine the π electron delocalization. From the X-ray structure analysis of 49 (see Fig. 8), the following structural features were observed.

(1) The 16-membered ring is planar, (2) No bond alternation is observed. (3) Bond distances (each C-C bond distance: 1.4Å) and angle of chemically equivalent parts of the molecule show good coincidences. From these observations the molecular symmetry of 49 is concluded essentially to be D_{2h} . This X-ray data indicates that 49 is a first example in which π system having peripheral 16 π and central 8 π (COT) structures is planar and has completely delocalized π electrons. The ¹H-NMR spectra of 49 appear at δ (CD₂Cl₂) 6.57 (t, 2H, H-3,11, $J=3.66$ Hz), 7.14 (d, 4H, H-2,4,-10,12, $J=3.66$ Hz), 7.93 (s, 2H, H-7,15). It is to note that ¹H resonance signals don't exhibit any upfield shifts due to a paramagnetic ring current expected peripheral 16 π or central 8 π system. The equivalent vicinal coupling constants ($J_{2,3}=J_{3,4}=\dots$

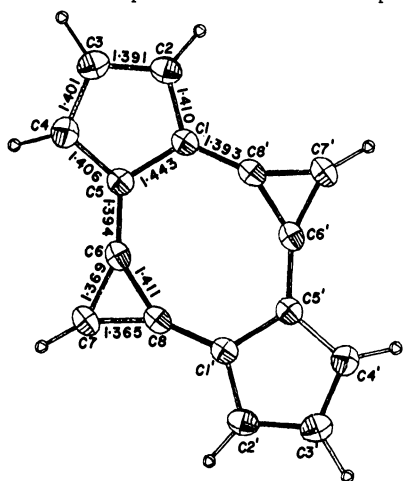
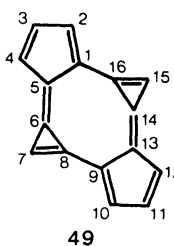


Fig. 8 X-ray structure of 49

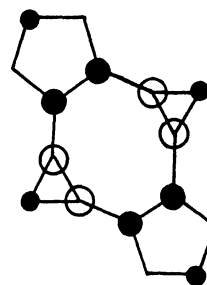
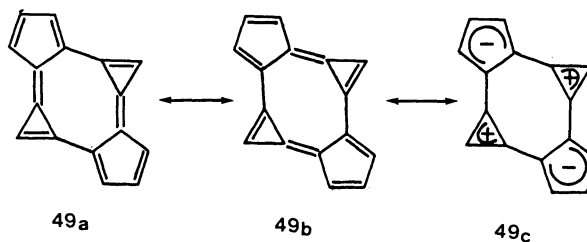


Fig. 9 Positive and negative charge distribution in 49.
 ○ positive charge
 ● negative charge
 The area of circle corresponds to magnitude of the charge

3.66 Hz) also indicates that no bond alternation occurs in C₂-C₃ and C₃-C₄ bonds. The ¹³C-NMR spectra of 49 appear at δ (CD₂Cl₂) 110.20 (C-1,5,9,13), 117.81 (C-7, 15, $J_{13C-H}=235.5$ Hz), 124.67 (C-3,11, $J_{13C-H}=164.4$ Hz) 130,50 (C-2,4,10,12, $J_{13C-H}=167.9$ Hz), 140.87 (C-6,8, 14,16). This ¹³C-NMR spectra supports the D_{2h} symmetry. The charge distribution on each carbon atom estimated from ¹³C-NMR chemical shifts accords with MINDO/3 charge distribution. The positive and negative charge distribution in 49 is shown in Fig. 9. This figure shows that (1) the polar structure of five membered ring is close to pentadienide anion and (2) the polar structure of three membered ring is close to allylic cation. Thus 49 is considered to be stabilized by the resonating contribution of two covalent structures (49a, 49b) and one polarized structure (49c).



Acknowledgement

I would like to express my appreciation to the following collaborators who have contributed to this work: Prof. S. Yoneda, Prof. H. Ogoshi, Prof. H. Konishi, Dr. Y. Kamitori, Dr. S. Araki, Dr. S. Miki, M. Shibata, S. Kida, Prof. J. A. Ibers, Dr. Y. Kai, Prof. N. Kasai. I wish also to thank the Ministry of Education, Science and Culture, for financial support.

REFERENCES

1. R. Gleiter and R. Hoffmann, J. Am. Chem. Soc. **90**, 5457 (1968).
2. Z. Yoshida, Abstracts 6th Symposium on Chemistry of Nonbenzenoid Aromatic Compounds, Fukuoka, October (1973), Abstracts, 2nd International Symposium on the Chemistry of Novel Aromatic Compounds, Lindau, September (1974).
3. L. D. McKeever and R. Waack, J. Organometal. Chem. **28**, 145 (1971).
4. K. Öfele, Angew. Chem. **80**, 1032 (1968).
5. K. Öfele, J. Organometal. Chem. **22**, C9 (1970).
6. G. Huttner, S. Schelle and O. S. Mills, Angew. Chem. **81**, 536 (1969).
7. D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, Chem. Soc. Rev. **2**, 99 (1973).
8. R. D. Wilson, Y. Kamitori, H. Ogoshi, Z. Yoshida and J. A. Ibers, J. Organometal. Chem. **173**, 199 (1979).
9. D. R. Russell and P. . Tucker, J. Chem. Soc. Dalton. 1743 (1975).
10. A. T. Ku and M. Sundaralingam, J. Am. Chem. Soc. **94**, 1688 (1972).
11. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., John Wiley & Sons, New York 1977, p. 279.
12. K. Öfele, J. Organometal. Chem. **12**, p. 42 (1968).
13. P. J. Stang and M. G. Mangum, J. Am. Chem. Soc. **97**, 3854 (1975).
14. W. E. Billups and A. J. Blackeney, ibid. **98**, 7817 (1976).
15. K. Komatsu, K. Masumoto and K. Okamoto, Chem. Commun. 232 (1977).
16. D. E. Dorman, and J. D. Roberts, J. Org. Chem. **38**, 1026 (1973), ibid. **38**, 2644 (1973).
17. J. P. C. M. van Dongen, M. J. A. de Bie, and R. Steuer, Tetrahedron Lett., 1371 (1973).
18. H. Prinzbach, U. Fischer, Helv. Chim. Acta **50**, 1692 (1967).
19. H. Prinzbach, Pure and Appl. Chem. **28**, 281 (1971).
20. T. J. Katz, P. J. Garratt, J. Am. Chem. Soc. **85**, 2852 (1963), **86**, 5194 (1964).
21. E. A. Lalancette, R. E. Benson, J. Am. Chem. Soc. **85**, 2853 (1963), ibid. **87**, 1941 (1965).
22. W. Grimme, M. Kaufold, U. Dettmier, E. Vogel, Angew. Chem. **78**, 643 (1966).
23. P. Radlick, W. Rosen, J. Am. Chem. Soc. **88**, 3461 (1966).
24. I. Murata, K. Nakasuji, T. Morita, Chem. Lett. 743 (1974).