Cyclopropenylium Cations, Cyclopropenones, and Heteroanalogues—Recent Advances

Koichi Komatsu* and Toshikazu Kitagawa

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received July 23, 2002

Contents

I. Introduction 1371
II. Synthesis of Cyclopropenylium Cations 1372
A. Cations Having Carbon and Silicon Substituents 1372
B. Cations Having Heteroatom Substituents 1376
1. Trihalocyclopropenylium Cations 1376
2. Cyclopropenylium Cation with Oxygen Substituent(s) 1376
3. Cyclopropenylium Cation with Nitrogen Substituent(s) 1377
4. Cyclopropenylium Cation with Chalcogen Substituent(s) 1380
C. Cyclotrigermenylium Cation and Homocyclotrisilenylium Cation 1382
D. X-ray Structure Determination 1384
III. Reactions of Cyclopropenylium Cations 1385
A. Reactions with Carbon Nucleophiles To Give Cyclopropenyl Compounds 1385
1. Cation–Anion Combination Reactions 1385
2. Carbocation–Carbanion Salt Formation 1388
B. Reactions with Heteroatom Nucleophiles 1391
C. Reactions with Nucleophiles with Ring Opening 1392
1. Formation of Five-Membered Rings 1392
2. Formation of Six-Membered Rings 1394
3. Formation of Seven-Membered Rings 1395
4. Formation of Linear Unsaturated Systems 1395
D. Reduction and Oxidation Reactions 1396
E. Formation of Metal Complexes 1398
1. Formation of σ-Complexes 1398
2. Formation of π-Complexes 1400
IV. Synthesis of Cyclopropenones and Heteroanalogues 1403
A. Cyclopropenones 1403
B. Sulfur and Selenium Analogues 1405
C. Nitrogen and Phosphorus Analogues 1406
V. Reactions of Cyclopropenones and Heteroanalogues 1407
A. Reactions with Electrophiles 1407
B. Reaction at the C=X Double Bond 1408
C. Cycloaddition to the Three-Membered Ring 1410
1. Addition to C=C Double Bond 1410
2. Addition with Cleavage of C–C Single Bond 1412
D. Reaction with Nucleophiles 1415
1. Ring Expansion 1415
2. Nucleophilic Addition with Ring Opening 1416
E. Oxidation and Reduction 1418
F. Rearrangement 1419
G. Decarbonylation 1419
H. Formation of Metal Complexes 1420
VI. Summary 1422
VII. References 1422

* Corresponding author. Phone: (81) 774-38-3172. Fax: (81) 774-38-3178. E-mail: komatsu@scl.kyoto-u.ac.jp.

I. Introduction

The cyclopropenylium cation is the smallest member of the Hückel aromatic systems, and numerous investigations have been carried out on this class of cation[1] since the first synthesis of triphenylcyclopropenylium perchlorate by Breslow.[2] Despite the apparent molecular strain inherent in such a small ring with two π-electrons delocalized over three 2p orbitals, this type of cations is now known to have considerable thermodynamic stability, owing to the Hückel aromaticity. An empirical parameter used as a measure of thermodynamic stability of carbocations, the pK_{R^+} value, which corresponds to the pH of the solution when the carbocation is half-neutralized, ranges from −0.67 to 10.0 for the cyclopropenylium cations with various substituent(s),[1b] while the value for the parent cation is quite low (−7.4).[3]

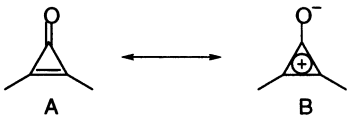
The study on cyclopropenylium cations has been developed mostly on the basis of the theoretical interest from the viewpoint of physical organic chemistry. However, synthesis utilizing the cyclopropenylium cation as a three-carbon building block has also become an important aspect of the study in recent years. Thus, not only the derivatives with various substituents have been synthesized, but various novel reactions of these cations have been investigated, which have afforded products with intriguing structures from the viewpoints of both theoretical interest and the importance in application. Particularly, it is to be noted that organometallic chemistry involving cyclopropenylium cations has been developed in the past one to two decades.

The chemical behavior of cyclopropenones is largely affected by its polarized nature, i.e., the contribution of the resonance structure in which a negative charge lies on oxygen (A↔B). This leads to enhanced nucleophilicity of the oxygen atom compared to ordinary carbonyl compounds. The cationic part of this structure is the cyclopropenylium cation with Hückel aromaticity, which makes the contribution of structure B quite important. The basic physical properties of cyclopropenone, which can be mostly understood by the aromatic stabilization, have been summarized in earlier reviews[4] and are not discussed here.

10.1021/cr010011q CCC: $44.00
Published on Web 03/19/2003

Koichi Komatsu was born in 1942 in Kyoto. After spending one year at Davidson College, NC, he graduated from Kyoto University in 1966. He studied at the graduate school of Kyoto University and became Instructor in 1971. He received his Ph.D. degree for his studies on one-electron reduction of carbocations in 1974. Then he conducted postdoctoral research on polyquinocycloalkanes with Professor Robert West at the University of Wisconsin, Madison, USA, in 1975–1976. He returned to Kyoto University and, after serving as Lecturer (1984–1989) and Associate Professor at the Department of Hydrocarbon Chemistry (1989–1993) and at the Institute for Chemical Research (1993–1995), he became Professor at the Institute for Chemical Research of Kyoto University in 1995. His research activities have been focused on carbocation chemistry, structural and physical organic studies on cyclic π-conjugated systems, and the fullerene chemistry. He received the Divisional Award of the Chemical Society of Japan (in Organic Chemistry) in 1997 and Alexander von Humboldt Research Award in 2002.

Toshikazu Kitagawa completed his undergraduate study in 1980 and received his Ph.D. degree in 1986 from Kyoto University under the guidance of Professor Kunio Okamoto and Professor Ken'ichi Takeuchi. He was a Research fellow of the Japan Society for the Promotion of Science in 1985–1986. He worked as a postdoctoral fellow at Harvard University (1986–1988, Professor William von E. Doering), and at Institute for Molecular Science (1989, Professor Kazuhiro Nakasuji). He was appointed as Instructor in 1990 and as Lecturer in 1995 at Kyoto University, where he has been an Associate professor since 1998. His major interest is directed to the synthesis of unusual organic molecules and structure and property of reactive intermediates.



Another factor that determines the properties of cyclopropenone is the large strain in the three-membered ring. This accounts for the high reactivity of this molecule, since the strain is released in most reactions. A balance of the aromatic stabilization and the magnitude of strain, which controls the stability of cyclopropenone, however, is still controversial.[5]

Cyclopropenone is an amphiphilic molecule, reacting readily with both nucleophilic and electrophilic reagents. It is also reactive toward dipolar reagents and compounds having a reactive π-system. The reaction pattern is sometimes complex, but recent extensive investigations have established the utility of these molecules as building blocks for the construction of larger molecules. The majority of investigations have been conducted for diphenylcyclopropenone, the first cyclopropenone reported in 1959 by Breslow et al.[6] and Vol'pin et al.,[7] but cyclopropenones containing a variety of substituents, in particular, some unstable derivatives such as fluoro- and hydroxycyclopropenones, have been synthesized recently. Important developments have been also attained for the chemistry of the heteroanalogues of cyclopropenones containing group 15 or 16 elements, S, Se, N, or P, though those containing heavier elements of these groups have not been reported to date.

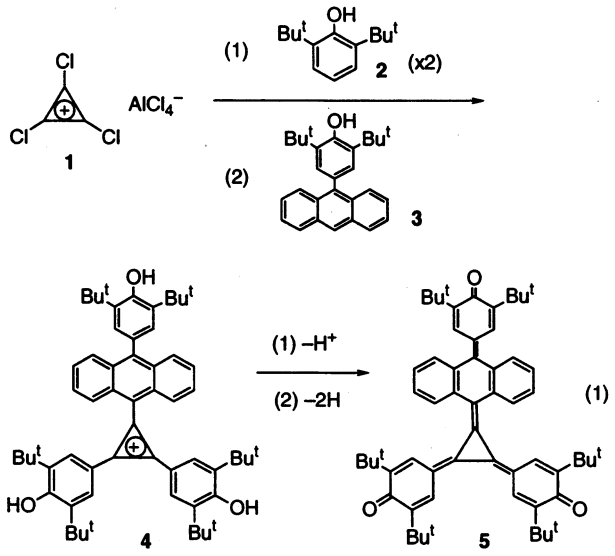
This article covers the recent topics in the chemistry of cyclopropenylium cations and cyclopropenones, as well as the heteroanalogues (S, Se, N, or P) of the latter, focusing on their synthesis, structures, properties, and reactions reported mainly in the past two decades.

II. Synthesis of Cyclopropenylium Cations

A. Cations Having Carbon and Silicon Substituents

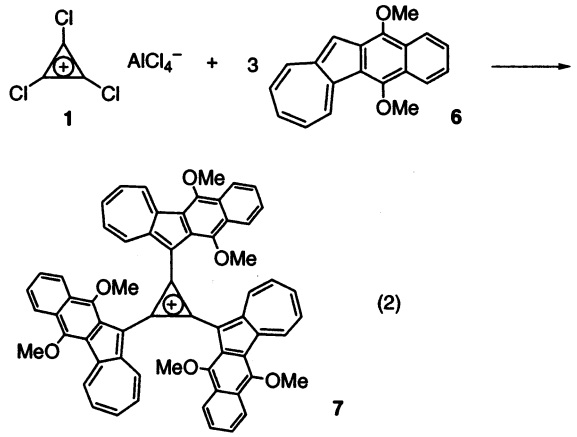
The direct synthetic method for the cyclopropenylium cation is essentially the combination of the C_1 and C_2 building blocks, i.e., the addition of a carbene or carbenoid species to a triple bond, followed by ionization of the produced cyclopropene to the cation. Alternatively, cyclopropene derivatives are prepared by dehydrohalogenation of halocyclopropanes or by addition of organometallic reagents to cyclopropenones. Various methods have also been reported for the exchange of the substituents, to give novel derivatives of cyclopropenylium cations.

One of the most versatile reactions for this last method involves the use of a Friedel−Crafts type reaction of the trichlorocyclopropenylium cation (**1**), which was first discovered by R. West.[8] This method can afford a wide variety of cyclopropenylium cations substituted with various different π-conjugated systems. Just to show one recent example, the reaction of **1**·$AlCl_4^-$ with 2 equiv of phenol **2**, followed by addition of 9-anthrylphenol **3**, afforded cation **4**, which could be transformed into tris-quinone **5**, having the longest-wavelength absorption at 672 nm, in 44% yield (eq 1).[9] It should be emphasized here that many works reported in this review would not have been possible without the seminal contribution of West, who made tetrahalocyclopropene and trihalogenocyclopropenylium systems available for the first time and subsequently used them as multifunctional electrophiles.[8] Retrospectively, it was this work that made all the fully heteroatom-substituted cyclopropenylium systems, including metallo-organic ones and many new carbon-substituted ones, acces-



sible for the first time and in a convenient way, as will be described later.

As an application of this method, the reaction of **1**·$AlCl_4^-$ with 3 equiv of naphth[2,3-*a*]azulene **6** gave cation **7**, having the longest-wavelength absorption at 592 nm, in 42% yield (eq 2).[10]

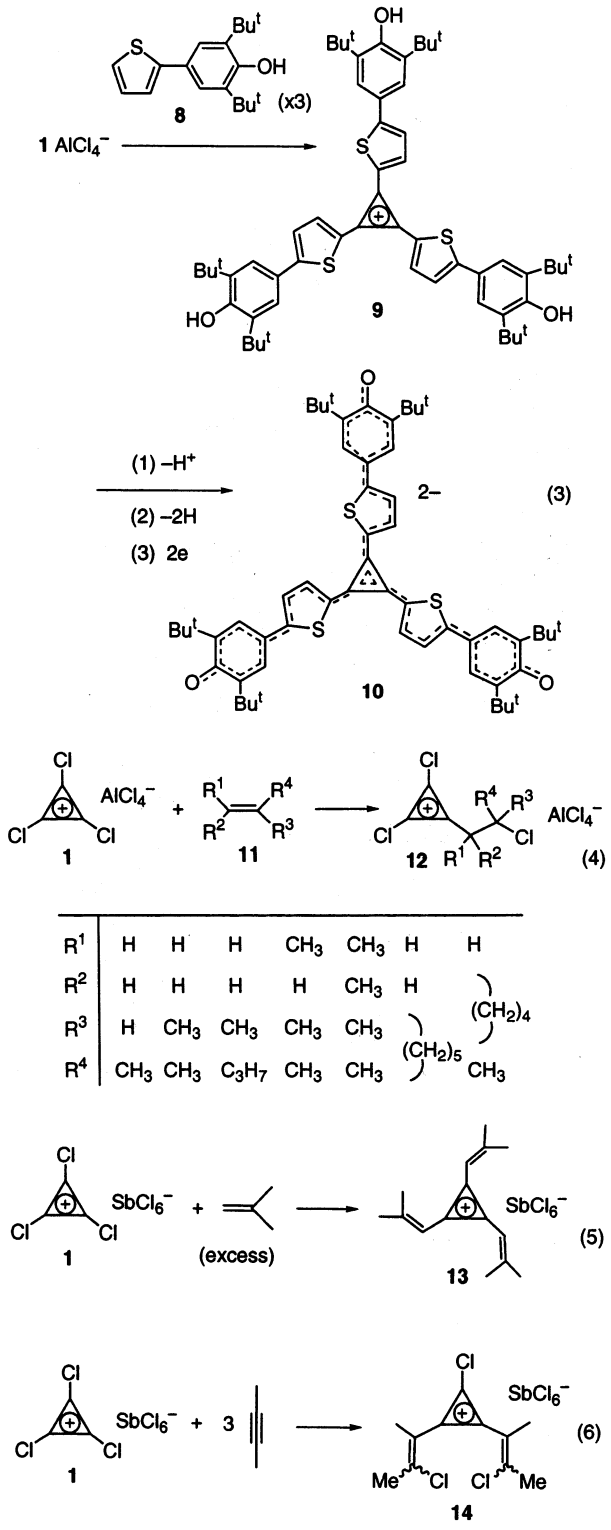


A derivative of tris(2-thienyl)cyclopropenylium cation **9** was prepared in 37% yield by a similar reaction with thienylphenol **8** and was transformed into dianion **10** with a highly delocalized π-system, having the longest-wavelength absorption at 693 nm (eq 3).[11]

This method is effective particularly for the reaction with activated π-systems. When cation **1** was allowed to react with simple alkenes **11**, only monosubstitution occurred to give cyclopropenylium cations **12** in moderate yields (28−60%) (eq 4).[12]

This reaction is sensitive to the nature of the counterion.[13] When the hexachloroantimonate salt of cation **1** (**1**·$SbCl_6^-$) was allowed to react with an excessive amount of 2-methylpropene, the first trivinylcyclopropenylium salt **13** was obtained in 15% yield (eq 5). Additionally, the two-fold addition of 2-butyne, to give the divinylcyclopropenylium salt **14**, was possible (eq 6).[13]

On the other hand, the reaction of the tetrachloroaluminate salt of cation **1** with excessive bis(trimethylsilyl)acetylene proceeded to give triafulvene **16** via formation of tris(trimethylsilyl)ethynylcyclopropenylium cation **15** only as an intermediate (eq 7).[14]



When 1,2-dichloro-3-phenylcyclopropenylium cation (**17**)[15] was allowed to react with 2 equiv of silylenol ether **18**, novel triafulvene derivatives, **19**, having a cyclic "7-hydroxy-2,4,6-heptatrien-1-one"-type structure with intramolecular hydrogen bonding were obtained in 32−78% yield (eq 8). One representative highly symmetrical structure of **19c** was determined by X-ray crystallography (Figure 1).[16]

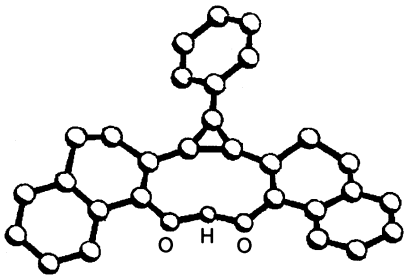
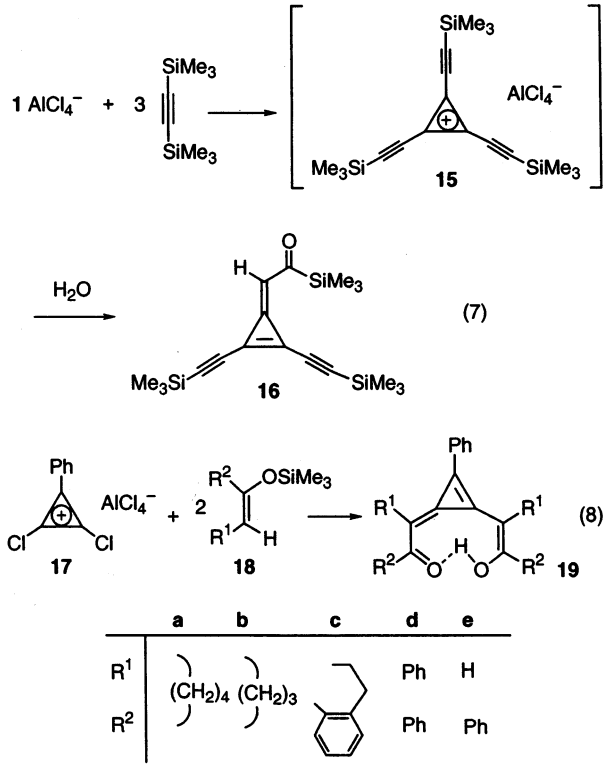
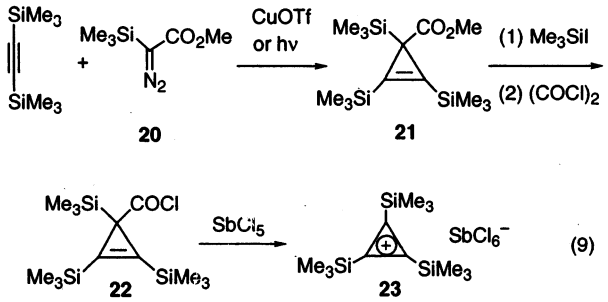


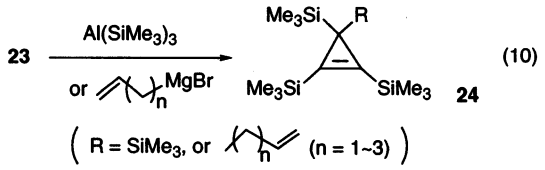
Figure 1. X-ray crystal structure of **19c**. [Reprinted with permission from ref 16. Copyright 2002 Georg Thieme Verlag.]



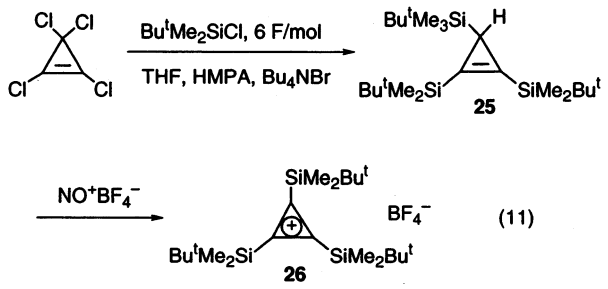
One of the recent reactions to be noted for the combination of a C_1 unit to a C_2 unit is represented by the synthesis of tris(trimethylsilyl)cyclopropenylium cation (**23**), as shown in eq 9.[17] Thus, either

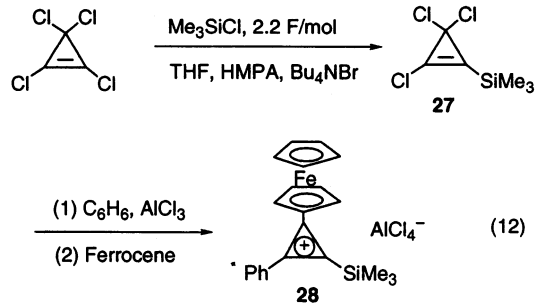


a Cu(I)-catalyzed thermal reaction or a photochemical reaction of bis(trimethylsilyl)acetylene with diazoacetate **20** afforded cyclopropenecarboxylate **21**, which was hydrolyzed and transformed to the first cyclopropenylium cation fully substituted with silicon, **23**, by treating the cyclopropenecarbonyl chloride **22** with $SbCl_5$. The salt **23**·$SbCl_6^-$ is a stable colorless crystal, exhibiting the ^{13}C NMR chemical shift of the three-membered ring at δ 214.3 ppm. The structure of this salt was determined by X-ray crystallography and was also examined by theoretical calculations.[18] The pK_{R^+} value, which is a measure of the thermodynamic stability of carbocations, was estimated to be around 4 on the basis of the calculations in the gas phase.[18] Cation **23** reacted with $Al(SiMe_3)_3$ and with alkenylmagnesium bromide to give the corresponding tetrasubstituted cyclopropenes **24** (eq 10).[19]



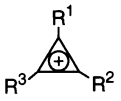
It is to be noted that the electrochemical reduction of tetrachlorocyclopropene in the presence of *tert*-butyldimethylchlorosilane afforded the corresponding trisilylcyclopropene **25** (12−15%), which was transformed into tris(*tert*-butyldimethylsilyl)cyclopropenylium cation **26** by oxidation with $NO^+BF_4^-$ quantitatively (eq 11).[20] The ^{13}C NMR signal of the three-membered-ring carbon of **26** was observed at δ 217.1 ppm. When the amount of electric current was reduced (in the presence of trimethylchlorosilane), the trichlorocyclopropene **27**, having only one trimethylsilyl group at C1-position, was obtained in 78% yield. This cyclopropene was allowed to react with benzene and then with ferrocene under Friedel−Crafts conditions to give cyclopropenylium cation **28** (eq 12).[21]





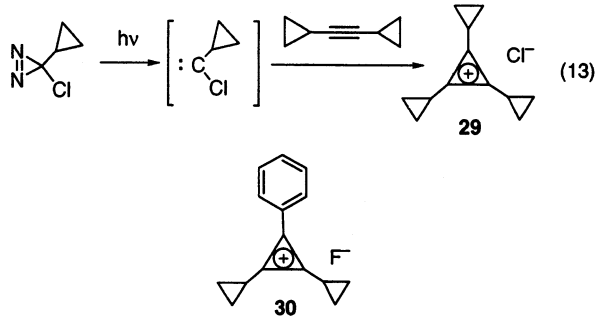
As another example of the combination of a C_1 unit with a C_2 unit, cyclopropylchlorocarbene, generated in situ, rapidly reacted with dicyclopropylacetylene to give tricyclopropylcyclopropenylium chloride (**29**, ~60%) as a colorless crystal (eq 13).[22−24] By a similar method, dicyclopropylphenylcyclopropenylium cation (**30**) was also synthesized (33%).[24] By comparison of the pK_{R^+} values of a series of cyclopropenylium cations with sequential changing of the substituent

Table 1. pK_{R^+} Values of Cyclopropyl- and Phenyl-Substituted Cyclopropenylium Cations[a]



R^1	R^2	R^3	anion	pK_{R+}	Ref
Ph	Ph	Ph	Br^-	3.1	26
Ph	Ph	Ph	BF_4^-	3.4	25
	Ph	Ph	BF_4^-	5.04	25
		Ph	BF_4^-	7.09	24
			Cl^-	9.4	23,24
			BF_4^-	10.0	22

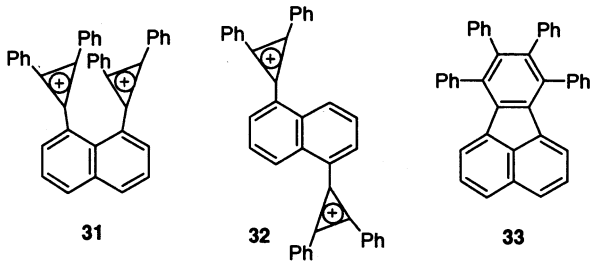
[a] Determined by potentiometric titration in H_2O−MeCN (1:1).



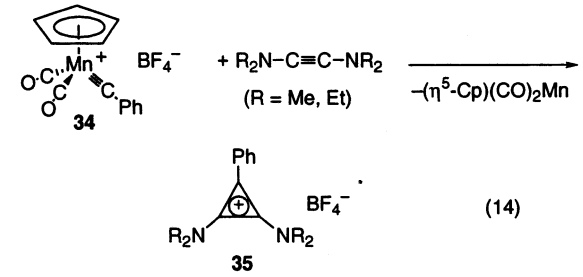
(13)

from a phenyl group to a cyclopropyl group (Table 1), it is apparent that each cyclopropyl-for-phenyl substitution stabilizes the cyclopropenylium cation by about 2 pK units.[24−26] The ^{13}C NMR signal of the three-membered-ring carbon of cation **29** was observed at δ 169.2 ppm, which is considerably upfield shifted due to the decrease of the positive charge in this ring by cyclopropyl conjugation. This is reflected in the ^{13}C NMR signals for the α- and β-carbons of the cyclopropyl group, which were observed at δ 8.65 and 15.79 ppm, respectively. The greater deshielding of the β- relative to the α-carbons is consistent with significant positive charge transferred to the β-cyclopropyl carbons. The X-ray crystal structures were determined for cations **29** and **30**, and the cyclopropyl group was shown to take the orthogonal, i.e., bisected, conformation to the three-membered cationic plane for the most effective charge delocalization.[27]

The double addition of chlorophenylcarbene to 1,8- and 1,5-bis(phenylethynyl)naphthalenes afforded the dications **31** and **32** after ionization using trityl tetrafluoroborate.[28] In the dication **31**, the face-to-face arrangement of the two cyclopropenylium rings was proved by a considerable upfield shift observed for the ^{1}H NMR signals of phenyl protons. Due to the electrostatic repulsion between the two positively charged moieties, dication **31** (pK_{R^+} −2.08) was found to be destabilized as compared with **32** (pK_{R^+} −0.42) by 1.66 pK units. The one-electron reduction of dication **31** resulted in the formation of fluoranthene **33** (80%), possibly via formation of an intramolecular bis(cyclopropenyl) intermediate.

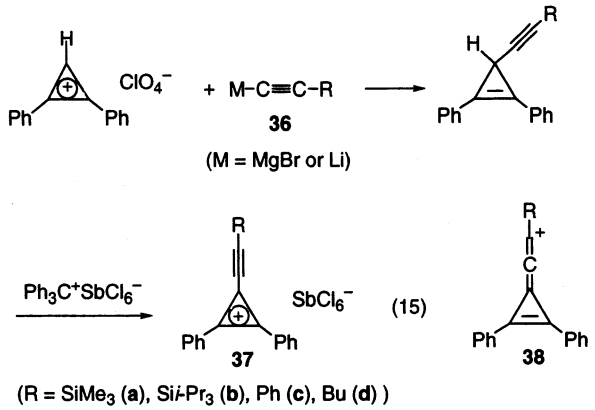


When the cationic carbyne moiety was added to an acetylene, a cyclopropenylium cation **35** was directly formed in 60% yield, as exemplified by the reaction of [(η^5-C_5H_5)$(CO)_2$Mn≡CPh]$^+$ (**34**) with bis(dialkylamino)acetylenes (eq 14).[29] This is the first example of the transfer of an electrophilic carbyne ligand to the carbon−carbon triple bond.



(14)

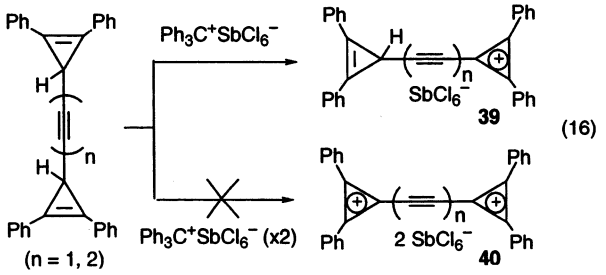
As has been mentioned, triethynylcyclopropenylium cation **15** was found to be present only as an unstable intermediate (stable in solution only below −40 °C).[14] In contrast, the cyclopropenylium cations having only one 1-alkynyl group **37** were prepared as stable salts, utilizing the reaction of diphenylcyclopropenylium cation with appropriate acetylenic nucleophiles **36**, followed by hydride abstraction (eq 15).[30] Although the contribution of the allene-type



(15)

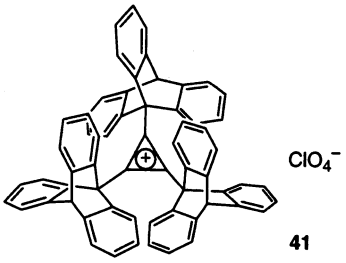
resonance structure, such as **38**, is not favorable because of the decrease in the aromatic character in the three-membered ring, such a contribution is present to some extent, as shown by the downfield shift of the ^{13}C NMR signal of the γ-carbon by 52.24 ppm (for the phenylethynyl derivative) as compared with the neutral cyclopropene precursor. The pK_{R^+} values for cations **37a** and **37c** were determined to be 2.93 and 3.00, while the value for the triphenylcyclopropenylium cation was found to be 3.15 under the same conditions [in H_2O−CH_3CN (1:1)]. Thus, the acetylene substituents appear to have roughly the

same capability to stabilize the cation as a phenyl group. Using the same method, monocation **39** was synthesized, but dication **40** could not be obtained (eq 16).



(16)

By the use of the reaction of bis(9-triptycyl)-cyclopropenone with 9-triptycyllithium, followed by treatment with $HClO_4$, tris(9-triptycyl)cyclopropenylium perchlorate (**41**) was synthesized (24−67%),[31] and the X-ray crystal structure was determined.

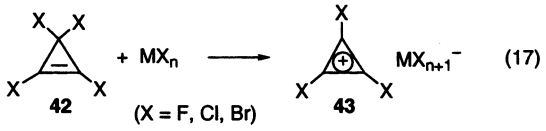


From the results of the variable-temperature NMR study, it was shown that torsional motion of the three triptycyl rotors is frozen because uncorrelated as well as correlated rotation is mechanically disallowed, as in a securely meshed gear. The rotational barrier for the triptycyl group was estimated to be higher than 21.0 kcal mol^{-1}. The pK_{R^+} value of **41** was determined to be 8.2 [in H_2O-CH_3CN (2:3)],[31b] which falls into the range obtained for other trialkylcyclopropenylium cations or slightly higher; the pK_{R^+} value is 7.4 for the trimethyl derivative,[32] 7.0 for the tripropyl derivative,[32] and 6.5 for the tri-*tert*-butyl derivative[32] [all measured in H_2O-CH_3CN (1:1)].

B. Cations Having Heteroatom Substituents

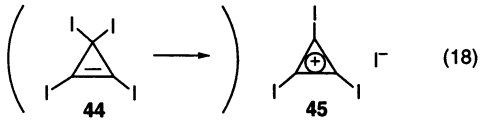
1. Trihalocyclopropenylium Cations

The trichloro-,[8b] tribromo-,[8b] and trifluoro derivatives[33] of cyclopropenylium cation salts **43** have been prepared by the halide ion abstraction reaction of the corresponding tetrahalocyclopropenes **42** with appropriate Lewis acids in a pioneering work by West (eq 17), and their vibrational spectra have been studied.[8b,33]

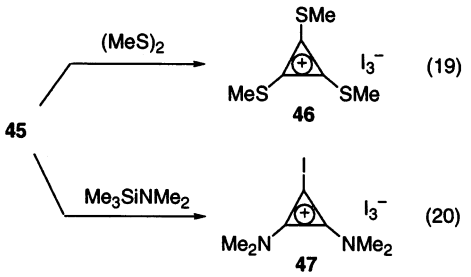


(17)

In sharp contrast to the tetrahalocyclopropenes **42** (X = F, Cl, Br), which are covalent compounds, the tetraiodo derivative **44** is already ionized by itself into the salt, triiodocyclopropenylium iodide (**45**) (eq 18).[34] Just like the reaction of **42** (X = Cl),[35] triiodo compound **45** underwent substitution, as shown in eqs 19 and 20, to give cations **46** and **47**. (***Caution:*** *The salt **45** is highly explosive, not only in the dry solid state, but also upon dissolution in polar solvents such as CH_3OH and CH_3CN!*)



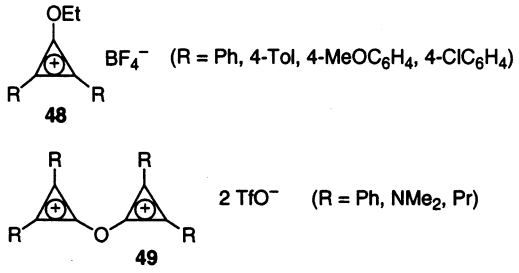
(18)



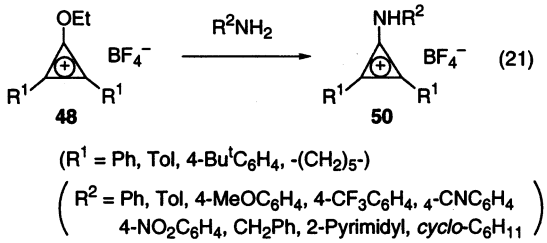
(19)
(20)

2. Cyclopropenylium Cation with Oxygen Substituent(s)

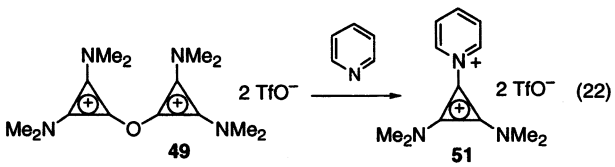
Cyclopropenones are versatile precursors to the cyclopropenylium cations, as will be described later. By treatment with an equimolar amount of trialkyloxonium salts, cyclopropenones were converted to the corresponding alkoxycyclopropenylium salts **48**.[36] When treated with trifluoromethanesulfonic anhydride, cyclopropenones were converted to bis(cyclopropenyliumyl) ether dication **49**.[37]



Both cations **48** and **49** react with nitrogen nucleophiles to give amino- or pyridyl-substituted cations **50** (65−95%)[38] and **51** (87%),[39] respectively (eqs 21 and 22).



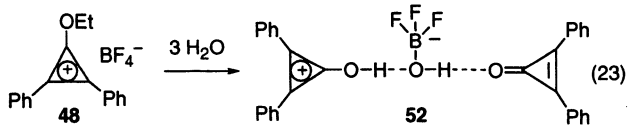
(21)



(22)

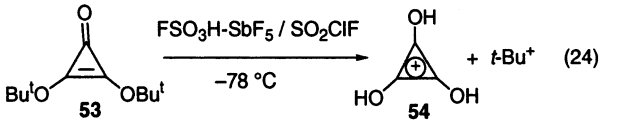
Upon hydrolysis of 1-ethoxy-2,3-diphenylcyclopropenylium tetrafluoroborate, a complex hydrogen-bonded salt of protonated diphenylcyclopropenone **52**

was formed (eq 23), the structure of which was determined by X-ray crystallography.[40] The $BF_3(OH)^-$



group is present in the middle of the symmetrically hydrogen-bonded cyclopropenone and hydroxycyclopropenylium cation moieties, and the structural parameters of the two cyclic C_3 units take values between those of cyclopropenone and the hydroxycyclopropenylium cation.

The trihydroxycyclopropenylium cation (**54**), which is equal to protonated deltic acid, was prepared in solution for the first time by protolysis of di-*tert*-butyl deltate (**53**) by FSO_3H or FSO_3H:SbF_5 in SO_2ClF at −78 °C (eq 24).[41] The observed ^{13}C NMR signal for



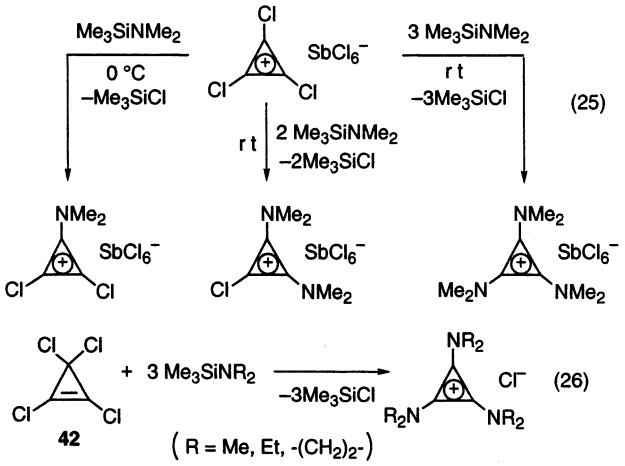
the three-membered-ring carbon (δ 128.7 ppm) is greatly upfield shifted for the cyclopropenylium cation, due to the charge delocalization to three oxygen atoms, and is in fairly good agreement with the calculated value (δ 133.3 ppm) obtained using the IGLO/II method based on the MP2/6-31G* optimized geometry.

3. Cyclopropenylium Cation with Nitrogen Substituent(s)

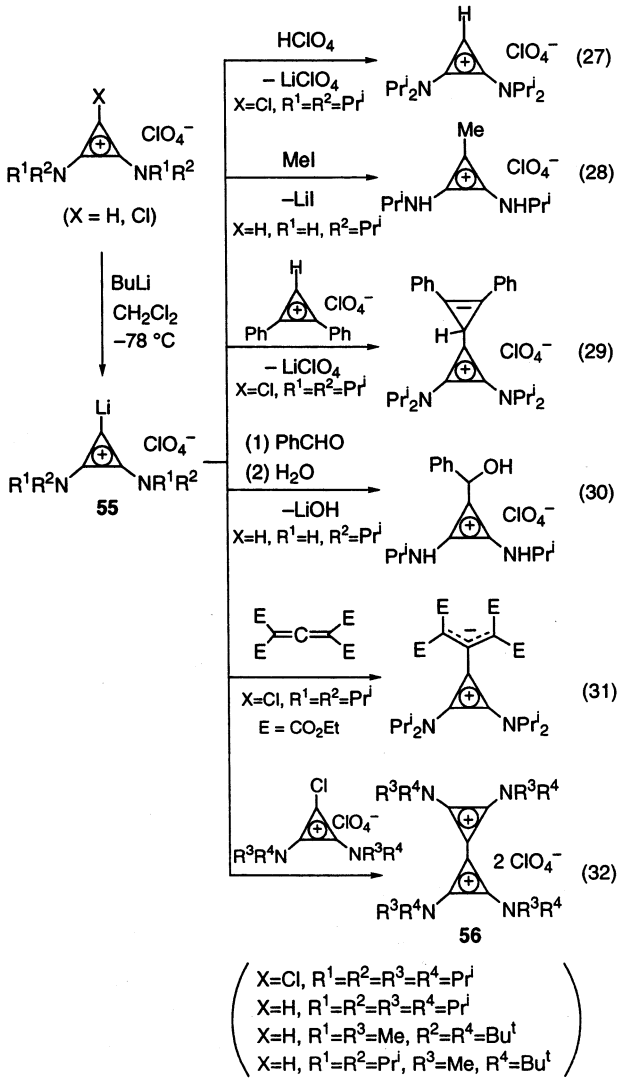
Since the first synthesis of tris(dialkylamino)cyclopropenylium cations,[42] there have been reported various derivatives of bis- or tris(diorganylamino)cyclopropenylium cations,[43] as will be shown in this and later sections.

The transamination reaction of trichlorocyclopropenylium hexachloroantimonate (**1**·$SbCl_6^-$) with trimethylsilyldialkylamines can afford a series of $SbCl_6^-$ salts of dialkylaminodichloro-, bis(dialkylamino)chloro-, and tris(dialkylamino)cyclopropenylium cations, depending on the reaction conditions (eq 25).[44] In a simpler procedure, the reaction of tetrachlorocyclopropene (**42**; X = Cl) with 3 equiv of trimethylsilyldialkylamines smoothly gives the corresponding tris(dialkylamino)cyclopropenylium chlorides quantitatively (eq 26).[45]

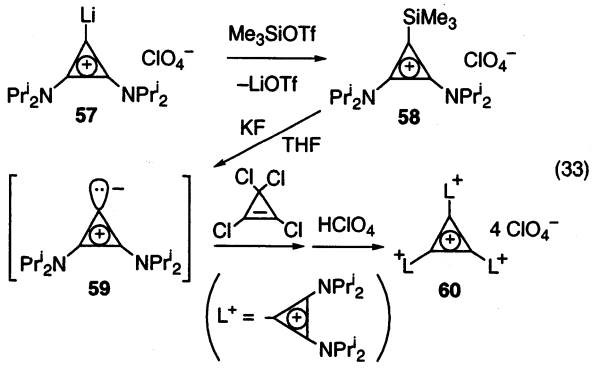
One of the most remarkable properties of the 1,2-diaminocyclopropenylium cation or its 3-chloro derivative is the facile metalation of the unsubstituted or chloro-substituted carbon by alkyllithium or aryl Grignard reagents.[46] This is attributed to the low reactivity of the organometallic reagent in the nucleophilic attack on the cyclopropenylium ring due to its cyanine-type resonance structure and also to the virtually sp-hybridized character of the exocyclic single bond of the cyclopropenylium ring. Especially, the 3-lithiated derivative of the 1,2-diaminocyclopropenylium cation can be used as a versatile synthetic intermediate for preparation of a variety of cyclopropenylium cations of structural interest. For example, as shown below, 1,2-diamino-3-lithiocyclo-



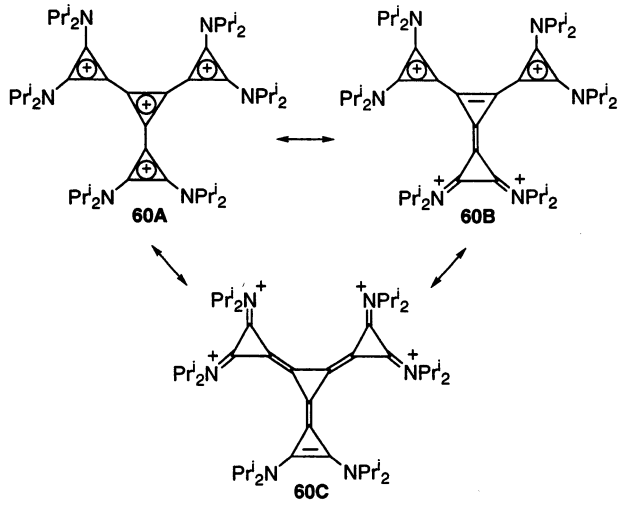
propenylium cation **55** underwent protonation (eq 27),[46] methylation (eq 28),[47] cyclopropenylation (eq 29),[46] carbonyl addition (eq 30),[48] addition to allenes to give dipolar zwitterionic species (eq 31),[49] and coupling with chlorocyclopropenylium cations to afford bis(cyclopropenylium) dications **56**, which can be regarded as triafulvalenyl dications (eq 32).[46,50] A similar Grignard reagent, the 1,2-diamino-3-bromomagnesiocyclopropenylium cation, could also be prepared and exhibited analogous reactivity.[51]



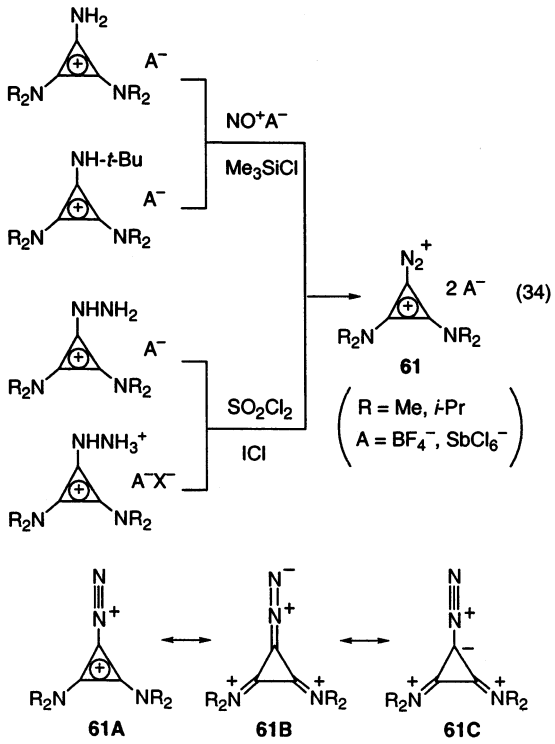
Furthermore, 1,2-diamino-3-(trimethylsilyl)cyclopropenylium cation **58**, obtained by the reaction of **57** with trimethylsilyl triflate, was found to react with tetrachlorocyclopropene in the presence of F^- ion to give the stable salt of a highly symmetrical stable tetracation **60** (eq 33).[52] The reaction appar-



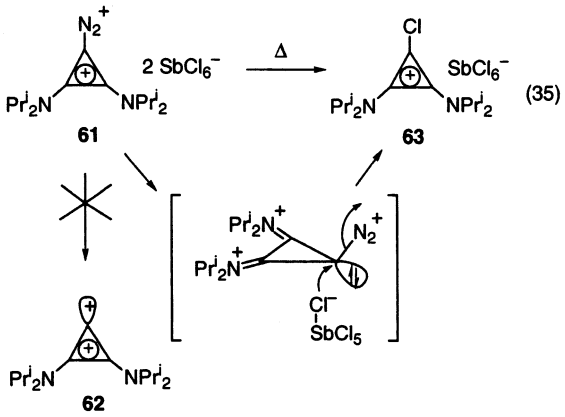
ently proceeds through the formation of a nucleophilic carbene **59**. The ^{13}C NMR signal of the central three-membered-ring carbon of **60** appeared at δ 120 ppm, indicating that the dimethylaminocyclopropenylio group has a donor strength comparable with that of a dialkylamino group. The tetracation **60** can be formulated as a resonance hybrid of aromatic (**60A**), fulvenoid (**60B**), and radialenoid (**60C**) structures.



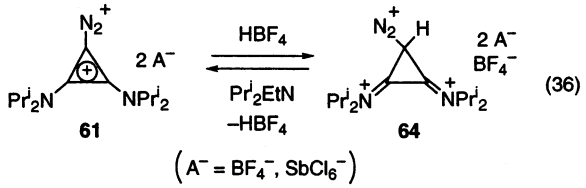
As the first cyclopropenylium cations having a diazonium function, cations **61** were synthesized as stable but moisture-sensitive salts via several pathways, as shown in eq 34.[53] These systems represent the first examples of a diazonium function attached to an sp-hybridized carbon. Since the $SbCl_6^-$ salts were only very slightly soluble in common organic solvents and the BF_4^- salts reacted with solvent such as CH_3CN with decomposition, unfortunately no NMR data could be obtained for these cations. The result of theoretical calculations (MNDO) implied that the bonding situation in this type of cation is conceived as a resonance hybrid made up from a donor-stabilized aromatic diazonium system (**61A**) and an acceptor-stabilized cycloaliphatic diazo systems (**61B**, **61C**).



Thermolysis was conducted on cation **61** (R= *i*-Pr, A = $SbCl_6^-$) to see if the reaction via a dicationic intermediate with an empty sp-hybridized orbital on C-1 (**62**) would be realized by nitrogen extrusion.[53] However, the results of the experiment, which afforded 1-chloro-2,3-diaminocyclopropenylium cation **63** ($SbCl_6^-$ salt) in 25% yield, as well as theoretical calculations, suggested that an S_N2-like bimolecular substitution, as shown in eq 35, would have been involved.

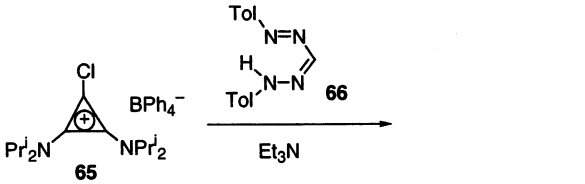


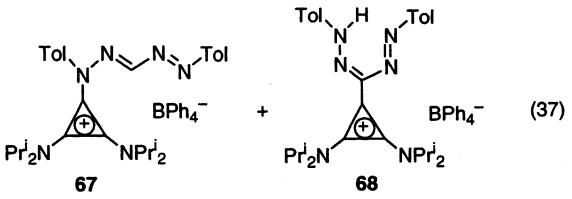
It is also reported that the cyclopropenyliumyl−diazonium system **61** (R = *i*-Pr; A = BF_4, $SbCl_6$) can be protonated on C-1 to give a stable tricationic alkanediazonium system **64** (eq 36).[53] This represents

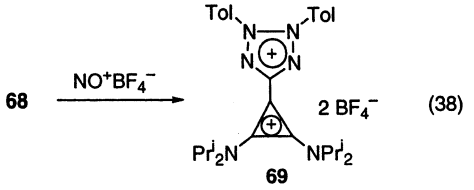


the first electrophilic attack on the π-system of a cyclopropenylium ion. This kind of reaction has been foreshadowed in an earlier paper by Weiss and Priesner,[54] in which electrophilic deuteration of a diaminocyclopropenylium system is demonstrated. These reactions are the only electrophilic attacks on a cyclopropenylium core known to date, and they have been the subject of a comprehensive theoretical study.[55]

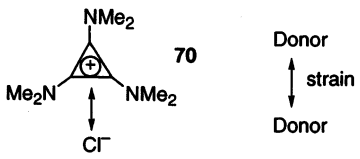
To examine the regioselectivity of the reaction of an anion of formazan (1,2,4,5-tetraaza-1,3-pentadiene), the 1,5-di-*p*-tolyl derivative **66** was allowed to react with 1-chloro-2,3-diaminocyclopropenylium cation **65** (BPh_4^- salt) in the presence of triethylamine. Two cyclopropenylium salts, **67** and **68**, were formed in 8% and 4% yield, respectively (eq 37).[56] The cation **68** was further oxidized with $NO^+BF_4^-$ to give the cyclopropenyliotetrazolium salt **69** as colorless crystals (eq 38).







The tris(dimethylamino)cyclopropenylium cation (**70**) is a very unusual cation which can act as an electron-rich "donor" species with a high-lying HOMO, despite the presence of a positive charge. Therefore, its salt, such as the chloride (**70**·Cl^-), can be regarded as a "donor−donor" system, which should have "ion pair strain" (a strong closed-shell repulsion between the electron-rich components).[57] This is demonstrated



by almost the same $E_{1/2}$ value of about +1.4 V (vs Ag/AgCl) for the oxidation of both cation **70** and the chloride ion. These considerations suggest that the salts of cation **70** would be effective sources of naked halide ions. In fact, the 1:1 adducts of **70**·Cl^- and various carboxylic acids or phenols have been isolated, and the formation of strong hydrogen bonds

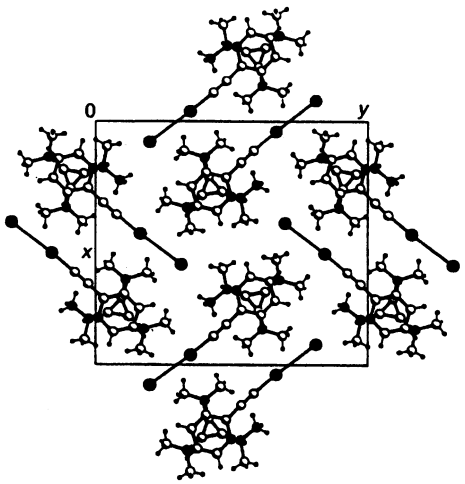
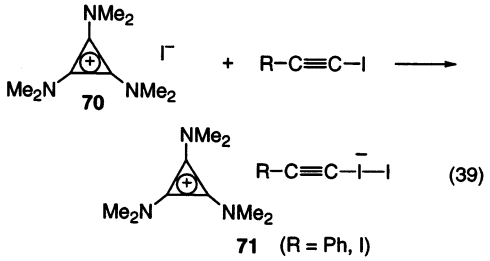


Figure 2. Crystal structure of **71** (R = Ph). [Reprinted with permission from ref 58. Copyright 2002 Wiley-VCH.]

between the O−H groups and Cl^- ions was shown by X-ray crystallography on these adducts.[57]

The above-mentioned activation of the halide ions can be applied to even the "soft" iodide ions to form novel hypervalent adducts with organic iodides as σ^* acceptors. Thus, the reaction of tris(dimethylamino)-cyclopropenylium iodide (**70**·I^-) with 1-iodo-2-phenylacetylene and with diiodoacetylene gave the salts **71**, which are the first examples of stable nσ^* adducts between iodide ion and C(sp)-bonded iodine centers (eq 39).[58] The structures of the adducts were determined by X-ray crystallography. The I−I distance of 3.44 and 3.40 Å in the anion of **71** (R = Ph, I) is very long in comparison to that in molecular iodine (2.66 Å) but considerably shorter than the sum of the van der Waals radii of iodine (4.35 Å).



The crystal structures of **71** (R = Ph, I) are shown in Figures 2 and 3.[58] Particularly in the case of **71** (R = I), a novel hypervalent one-dimensional polymer is formed. The bifunctional σ^* acceptor centers of diiodoacetylene are each connected by an iodide ion which functions as bifunctional lone pairs: the cationic moieties **70** are arranged above the partially anionic iodine center at a distance of 3.36 Å and form a stacking structure.

It is to be noted that a similar type of 1:1 "n→σ^* adducts" **72** was formed also between the salt **70**·I^- and iodoarenes with electron-withdrawing substituents (eq 40).[59]

By the reaction with triphenylphosphine, 1-chloro-2,3-bis(dimethylamino)cyclopropenylium cation was converted to 1,2-diamino-3-phosphoniocyclopropenylium cation **73**.[60,61] The characteristic nature of this dication, having a contribution of a radialene-type

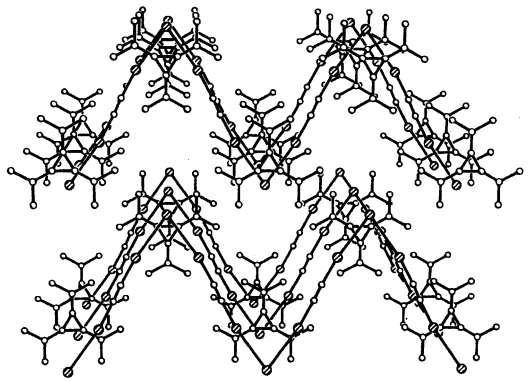
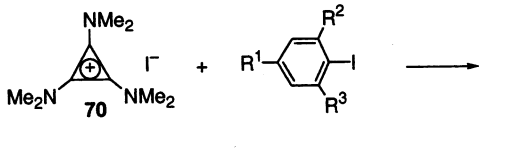


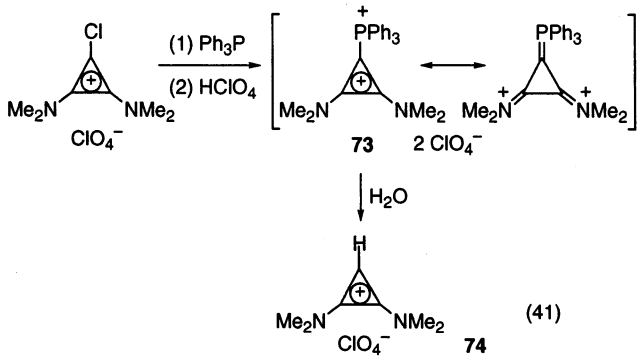
Figure 3. Crystal structure of **71** (R = I). [Reprinted with permission from ref 58. Copyright 2002 Wiley-VCH.]



(40)

R^1	R^2	R^3
CN	H	H
NO_2	H	H
NO_2	NO_2	H
NO_2	NO_2	NO_2

structure, has been discussed.[60] Hydrolysis of **73** afforded 1,2-diaminocyclopropenylium perchlorate **74** as bright yellow crystals in 93% yield (eq 41).[61]

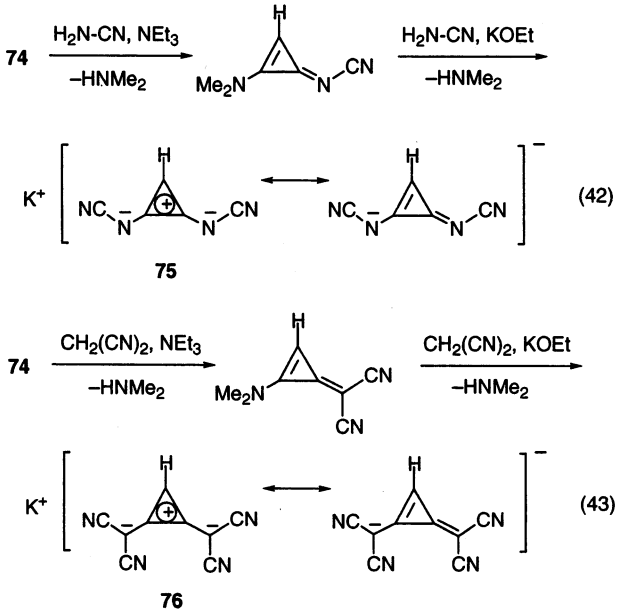


(41)

Treatment of **74** with H_2N-CN and Et_3N and then EtOK successively substituted the dimethylamino group with the cyanoimino group to give salt **75** (eq 42). The ^{13}C NMR chemical shift of the three-membered ring of **75** was δ 110.1 (CH) and 151.0 ppm (C−N), thus indicating the cyclopropenylium character of the central ring.[61] In the similar manner, the use of malononitrile instead of H_2N-CN afforded potassium or tetrabutylammonium salt **76** (eq 43).

4. Cyclopropenylium Cation with Chalcogen Substituent(s)

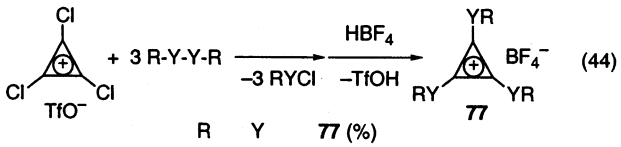
Tris(methylchalcogeno)- or tris(phenylchalcogeno)-cyclopropenylium tetrafluoroborates **77** were prepared by the use of oxidative cleavage of dimethyl dichalcogenides by trichlorocyclopropenylium triflate



(42)

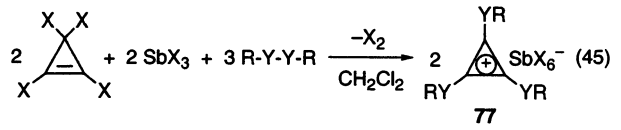
(43)

(eq 44).[35a] This method was further developed to give the hexahaloantimonate or tribromide salts of **77** in a simpler manner, directly from tetrahalocyclopropene, in much higher yield and purity (eqs 45 and 46).[62]



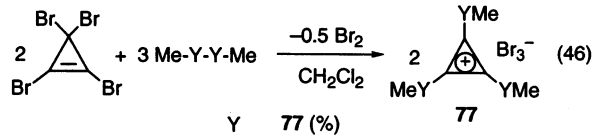
(44)

R	Y	77 (%)
Me	S	40
Me	Se	40
Me	Te	40
Ph	S	60-80
Ph	Se	60-80



(45)

X	Y	R	77 (%)
Cl	S	Me	94
Cl	S	Ph	86
Cl	Se	Me	92
Cl	Se	Ph	89
Br	S	Me	87

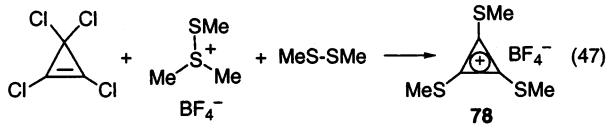


(46)

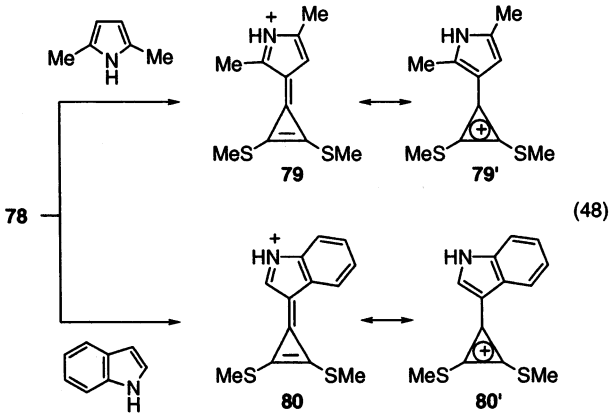
Y	77 (%)
S	95
Se	92
Te	94

Tris(methylthio)cyclopropenylium tetrafluoroborate **78** was also obtained by the reaction of tetrachlorocyclopropene with dimethyl(methylthio)sulfonium tetrafluoroborate and dimethyl disulfide in 70% yield (eq 47).[63]

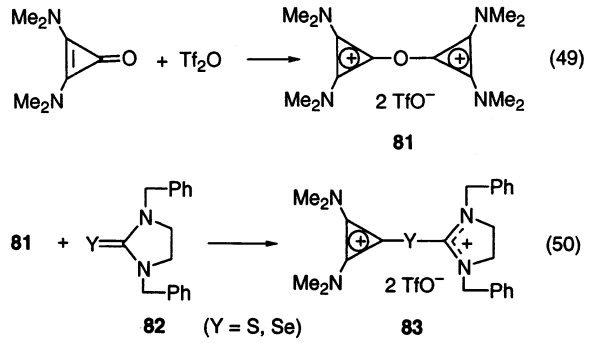
Cation **78** reacts with 2,5-dimethylpyrrole or with indole to give the azacalicenium salts **79** and **80**, in



which the contribution of cyclopropenylium structures **79′** and **80′** are dominating (eq 48).[63]

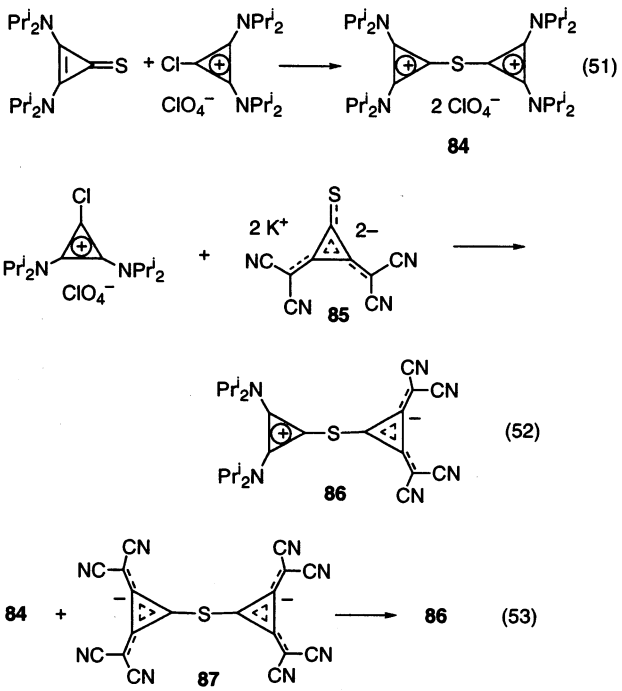


By the reaction with 0.5 equiv of triflic anhydride, bis(dimethylamino)cyclopropenone was converted into the ditriflate salt of bis(cyclopropenyliumyl) ether dication **81**, which was the first bis(carbenium) dication linked by a single atom (eq 49).[64] The reaction of this dication ether **81** with cyclic thione or selone (**82**) then afforded the sulfur- and selenium-bridged dications **83** (Y = S or Se) (eq 50).[65]

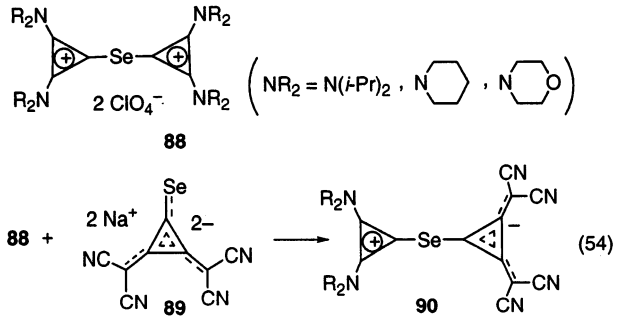


The corresponding bis(cyclopropenyliumyl) sulfide dication **84** was synthesized by the reaction of bis(diisopropylamino)cyclopropenethione with 1-chloro-2,3-bis(diisopropylamino)cyclopropenylium perchlorate (eq 51).[66,43] The reaction of 1-chloro-2,3-bis(diisopropylamino)cyclopropenylium perchlorate with the potassium salt of the dicyanomethylene derivative of thiodeltate **85** afforded thiocarbonyl ylide **86** in 69% yield (eq 52).[67] The same product (**86**) was obtained also by the reaction of the bis(cyclopropenyliumyl) sulfide dication **84** with the sulfur-bridged delocalized dianion **87**, in 51% yield (eq 53).[67] Comparison of the ^{13}C NMR data of the corresponding dication, dianion, and ylide suggests that there is almost no electronic interaction between the cationic and anionic moieties in the ylide **86**.

In the same way, selenium-bridged bis(cyclopropenyliumyl) dication **88** was obtained by the reaction of diaminocyclopropeneselone with 1-chloro-2,3-diaminocyclopropenylium cation,[68] and its reaction



with the sodium salt of a dicyanomethylene derivative of selenodeltate **89** gave the selenocarbonyl ylide **90** (eq 54).[69]



Additionally, the selone function in the diaminocyclopropeneselones **91**, which were readily accessible from the cyclopropenylium salts **92** and sodium hydrogen selenide, was sufficiently nucleophilic to displace triethylamine from the zwitterions **93** to give **90** or **95** (eq 55).[69] Via another route, **93** was converted with sodium hydrogen selenide into the sodium salt **94**, which reacted with the perchlorate salt of 1-chloro-2,3-diaminocyclopropenylium cation **92** to yield selenocarbonyl ylide **90** (eq 56). As in the case of the thiocarbonyl ylide, the ^{13}C NMR chemical shifts of the cationic terminus and anionic terminus in **90** were found to be almost identical to those in the dication **88** and in the dianion **96**.

The observation of two NMR signals each for the nitrile carbon atoms and the carbon atoms in the α-position to the piperidine nitrogen in **90** (NR_2 = piperidine) points to hindrance to rotation and thus to a high bond order for the corresponding bonds connected to the two kinds of three-membered rings.[69] The structure of the ylide **90** (R = *i*-Pr) was determined by X-ray crystallography (Figure 4).[69] The planar anionic moiety lies in a mirror plane. The cationic three-membered ring was found to be per-

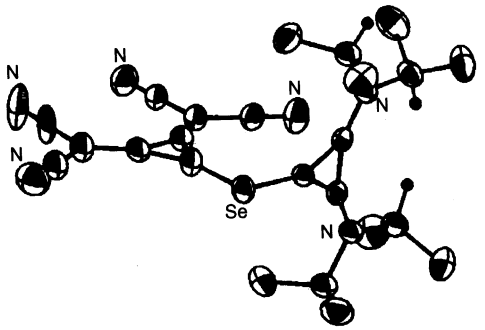
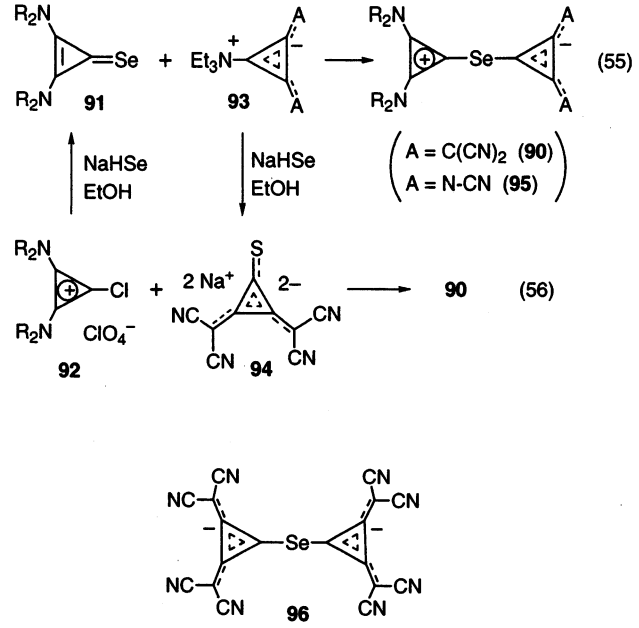
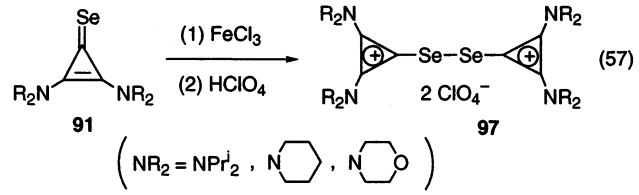


Figure 4. X-ray crystal structure of ylide **90** (R = *i*-Pr). [Reprinted with permission from ref 69. Copyright 2002 Wiley-VCH.]

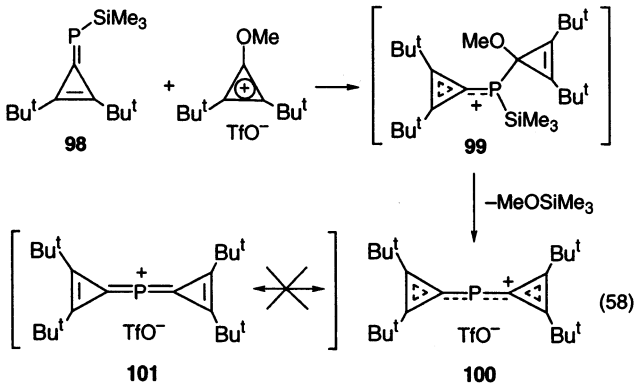


pendicular to the anionic ring and is bisected by the mirror plane. In agreement with the NMR data, the bonds to the ring substituents showed a high degree of double bond character.

When diaminocyclopropeneselone **91** was oxidized with $FeCl_3$, the bis(cyclopropenyliumyl) dication, connected by a diselenide bridge (**97**), was obtained in high yield (eq 57).[68]

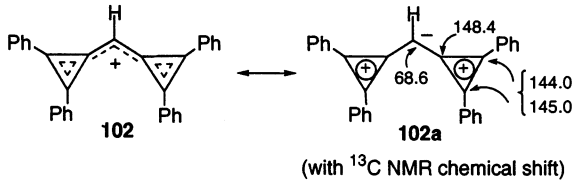


In contrast to the reaction of cyclopropenethione or -selone with chlorocyclopropenylium cation, giving the sulfur- or selenium-bridged dication, the reaction of silylphosphatriafulvene **98** with 1,2-di-*tert*-butyl-3-methoxycyclopropenylium cation afforded a fully π-conjugated monocation **100** by elimination of methoxytrimethylsilane from the first formed adduct **99** (eq 58).[70] The full delocalization of the positive charge is demonstrated by the relatively downfield shifted and symmetrical ^{13}C NMR signals for the three-membered-ring carbons (δ 179.1 ppm for C-1 and

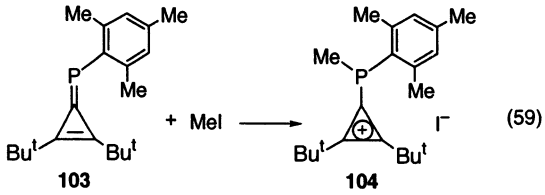


173.3 for C-2,3) and the single ^1H NMR signal (δ 1.50 ppm) for the *tert*-butyl protons. The upfield shift of the ^{31}P NMR signal (δ −46.8 ppm) is not quite in agreement with a resonance structure such as **101**.

In the case of the previously reported carbon analogue **102**, the ^{13}C NMR chemical shift of the central methine carbon was also upfield shifted, and the contribution of a structure such as **102a** was supposed.[71] In this cation, the signals of the cyclopropenylium carbons appeared unsymmetrically, indicating a hindered rotation around the central carbon−cyclopropenyl bond.



The reaction of phosphatriafulvene **103** with methyl iodide also afforded cyclopropenylium iodide **104**, having a phosphorus substituent as yellow crystals in 90% yield (eq 59).[72] The ^{13}C NMR signals of the cationic carbons appeared at δ 184.3 (C-1) and 180.7 ppm (C-2,3), while the ^{31}P NMR signal was observed at δ −40.0 ppm.



C. Cyclotrigermenylium Cation and Homocyclotrisilenylium Cation

As the first example of a germyl cation free from any coordination of solvent or counteranion, the germanium analogue of cyclopropenylium cation **106**, i.e., a cyclotrigermenylium cation with 2π electrons delocalized over the three-membered ring having three tri-*tert*-butylsilyl (**106a**) or tri-*tert*-butylgermyl groups (**106b**), was synthesized as tetraarylborate salts, by abstraction of the tri-*tert*-butylsilyl or -germyl group (eq 60).[73−75] The salts **106**·Ar_4B^- were isolated as moisture- and air-sensitive yellow to yellow-orange crystals in more than 80% yield. While a solution of the TPB salt of **106a** in a CH_2Cl_2 solution was stable only below −78 °C, the TFPB and

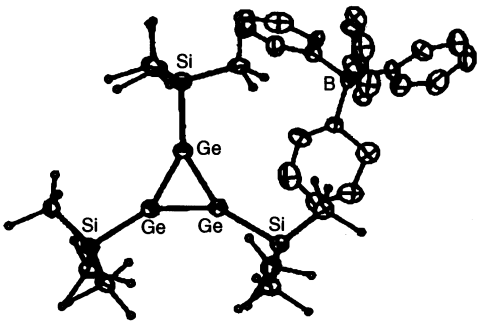
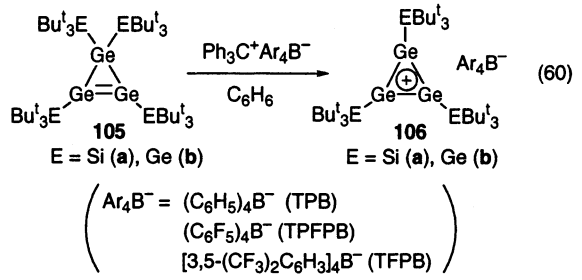
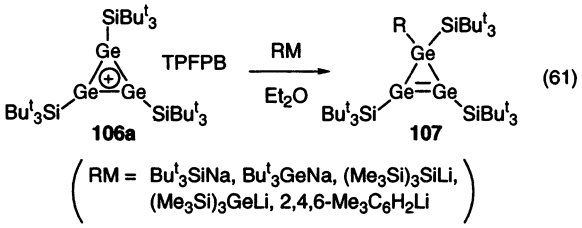


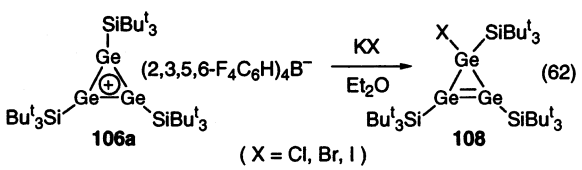
Figure 5. X-ray crystal structure of cyclotrigermenium salt **106a**·TPB. [Reprinted with permission from ref 73. Copyright 2002 American Association for the Advancement of Science.]



TPFPB salts of **106a** and **106b** were found to be stable at room temperature. X-ray crystallography was conducted on **106a**·TPB[73] and **106a**·TFPB.[74] As shown in Figure 5,[73] the result on **106a**·TPB indicated that the three Ge atoms form a nearly equilateral triangle, with an averaged Ge−Ge bond length of 2.326(4) Å, which is intermediate between the Ge=Ge double bond [2.239(4) Å] and the Ge−Ge single bond [2.522(4) Å] of the precursor **105a**.[76] Thus, the positive charge is delocalized over three Ge atoms to produce a structure similar to that of the cyclopropenylium cation. The Si atoms of the *t*-Bu$_3$Si substituents are located in approximately the same plane as the three-membered ring.

The cation **106a** reacted with Group 14 or carbon nucleophiles of rather large size to give unsymmetrically substituted derivatives of cyclotrigermenes **107** in more than 73% yield (eq 61).[77] Further, **106a** reacted with potassium halides to give halogen-substituted cyclotrigermenes **108** in 60−74% yield (eq 62).[78] It is to be noted that the halogen atom migrates





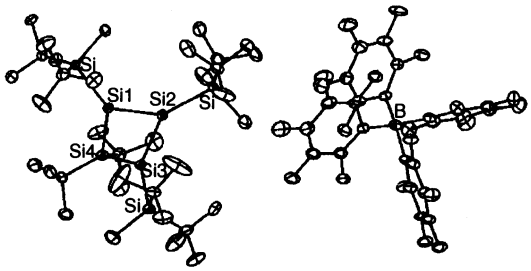
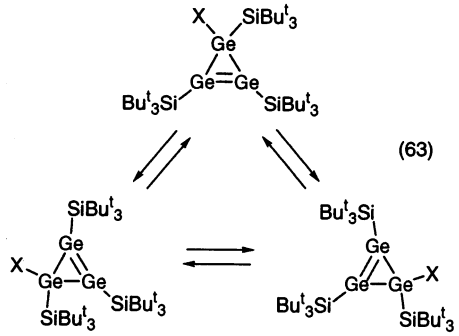
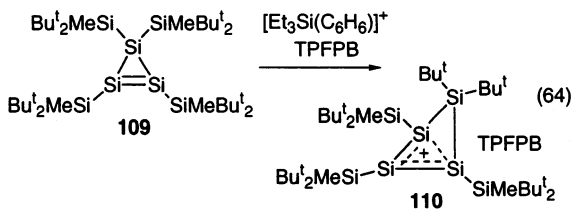


Figure 6. X-ray crystal structure of homocyclotrisilenylium salt **110**·TPFPB.

on the three-membered ring rapidly on the NMR time scale. From the results of dynamic NMR studies, the activation energy for this migration was determined to be 15.2 kcal mol^{-1} for X = Cl, 12.9 kcal mol^{-1} for X = Br, and 10.4 kcal mol^{-1} for X = I. The activation parameters were essentially independent of concentration and solvent polarity, suggesting that the halogen atom migrates intramolecularly, without intermediate formation of the cyclotrigermenylium cation (eq 63), which is different from the case of cyclopropenylium halides or azide.[79] The activation energies clearly indicate that the heavier halogen atom migrates more readily.

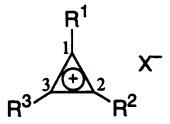


In sharp contrast to the above reaction (eq 60), the attempted silyl group abstraction from cyclotrisilene **109** with trityl tetraarylborate was unsuccessful. However, a reaction of **109** with [Et$_3$Si(benzene)]$^+$TPFPB was found to give a totally new salt of a free silyl cation in the condensed phase, the homocyclotrisilenylium cation **110**,[80] which is a silicon analogue of a homocyclopropenylium cation (eq 64). The reaction apparently took place by way of



abstraction of a methyl group on the saturated silicon atom by the [Et$_3$Si(benzene)]$^+$ cation, followed by rearrangement with a ring enlargement. The structure of salt **110**·TPFPB was determined by X-ray crystallography, as shown in Figure 6. The four-membered ring was found to be folded, the dihedral angle between the positively charged plane, Si1−Si2−Si3, and the plane, Si1−Si4−Si3, being 46.6°.

Table 2. Selected Lengths for the Endocyclic and Exocyclic Bonds in Cyclopropenylium Salts

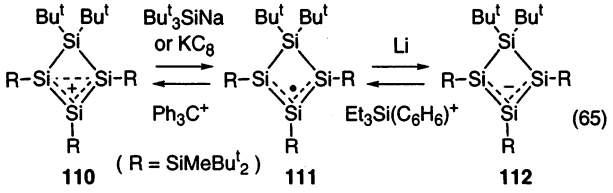


				bond length (Å)						
R^1	R^2	R^3	X	C1−C2	C2−C3	C3−C1	C1−R^1	C2−R^2	C3−R^3	ref
Ph	Ph	Ph	ClO_4	1.376	1.373	1.370	1.417	1.434	1.458	83
Ph	Ph	Ph	$TeBr_6$	1.373	1.384	1.396	1.446	1.433	1.426	85
Tript[a]	Tript[a]	Tript[a]	ClO_4	1.379(7) (average)			—[j]	—	—	86
c-Pr[b]	*c*-Pr[b]	*c*-Pr[b]	SbF_6	1.37(3) (average)			—	—	—	24
Ph	*c*-Pr[b]	*c*-Pr[b]	ClO_4	1.359(8) (average)			—	—	—	24
$Me_3SiC{\equiv}C$	Ph	Ph	$SbCl_6$	1.365(4)	1.379(4)	1.368(4)	1.401(4)	—	—	30
$Pr^i{}_3SiC{\equiv}C$	Ph	Ph	$SbCl_6$	1.358(4)	1.375(4)	1.367(5)	1.397(5)	—	—	30
$PhC{\equiv}C$	Ph	Ph	$SbCl_6$	1.363(7)	1.364(7)	1.362(7)	1.402(7)	—	—	30
t-Bu	*t*-Bu	*t*-Bu	HCl_2	1.372(1) (average)						87
Me_3Si	Me_3Si	Me_3Si	$SbCl_6$	1.391(4)	1.384(4)	1.375(4)	1.897(3)	1.897(3)	1.897(3)	18
PhS	PhS	PhS	ClO_4	1.368(3)	1.376(3)	1.372(3)	1.674(2)	1.685(2)	1.677(2)	88
Me_2N	Me_2N	Me_2N	ClO_4	1.363	1.362	1.363	1.326	1.337	1.337	84
Me_2N	Me_2N	Me_2N	$SbCl_6$	1.37(1)	1.37(1)	1.37(1)	1.318(5)	1.318(5)	1.318(5)	89
Me_2N	Me_2N	Me_2N	$NbCl_6$	1.380(3)	1.380(2)	1.380(3)	1.322(2)	1.322(2)	1.322(2)	90
Me_2N	Me_2N	Me_2N	$TaCl_6$	1.371(4)	1.371(2)	1.371(4)	1.323(3)	1.323(3)	1.323(3)	90
Me_2N	Me_2N	Me_2N	TCNQ[c]	1.395(9)	1.354(9)	1.378(11)	1.305(10)	1.324(7)	1.319(9)	91
Me_2N	Me_2N	Me_2N	DDQ[d]	1.375(4)	1.379(4)	1.379(4)	1.334(3)	1.317(4)	1.322(4)	92
NC_5H_{10}[e]	NC_5H_{10}[e]	NC_5H_{10}[e]	ClO_4	1.371(4)	1.382(4)	1.391(4)	1.322(4)	1.349(4)	1.329(4)	93
Cl	*i*-Pr_2N	i-Pr_2N	ClO_4	1.332(4)	1.427(5)	1.330(4)	1.724(3)	1.299(4)	1.272(4)	93
Py^+[f]	Me_2N	Me_2N	BF_4, E_5Cp[g]	1.358(8)	1.400(9)	1.345(8)	1.395(8)	1.299(7)	1.299(8)	94
Py^+[f]	Me_2N	Me_2N	$2E_5Cp$[g]	1.368(6)	1.424(6)	1.381(6)	1.394(5)	1.282(6)	1.289(5)	94
$[(Me_2N)_2C_3^+]O$[h]	Me_2N	Me_2N	ClO_4	1.331(12)	1.418(12)	1.361(12)	1.348(11)	1.304(11)	1.285(11)	64
Cl	Cl	Cl	$AlCl_4$	1.355(5)	1.357(5)	1.365(5)	1.629(3)	1.630(3)	1.634(4)	95
FeL_2Cp[i]	FeL_2Cp[i]	FeL_2Cp[i]	SbF_6	1.388(9)	1.375(9)	1.394(9)	1.913(6)	1.917(6)	1.919(7)	96

[a] 9-Triptycyl. [b] Cyclopropyl. [c] Radical anion of tetracyanoquinodimethane. [d] Radical anion of 2,3-dichloro-5,6-dicyanobenzoquinone. [e] Piperidino-. [f] Pyridyl-1-. [g] Pentakis(methoxycarbonyl)cyclopentadienide. [h] 2,3-Bis(dimethylamino)cyclopropenylium-1-yloxy-. [i] $Fe(CO)_2Cp$. [j] —, no data.

The distance between Si1 and Si3 was 2.692(2) Å, indicating the presence of considerable 1,3-orbital interaction to endow the homoaromaticity to cation **110**. The bond lengths of Si1−Si2 and Si2−Si3 were 2.240(2) and 2.244(2) Å, respectively, which are intermediate between the Si═Si double bond [2.138(2) Å] and the Si−Si single bond [2.364(3) and 2.352(3) Å] of the precursor **109**.

When the silyl cation salt **110**·TPFPB was treated either with *t*-Bu_3SiNa or with potassium graphite (KC_8) in ether, one-electron reduction took place, to give the cyclotetrasilenyl radical **111** as the first isolable silyl radical, as red-purple crystals in 67% yield (eq 65).[81] X-ray crystallography indicated that the four-membered ring is now almost planar, and **111** is regarded as an allyl-type radical. This radical can be further reduced with lithium metal to give the lithium salt of the anion **112** (eq 65).[82] X-ray crystal-



lography on the crystal **112**[Li(thf)]$^+$ showed that the four-membered ring deviates from planarity, and the lithium metal is bonded to Si3 with strong interaction with Si1═Si2 double bond. Anion **112** can be oxidized back to radical **111** by the reaction with [Et_3Si-(benzene)]$^+$TPFPB in benzene, and radical **111**, in turn, undergoes one-electron oxidation to regenerate cation **110** by the reaction with triphenylmethyl cation in benzene. Thus, this cyclotetrasilenyl system represents a new two-step, one-electron redox system.

D. X-ray Structure Determination

The first X-ray crystallography on the cyclopropenylium cation was conducted on a perchlorate salt of the triphenyl derivative.[83] The C−C bond length of the cyclopropenylium ring was found to be 1.373 ± 0.005 Å, appreciably shorter than the benzene C−C bond (1.398 Å). The average exocyclic single bond length of 1.436 Å is also considerably shorter than the normal $C(sp^2)-C(sp^2)$ single bond, reflecting the increased s character in the hybridization of the cyclopropenylium carbon. The phenyl groups are twisted in a propeller-like arrangement, making angles of 7.6, 12.1, and 21.2° with respect to the cyclopropenylium plane.

The second analysis was made on tris(dimethylamino)cyclopropenylium perchlorate.[84] The average C−C bond length of the three-membered ring was 1.363 Å, and the average exocyclic C−N bond length was 1.333 Å, which was intermediate between the length of a normal $C(sp)-N(sp^2)$ single bond (1.40−1.42 Å) and that of a C═N double bond (1.29 Å).

Since then, the analysis has been made on cyclopropenylium salts with various structures.[18,24,30,64,85−96] In general, the C−C bond length of the cyclopropenylium ring is similar to the values shown in the

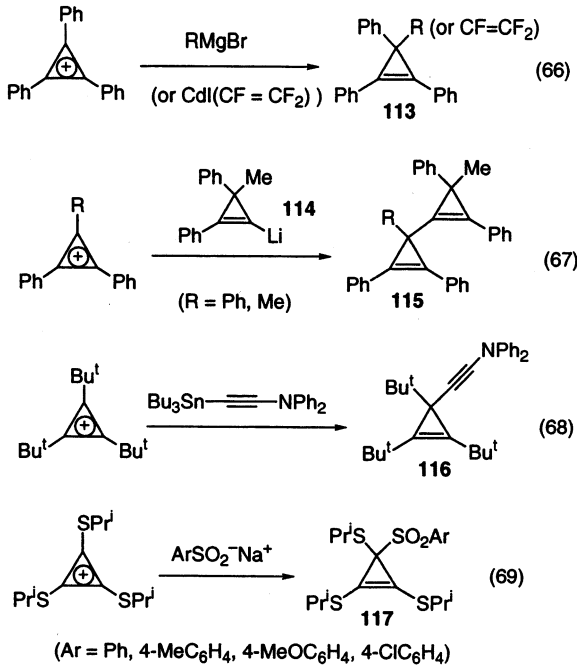
above two examples. The exact bond lengths for these bonds and exocyclic bonds are summarized in Table 2.

III. Reactions of Cyclopropenylium Cations

A. Reactions with Carbon Nucleophiles To Give Cyclopropenyl Compounds

1. Cation–Anion Combination Reactions

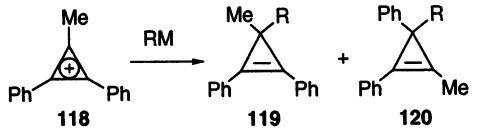
One of the most basic reactions of carbocations is the cation−anion combination reaction.[97] Thus, the reactions of cyclopropenylium cations with various carbon nucleophiles, i.e., organometallic reagents such as Grignard reagents and organolithium as well as organocadmium and organotin reagents, afford the corresponding 3-substituted cyclopropenes in fair to good yields. This is exemplified by the reaction of triphenylcyclopropenylium cation with various Grignard reagents and with perfluorovinylcadmium iodide to give 3-substituted 1,2,3-triphenylcyclopropenes **113** in excellent yield (76−96%) (eq 66).[98,99] The unsymmetrical dimers of cyclopropene **115** were also obtained in high yields by the reaction of the cyclopropenylium cation with 1-lithiocyclopropene derivative **114** (eq 67).[100] The reaction of tri-*tert*-butylcyclopropenylium bromide with (diphenylaminoethynyl)tributyltin also afforded the corresponding 3-ethynylcyclopropene derivative **116** in 53% yield (eq 68).[101] The reaction of tris(isopropylthio)cyclopropenylium perchlorate with sodium arene-*p*-sulfinate gave the corresponding 3-arenesulfonylcyclopropene **117** (eq 69).[102]

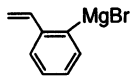
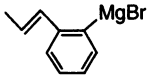
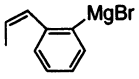
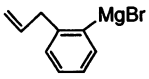
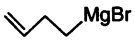
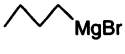
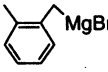
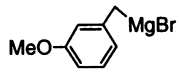


Reactions of unsymmetrically substituted cyclopropenylium cations, such as the 1,2-diphenyl-3-methyl derivative **118**, with Grignard and organolithium reagents were extensively studied.[98,103,104] As shown in Table 3, in most cases, symmetrical isomers **119** were major products, while unsymmetrical isomers **120** became major products for the reactions with benzyl-type Grignard reagents. From this tendency, it was suggested that, for the latter reaction, a single-electron-transfer pathway might be involved in the cation−anion reaction. This cyclopropenyl radical prefers to localize the odd electron on the phenylated carbon, thereby accounting for the preferential formation of the 1,3-diphenyl-substituted unsymmetrical isomers.[98]

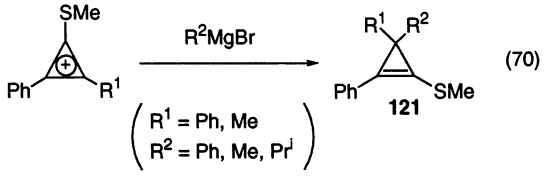
When 1-(methylthio)-2,3-diphenylcyclopropenylium (or 1-(methylthio)-2-methyl-3-phenylcyclopropenyli-

Table 3. Reactions of Cation 118 with Organometallic Reagents

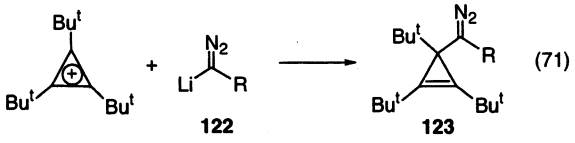


RM	119	120	ref
	64%	7%	103a
	90%	0%	103d
	55%	6%	103d
	38%	11%	103c
	71%	24%	103c
	49%	18%	103b
	50%	9%	103b
	76%	24%	104
	54%	46%	104
	52%	48%	104
	55%	45%	104
	64%	36%	104
	41%	59%	104
	36%	64%	104

um) bromide was allowed to react with various Grignard reagents, the attack of the anionic reagent occurred preferentially at the carbon bearing the phenyl (or methyl) group, to give 1-methylthio-1-cyclopropene derivative **121** as the major product (eq 70).[105−107] The thermolysis of the 1-methylthio-1-cyclopropene derivative afforded methylthio-substituted indene and/or butadiene derivatives in good yields.

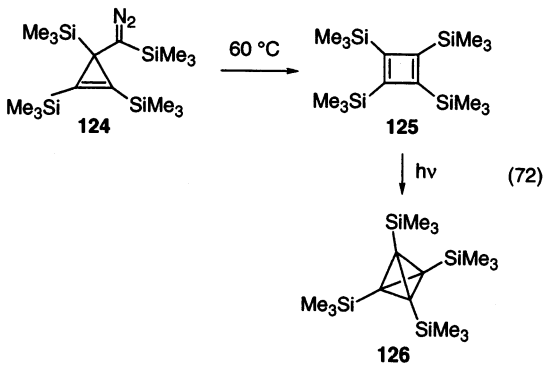


The tri-*tert*-butylcyclopropenylium cation was allowed to react with lithiated diazomethanes **122**, to give the cyclopropenyldiazomethanes **123** (eq 71), some of which were used as precursors to the kinetically stabilized cyclobutadienes and then to tetrahedrane derivatives (see below).[108−111]

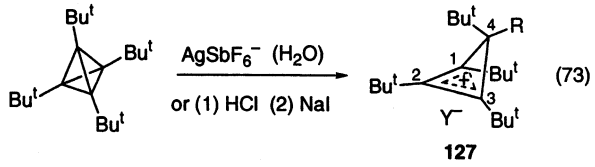


R	Yield (%)	ref
-Si(Ph)Me$_2$	25	108
-Si(OPr^i)Me$_2$	25	108
-GeMe$_3$	20	109
-1-Ad*	8	110
-Pr^i	15	110
-Bu^t	14	111
-SiMe$_3$	15	111
	26	117

The same methodology was applicable to the reaction of tris(trimethylsilyl)cyclopropenylium cation with **122** (R = SiMe$_3$), to give the tetrakis(trimethylsilyl) analogue of **123** (i.e., **124**), which was thermally converted to the tetrakis(trimethylsilyl)cyclobutadiene **125**[112] and then to a novel trimethylsilyl derivative of tetrahedrane **126** (eq 72).[113]

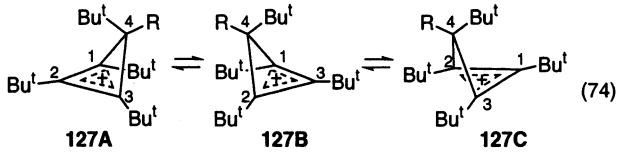


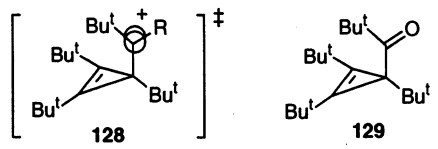
The highly stable hexafluoroantimonate salt of homocyclopropenylium cation **127** (R = OH, Y = SbF_6^-) was obtained in nearly quantitative yield by oxidative ring opening of tetra-*tert*-butyltetrahedrane with $AgSbF_6$ in moist ether (eq 73). Additionally, the



triiodide salt of the analogous cation **127** (R = H, Y = I_3^-) was obtained by treatment with hydrogen chloride in CH_2Cl_2, followed by anion exchange.[114] The precise structures of **127** (R = OH, Y = SbF_6^-) and **127** (R = H, Y = I_3^-) were determined by X-ray crystallography.[114] Their X-ray structures are quite similar. The characteristic features are the bending angle of the four-membered ring, which is 37.3° for **127** (R = H) and 36.4° for **127** (R = OH), and the distance between the C-1 and C-3 carbons, which is 1.806(6) Å for **127** (R = H) and 1.833(4) Å for **127** (R = OH), indicating considerable 1,3-interaction in the homocyclopropenylium structure.

Another characteristic feature of the cation **127** (R = OH) is its fluxional behavior, that is, a "walk" rearrangement.[115] The ^{1}H NMR spectrum exhibited only two signals for *t*-Bu protons and one signal for the OH proton at room temperature. On cooling of the sample to −10 °C, one of the *t*-Bu signal split into two signals in the intensity ratio of 2:1, while the other two signals remained unchanged. In accord with this, the ^{13}C NMR spectrum at room temperature exhibited only four signals, at δ 29.3 (*t*-Bu on C-4), 30.9 (*t*-Bu on C-1,2,3), 41.2 (quaternary, *t*-Bu on C-4), and 101.2 ppm (C-4). All other signals were broadened and hidden under noise. At −20 °C, the expected signals were observed at δ 29.1 (*t*-Bu on C-4), 30.6 (*t*-Bu on C-1,3), 31.3 (*t*-Bu on C-2), 34.9 (quaternary, *t*-Bu on C-2), 38.1 (quaternary, *t*-Bu on C-1,3), 40.9 (quaternary, *t*-Bu on C-4), 101.0 (C-4), 161.5 (C-1,3), and 184.9 ppm (C-2). The reversible changes in the spectra implied a dynamic process in which the olefinic ring portions in **127** are equilibrated, while C-4 and the substituents attached to it did not show any change. This observation is explained by the occurrence of the "walk" rearrangement among **127A**, **127B**, and **127C** (eq 74). From

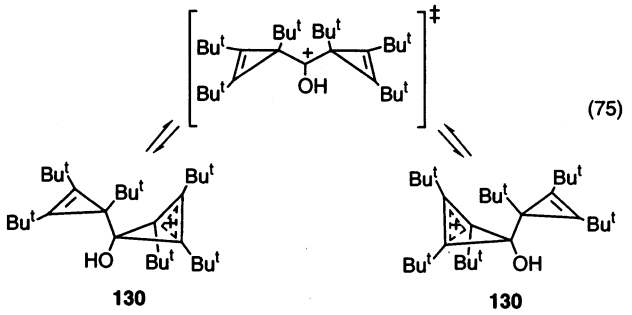




the coalescence temperature, an activation barrier of $\Delta G^{\ddagger}$ was calculated as 15 kcal mol^{-1}. Since the orientation of substituents at C-4 remained unchanged, the bond cleavage must have taken place

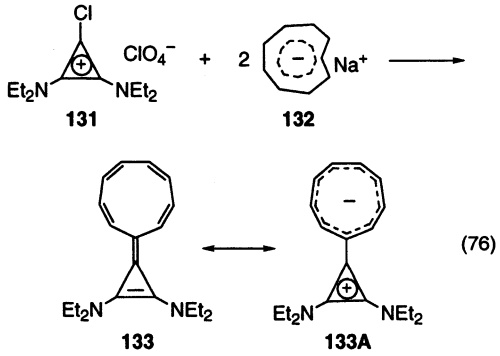
via the transition-state structure **128**. Actually, the cyclopropenylcarbinyl cation having the same geometry as **128** (R = OH) was generated by dissolving the ketone **129** in magic acid at low temperature (−90 °C) and confirmed by ^{1}H and ^{13}C NMR spectroscopy.[116]

A similar "walk" rearrangement and a further intramolecular exchange of the positive charge between the cyclopropenyl and homocyclopropenylium cation moieties were observed for the cyclopropenyl-substituted homocyclopropenylium cation **130**, as shown in eq 75.[117]



(75)

The reaction of 1-chloro-2,3-bis(diethylamino)cyclopropenylium perchlorate (**131**) with sodium (*Z*,*Z*,*Z*,*E*)-cyclononatetraenide (**132**) at −60 °C proceeded with a configurational change in the nine-membered ring, to give the nonatriafulvalene **133** as pale yellow crystals in 54% yield (eq 76).[118] The contribution of

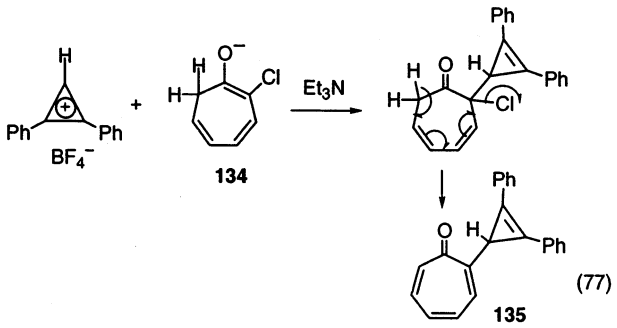


(76)

the dipolar structure with Hückel aromaticity, **133A**, was shown to be quite large, as judged from the downfield shift (averaged $\Delta\delta$ 1.2 ppm) of the ^{1}H NMR chemical shift of the nine-membered ring protons as compared with those of nonpolar nonafulvene and the similarity of the ethyl protons' shift to those of **131**; furthermore, the ^{13}C NMR signals of the nine-membered-ring carbons were upfield shifted by an average $\Delta\delta$ of 16 ppm as compared with those of nonpolar nonafulvene.

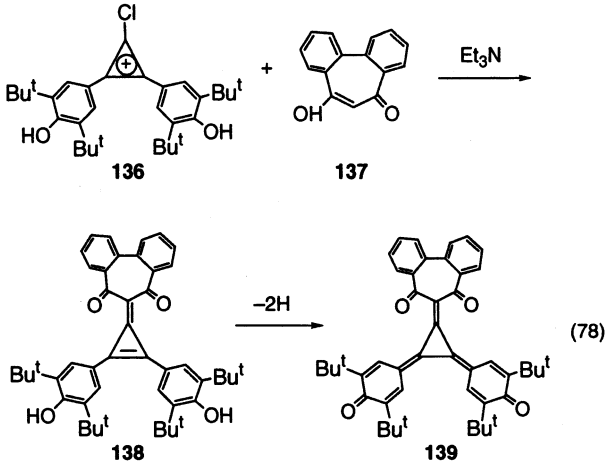
Diphenylcyclopropenylium tetrafluoroborate reacted with the enolate of 2-chlorotropone **134**, which is considered as the tropone with reverse polarity (umpolung), in the presence of triethylamine, to give 2-cyclopropenyltropone **135** in 75% yield (eq 77).[119]

With an intention to construct an extensively π-conjugated system, the 1,2-diaryl-3-chlorocyclopropenylium ion **136** was allowed to react with dibenzo-β-tropolone **137** in the presence of triethylamine, to give triafulvene derivative **138** in 20% yield (eq 78).[120]



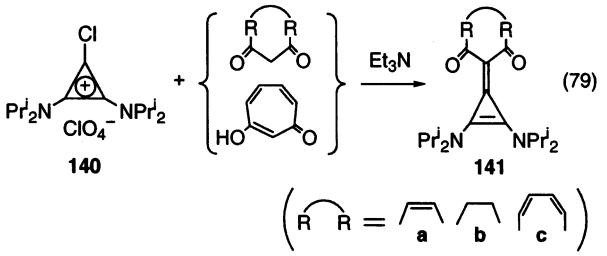
(77)

The oxidation of **138** under basic conditions afforded the planar and fully conjugated diquinocyclopropane **139**, which has the longest-wavelength absorption at 619 nm. This methodology of the synthesis of various types of polyquinocycloalkanes was first found and developed by West.[121]



(78)

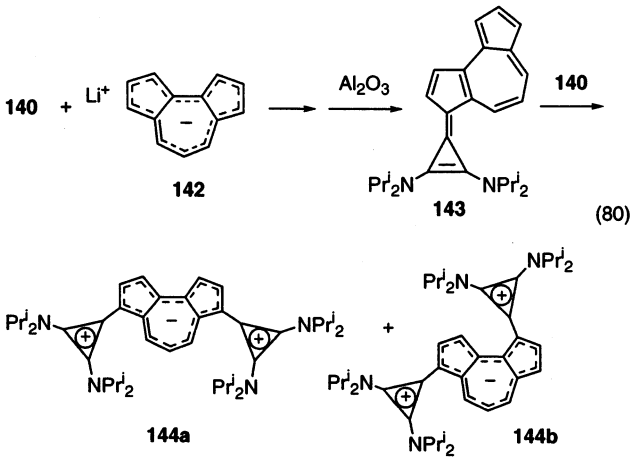
Similarly, 1-chloro-2,3-bis(diisopropylamino)cyclopropenylium perchlorate (**140**) reacted with a series of cyclic 1,3-diketones (or its enol) to give triafulvene derivatives **141** (eq 79).[122] The results of ^{13}C NMR indicated that the polarization of the central bond in **141** decreases in the order **141a**, **141b**, **141c**.



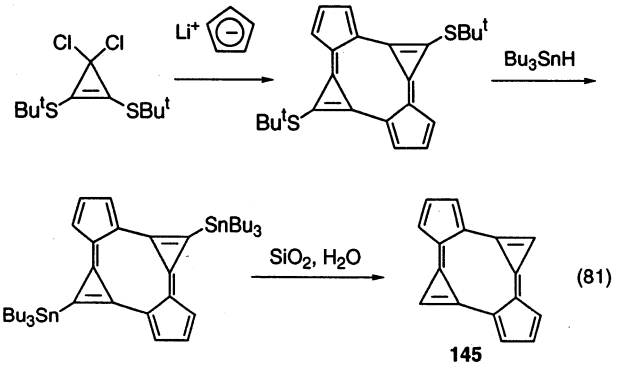
(79)

The reaction of cation **140** with cyclopent[*e*]azulenide ion (**142**) was also conducted. When treated with basic alumina, the product mixture afforded selectively the calicene-fused azulene **143** as red-purple crystals in 32% yield (eq 80).[123] This product was further reacted with cation **140** to give a 2:3 mixture of the adducts **144a** and **144b**, in which a large contribution of the tripolar mesomeric forms is apparent from the spectral data.

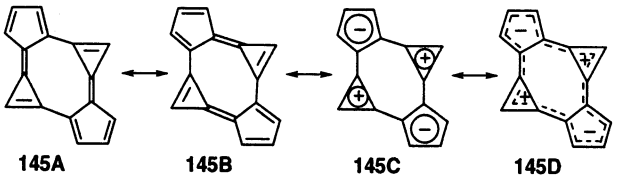
The dimer of calicene, the cyclic bicalicene **145**, was synthesized, as shown in eq 81, by the reaction of



1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropene and cyclopentadienide anion as a key step.[124b] The struc-

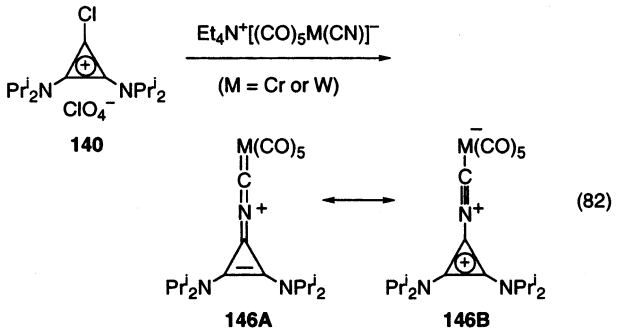


ture of **145** was determined by X-ray crystallography.[124a] The skeleton was found to be planar, and almost no bond alternation was observed, indicating the presence of D_{2h} symmetry. From the ^{1}H NMR data,[124b] there is no paramagnetic ring current expected for a peripheral 16π system. Its electronic structure is expressed by resonance structues **145A**, **145B**, **145C**, and **145D**. The resonance stabilization



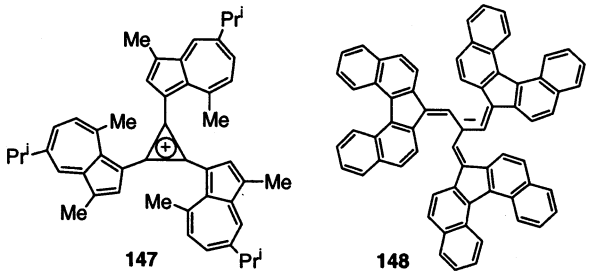
energy, calculated by the graph-theoretical method,[125] was found to be 0.193β for **145**, considerably larger than that of calicene (0.038 β). This stability of **145** is attributed to the large contribution of the tetrapolar structure **145C** and **145D** to the ground state. From the ^{13}C NMR data, 36−45% polarization was estimated to be present in **145**.

The reaction of 1-chloro-2,3-bis(diisopropylamino)-cyclopropenylium salts (**140**) with a cyano-metal complexes, $Et_4N[(CO)_5M(CN)]$ (M = Cr or W), in CH_2Cl_2 afforded the 2-azaallenylidene complexes **146** in fair yields (eq 82).[126] The result of X-ray crystallography on **146** (M = W) indicated that its structure is best described as a resonance hybrid of two canonical forms, the cumulene form **146A** and the isocyanide form **146B**, with cyclopropenylium character.



2. Carbocation–Carbanion Salt Formation

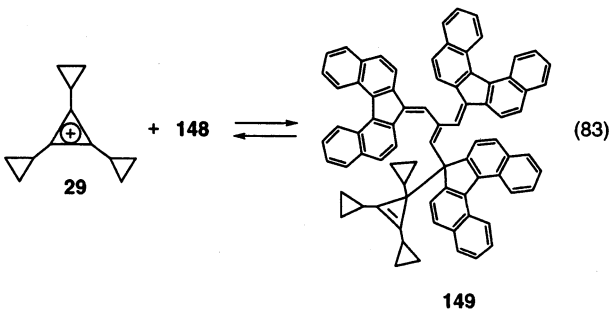
Although it is common knowledge that the combination of a carbocation and a carbanion provides a covalent bond by C−C σ-bond formation, it can form a carbocation−carbanion salt when the cationic and anionic species have sufficiently high thermodynamic stability. Thus, the first "hydrocarbon salt" was prepared by mixing the THF solutions of tris(3-guaiazulenyl)cyclopropenylium cation (**147**), which is the most stable all-hydrocarbon cyclopropenylium cation, with a pK_{R^+} value ≥10,[127] and tris(7*H*-dibenzo-



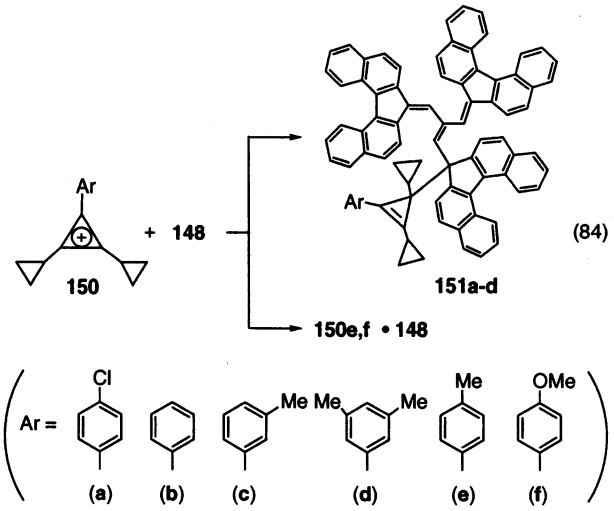
[*c*,*g*]fluorenylidenemethyl)methide anion (**148**), which is the most stable hydrocarbon anion, with a pK_a value for **148**-H of ∼6.[128] The salt was recrystallized from DMSO to give stable greenish-black crystals in ≥60% yield.[129] The UV−vis and IR spectra of the hydrocarbon salt **147·148** were expressed by the superposition of the spectra of cationic and anionic moieties, and no charge-transfer band was observed.

The "hydrocarbon salt" was also formed, in 60% yield, by mixing the THF solutions of tricyclopropylcyclopropenylium cation (**29**) and the anion **148**.[130] When dissolved in chloroform, however, the salt **29·148** rapidly underwent C−C bond formation, to give the covalent compound **149**, which was identified by ^{1}H NMR measurements. This covalent hydrocarbon could exist only in solution, since evaporation of the solvent or recrystallization upon cooling afforded the salt **29·148** (eq 83).

To examine the limit of the carbocation stability, which controls the formation of salts or covalent compounds, against carbanion **148**, a series of 1-aryl-2,3-dicyclopropylcyclopropenylium cations **150a**−**f** were synthesized.[131] The electrochemically determined value of reduction potential of these cations increased in the order **150a** (−1.412 V vs Ag/$AgNO_3$) < **150b** (−1.525 V) < **150c** (−1.532 V) < **150d** (−1.566 V) < **150e** (−1.583 V) < **150f** (−1.632 V).



This order can be supposed to reflect the order of each cation's thermodynamic stability.[132] The pK_{R^+} value of **150b** was determined to be 7.09 ± 0.05,[24] and that of **150e** was determined to be 7.29 ± 0.20. Despite the similar thermodynamic stabilities of **150a**−**f**, products from the reaction of these cations with anion **148** were quite distinguishable. When a THF−acetonitrile solution of any one of **150a**−**d** (ClO_4^- or BF_4^- salts) was added to a deep-green-colored THF solution of carbanion **148**, the color immediately turned brownish-orange, and the covalent hydrocarbons **151a**−**d** were formed in almost quantitative yields (eq 84).[131] In contrast, the deep green color of



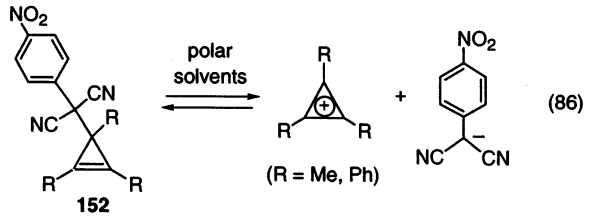
148 persisted when a solution of the ClO_4^- salt of **150e** or **150f** was added to the THF solution of **148**, and the corresponding "hydrocarbon salt" was obtained as a dark green powder upon evaporation of the solvent. Thus, the borderline between the occurrence of the two types of reactions turned out to be present between the cations **150d** and **150e**. The slight difference (0.017 V) in the reduction potentials of these cations suggests that only a slight difference (0.4 kcal/mol) in thermodynamic stability can switch the type of bond.

When dissolved in DMSO, both covalent compounds **151a**−**d** and salts **150e**,**f**·**148** were found to form equilibrated solutions consisting of the heterolytically dissociated carbocations/carbanions and the covalent compounds (eq 85). The degree of dissocia-

$$\mathbf{150} + \mathbf{148} \overset{\text{DMSO}}{\rightleftharpoons} \mathbf{151} \qquad (85)$$

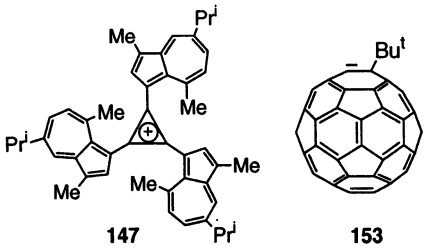
tion was apparently dependent on the thermodynamic stability of the carbocations, the $\Delta G°$ value of heterolysis being correlated to the reduction potential of the cations.[131a]

This kind of equilibrated heterolysis of carbon−carbon covalent bonds, to form carbocations and carbanions, was first found by Arnett and co-workers for the covalent compound **152**, formed from trimethyl- and triphenylcyclopropenylium cations and (*p*-nitrophenyl)dicyanomethyl anion (eq 86).[133] They

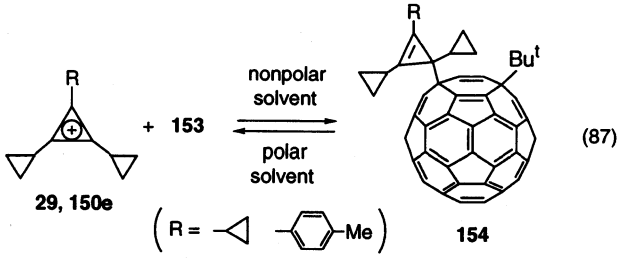


measured heats of reaction between a large variety of carbocations (including trimethyl- and triphenylcyclopropenylium ions) and carbanions and obtained heats of heterolysis for the corresponding covalent compounds by changing the sign ($\Delta H_{het} = -\Delta H_{rxn}$). On the basis of the results of this systematic study, they successfully demonstrated that the heats of heterolysis are correlated with thermodynamic stability indexes of the carbocation (pK_{R^+}) and of the carbanion (pK_a of conjugate acid): $\Delta H_{het} = apK_a + bpK_{R^+}$ + constant.[134,97a] Furthermore, heats of homolysis have been determined by combining heats of heterolysis with redox potentials for a series of carbocations and carbanions.

The acidity (pK_a) of the *tert*-butyl derivative of 1,2-dihydro[60]fullerene (*t*-BuC_{60}H) has been determined to be 5.7,[135] which is among the lowest values for hydrocarbon molecules; i.e., this is one of the most acidic hydrocarbons. Thus, a similar type of "hydrocarbon salt" was successfully synthesized from the cation **147** and the *t*-BuC_{60} anion (**153**).[136]



In contrast, the reaction of the *t*-BuC_{60}^- anion (**153**) with tricyclopropylcyclopropenylium cation (**29**) and 1,2-dicyclopropyl-3-(4-methylphenyl)cyclopropenylium cation (**150e**) underwent C−C covalent bond formation to give 1-*tert*-butyl-4-(2-cyclopropen-1-yl)-1,4-dihydro[60]fullerenes **154** (eq 87).[137] The newly



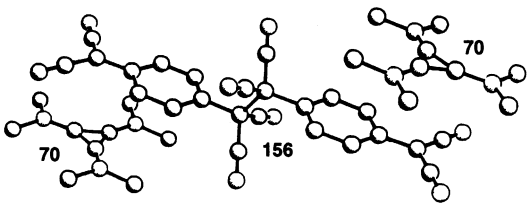


Figure 7. X-ray crystal structure of crystal A ((**70**)$_2$·**156**). [Reprinted with permission from ref 91. Copyright 2003 Taylor & Francis Ltd. (http://www.tandf.co.uk/journals).]

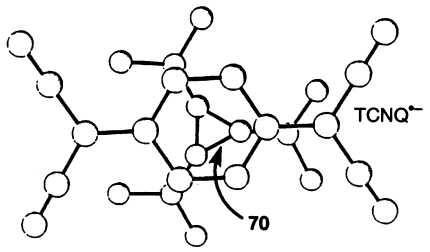
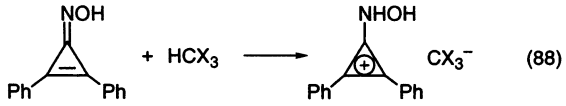


Figure 8. X-ray crystal structure of crystal B (**70**·TCNQ$^{\bullet-}$). [Reprinted with permission from ref 91. Copyright 2003 Taylor & Francis Ltd. (http://www.tandf.co.uk/journals).]

formed C−C bond was found to undergo reversible heterolysis in polar solvents to give the original ions. Tri-*tert*-butylcyclopropenylium cation, although less stable (pK_{R^+} 6.5)[138] than **29**, did not cause any C−C bond formation with the carbanion **153**, indicating that steric hindrance effectively suppresses carbocation−carbanion coordination.

When strong carbon acids such as nitroform (HC(NO$_2$)$_3$) and cyanoform (HC(CN)$_3$) were allowed to react with diphenylcyclopropenone oxime, carbocation−carbanion salts 1-(hydroxyamino)-2,3-diphenylcyclopropenylium trinitromethide (**155a**) and tricyanomethide (**155b**) were obtained as yellow solids in 85% and 65% yield, respectively (eq 88).[139]



155a (X = NO$_2$), **155b** (X = CN)

Tris(dimethylamino)cyclopropenylium cation (**70**) formed salts with the tetracyanoquinodimethane (TCNQ) radical anion. These salts afforded two different crystals, depending on the polarity of the solvent.[91] From an acetone−water mixed solvent, a yellow-colored crystal was obtained. Its structure was determined, by X-ray crystallography, to be the 2:1 complex (crystal A) of cation **70** and a dimer of TCNQ radical anion (**156**). As shown in Figure 7, the TCNQ moiety is dimerized by forming a long (1.62 Å) σ-bond between the dicyanomethylene carbons. On the other hand, when the salt was dissolved in acetonitrile−xylene and heated to 100 °C to evaporate off acetonitrile, a black crystal was obtained (crystal B). X-ray crystallography of this crystal indicated its structure to be the 1:1 complex of cation **70** and TCNQ radical anion, overlapped in a face-to-face arrangement, forming a mixed stack (Figure 8). A variable-temperature EPR experiment indicated that the diamagnetic form of crystal A changes to the paramagnetic form of crystal B upon heating at 79 °C, and upon

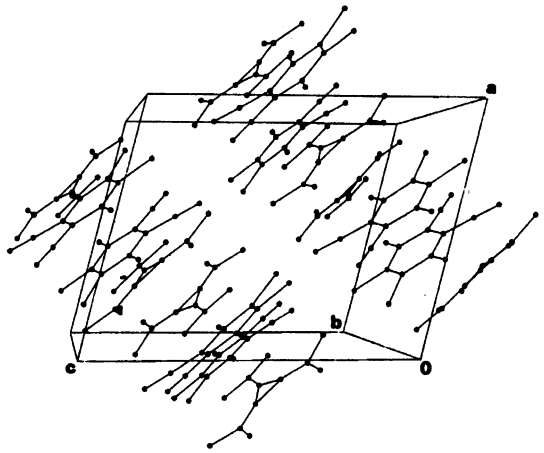
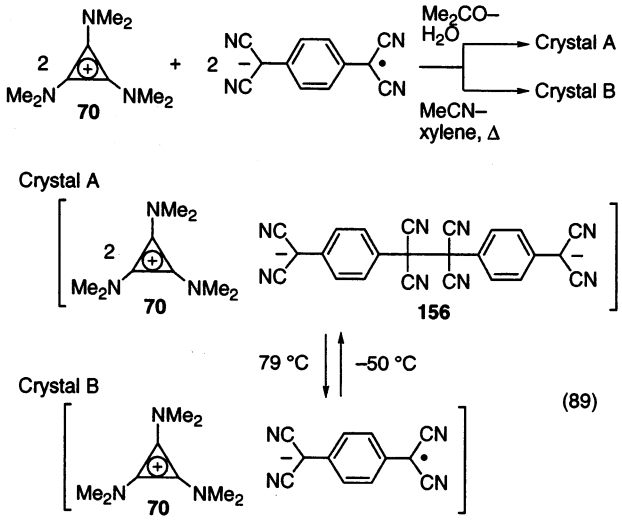


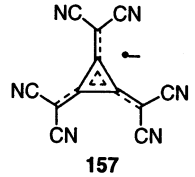
Figure 9. View of **70**·DDQ$^{\bullet-}$ unit cell packing.

cooling to −50 °C the σ-bond formation between the TCNQ radical anions takes place again (eq 89).



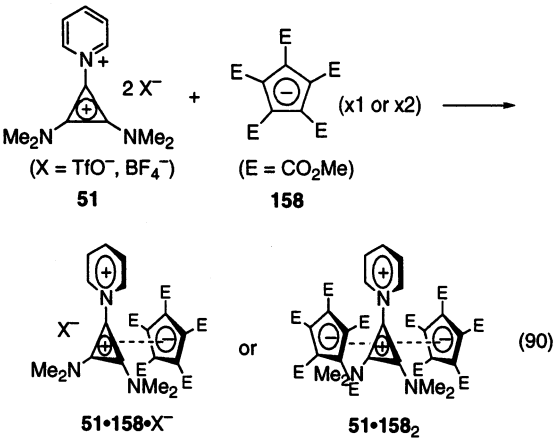
Similarly, the salt of cation **70** (D$^+$) and the 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) radical anion (A$^-$) formed a 1:1 crystal, for which X-ray crystallography indicated that cationic and anionic moieties were superposed in a face-to-face arrangement (as in Figure 8), despite the difference in their symmetries, D_{3h} for **70** and C_{2v} for DDQ.[92] Additionally, the stacking pattern of ...D$^+$A$^-$A$^-$D$^+$... was observed, as shown in Figure 9. This is due to the tendency of the two DDQ$^-$ moieties to form dimers.

Cation **70** also formed a complex with the radical anion of hexacyanotrimethylenecyclopropanide (**157**) as a purple solid, which turned out to have antiferromagnetic coupling.[140]



When the triflate or tetrafluoroborate salt of *N*-[2,3-bis(dimethylamino)cyclopropenyliopyridinium dication (**51**) was mixed with 1 or 2 equiv of pentakis(methoxycarbonyl)cyclopentadienide anion (**158**), a

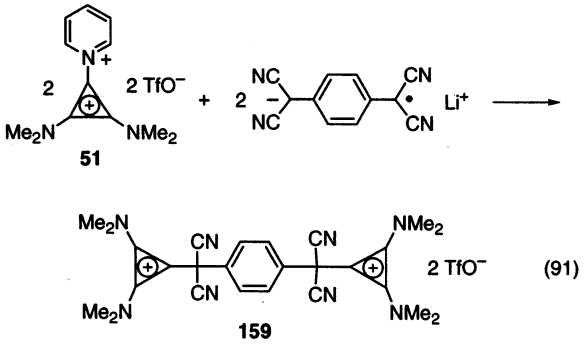
yellow-colored charge-transfer complex (**51·158**·X^- or **51·158**$_2$) was formed (eq 90).[141] The charge-transfer



(90)

band was observed at 410−420 nm for both of these complexes. The structures of these complexes were determined by X-ray crystallography. The crystal of **51·158**·X^- consisted of infinite stacks, in which dications and cyclopentadienide rings alternated in a sandwich-type manner. It was the cyclopropenylium and not the pyridinium ring which was nearly at the face-to-face position with the anionic C_5 ring, and the intermolecular spacing was 3.39−3.46 Å. On the other hand, in the crystal of **51·158**$_2$, columns consisting of discrete anion−dication−anion units are found, with the rings oriented approximately parallel with each other. Again, the anions were associated with the cyclopropenylium rather than the pyridinium ring, with an intermolecular spacing of 3.44−3.51 Å.

In contrast, when equimolar amounts of dication **51** and the lithium salt of the tetracyanoquinodimethane (TCNQ) radical anion were combined, no isolable charge-transfer complex was obtained. Rather, the novel dicationic salt **159** was formed in 91% yield (eq 91).[141] The salt **159** apparently resulted from an addition−elimination reaction of TCNQ radical anion at the three-membered ring of **51**.



(91)

B. Reactions with Heteroatom Nucleophiles

Upon reaction with alkoxide or hydroxide ions, the cyclopropenylium cations bearing no heteroatom substituent afford the derivatives of cyclopropenyl ether,[142] while the monochloro-[8b,35a,127,143] or triaminosubstituted cations[144] give the corresponding cyclopropenone derivatives. The reactions affording cyclopropenones and their heteroanalogues (=S, =Se, =NR) will be described in later sections.

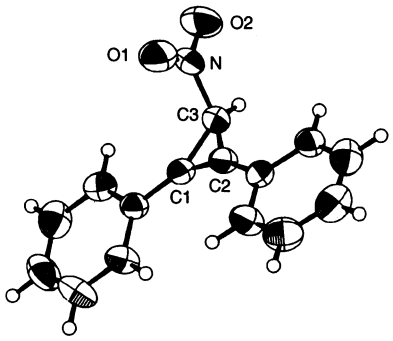
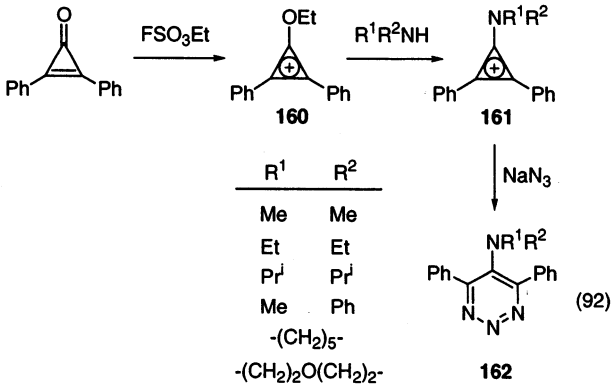


Figure 10. X-ray crystal structure of **163**.

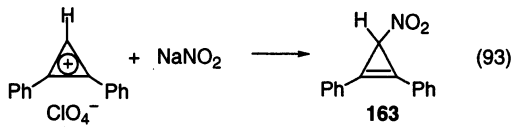
The 1-ethoxy-2,3-diphenylcyclopropenylium cation (**160**), prepared in situ from the corresponding cyclopropenone and ethyl fluorosulfate, reacted with various secondary amines to give 1-amino-2,3-diphenylcyclopropenylium fluorosulfates (**161**) in moderate yields.[145] Further reaction of **161** with sodium azide afforded 5-amino-1,2,3-triazines **162** in good yields (73−93%) (eq 92).



(92)

The cyclopropenylium cations having *tert*-butyl or aryl substituents also react with azide ion to give the covalent cyclopropenyl azides in fair to good yields.[79b,146]

The product obtained from the reaction of diphenylcyclopropenylium perchlorate (***Caution:*** *This perchlorate is explosive!*) with sodium nitrite in 67% yield (eq 93)[147] was determined to be the first nitrocyclopropene derivative, 1,2-diphenyl-3-nitrocyclopropene (**163**), by X-ray crystallography.[148] As shown in

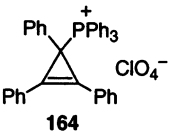


(93)

Figure 10, the plane of the NO_2 group bisects the three-membered ring for the maximum interaction between the Walsh-type HOMO of the cyclopropene moiety and the LUMO of NO_2. The bonds C1−C3 [1.483(6) Å] and C2−C3 [1.482(6) Å] are significantly shorter than typical bonds in cyclopropenes with π-acceptor substituents,[149] which fall in the range 1.500−1.544 Å. In addition, the C3−N bond [1.523(6) Å] is significantly longer than the 1.476−1.486 Å range exhibited by nitrocyclopropanes.[150] These struc-

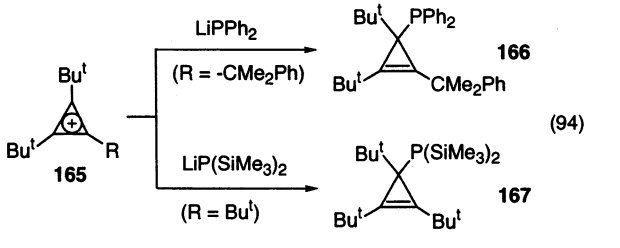
tural characteristics imply the presence of some ionic character in the nitrocyclopropene **163**, which is in agreement with its ready ionization.[147]

The reaction of triphenylcyclopropenylium perchlorate with triphenylphosphine gave (cyclopropenyl)-triphenylphosphonium perchlorate **164** in quantitative yield.[151]

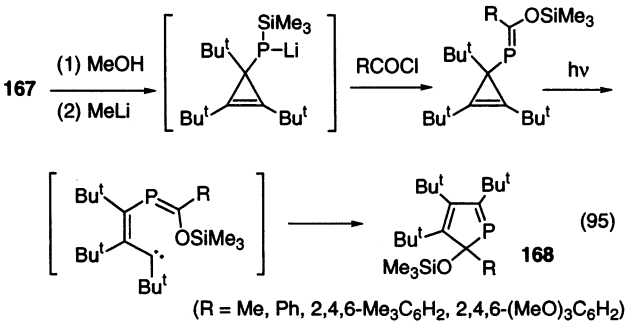


164

The reactions of *tert*-butyl-substituted cyclopropenylium cations **165** with lithium diphenylphosphide[152] or bis(trimethylsilyl)phosphide[153] afforded the corresponding 3-phosphinocyclopropenes **166** and **167** in 85% and 92% yield, respectively (eq 94). The [bis(trimethylsilyl)phosphino]cyclopropene **167** can undergo further reactions to afford 2*H*-phosphole derivatives **168**, as shown in eq 95.[153]



(94)



(95)

(R = Me, Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-$(MeO)_3C_6H_2$)

Similarly, tri-*tert*-butylcyclopropenylium cation smoothly reacted with polysilyllithium reagents to give 3-silylcyclopropenes **169** in good yields (eq 96).[154] X-ray crystallography of some of the products **169** (R = phenyl, 2,4,6-trimethylphenyl) indicated that the C(cyclopropenyl)−Si bond was elongated [1.940(4) and 1.959(4) Å, respectively] compared with the typical value of the C−Si bond length of 1.89 Å due to the severe steric congestion around this bond.

(96)

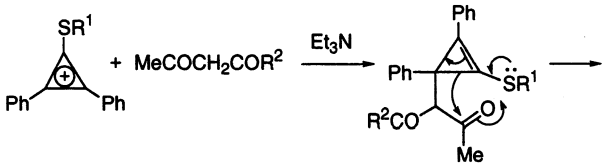
(R = $SiMe_3$, Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-$Pr^i_3C_6H_2$)

C. Reactions with Nucleophiles with Ring Opening

1. Formation of Five-Membered Rings

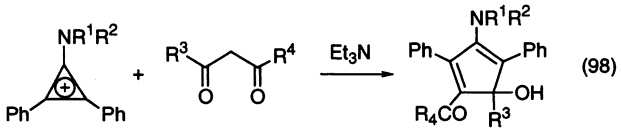
Cyclopropenylium cations can serve as three-carbon building blocks in organic synthesis. Thus, cyclopropenylium cations having phenyl, amino, and alkylthio substituents react with nitrogen nucleophiles such as hydrazine, aliphatic amines, and azides to give five- or six-membered nitrogen heterocycles.[155−158]

On the other hand, 1-(alkylthio)-2,3-diphenylcyclopropenylium ions reacted with 2,4-pentanedione or ethyl acetylacetate in the presence of triethylamine to give cyclopentadienol derivatives **170** in moderate yields.[159] The reaction involves the initial attack of the carbanionic species to the phenyl-substituted carbon of the three-membered ring and a subsequent ring enlargement, as shown in eq 97. In the same way, 1-(dialkylamino)-2,3-diphenylcyclopropenylium tetrafluoroborate reacted with 1,3-diketones to give 3-amino-2,4-cyclopentadien-1-ol derivatives **171** selectively (eq 98).[160]



(97)

(R^1 = Me, Et, CH_2Ph R^2 = Me, OEt)



(98)

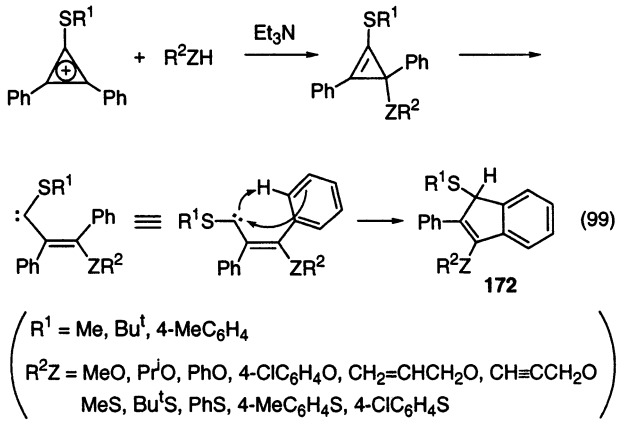
R^1	R^2
Me	Me
Et	Et
Me	Ph
-$(CH_2)_4$-	
-$(CH_2)_5$-	
-$(CH_2)_2O(CH_2)_2$-	

R^3	R^4
Me	Me
Me	Ph
Ph	Ph
Me	OMe
Me	OEt
Me	O-Bu^t
OEt	OEt
-$(CH_2)_2$-	
-$(CH_2)_3$-	
-$CH_2CMe_2CH_2$-	

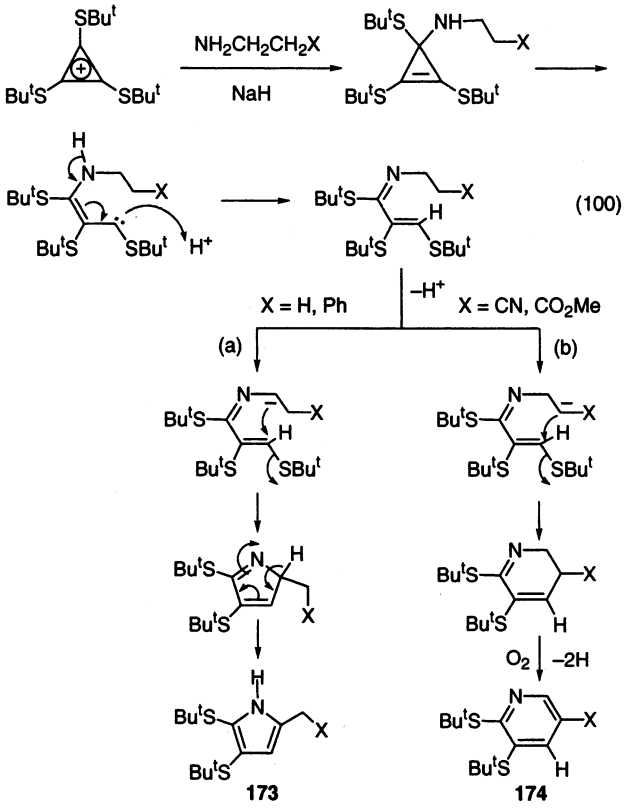
171

The reaction of 1-alkylthio- or 1-arylthio-2,3-diphenylcyclopropenylium ions with alcohols, phenols, and thiols in the presence of triethylamine at 80 °C afforded 1-alkylthio- or 1-arylthio-1*H*-indenes **172** in fair to moderate yields.[161] This reaction apparently proceeds through the formation of the corresponding 1-alkylthio- or arylthio-1-cyclopropene derivatives, followed by the cyclopropene → vinylcarbene rearrangement, as shown in eq 99. In the case of the reaction with *N*-methylaniline, the indene **172**, with N(Me)Ph group for ZR^2, was obtained.[162]

The reaction of tris(*tert*-butylthio)cyclopropenylium perchlorate with derivatives of primary amines and *β*-amino acids was investigated in detail as a new methodology for heterocycle synthesis.[163] The reaction was highly dependent on the structure of the

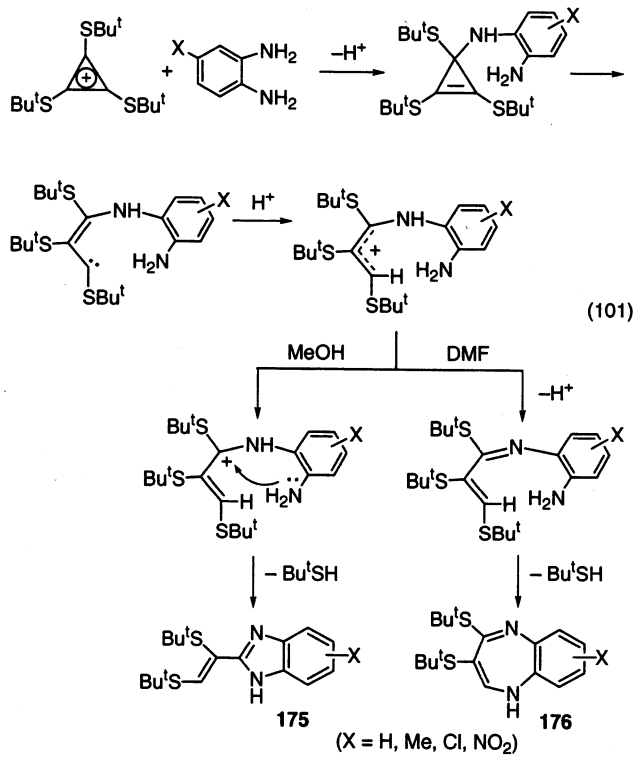


amine. Thus, when the reaction was conducted with ethylamine or 2-phenylethylamine in the presence of NaH in DMF, 2,3-bis(*tert*-butylthio)pyrrole derivatives **173** were obtained in 65−69% yields (eq 100a), whereas the reaction with various derivatives of *β*-amino acids gave 2,3-bis(*tert*-butylthio)pyridine derivatives **174** in fair to good yields (eq 100b). The reaction is considered to proceed via the cyclopropene → vinylcarbene rearrangement.

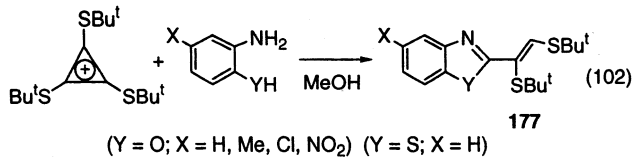


Similarly, the reaction of 1-alkylthio- or 1-arylthio-2,3-diphenylcyclopropenylium cations with *N*-alkyl- or *N*-arylbenzylamines gave 1-alkyl- or 1-aryl-2,3-diphenylpyrroles.[164]

On the other hand, the reaction of tris(*tert*-butylthio)cyclopropenylium perchlorate with *o*-phenylenediamine, having various substituents, in methanol afforded (*Z*)-2-[1′,2′-bis(*tert*-butylthio)vinyl]benzimidazole derivatives **175**, while 1*H*-3,4-bis(*tert*-butylthio)-1,5-benzodiazepine derivatives **176** were obtained when the reaction was conducted in DMF.[165] Equation 101 sums up a plausible mechanism for this transformation.



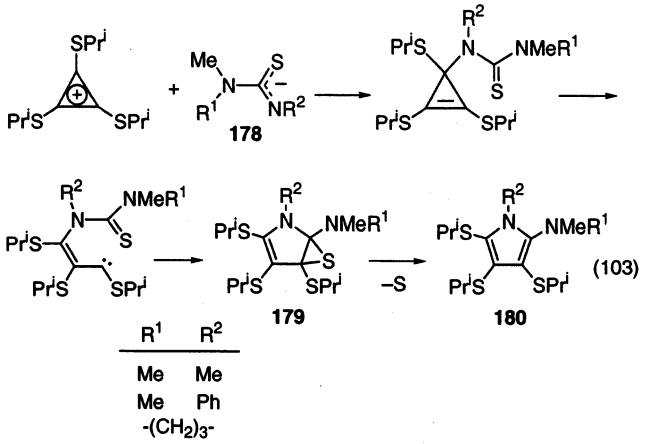
The reaction of the same trithiocyclopropenylium cation with *o*-aminophenols and with *o*-aminothiophenol in methanol afforded the corresponding benzoxazoles **177** (Y = O) and benzothiazole **177** (X = H, Y = S) in good yields (eq 102).[163]

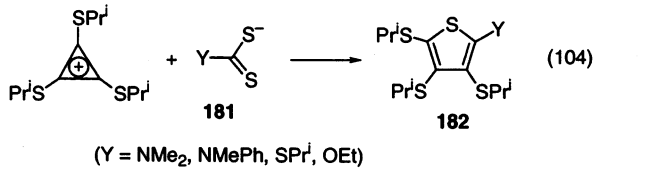


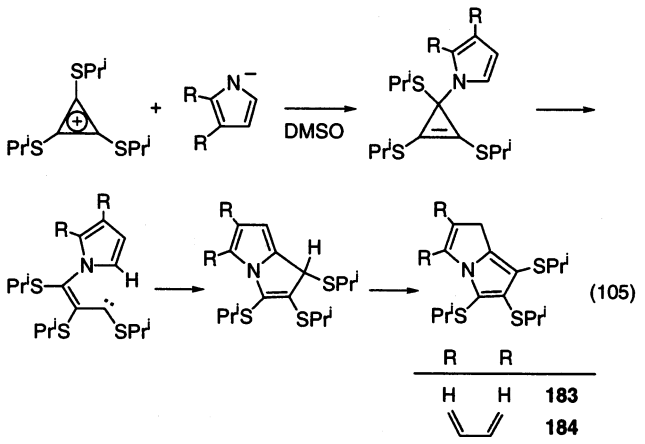
When tris(isopropylthio)cyclopropenylium perchlorate was allowed to react with thioureid anions **178** in acetonitrile at room temperature, the vinylcarbene intermediates underwent intramolecular cyclization to thiiranes **179**, which afforded 2,3,4-tris(isopropylthio)pyrroles **180** in good yields (eq 103).[164] In exactly the same way, the reaction with carbodithioate anions **181** gave 2,3,4-tris(isopropylthio)thiophenes **182** (eq 104).[165]

Similar reactions were applied to the synthesis of various nitrogen-containing polycyclic aromatic compounds. For example, the reaction of tris(isopropylthio)cyclopropenylium perchlorate with pyrrole and with indoles in the presence of NaH in DMSO afforded 1*H*-pyrrolizine **183** and fluorazene **184** in fair to good yields (eq 105).[166,167]

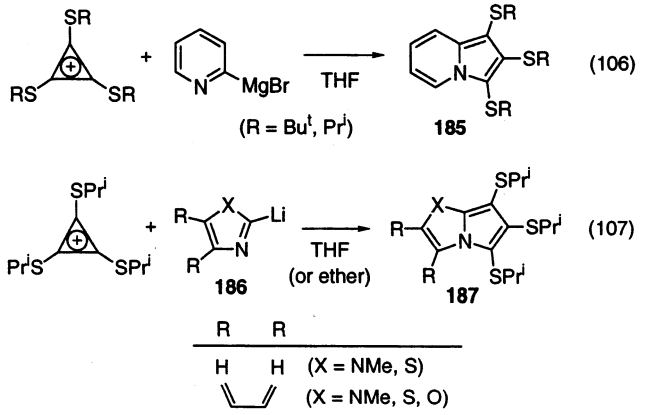
Additionally, via the cyclopropene → vinylcarbene rearrangement, the reaction of tris(isopropylthio)- and tris(*tert*-butylthio)cyclopropenylium perchlorates with 2-pyridylmagnesium bromide in THF gave 1,2,3-tris(alkylthio)indolizines **185** in good yields (99% and 72%, respectively; eq 106),[168,169] while the reaction of tris(isopropylthio)cyclopropenylium perchlorate with



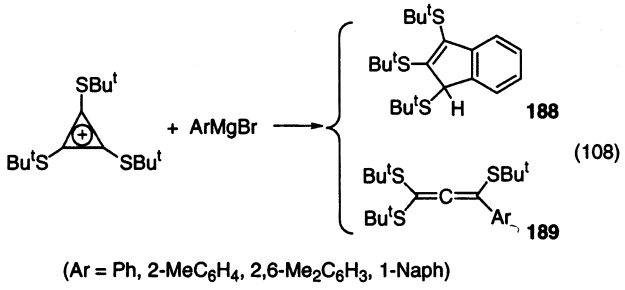




2-lithiated azoles **186** in THF or ether yielded pyrrolo[2,1-*b*]azoles **187** in good yields (50−98%; eq 107).[169]

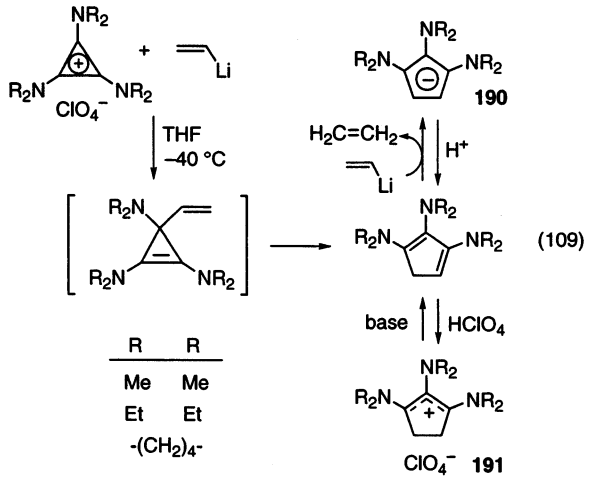


When tris(*tert*-butylthio)cyclopropenylium perchlorate was allowed to react with various arylmagnesium bromides in THF at room temperature, *tert*-butylthio-substituted indenes **188** and allenes **189** were obtained (eq 108).[170] In contrast to the reaction of 1-methylthio-2,3-diphenylcyclopropenylium cat-



ions,[105−107] no cyclopropene derivative was isolated, indicating that the cyclopropene ring with three *tert*-butylthio groups undergoes ring cleavage much more readily than the ring with two phenyl groups.

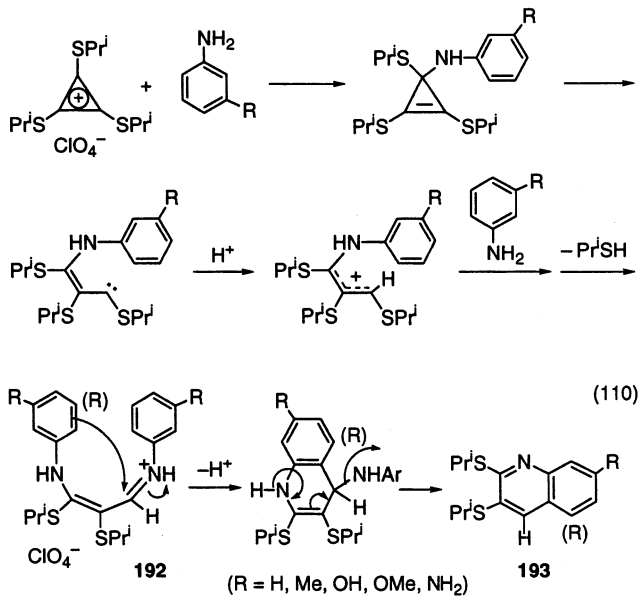
Tris(dialkylamino)cyclopropenylium perchlorate reacted with 2 equiv of vinyllithium in THF at low temperature (−40 °C); then, during warming of the reaction mixture, evolution of ethylene occurred, and there resulted formation of the 1,2,3-tris(dialkylamino)cyclopentadienide ion **190**, as observed by NMR.[171] Upon acidification of the reaction solution, **190** was doubly protonated to give cyclic 1,2,3-tris(dialkylamino)vinamidinium perchlorates **191** in 60−70% yields (eq 109).



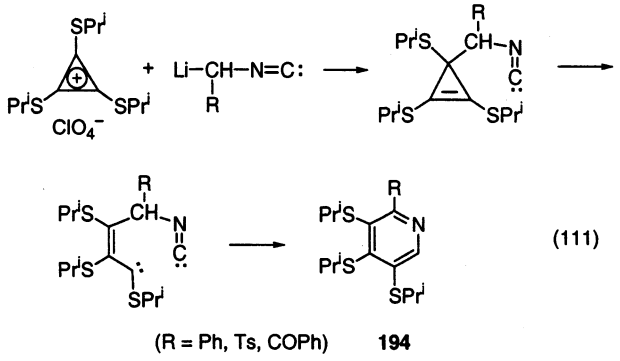
2. Formation of Six-Membered Rings

As described in the preceding section, the reaction of cyclopropenylium cations with various nucleophiles often proceeds by way of ring cleavage of the first formed cyclopropenes, to give vinylcarbene intermediates and subsequent intramolecular cyclization affording ring-expanded products. The same mechanism applies to the ring expansion to six-membered-ring heterocycles.

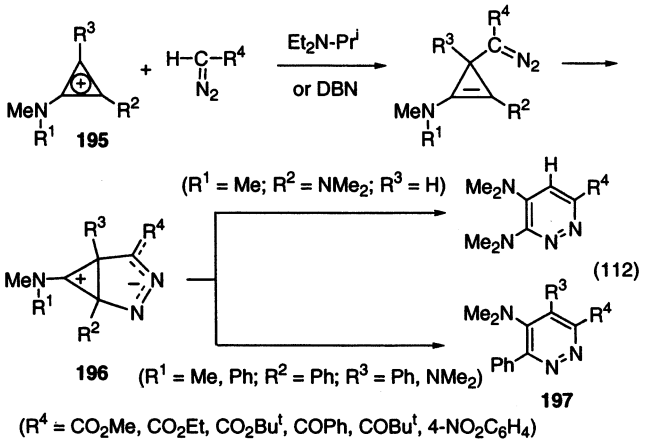
When tris(isopropylthio)cyclopropenylium perchlorate was allowed to react with 2 equiv of meta-substituted anilines in DMF at 85 °C, 5- and 7-substituted quinolines **193** were obtained in high yields. When the reaction was conducted at room temperature, iminium salts **192** were isolated in quantitative yield. Therefore, the reaction is considered to proceed via protonation of the vinylcarbene intermediate and subsequent amination with the second equivalent of aniline, followed by the ring closure of **192**, with elimination of an aniline molecule (eq 110).[167,172]



On the other hand, the reaction of tris(isopropylthio)cyclopropenylium perchlorate with derivatives of α-lithiated isocyanide in THF at −60 °C to room temperature gave 2-substituted 3,4,5-tris(isopropylthio)pyridines **194** in moderate to good yields (eq 111).[173]

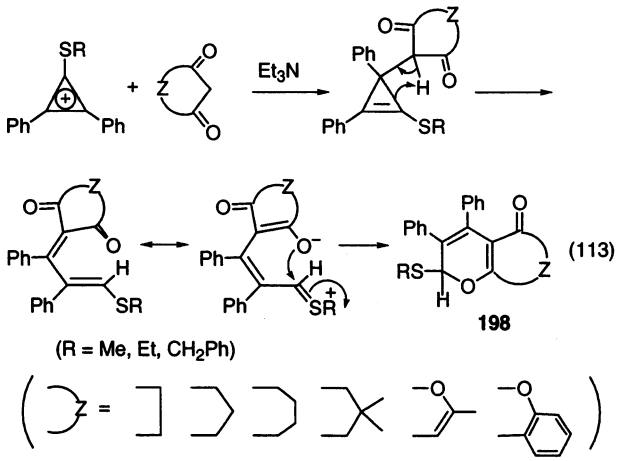


The aminocyclopropenylium cation **195** reacted with various diazomethane derivatives in dichloromethane or in acetonitrile in the presence of ethyldiisopropylamine or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) at room temperature to give selectively 4-aminopyridazine derivatives **197** (eq 112).[174] The reaction



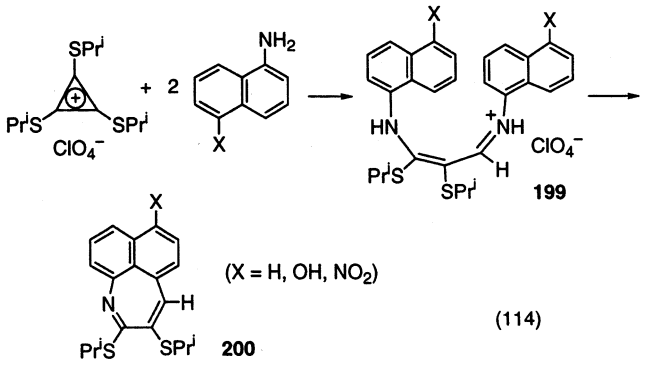
was interpreted in terms of an initial electrophilic substitution of the diazoalkane, to give diazomethylcyclopropenes, which undergo [1.5] cyclization to form zwitterion **196** and valence bond isomerization to the pyridazine derivatives. In exactly the same way, triaminocyclopropenylium cations were converted to the 3,4,5-triaminopyridazine derivatives.

When 1-alkylthio-2,3-diphenylcyclopropenylium cations were allowed to react with cyclic 1,3-diketones in benzene in the presence of triethylamine at room temperature, the corresponding 2-alkylthio-2*H*-pyrans **198** were obtained in good yields.[175] The reaction was interpreted to proceed by ring cleavage of the first-formed 1-alkylthiocyclopropene, followed by formation of the six-membered ring (eq 113).



3. Formation of Seven-Membered Rings

Tris(isopropylthio)cyclopropenylium perchlorate reacted with 2 equiv of 1-naphthylamine or 5-amino-1-naphthol in acetonitrile or in DMF at 80−85 °C to give 2,3-bis(isopropylthio)naphth[1,8-*bc*]azepines **200** in high yields (eq 114).[167,176] When the reaction was

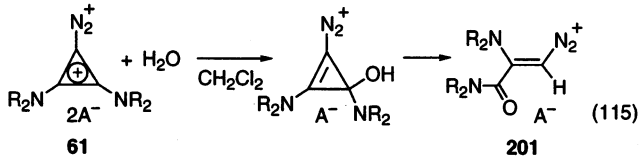


conducted at 25 °C, the iminium salts **199** were obtained as the main products. Thus, the reaction is considered to proceed through protonation of the vinylcarbene intermediate, followed by a reaction with the second molecule of naphthylamine, as in the first example in the previous section.

4. Formation of Linear Unsaturated Systems

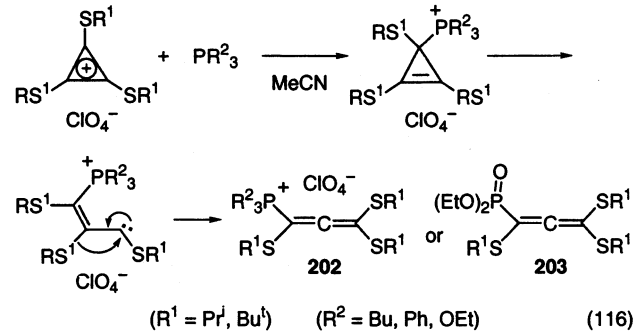
The hydrolysis of cyclopropenyliumyldiazonium salts **61** with water in CH_2Cl_2 smoothly afforded, in high yields, the *Z*-isomer of a new class of function-

ally substituted vinyldiazonium salts **201** in a highly stereospecific manner (eq 115).[53] According to charge



distribution and LUMO structure of **61** calculated by MNDO, this reaction is considered to proceed through the selective nucleophilic attack of the hydroxide ion to C-2,3 carbons, followed by a synchronous ring opening and hydrogen migration.

The reaction of tris(alkylthio)cyclopropenylium perchlorates with tributyl-, triphenyl-, and triethoxyphosphines in acetonitrile afforded the tris(alkylthio)-substituted allenic phosphonium salts **202** or phosphonates **203** in good yield (eq 116).[151] This reaction

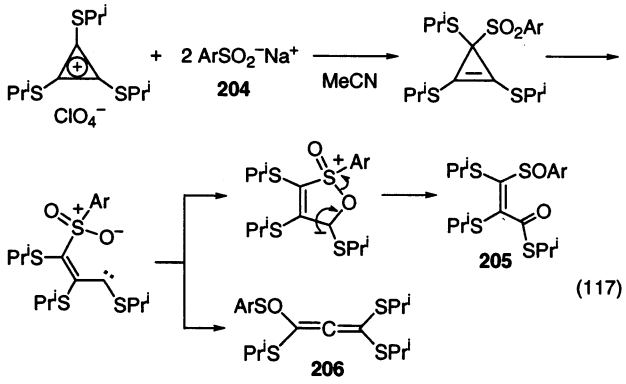


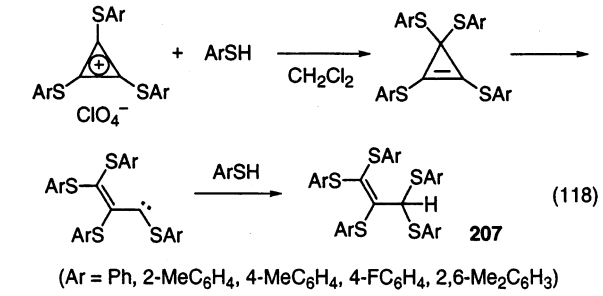
is interpreted as the cyclopropene → vinylcarbene rearrangement, followed by a 1,2-shift of the alkylthio group to the carbenic carbon. This is in contrast to the reaction of the triphenylcyclopropenylium cation (see section III.B), which gave only the cyclopropenylphosphonium salt. Apparently, alkylthio substituents promote the cleavage of the cyclopropene ring.

When tris(isopropyl)cyclopropenylium perchlorate was allowed to react with 2 equiv of sodium arylsulfinates **204** in refluxing acetonitrile, *S*-isopropyl 2,3-bis(isopropylthio)-3-(arylsulfinyl)propenethioate (**205**) and 1,1,3-tris(isopropylthio)-3-arenesulfonylpropadiene (**206**) were obtained in high total yield, with the former as the major product (eq 117).[102] The reaction pathway for the formation of **205** can be interpreted as the formation of the vinylcarbene intermediate, followed by intramolecular transfer of the sulfonyl oxygen to the carbenic carbon, while the pathway to **206** involves the 1,2-shift of the alkylthio group.

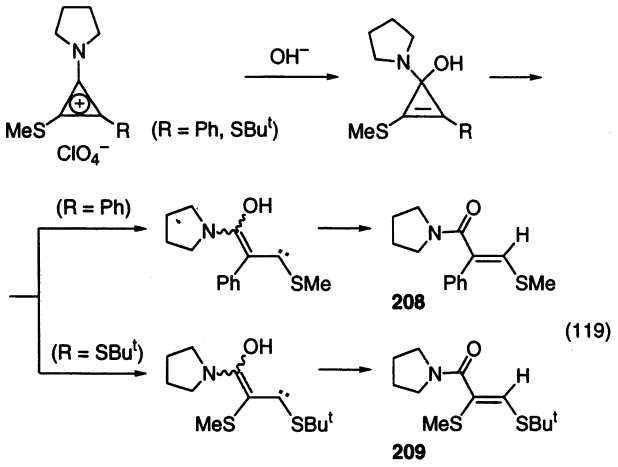
In a similar manner, tris(arylthio)cyclopropenylium perchlorate reacted with an excessive amount of arenethiols to give 1,1,2,3,3-pentakis(arylthio)-1-propenes **207**, possibly by insertion of the carbenic carbon into the S−H bond of arenethiols (eq 118).[88,177]

When the perchlorate salts of 1-(*tert*-butylthio)-2-(methylthio)-3-pyrrolidinylcyclopropenylium and 1-(methylthio)-2-phenyl-3-pyrrolidinylcyclopropenylium cations were allowed to react with aqueous NaOH, (*E*)- and (*Z*)-α,β-unsaturated amides **208** and **209**, which have the electron-donating alkylthio group at the β-position, were obtained in high yields (eq 119).[178] These reactions are considered to proceed





via formation of vinylcarbenes, in which the carbenic carbon is stabilized by the more-electron-donating alkylthio groups, followed by migration of the double bond and protonation.

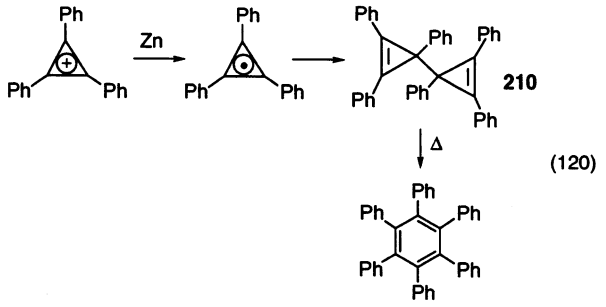


Essentially in the same way, the cyclopropenes obtained by the reaction of (alkylthio)cyclopropenylium cations with Grignard reagents (section III.A.1) were transformed into linear unsaturated compounds via ring cleavage to vinylcarbenes.[105,106]

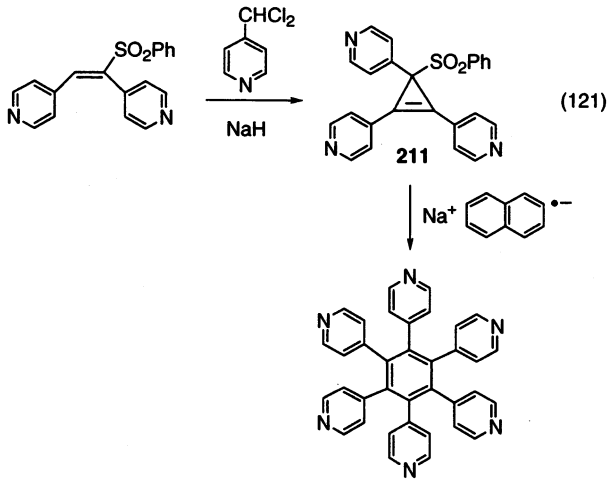
D. Reduction and Oxidation Reactions

In his pioneering work, Breslow showed that, upon one-electron reduction with zinc powder, triphenylcyclopropenylium cation gives the corresponding radical, which readily undergoes dimerization to the bi(cycloprop-2-en-1-yl) derivative **210**, and this dimer thermally rearranges to hexaphenylbenzene (eq 120).[179]

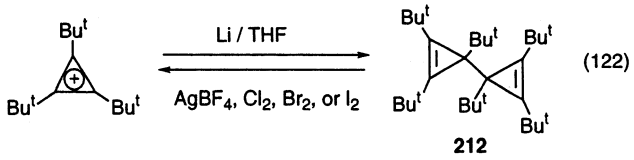
As a possible precursor to the cyclopropenyl anion, 1,2,3-tri(4-pyridyl)-3-benzenesulfonylcyclopropene **211**



was synthesized in 72% yield (eq 121).[180] Treatment of sulfone **211** with sodium naphthalenide in THF at −78 °C afforded hexa(4-pyridyl)benzene in 80% yield via formation of the corresponding cyclopropenyl radical. The N-methylated derivatives underwent the same transformations.



When tri-*tert*-butylcyclopropenylium tetrafluoroborate was allowed to react with lithium powder in THF for 2 days, bi(2-cyclopropen-1-yl) **212** was isolated in 23% yield (eq 122).[181] The molecular structure of **212**



was determined by X-ray crystallography, as shown in Figure 11. The two cyclopropenyl rings were found to be in a gauche conformation, with the twist angle of C1−C3−C3′−C2′ being 87.3°. The length of the central bond connecting the two three-membered rings was elongated to 1.570(3) Å. Neither pyrolysis nor photolysis of bi(2-cyclopropen-1-yl) **212** afforded hexa-*tert*-butylbenzene. Two-electron oxidation of **212** with either $Ag^+BF_4^-$, Cl_2, Br_2, or I_2 regenerated the original tri-*tert*-butylcyclopropenylium cation.

As has been mentioned in section III.A.1, the reaction of 1-methyl-2,3-diphenylcyclopropenylium cation with Grignard reagents appears to involve a one-electron-transfer process.[98] In this connection, the one-electron reduction of 1-methyl-2,3-diphenylcyclopropenylium cation with activated magnesium[182] was conducted in ether at −78 °C to give bis(2-methyl-1,3-diphenylcyclopropen-1-yl) (**213**, 21%), 1,2-

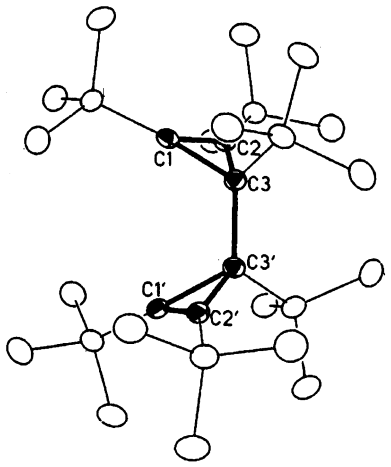
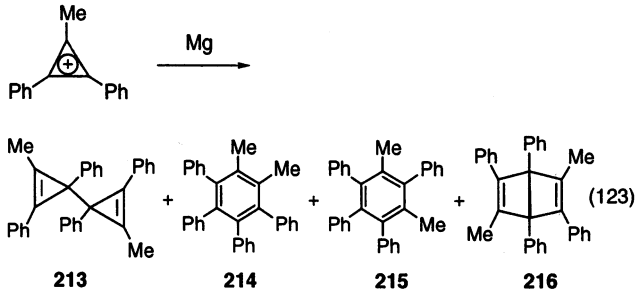
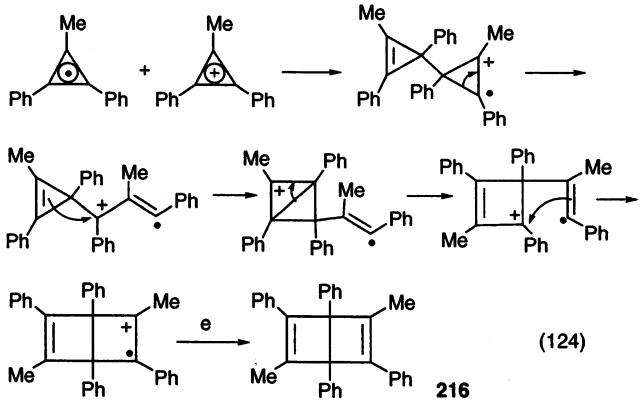


Figure 11. X-ray structure of biscyclopropenyl **212**. [Reprinted with permission from ref 181. Copyright 2002 Wiley-VCH.]

dimethyl-3,4,5,6-tetraphenylbenzene (**214**, 17%), 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (**215**, 25%), and 2,5-dimethyl-1,3,4,6-tetraphenylbicyclo[2.2.0]hexa-2,5-diene (**216**, 37%) (eq 123).[98] Compound **213** was



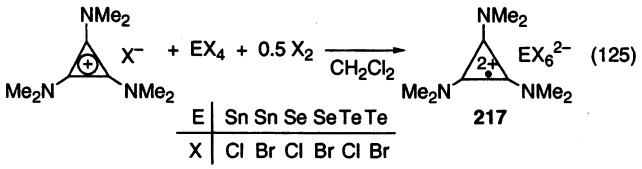
apparently formed by coupling of the cyclopropenyl radical at the carbon bearing a phenyl group. The formation of Dewar benzene **216** was interpreted as the pathway involving the reaction of cyclopropenyl radical with the original cation, as shown in eq 124.[98] Biscyclopropenyl **213** and Dewar benzene **216** were also produced by an electrolytic reduction of 1-methyl-2,3-diphenylcyclopropenylium cation.



The photoirradiation of triphenylcyclopropenylium or 1-(2-methoxy-1-naphthyl)-2,3-diphenylcyclopropenylium tetrakis(pentafluorophenyl)gallates in moist acetonitrile also afforded hexaphenylbenzene or a mixture of isomeric hexaarylbenzenes.[183] The reaction is supposed to proceed via biscyclopropenyl

derivatives, formed by coupling of the cyclopropenyl radicals produced by photoreduction.

Compared to the reduction of cyclopropenylium cations, the example of their oxidation is much more limited, since it requires the presence of a relatively high-lying HOMO. Thus, only the triaminocyclopropenylium cation can be further oxidized to the state of radical dication. The tris(dimethylamino)cyclopropenylium cation was first electrochemically oxidized to give a deep red radical dication and was studied with ESR, but this species could not be isolated under these conditions.[184] In contrast, when tris(dialkylamino)cyclopropenylium chloride was treated with $SbCl_5$ in CH_2Cl_2, the radical dication salt, [tris(dialkylamino)cyclopropendiylium]$^{\bullet 2+}SbCl_6^{2-}$ (**217**), was obtained as brick-red microcrystals in yields higher than 90%.[45] Additionally, when tris(dimethylamino)-cyclopropenylium halide was reacted with MX_4 (M = Sn, Se, or Te; X = Cl or Br) in the presence of either $SOCl_2$ (when X = Cl) or Br_2 (when X = Br), the radical dication salts, [tris(dimethylamino)cyclopropendiylium]$^{\bullet 2+}MX_6^{2-}$ (**217**), were obtained in 81−91% yield (eq 125).[45,185] In these ion pairs, the outer-sphere



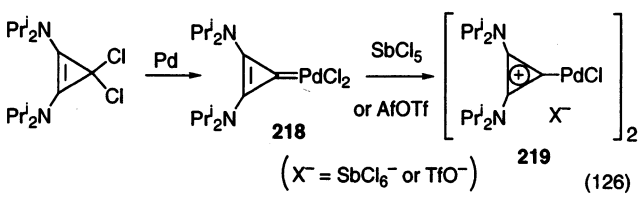
(125)

charge-transfer interaction was observed, in which the complex anion acts as the electron donor. With 48-electron systems SnX_6^{2-}, the bromo complex was found to be a better donor (with the charge-transfer (CT) band observed at 585 nm) than the chloro complex (no CT band observed). In contrast, with 50-electron systems TeX_6^{2-}, the chloro complex (with the CT band at 700 nm) was a better donor than the bromo complex (with the CT band at 595 nm). This electronic interaction between the SOMO of the organic moiety as an acceptor and the a_{1g}* HOMO of the anion as a donor was rationalized on the basis of a simple qualitative MO argument.[186]

E. Formation of Metal Complexes

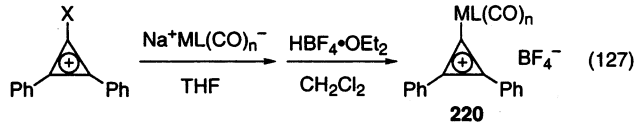
1. Formation of σ-Complexes

As the first example of a coordinatively unsaturated transition-metal-substituted cyclopropenylium cation, the salts **219** were obtained by Cl^- abstraction from carbene complex **218**, which are readily accessible from 3,3-dichlorocyclopropenes and Pd black (eq 126).[187]



(126)

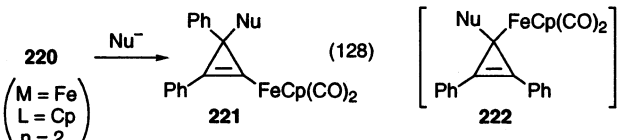
Similar cyclopropenylium cations, directly connected to transition metals by σ-bond(s), can also be synthesized by reaction of the cyclopropenylium cations with metalate anions. For example, cyclopropenylium complexes **220** were synthesized by the reaction of diphenylcyclopropenylium cation, having a methoxy or chloro substituent, with sodium salts of $CpFe(CO)_2^-$ and $Mn(CO)_3^-$ in THF, followed by treatment with ether/tetrafluoroboric acid in CH_2Cl_2, in 52−59% yields (eq 127).[188,189] The cyclopropenylium cations with dialkylamino substituents in place of phenyl groups undergo a similar reaction.[188]



(127)

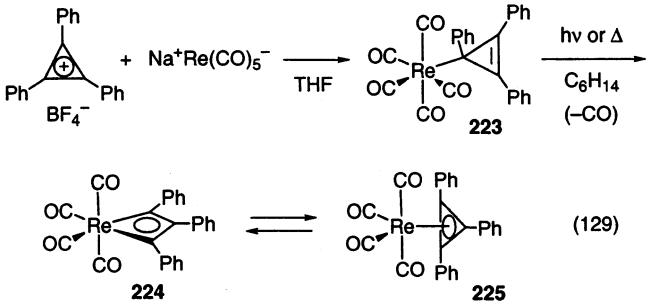
(X = OMe, Cl) (M = Fe, L = Cp, n = 2; M = Mn, L = none, n = 3)

Thus-formed cyclopropenylio-metal complexes such as **220** (M = Fe, L = Cp, *n* = 2) can readily react with nucleophiles selectively at the cyclopropenylium carbon carrying the phenyl group, to give cyclopropene **221** in moderate to fair yields (eq 128).[189] The positional isomer **222** should be highly unstable, because it can be viewed as a derivative of the antiaromatic cyclopropenide anion.



(128)

The reaction of triphenylcyclopropenylium tetrafluoroborate with $Na^+Re(CO)_5^-$ afforded pentacarbonyl(η^1-1,2,3-triphenylcyclopropenyl)rhenium compound **223** in 70% yield (eq 129).[190] Upon UV



(129)

irradiation (or by refluxing in hexane), **223** was converted to dark green tetracarbonyl(η^2-1,2,3-triphenylpropenetriyl)rhenium complex **224** in 25% yield. X-ray crystallography on **224** indicated a complete planarity for the central four-membered ring. Although the ^{13}C NMR spectrum of **224** at −50 °C was consistent with the X-ray structure, at higher temperatures coalescence was observed for the four-membered-ring carbons. This is ascribed to the rapid interconversion between **224** and the η^3-cyclopropenyl complex **225** on the NMR time scale.

Bis(diisopropylamino)cyclopropenylium perchlorate can be lithiated with butyllithium at −78 °C to give a complex of nucleophilic carbene **226**. Upon addition of photochemically generated metal carbonyl complex

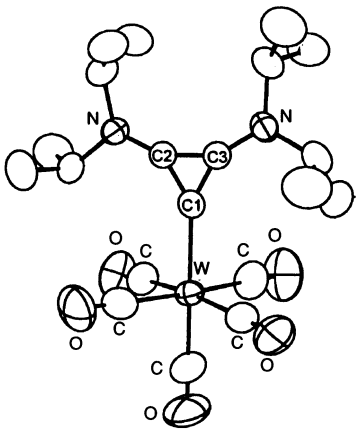
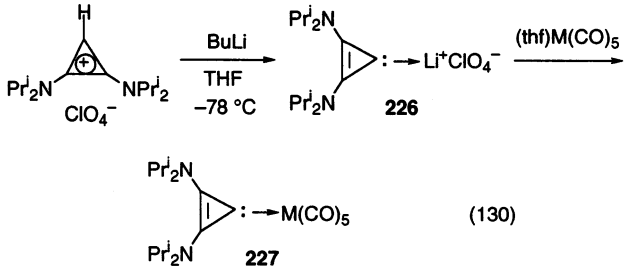
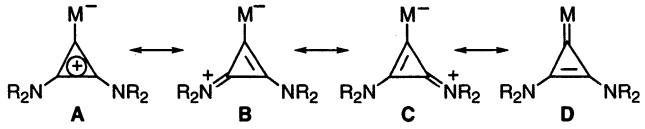


Figure 12. X-ray structure of carbene complex **227** (M = W). [Reprinted with permission from ref 191. Copyright 2002 Elsevier Science.]

$(thf)M(CO)_5$ (M = Cr, W), carbene complexes **227** (M = Cr, W) were obtained as yellow crystals (eq 130).[191] The molecular structure of **227** (M = W) was

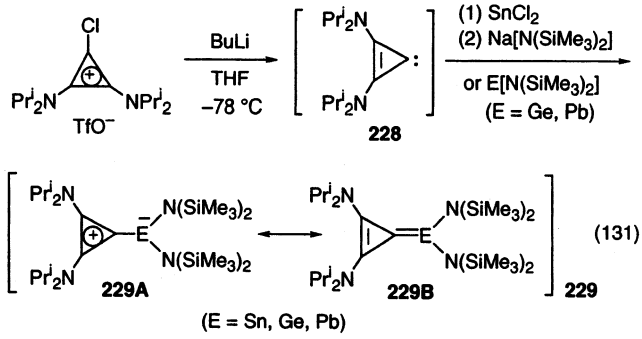


determined by X-ray crystallography (Figure 12). The bond lengths of the three-membered ring were found to be 1.360(7) (C2−C3), 1.376(7) (C1−C2), and 1.373(7) Å (C1−C3). Obviously, the mesomeric structures **A**−**D** are contributing. The ^{13}C NMR signal for the carbene carbon appeared at δ 151.1 ppm for M = Cr and 136.7 ppm for M = W.

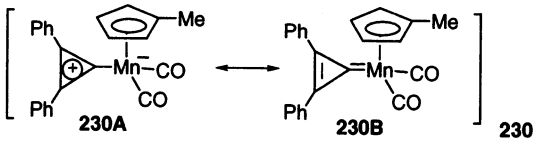


Similarly, nucleophilic carbene **228** was generated by the reaction of 1-chloro-2,3-bis(diisopropylamino)-cyclopropenylium triflate with butyllithium at low temperature, and it was converted to the first cyclopropenylidene metal complexes having the main-group elements (E = Ge, Sn, Pb) **229** as thermally stable yellow crystals (eq 131).[192] X-ray crystallography, conducted for all the compounds **229**, indicated that the distances between the E atom and the carbene carbon are appreciably longer than those in metalaethenes. Additionally, the C−C bonds in the three-membered rings are almost equivalent (1.37−1.39 Å). The ^{13}C NMR signals for the ring carbons for **229** are all observed at the range δ 145−150 ppm. These facts suggest that the contribution of the canonical form **229A** is larger than that of form **229B**.

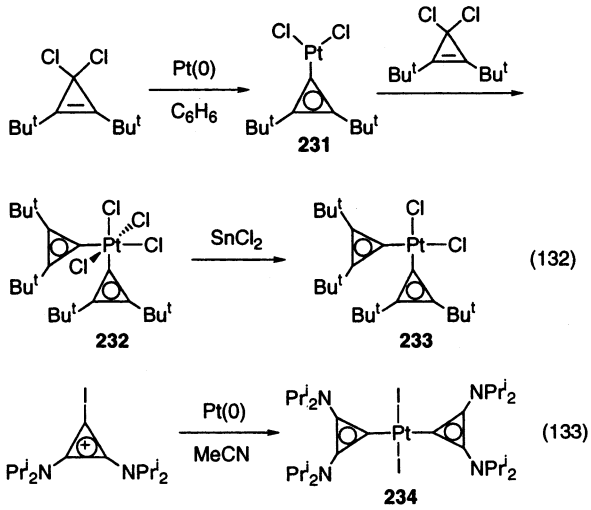
For the preparation of another cyclopropenylidene metal complex, the reaction of 3,3-dichloro-1,2-diphenylcyclopropene with sodium salts of $(MeCp)(CO)_2$-



$MnEPh_3^-$ (E = Si, Ge, Sn) was conducted in THF to give the complex **230** in reasonable yields by elimination of Ph_3ECl and NaCl.[193] Again, this complex is considered to be stabilized by the contribution of the dipolar ionic structure **230A**.



For the preparation of platinum complexes of di-*tert*-butyl- and bis(diisopropylamino)cyclopropenylidene, the reactions of 1,2-di-*tert*-butyl-3,3-dichlorocyclopropene and 1-iodo-2,3-bis(diisopropylamino)-cyclopropenylium iodide with Pt(0) were conducted in benzene and in acetonitrile, respectively (eqs 132 and 133).[194] As shown in eq 132, the oxidative addition of the second cyclopropene to intermediate **231** took place to give the Pt(IV) complex **232**, which could be reduced with $SnCl_2$ to the *cis*-Pt(II) complex **233**. In contrast, the *trans*-Pt(II) complex **234** was formed in the latter reaction (eq 133).



Finally, the first cyclopropenylium cation salts having three σ-metal substituents, **235**, were synthesized by the reaction of trichlorocyclopropenylium hexafluoroantimonate with 3 equiv of metalate anions in THF at −78 °C (eq 134).[96] Typically, the cyclopropenylium salt having three $Fe(CO)_2Cp$ units (**235**: M = Fe, $L_n = (CO)_2Cp$) was obtained as dark amber-brown crystals in 65% yield, and its structure was determined by X-ray crystallography, as shown

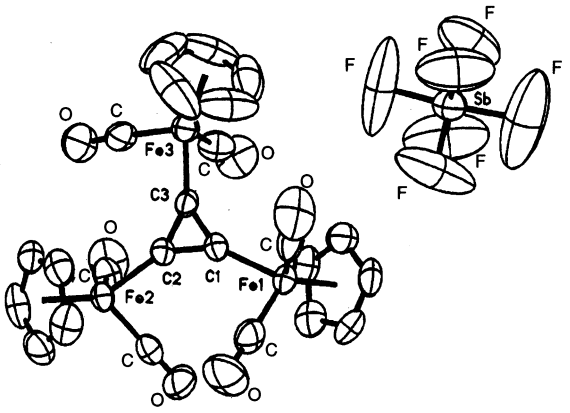
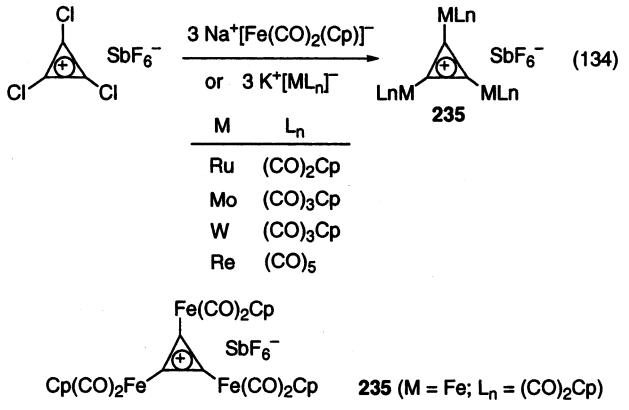


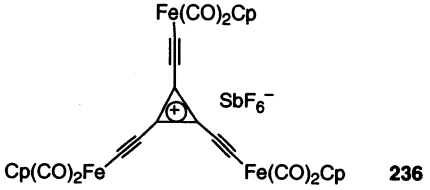
Figure 13. X-ray structure of cyclopropenylium salt **235** (M = Fe, Ln = $(CO)_2Cp$).



in Figure 13.[96a] The lengths of the three-membered ring were averaged to 1.39(1) Å, which is in a rather normal range for the cyclopropenylium cations (Table 2). The average $Fe-C_{ring}$ bond length, 1.92 Å, falls near the middle of the range of Fe−C bonds with multiple-bond character and is about the same as $Fe-C_{sp}$ bonds (1.9 Å).[195] A theoretical study has shown that the iron−cyclopropenyl bond is mainly of σ character, with a smaller, but important, π contribution.[196]

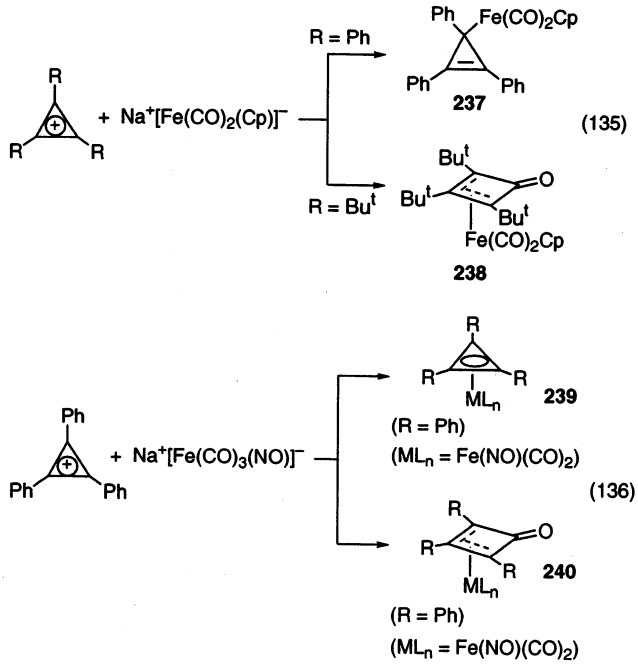
For **235**, the cyclopropenyl carbon exhibited ^{13}C NMR signals at δ 256.6 (M = Fe), 251.3 (M = Mo), 224.4 (M = W), and 237.83 ppm (M = Re), which are downfield of most organic cyclopropenylium cations (δ 118−175 ppm).[197]

Exactly in the same way, the reaction of the trichlorocyclopropenylium cation with 3 equiv of $[Fe(C{\equiv}CSiMe_3)(CO)_2(Cp)]$ afforded the tris-metal-capped triethynylcyclopropenylium hexafluoroantimonate **236** as a rather unstable brown powder in 53% yield.[96b]

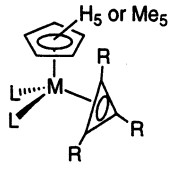


2. Formation of π-Complexes

The reactions of cyclopropenylium cations with low-valent metal centers can lead to (η^3-cyclopropenyl)-metal, (η^1-cyclopropenyl)metal, and (η^3-oxocyclobutenyl)metal complexes, depending on the metal, ligand, and substituents on the three-membered ring. For example, triphenylcyclopropenylium cation was shown to react with $[Fe(Cp)(CO)_2]^-$ to afford η^1-cyclopropenyl compound **237**,[188a,198] whereas tri-*tert*-butylcyclopropenylium cation reacted with the same anion to afford only the ring-expanded η^3-oxocyclobutenyl complex **238** (eq 135).[199] In contrast, the reaction of the triphenylcyclopropenylium cation with $[Fe(NO)(CO)_3]^-$ gave the η^3-cyclopropenyl complex **239** (R = Ph, ML_n = $Fe(NO)(CO)_2$) in 31% and the η^3-oxocyclobutenyl complex **240** (R = Ph, ML_n = $Fe(NO)(CO)_2$) in 19% yield (eq 136).[200]



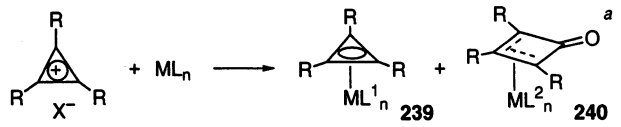
Reactions of cyclopropenylium cations affording these representative products **239** and **240**, reported in the past two decades,[200−204] are summarized in Table 4.



239 (R = Me, Ph)
(ML_n = $RuCpX_2$, $RuCp^*X_2$, $MoCp(CO)_2$)

The halide ligands in η^3-cyclopropenyl complexes **239** having phenyl or methyl substituents were substitutionally labile, and metathetical reactions of a methanol solution of **239** (R = Ph, ML_n = $RuCpCl_2$) with NaBr or KI gave the halogen-exchanged products **239** (R = Ph, ML_n = $RuCpBr_2$) or **239** (R = Ph, ML_n = $RuCpI_2$).[203] The Cp* complexes **239** (R = Ph, Me; ML_n = $RuCp^*Br_2$) and **239** (R = Ph, Me; ML_n = $RuCp^*I_2$) were also prepared in the same way. The result of NMR measurements indicated that the cyclopropenyl ring is conformationally static on the NMR time scale for the Ru complexes **239** (R =

Table 4. Reactions Affording η^3-Cyclopropenyl (239) and η^3-Oxocyclobutenyl Metal Complexes (240)



R	X^-	ML_n[b]	**239**, ML^1_n	**240**, ML^2_n	ref
Ph	PF_6^-	$Mo(CO)_3(MeCN)_3$	$Mo(CO)_2Cp$[c]		201
Ph, Ph, Bu^t	PF_6^-	$Mo(CO)_3(MeCN)_3$	$Mo(CO)_2Cp$[c]		201
Ph, Ph, Bu^t	PF_6^-	$W(CO)_3(MeCN)_3$	$W(CO)_2Cp$[c]		201
Ph	Cl^-	$Mo(CO)_3(MeCN)_3$		$MoCp(CO)_2$[c]	201
Ph	Br^-	$Mo(CO)_3(MeCN)_3$		$MoCp(CO)_2$[c]	201
Ph	PF_6^-	$Na^+[CrCp^*(CO)_3]^-$		$CrCp^*(CO)_2$	202
Ph	PF_6^-	$Na^+[MoCp^*(CO)_3]^-$		$MoCp^*(CO)_2$	202
Me	BF_6^-	$Na^+[MoCp^*(CO)_3]^-$		$MoCp^*(CO)_2$	202
Ph, Ph, H	ClO_4^-	$Na^+[MoCp^*(CO)_3]^-$		$MoCp^*(CO)_2$	202
Ph, Ph, Bu^t	PF_6^-	$Na^+[MoCp^*(CO)_3]^-$		$MoCp^*(CO)_2$	202
Ph, Ph, Me	BF_4^-	$Na^+[MoCp^*(CO)_3]^-$		$MoCp^*(CO)_2$	202
Ph	PF_6^-	$Na^+[WCp^*(CO)_3]^-$		$WCp^*(CO)_2$	202
Ph, Ph, H	ClO_4^-	$Na^+[WCp^*(CO)_3]^-$		$WCp^*(CO)_2$	202
Ph, Ph, Bu^t	PF_6^-	$Na^+[CrCp^*(CO)_3]^-$		$CrCp^*(CO)_2$	202
Bu^t	BF_4^-	$PPN^+[Co(CO)_4]^-$	$Co(CO)_3$	$Co(CO)_3$	200
Ph	BF_4^-	$Co_2(CO)_8$	$Co(CO)_3$	$Co(CO)_3$	200
Ph, Ph, Bu^t	BF_4^-	$Co_2(CO)_8$	$Co(CO)_3$	$Co(CO)_3$	200
Ph	BF_4^-	$Na^+[Fe(NO)(CO)_3]^-$	$Fe(NO)(CO)_2$	$Fe(NO)(CO)_2$	200
Ph	Cl^-	RuCp(COD)Cl	$RuCpCl_2$		203
Ph	Cl^-	$[RuCp^*Cl]_4$	$RuCp^*Cl_2$		203
Ph	Br^-	RuCp(COD)Br	$RuCpBr_2$		203
Ph	Cl^-	RuCp(COD)Br	RuCpBrCl		203
Ph	Br^-	$[RuCp^*Cl]_4$	$RuCp^*Br_2$		203
Me	BF_4^-	RuCp(COD)Cl	$RuCpCl_2$		203
Me	BF_4^-	$[RuCp^*Cl]_4$	$RuCp^*Cl_2$		203
Bu^t	BF_4^-	$PPN^+[Rh(CO)_4]^-$	$Rh(CO)_3$		204
Bu^t	BF_4^-	$PPN^+[Ir(CO)_4]^-$	$Ir(CO)_3$		204

[a] When the three R groups are Ph, Ph, and alkyl (or H), the two Ph groups are located at the C-2 and C-3 positions. [b] Cp* = pentamethylcyclopentadienyl; PPN^+ = bis(triphenylphosphiniminium); COD = 1,5-cyclooctadiene. [c] Complexes **239** and **240** were obtained by treatment of the crude product with cyclopentadienylthallium.

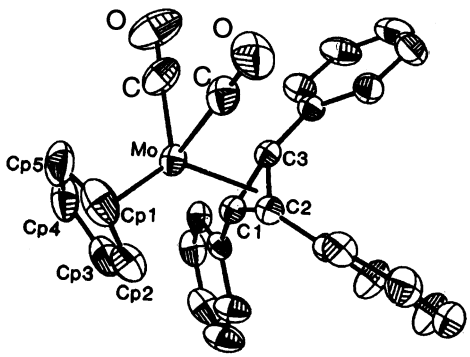


Figure 14. X-ray structure of (η^3-cyclopropenyl)molybdenum complex **239** (R = Ph, ML_n = $MoCp(CO)_2$).

Ph) having CpX_2 or Cp^*X_2 ligands. For a series of trimethylcyclopropenyl complexes **239** (R = Me; ML_n = $RuCpX_2$, $RuCp^*X_2$), dynamic NMR studies were conducted, and the $\Delta G^‡$ values for rotation of the trimethylcyclopropenyl ring were determined as follows: **239** (R = Me, ML_n = $RuCpCl_2$), $\Delta G^‡$(298 K) = 14.2 ± 0.4 kcal mol^{-1}; **239** (R = Me, ML_n = $RuCpBr_2$), $\Delta G^‡$ = 14.9 ± 0.3; **239** (R = Me, ML_n = $RuCpI_2$), $\Delta G^‡$(298 K) = 15.4 ± 0.4; **239** (R = Me, ML_n = $RuCp^*Cl_2$), $\Delta G^‡$(298 K) = 14.0 ± 0.4; **239** (R = Me, ML_n = $RuCp^*Br_2$), $\Delta G^‡$(298 K) = 14.5 ± 0.2; **239** (R = Me, ML_n = $RuCp^*I_2$), $\Delta G^‡$(298 K) 14.7 ± 0.4.[203]

The structure of **239** (R = Ph, ML_n = $MoCp(CO)_2$) was determined by X-ray crystallography, as shown in Figure 14.[201] The "bend-back angles", defined as the angle between the substituent-to-ring carbon bond and the vector from the ring carbon to the three-membered-ring centroid, were found to be 24.7°, 26.6°, and 34.4°.

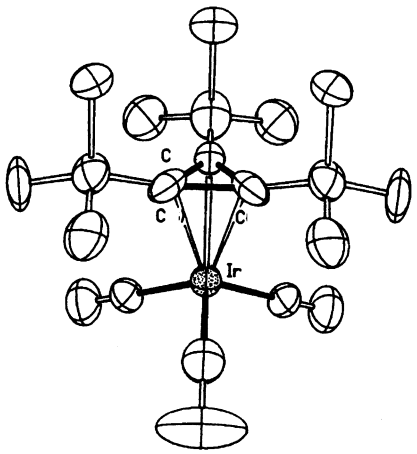


Figure 15. X-ray structure of (η^3-cyclopropenyl)iridium complex **239** (R = *t*-Bu, ML_n = $Ir(CO)_3$).

As a typical example of a Group 9 metal complex, the structure of **239** (R = *t*-Bu, ML_n = $Ir(CO)_3$) was also determined by X-ray crystallography, which indicated a symmetrical η^3-cyclopropenyl-to-Ir interaction, with the ring carbons staggered relative to the carbonyl ligands (Figure 15).[204] The "bend-back angles" were found to be 19.3°, 19.3°, and 15.0°.

In contrast to the above results, the deep blue crystal of vanadium complex **241**, synthesized by the reaction of tri-*tert*-butylcyclopropenylium tetrafluoroborate with $Na^+V(CO)_6^-$ under photoirradiation, was shown by X-ray structure analysis to be the first example of partial insertion of an early-transition-metal atom into the cyclopropene ring (Figure 16).[205] In the crystal structure, the V atom is not symmetrically bonded to the ring but lies much closer to one edge of the triangle. The angle ϕ between the

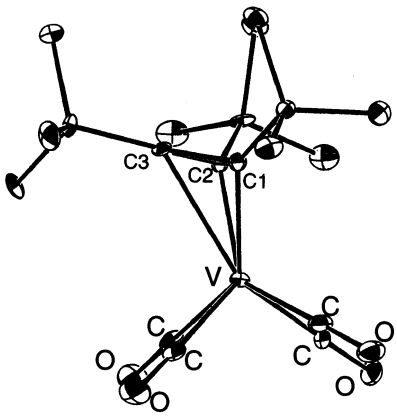
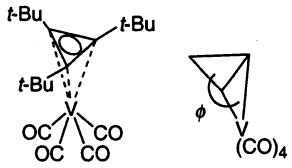


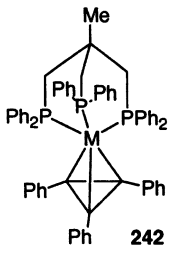
Figure 16. X-ray structure of vanadium complex **241**.



241

plane of the ring and that defined by V, C1, and C2 is 106.86°. The results of variable-temperature ^{13}C NMR measurements were also consistent with the presence of an appreciable amount of σ-character in the ring−metal bond.[205]

When the reactions of triphenylcyclopropenylium hexafluorophosphate with $[M(C_2H_4)(PPh_3)_2]$ (M = Ni, Pd, Pt) and "triphos" (1,1,1-tris(diphenylphosphinomethyl)ethane) were conducted in THF, the complexes **242** were obtained as red-orange (M = Ni), orange (M = Pd), and yellow (M = Pt) crystals in high yields.[206] As a representative example, the X-ray



242

structure of the Pt complex **242** (M = Pt) was examined. As shown in Figure 17, the platinum center was linked to the three phosphorus atoms of the ligand and to the cyclopropenyl unit in a symmetric η^3 fashion: the orientation of the cyclopropenyl ring was staggered with respect to the ligand. The "bend-back angles" were in the range 19.2−32.2°. Variable-temperature NMR spectroscopy indicated a temperature-dependent fluxionality of the cyclopropenyl ring, with the rotational barrier increasing in the order Ni < Pd < Pt. For the case of Pd complex **242** (M = Pd), the activation parameters for cyclopropenyl rotation were determined as follows: E_a = 43 ± 2 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 40 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −38 ± 9 J K^{-1} mol^{-1}, $\Delta G^{\ddagger}$ (298 K) = 52 ± 4 kJ mol^{-1}.[206]

By the reaction of triphenylcyclopropenylium bromide ($Ph_3C_3^+Br^-$) with complex $[Ni(COD)_2]$ (COD =

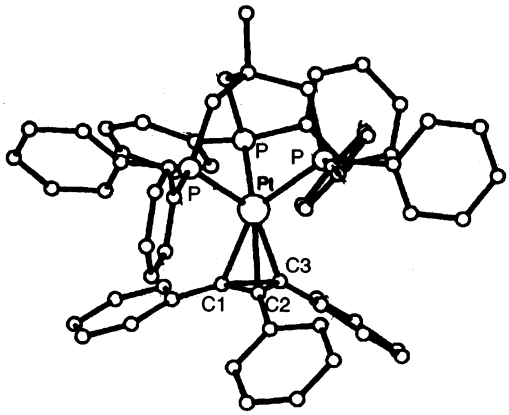


Figure 17. X-ray structure of platinum complex **242**. [Reprinted with permission from ref 206. Copyright 2002 the Royal Society of Chemistry.]

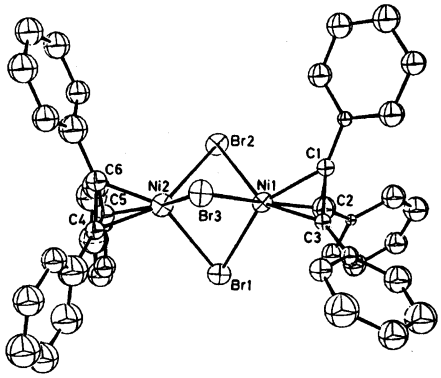
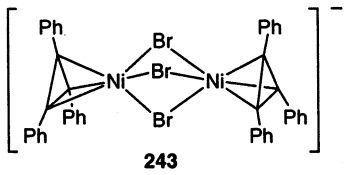


Figure 18. X-ray structure of anionic complex **243**. [Reprinted with permission from ref 207. Copyright 2002 Wiley-VCH.]

1,5-cyclooctadiene) in a molar ratio of 3:2 in THF, a salt of $Ph_3C_3^+$ and new anionic complex **243**, having the two eclipsed NiC_3Ph_3 fragments linked together by three bridging Br atoms, was formed as deep red crystals.[207] The X-ray crystal structure of this anionic



243

complex is shown in Figure 18. This is a quite rare example of an organometallic compound containing the triphenylcyclopropenylium moiety as the only organic ligand.

In contrast to the above examples, in which the cyclopropenyl ring is not cleaved, a reaction of triphenylcyclopropenylium tetrafluoroborate with the complex $[M(CO)_3(\eta^4\text{-COT})]$ (M = Fe, Ru; COT = cyclooctatetraene) in acetone afforded complex **244**.[208] Its structure was determined by X-ray crystallography of the hydride addition product **245** (ML_n = $Fe(CO)_3$) (Figure 19). The reaction is proposed to have proceeded according to eq 137, involving the cleavage of the cyclopropenyl ring.

Furthermore, when 1-methyl-2,3-diphenylcyclopropenylium tetrafluoroborate was allowed to react with a platinum complex $[(Ph_3P)_2Pt(C_2H_4)]$ in CH_2Cl_2,

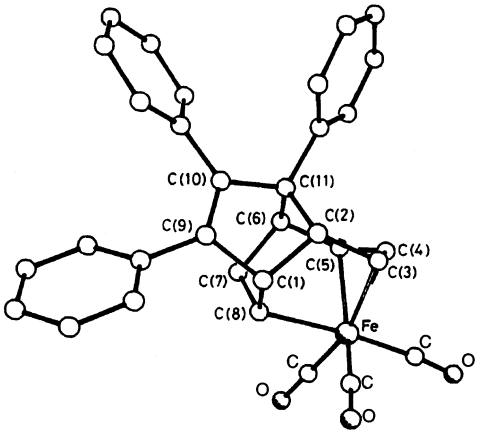


Figure 19. X-ray structure of complex **245** (ML_n = Fe-$(CO)_3$). [Reprinted with permission from ref 208. Copyright 2002 the Royal Society of Chemistry.]

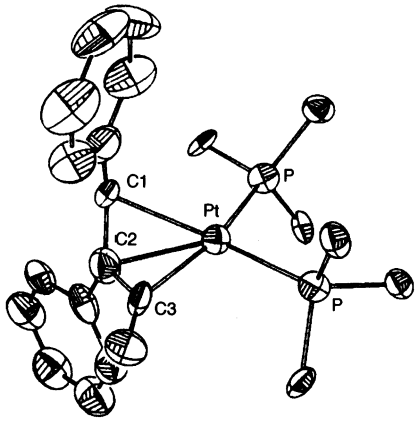
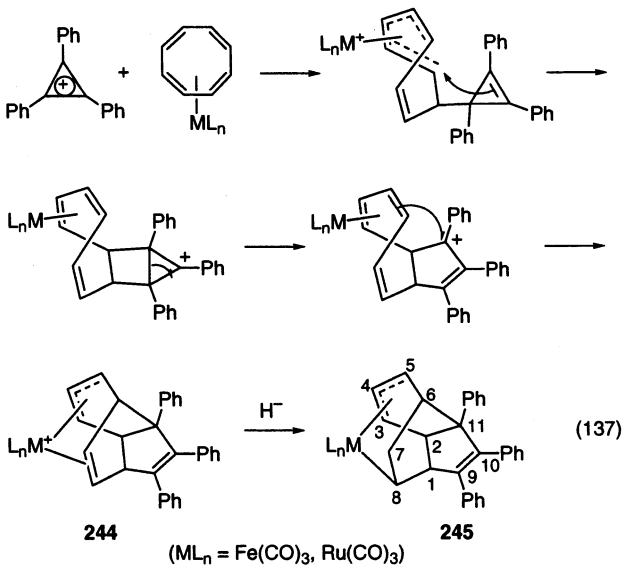
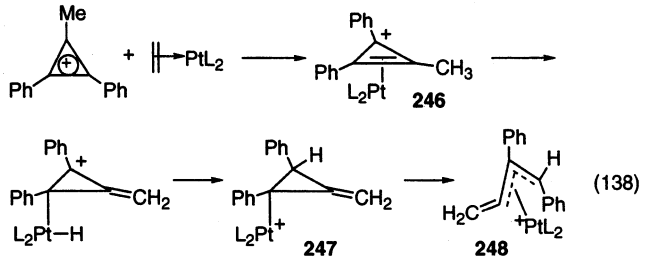


Figure 20. X-ray structure of complex **248**.



(137)

complex cation **248** was obtained as a bright yellow tetrafluoroborate salt in 85% yield.[209] The structure of **248** was unambiguously determined by X-ray crystallography, as shown in Figure 20. The mechanism for this reaction is not very clear, but one possibility is shown in eq 138 (the BF_4^- anion is deleted for clarity), which involves the initial formation of η^2-cyclopropenyl species **246**, metal-assisted H transfer to give the η^1-allylic complex **247**, and ring opening to afford **248**.



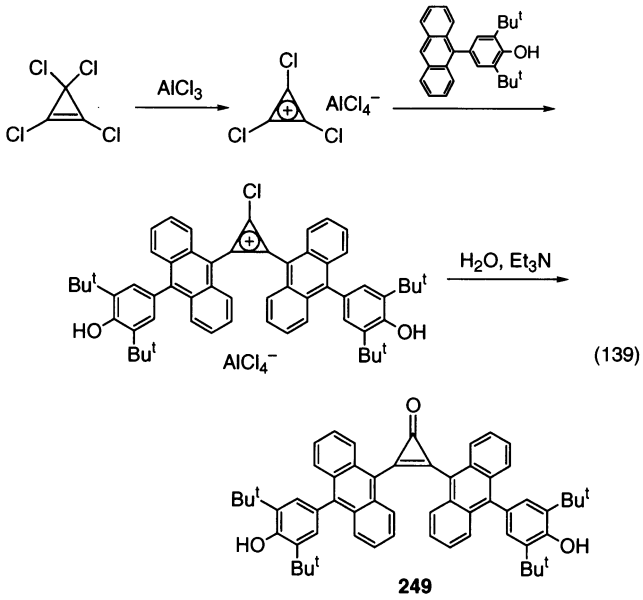
(138)

IV. Synthesis of Cyclopropenones and Heteroanalogues

A. Cyclopropenones

The construction of the three-membered ring of the cyclopropenone derivatives has been conducted in several ways. Transformation of cyclopropenylium ions or cyclopropenes, which already have a central three-membered ring, is the most widely used method for the synthesis of cyclopropenone derivatives. In other approaches, the three-membered ring is constructed either by [2 + 1] cycloaddition, i.e., the addition of a carbene to an acetylene C≡C bond, or by the ring closure of a C_3 component. Contraction of a larger ring by the loss of a small fragment also leads to the three-membered ring.

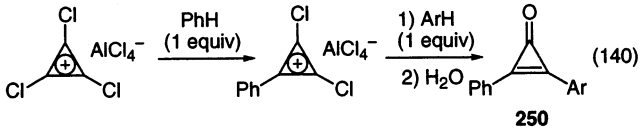
Reaction of two molecules of an aromatic compound with trichlorocyclopropenylium ion affords 1,2-diaryl-3,3-dichlorocyclopropene, which on aqueous workup gives cyclopropenone. This method, developed by West,[210] has been applied to the preparation of a wide variety of diarylcyclopropenones.[8c,121a,211,212,213] Using this procedure, bis[10-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-9-anthryl] derivative **249** was prepared in 67% yield (eq 139).[9]



(139)

The synthesis of nonsymmetric cyclopropenone has been done by stepwise arylation with two different aromatic compounds.[15a,213,214] For example, initial addition of 1 equiv of benzene to trichlorocyclopropenylium ion at 0 °C formed a stable intermediate

dichloro(phenyl)cyclopropenylium ion, which was further arylated by the addition of a second aromatic molecule to form the desired ketone **250** (eq 140).

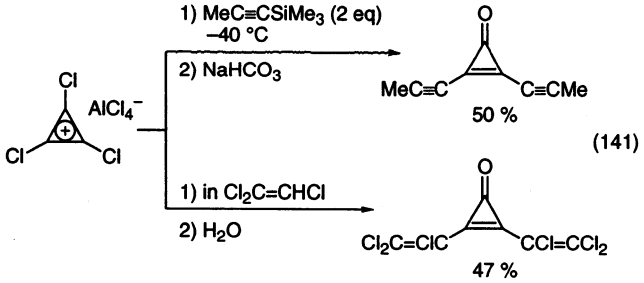


(140)

250

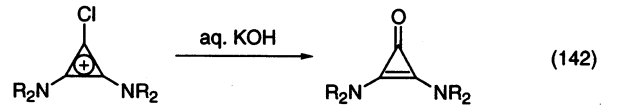
The stepwise substitution has been extended for the synthesis of alkoxy(aryl)cyclopropenones. This has been accomplished by the reaction with 3 equiv of an alcohol at low temperature, after the initial substitution of a chlorine atom by an aromatic group. The possible product, trialkoxy(aryl)cyclopropene or dialkoxy(aryl)cyclopropenylium ion, is readily hydrolyzed to give the ketones.[215]

Reaction of trichlorocyclopropenylium ion with 1-trimethylsilyl-1-propyne[14] and trichloroethene[216] gave dialkynyl- and dialkenylcyclopropenones, respectively (eq 141).



(141)

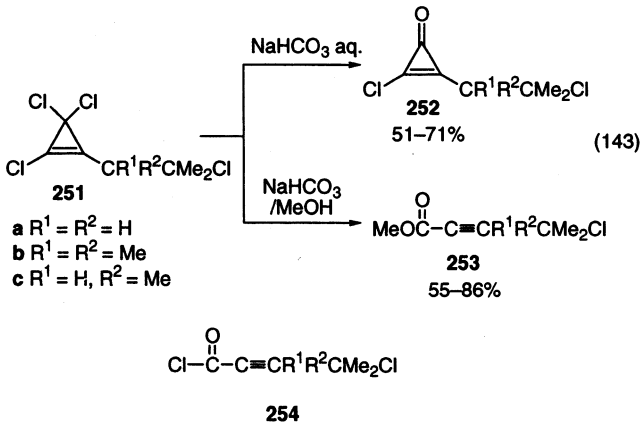
Alkaline hydrolysis of cyclopropenylium ions having a chloro[143,217] or a dialkylamino[218,219] substituent yielded the corresponding cyclopropenone. In the case of 1,2-bis(dialkylamino)-3-chlorocyclopropenylium ions, hydrolysis selectively occurred at the chloro-substituted carbon, to from bis(dialkylamino)cyclopropenone (eq 142).[143]



(142)

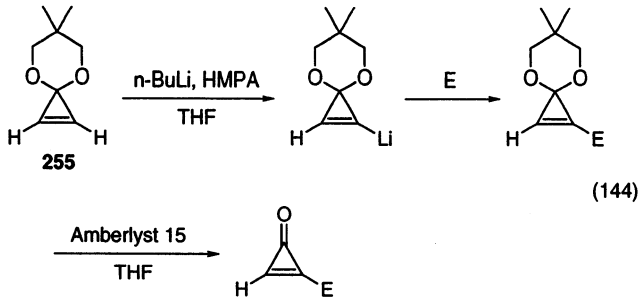
The hydrolysis of 3,3-dichlorocyclopropenes and the 3,3-dialkoxy derivatives (cyclopropenone acetals) yielded the corresponding ketone. 3,3-Dichlorocyclopropenes are readily hydrolyzed, as is normally seen in the aqueous workup of the addition of dichlorocarbene to an alkyne (see below). In the example shown in eq 143, the hydrolysis of **251** took place to form cyclopropenone **252** in aqueous $NaHCO_3$, but ring opening and successive elimination of chloride ion to give **253** occurred when a suspension of $NaHCO_3$ in methanol was used.[12] The latter reaction would involve rearrangement of cyclopropenones **252** to acid chlorides **254**, which were isolated when neat samples of **252b** and **252c** were heated at 100 °C.[220]

Acetal **255**, prepared by dehydrochlorination of 2,2-bis(chloromethyl)-5,5-dimethyl-1,3-dioxane, is a base-stable, protected cyclopropenone, to which a variety of groups can be introduced at the C-2 position via



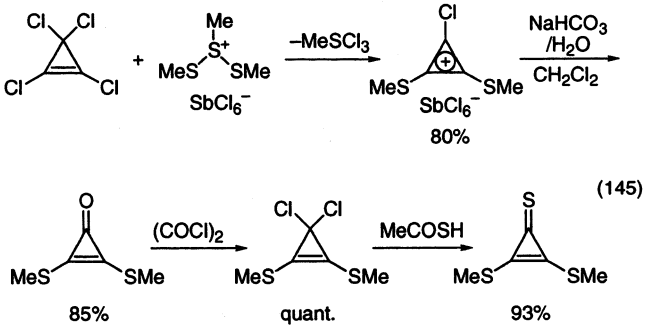
(143)

2-metalated derivatives. Deprotection after the addition to an electrophile, E (alkyl halide, ketone, or aldehyde), tends to cleave the cyclopropene ring, but this can be avoided by the use of Amberlyst 15, pretreated with 2,6-di-*tert*-butylpyridine (eq 144).[221]



(144)

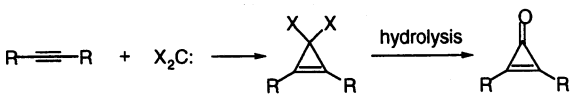
The reaction of tetrachlorocyclopropene with methyl(bismethylthio)sulfonium hexachloroantimonate yielded bismethylthiochlorocyclopropenylium ion, which could be efficiently converted to the corresponding cyclopropenone and thione (eq 145).[35a]



(145)

The oxidation of cyclopropenes at C-3 is a potentially useful method for the synthesis of cyclopropenones, but examples are few. Oxidation of 1-isopropyl-2-silylcyclopropene **256** (R = Pr^i) with dimethyldioxirane in acetone gave cyclopropenone **257**, together with a ring-opened product. On the other hand, similar treatment of the methyl derivative **256** (R = Me) gave spiro epoxide **258** (eq 146).[222] The difference in the behavior of **256** (R = Pr^i) and that of **256** (R = Me) was ascribed to the steric hindrance inherent in the isopropyl group; oxidation of the isopropyl group in **256** (R = Pr^i) is inhibited since the C−H bond in the isopropyl group is oriented in the plane of the

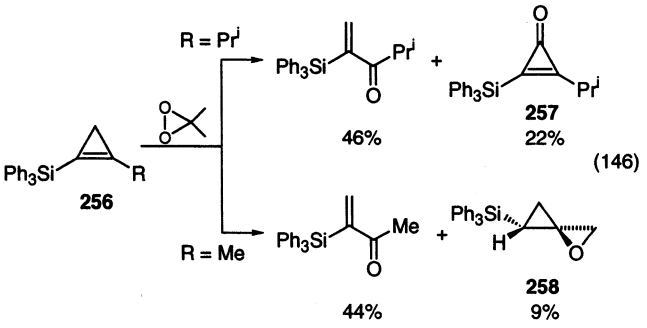
Table 5. Synthesis of Cyclopropenones by the Addition of Carbenes to Alkynes



carbene	method of carbene generation	starting compound	yield (%)	ref
Cl_2C:	$CHCl_3$/aqueous NaOH	1-phenylethynylnaphthalene	15	28b
Cl_2C:	$CHCl_3$/aqueous NaOH	$Bu^tOC{\equiv}COBu^t$	13−35	226
ClFC:	$CFCl_2$, CH_2Cl_2/aqueous NaOH	1-AdC≡CMes	34	227
Cl_2C:	$CHCl_3$, Bu^nLi, THF	dialkylacetylenes	16−90	224[a]
Cl_2C:	$CHCl_3$, Bu^nLi, THF	cyclooctyne	18	225[a]

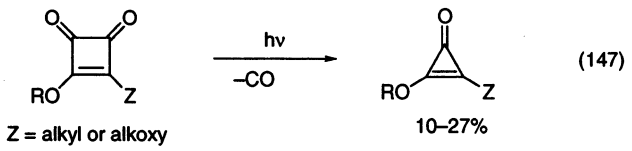
[a] 2-Ynone R−C≡C−CO−R was also obtained.

cyclopropene ring rather than allylically aligned with the π orbitals.

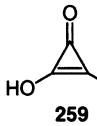


In contrast to the conversion of peripheral groups on the preconstructed three-membered ring, the ring can be directly built by [2 + 1] addition between a carbene and an alkyne or by ring closure of a 1,3-dihalopropan-2-one.[223] Addition of dihalocarbene to a C≡C bond formed a 3,3-dichlorocyclopropene, which on subsequent hydrolysis yielded a cyclopropenone (Table 5). The carbenes have been generated from a trihalomethane with aqueous NaOH or Bu^nLi. The reactions with aqueous NaOH have been carried out in two-phase media with the use of a phase-transfer catalyst. A monoadduct was obtained from 1,8-bis-(phenylethynyl)naphthalene by this method.[28b] In the reactions with Bu^nLi, which have been carried out in THF at low temperatures, the cyclopropenones were formed as minor products with larger amounts of 2-ynones.[224,225]

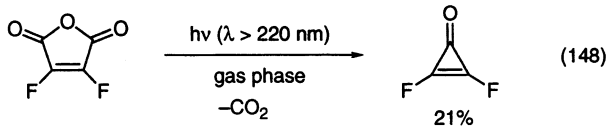
Ring contraction of dialkoxy- or alkoxy(alkyl)-cyclobutenediones by photolytic decarbonylation is an efficient method for the preparation of dialkoxy-[228−230] or alkoxy(alkyl)cyclopropenones[230] (eq 147).



The hydrolysis of dialkoxycyclopropenones has provided a synthetic route to a structurally interesting 2,3-dihydroxycyclopropenone **259**, known as deltic acid. The hydrolysis was successful when 2,3-bis-(trimethylsiloxy)- and 2,3-di-*tert*-butoxycyclopropenones were treated with butanol[228,229] and TFA,[231] respectively. Deltic acid is a fairly strong acid (pK_{a1} 2.57, pK_{a2} 6.03[232]), which on deprotonation gives a dianion $C_3O_3^{2-}$, the smallest member of the cyclic oxocarbons.[233] Single-crystal X-ray analysis showed short C−C single bonds and the long C=C bond, indicating a significant contribution of cyclopropenylium ion character.[231]



Photolysis of difluoromaleic anhydride in the gas phase yielded difluorocyclopropenone in 21% isolated yield (eq 148).[234] This is an unstable cyclopropenone



which decomposes at room temperature but can be stored for a long period of time at −78 °C. Fluorine is a strongly electronegative substituent, but it is also a π-electron donor. Experimental geometry, obtained by microwave spectra for ^{16}O and ^{18}O isotopomers, and ab initio calculations indicated that difluorocyclopropenone has a resonance energy comparable to that of parent cyclopropenone.

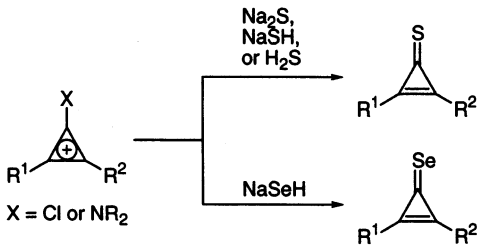
Photolysis of difluoro-[235] and monofluoromaleic anhydrides[236] in an argon matrix at 11 K also generated the corresponding fluorocyclopropenones, although the latter reaction was accompanied by the formation of a similar amount of fluoro(ketenyl)-carbene.

B. Sulfur and Selenium Analogues

Known synthetic methods for cyclopropenethiones can be divided into three types: (a) reaction of a cyclopropenylium ion with an appropriate nucleophilic substituent, (b) conversion of the carbonyl group of cyclopropenone to a thiocarbonyl group, and (c) construction of the three-membered ring by [2 + 1] addition. A few cyclopropeneselones are known which have been synthesized only from a cyclopropenylium ion with a selenium nucleophile.

Cyclopropenylium ions having dialkylamino substituents, in analogy with the formation of cyclopropenones by alkaline hydrolysis, underwent nucleophilic attack by sulfur and selenium nucleophiles (Na_2S,[66] NaSH,[66] H_2S,[61,237] NaSeH[237,238]) to form the corresponding thiones and selones (eq 149). When chlorobis(dialkylamino)cyclopropenylium ions were

treated with aqueous NaSH and NaSeH, the chloro substituent was replaced to give the bis(dialkylamino) derivatives.



(149)

Cyclopropenethiones also can be obtained from sulfur-substituted cyclopropenylium ions. Thus, tris(*tert*-butylthio)cyclopropenylium ion gave bis(*tert*-butylthio)cyclopropenethione in 90% yield upon refluxing with anhydrous $NaHCO_3$ in EtOAc.[239] Zinc reduction of tris(2-trimethylsilylethylthio)cyclopropenylium ion afforded bis(2-trimethylsilylethylthio)-cyclopropenethione (54%).[240] Acid-catalyzed hydrolysis of acetylthiocyclopropenylium ions gave the corresponding cyclopropenethiones in over 89% yields.[241]

Replacement of the oxygen atom of cyclopropenones with sulfur using reagents such as AcSH/HBF_4[242] and P_2S_5[243] is another method for the preparation of cyclopropenethiones. Similarly, 2-methyl-3-phenylcyclopropenethione was obtained in 19% yield by the reaction of 3,3-dichloro-1-methyl-2-phenylcyclopropene with AcSH.[244]

Carbon monosulfide, generated by decomposition of CS_2 in a discharge apparatus, reacted with $R_2NC{\equiv}CNR_2$ at −78 °C, affording bis(dialkylamino)cyclopropenethiones (R = Me, 67%; R = Et, 32%).[245] Reaction with $MeC{\equiv}CNEt_2$ gave methyl(diethylamino)cyclopropenethione in 24% yield. However, with diphenylacetylene, only polymerization of CS occurred.

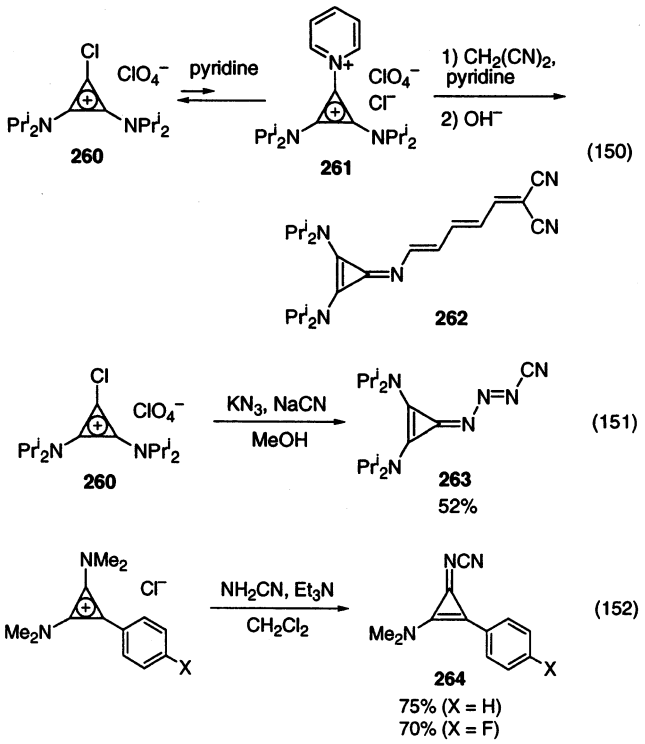
C. Nitrogen and Phosphorus Analogues

In analogy with the preparation of thiones and selones, the most important method for the synthesis of nitrogen and phosphorus analogues of cyclopropenone (cyclopropenimines and phosphatriafulvenes) is the reaction of cyclopropenylium ions with nitrogen and phosphorus nucleophiles.

Substitution of the chlorine atom in **260** with pyridine formed a dication **261**, which on subsequent treatment with malononitrile underwent ring opening to give an imine dye **262** (eq 150).[246] With KN_3 and NaCN, **260** was converted to a triazine nitrile **263** (eq 151).[247]

Chlorodipropylcyclopropenylium ion has been converted to dipropylcyclopropenone tosylhydrazone by $TsNHNH_2$.[217] Treatment of arylbis(dimethylamino)-cyclopropenylium ion with cyanamide gave a cyanoimine **264** (eq 152).[248,249]

Cyclopropenylium ions containing a monoalkylamino group (RHN−) are considered protonated cyclopropenimines and readily lose a proton with an

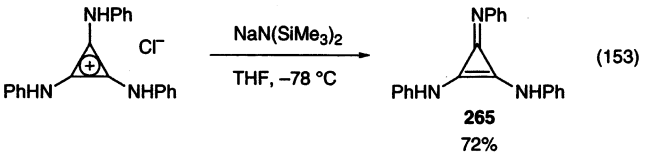


(150)

(151)

(152)

added base to form cyclopropenimines.[38,157,219,250] A nitrogen analogue of deltic acid **265** has been prepared according to eq 153.[250]



(153)

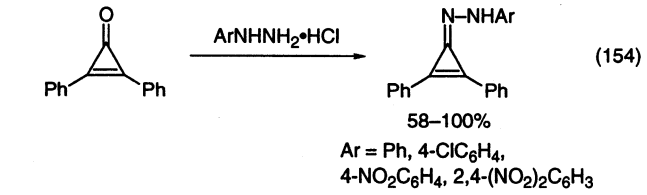
A phosphatriafulvene was obtained by the reaction of di-*tert*-butylmethoxycyclopropenylium ion with mesityltrimethylsilylphosphine in the presence of $EtPr^i_2N$.[70]

The transformations by nitrogen and phosphorus nucleophiles described so far indicate the high utility of cyclopropenylium ions having an electronegative atom, Cl or N, as a precursor of cyclopropenimines and phosphatriafulvenes. Such cyclopropenylium ions can be considered as synthetic equivalents to the corresponding cyclopropenones.

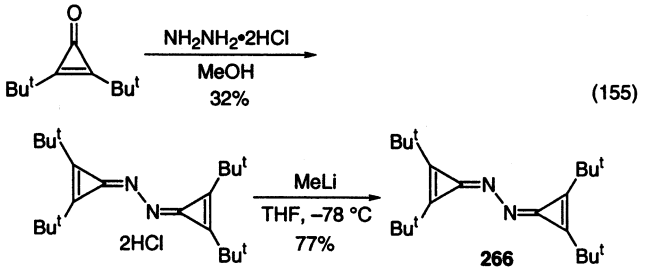
With hydrazines, cyclopropenones can be converted to the corresponding hydrazones (eq 154).[251] Reaction of unsubstituted hydrazine, NH_2NH_2, occurred at both nitrogen atoms, affording cyclopropenonazine **266** (eq 155).[252] Likewise, cyclopropenones were converted to oximes **267** by treatment with NH_2OH and subsequent neutralization of the initially formed hydrochlorides (eq 156).[253,254]

The reaction of diphenylcyclopropenone with isocyanates R−NCO (R = Ts, $Cl_3C(CO)$, $ClSO_2$) was reported to proceed with loss of CO_2, to give the corresponding imines having group R attached on nitrogen.[255]

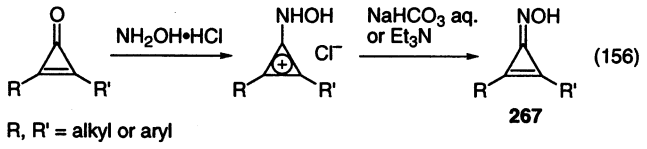
Cyclopropenethiones can be also converted to the corresponding imines. With the conjugate base of



(154)

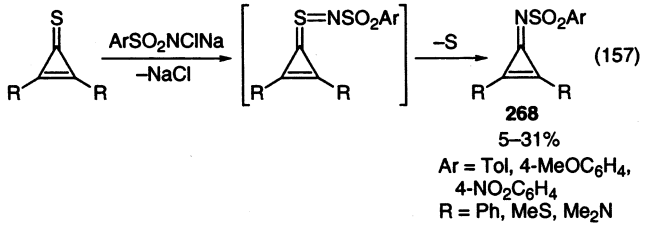


(155)



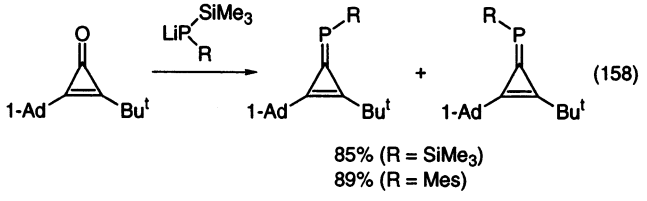
(156)

N-chloroarenesulfonamide ($ArSO_2N{-}Cl\ Na^+$), *N*-sulfonylcyclopropenimines **268** were obtained (eq 157).[256]

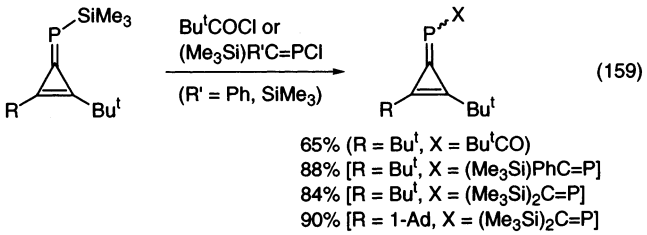


(157)

Phosphatriafulvenes have been prepared from di-*tert*-butylcyclopropenone using lithium trimethylsilylphosphides.[70,257,258] From (1-adamantyl)(*tert*-butyl)-cyclopropenone, mixtures of *E*- and *Z*-isomers were obtained (eq 158).[70] Pivaloyl chloride[258] and chloromethylenephosphanes[259] converted the 2,3-dialkyl-*P*-trimethylsilyl derivative to phosphatriafulvenes having a *P*-Bu^{t}CO or *P*-$(Me_3Si)RC{=}P$ substituent (eq 159). The 2,3,*P*-tri-*tert*-butyl-substituted phosphatriafulvene has been synthesized by the reaction of di-*tert*-butylcyclopropenone with $Bu^tP(SiMe_3)_2$ and $BF_3{\cdot}OEt_2$.[260]

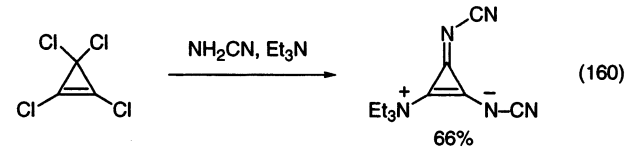


(158)



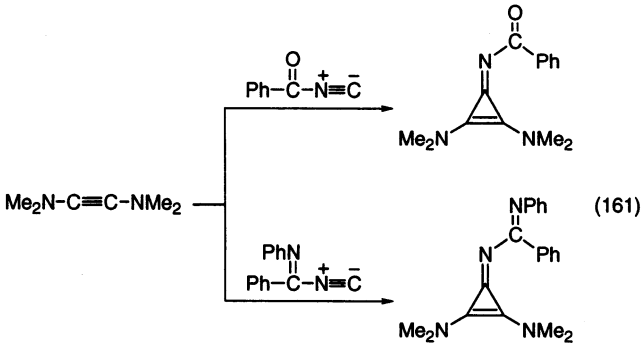
(159)

Reaction of tetrachlorocyclopropene with cyanamide in the presence of Et_3N gave a zwitterionic cyclopropenimine (eq 160).[261,262]

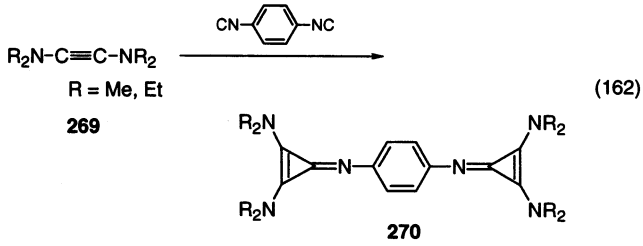


(160)

Cyclopropenimines were synthesized by [2 + 1] cycloaddition between isocyanides and acetylene derivatives (eq 161).[219] Diimine **270** was obtained by the reaction of 1,4-diisocyanobenzene with an ynediamine **269** (eq 162).[219]



(161)



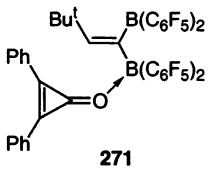
(162)

V. Reactions of Cyclopropenones and Heteroanalogues

A. Reactions with Electrophiles

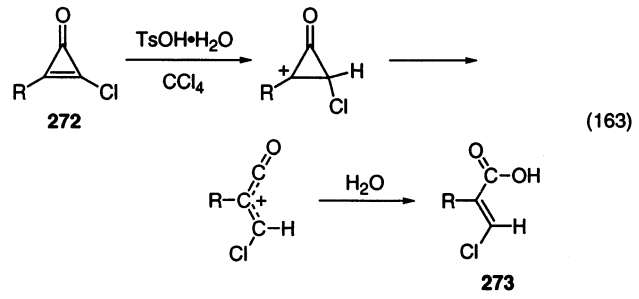
Strong electrophiles, E^+, are readily coordinated by the carbonyl oxygen of cyclopropenone (or the heteroatom X of the heteroanalogues) to form an adduct $-C^+-X-E$, which is stabilized by delocalization of the positive charge over the three-membered π system. Cyclopropenones and the heteroanalogues are thus good precursors for the synthesis of cyclopropenylium ions having a heteroatom substituent, as has been described in earlier sections. Metal complexation on X, which is discussed later, also comes under this category. Some other examples of this type of reactions are shown below.

Boron-centered Lewis acids form stable adducts with cyclopropenones. Diphenylcyclopropenone and diborane $Bu^tCH{=}C[B(C_6F_5)_2]_2$ gave an isolable 1:1 adduct **271**. The ^{19}F NMR data for this adduct



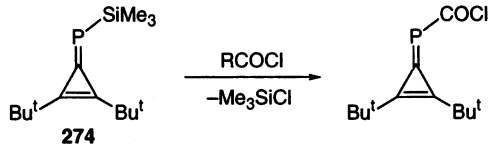
indicated that the carbonyl oxygen binds only one boron atom.[263] Interestingly, acetone formed a similar adduct, only reversibly. No binding was observed with benzophenone. The enhanced binding ability of diphenylcyclopropenone is a clear indication of its dipolar character.

Treatment of alkylchlorocyclopropenone **272** with $TsOH·H_2O$ in CCl_4 resulted in ring opening to give **273**. This result has been attributed to initial protonation on a vinylic carbon, rather than on the carbonyl oxygen (eq 163).[220]



(163)

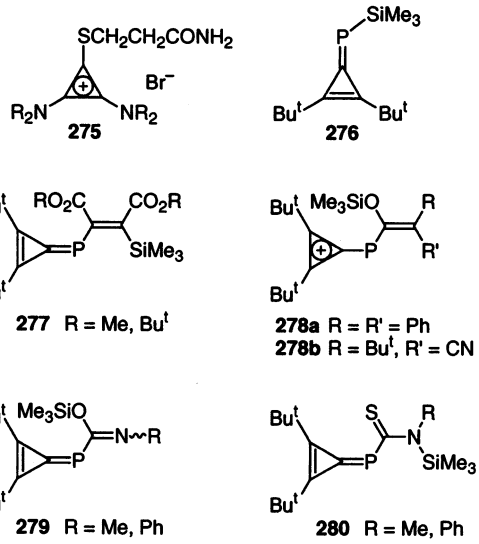
Alkylating reagents, such as alkyl halides (RX),[66,159,264] FSO_3Me,[237] and $(MeO)_2POH$,[66] effectively add an alkyl group on the sulfur atom of cyclopropenethione to give alkylthio-substituted cyclopropenylium ions. Similar substitution has been observed for the reaction with 2,4-$(NO_2)_2C_6H_3Cl$ to form an arylthiocyclopropenylium ion.[66] Cyclopropeneselones and phosphatriafulvene were reported to be methylated by FSO_3Me[237] and MeI,[72] respectively, to yield the corresponding cations. Compound **274** attacks carboxylic acid chlorides RCOCl, but concomitant elimination of the Me_3Si group occurred, leading to the neutral *P*-acyl derivative (eq 164).[257]



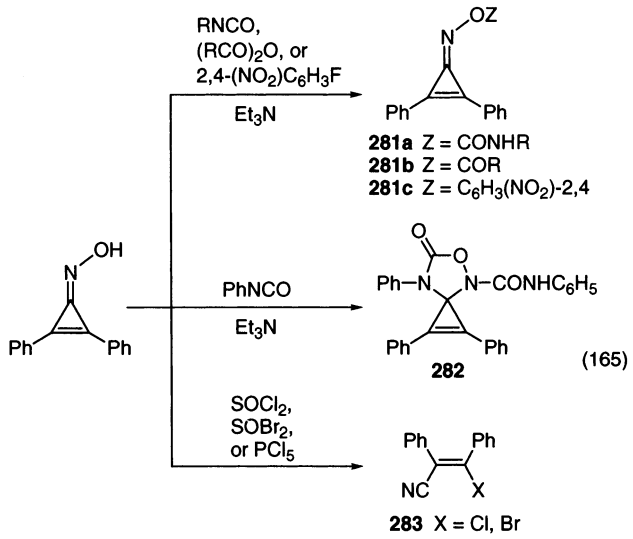
(164)

The fact that the phosphorus atom acts as an nucleophile in eq 164 appears unusual, since in the normal mode of polarization, a C=P group possesses positive character on phosphorus and negative character on the carbon atom, in harmony with the smaller electronegativity of the former compared to the latter. The C=P bond in phosphatriafulvenes is thus inverted, due to the aromaticity of the three-membered ring.

π-Electrophiles, such as alkenes and alkynes substituted with electron-withdrawing group(s), similarly attack cyclopropenethiones and phosphatriafulvenes. Examples for such reactions include reaction of bis(dialkylamino)cyclopropenethione with acrylamide/HBr to form cation **275**[66] and insertion of $RO_2CC{\equiv}CCO_2R$ to the P–Si bond of phosphatriafulvene **276** to give **277**[72,257] Compound **276** is also reported to react with ketenes RR′C=C=O, isocyanates R–NCO, and isothiocyanates R–NCS, giving insertion products **278**, **279**, and **280**, respectively.[72]



Reaction of diphenylcyclopropenone oxime with isocyanates R–NCO (R = acetyl, tosyl), acid anhydrides $(RCO)_2O$ (R = alkyl, aryl), and 2,4-$(NO_2)C_6H_3F$ in the presence of Et_3N have been reported to give *O*-substituted oximes **281a**, **281b**, and **281c**, respectively (eq 165).[265] When diphenylcyclopropenone oxime was treated with phenyl isocyanate, however, a 1:2 adduct **282** was obtained.[266] Reaction with halogenating reagents $SOCl_2$, $SOBr_2$, and PCl_5 resulted in ring opening to give **283**.[265]

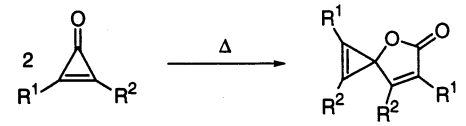


(165)

B. Reaction at the C=X Double Bond

Some of the reactions of cyclopropenones and their analogues involve changes in the structure at only the C=X (X = O, S, Se, N, and P) bond. The cyclopropene moiety is retained in these reactions; no ring opening nor loss of the C–C π bond occurs. The simplest reaction of this type would be the exchange of the oxygen atom of the carbonyl carbon of cyclopropenone with water, observed by using $H_2{}^{17}O$.[267]

Cyclopropenones undergo thermal dimerization to yield spirolactones (eq 166).[36a,268–273] This is a formal [3 + 2] cycloaddition between the carbonyl group of

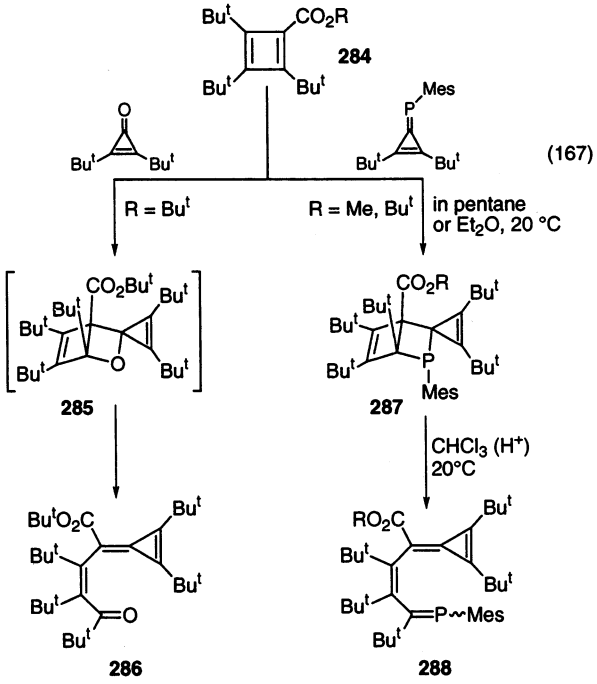


(166)

R^1	R^2	ref.
H	H	268
Me	H	269
Ph	Ph	36a,270,271
Ph	MeO	272
Cl	Cl	273

one molecule and the cyclopropene C−C single bond of another molecule, which can occur on the basis of the nature of cyclopropenones, which have both polarized and strained characters. This reaction is accompanied by decarbonylation (see below), which becomes predominant at high temperatures.

Kinetically stabilized cyclobutadiene **284** reacted slowly with di-*tert*-butylcyclopropenone to give triafulvene derivative **286** (eq 167).[274] Initial [4 + 2]

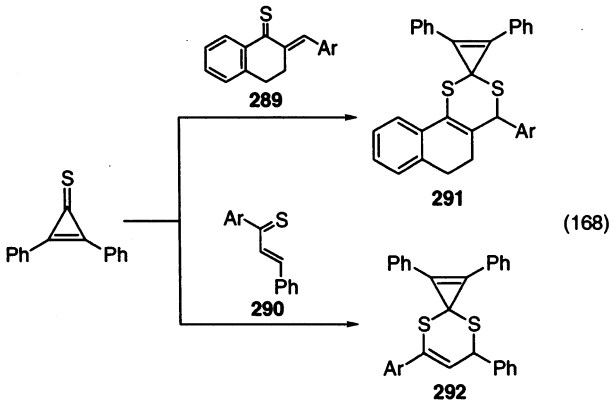


(167)

cycloaddition to form a oxabicyclohexene intermediate **285** has been suggested. The reaction of **284** with phosphatriafulvenes, on the other hand, stopped at this stage, giving phosphabicyclohexenes **287** as crystalline products.[275] In chloroform solution, **287** isomerized to triafulvenes **288** quantitatively at room temperature.

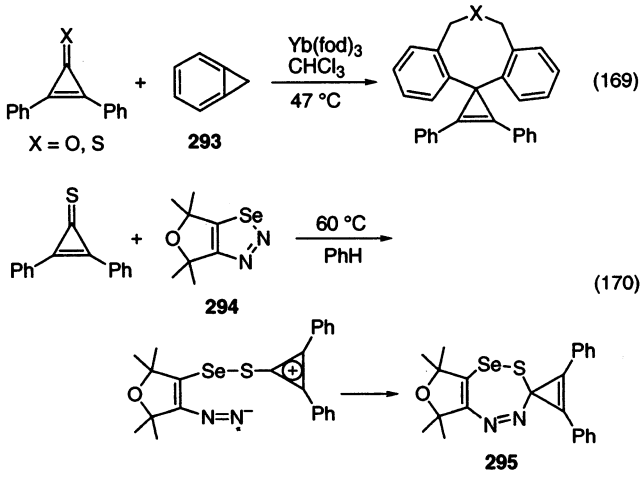
Diphenylcyclopropenethione underwent [4 + 2] cycloaddition with α,β-unsaturated thiones **289** and **290**, to form 1,3-dithiins **291** and **292**, respectively (eq 168).[276]

Addition of two molecules of cyclopropaparene **293** occurred to the C=X bond (X = O or S) of diphenylcyclopropenone or its sulfur analogue in the presence of $Yb(fod)_3$ catalyst (eq 169).[277] These reactions are consistent with the mechanism involving complexation of $Yb(fod)_3$ with an oxygen or sulfur atom and



(168)

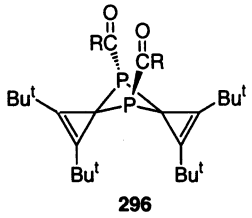
subsequent heterolytic cleavage of the cyclopropaparene ring.[278] Diphenylcyclopropenone underwent formal



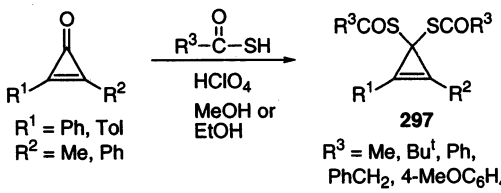
(169)

(170)

[2 + 2] cycloaddition with furoselenadiazole **294**, to give an adduct having a seven-membered heterocycle **295**. A stepwise, ionic mechanism has been proposed (eq 170).[279] Phosphatriafulvenes having an acyl group on P reversibly dimerized to form **296** by the head-to-tail cycloaddition at the C=P bond.[70]

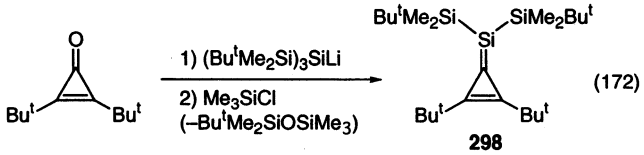


Cyclopropenones can be converted to acetals by treatment with Et_3O^+ and subsequent treatment of the resulting ethoxy-substituted cyclopropenylium ions with an alcohol or a thiol.[280] Reaction of cyclopropenones with thiocarboxylic acid RCOSH in the presence of an acid in MeOH or EtOH gave 3,3-bis(acylthio)cyclopropene **297** (eq 171).[242]

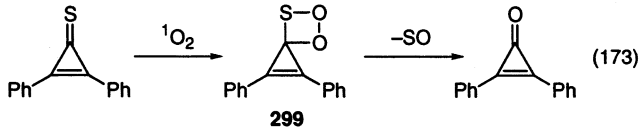


(171)

Another series of reactions at C=X involves replacement of the atom X with another element. Some examples of such transformations have been discussed in an earlier section, such as the synthetic method for the heteroanalogues from cyclopropenone. Other examples include the preparation of the first isolable silatriafulvene **298** from di-*tert*-butylcyclopropenone and $(Bu^tMe_2Si)_3SiLi$ (eq 172).[281] Reaction of diphenylcyclopropenethione with singlet oxygen, generated in situ by dye sensitization or by the decomposition of triphenyl phosphite ozonide, gave diphenylcyclopropenone in 65−75% yields. Decomposition of the initially formed 1,2,3-dioxathietane intermediate **299** has been proposed as a possible mechanism (eq 173).[282]

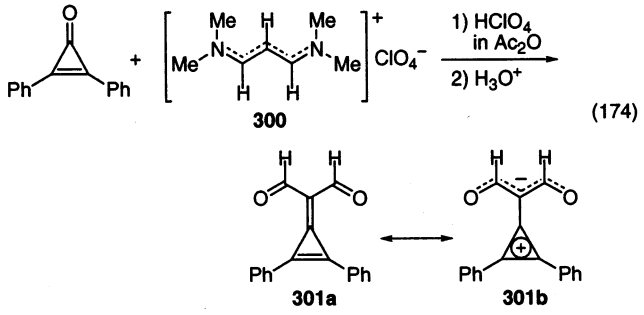


(172)



(173)

Acid-catalyzed condensation of diphenylcyclopropenone with the trimethinium salt **300** and subsequent hydrolysis gave malonaldehyde **301**. X-ray analysis of **301** indicated a slightly longer (C-3)−(C-4) double bond (1.37 Å) than expected for a normal C=C bond (ca. 1.34 Å), indicating a small contribution of the dipolar form **301b** (eq 174).[283]

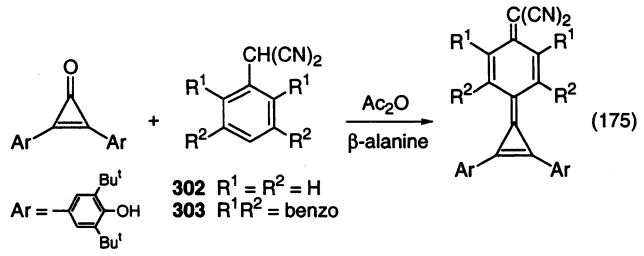


(174)

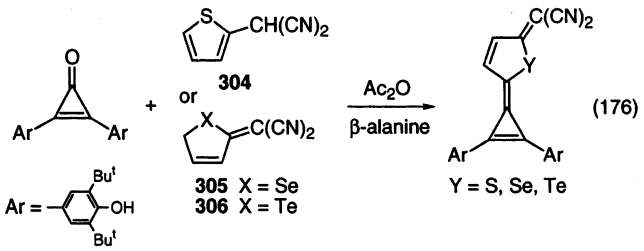
The carbonyl oxygens of cyclopropenones have been replaced by an aromatic ring by treatment with arylmalononitrile **302** and **303**,[284] thienylmalononitrile **304**,[285] 2-(dicyanomethylene)-2,5-dihydroselenophene **305**,[286] and its tellurium analogue **306**,[287] to afford cyclopropenes substituted with a quinoid ring (eqs 175 and 176).

C. Cycloaddition to the Three-Membered Ring

Cycloaddition at a bond of the three-membered ring is among the most commonly observed reactions of cyclopropenones and heteroanalogues with dipolar organic molecules and other compounds with a reactive π-system. The reaction can occur at both the



(175)



(176)

C=C and C−C bonds to give a 1:1 adduct, but further transformation of the primary product, such as rearrangement and fragmentation, is frequently observed. The reactions at C=C and C−C bonds are somewhat different in nature from each other and are described separately in this section.

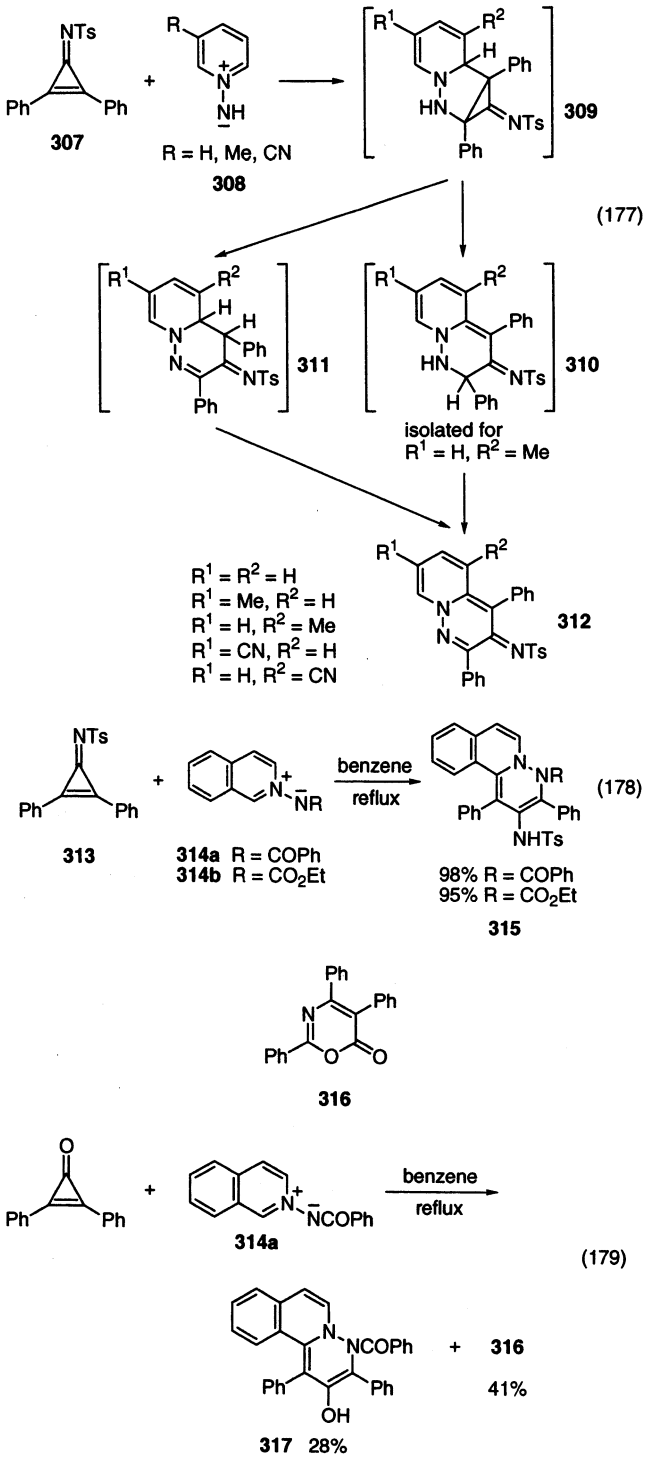
1. Addition to C=C Double Bond

The carbon−carbon π-bonds in the cyclopropenones are known to react with 1,3-dipoles and activated dienes, to form [3 + 2] and [4 + 2] cycloadditions, respectively. The initially formed adduct retains the cyclopropane ring, which is fused with a newly formed ring. Due to the high strain, these adducts usually undergo ring opening or decarbonylation.

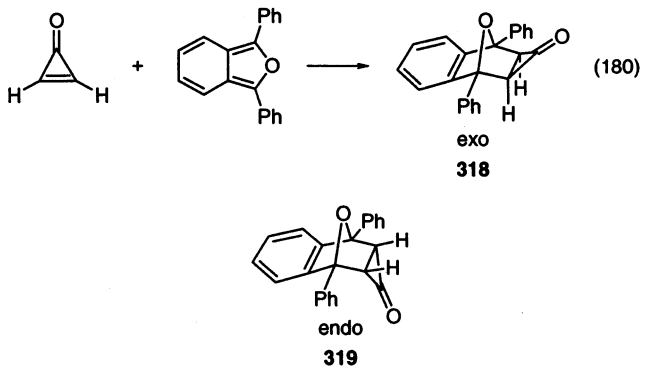
The reaction of diphenyl-*N*-tosylcyclopropenimine **307** with pyridinium *N*-amide **308**, generated in situ from *N*-aminopyridinium iodide and triethylamine, yielded cycloadduct **312** (65% for $R^1 = R^2 = H$) (eq 177).[288] A possible mechanism includes the formation of dihydro adduct **310** and/or **311** via 1,3-dipolar cycloaddition to form **309**. In the case $R^1 = H$, $R^2 =$ Me, the reaction stopped at **310**, which was isolated in 64% yield. This result provided evidence for the participation of intermediate **309**. The isolated intermediate **310** was quantitatively dehydrogenated to give **312** ($R^1 = H$, $R^2 =$ Me) upon heating at 120 °C in DMF.

Cyclopropenimine **313** reacts with isoquinolinium *N*-amides **314** to give [3 + 2] cycloadducts **315** in high yields (eq 178).[289] The high reactivity of isoquinolinium *N*-amides toward cycloaddition, compared to the reactivity of pyridinium amides, was demonstrated by their reaction with cyclopropenone. Although diphenylcyclopropenone underwent cycloaddition with pyridinium *N*-benzamides, with a loss of pyridine, to give 1,3-oxadin-6-one derivatives **316**,[290] a reaction with isoquinolinium *N*-benzamide **314a** afforded, in addition to **316**, simple cycloadduct **317** in 28% yield (eq 179).[289]

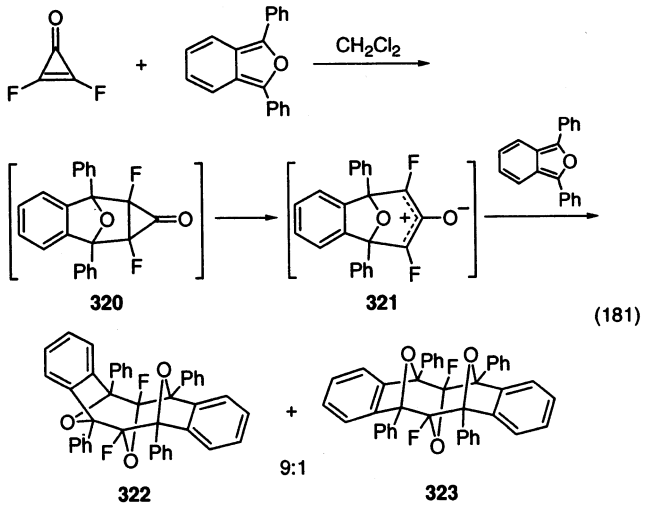
The C=C bond of cyclopropenones acts as a dienophile in Diels−Alder reactions. The adduct from the reaction of cyclopropenone with 1,3-diphenylisobenzofuran, first reported in 1972,[291,292] was analyzed



recently by single-crystal X-ray analysis and was demonstrated to be the exo isomer **318** (eq 180).[293] A small amount (1−2%) of endo adduct **319** could be detected by NMR at −30 °C which isomerized below room temperature to the more stable exo isomer with a half-life of ca. 1 h. This suggested a kinetic preference of approximately 50:1 for the formation of **318** over **319**. The preference for **318** was explained in terms of a transannular attractive interaction between the bridging oxygen and the cyclopropenone carbonyl carbon, which is in accord with the X-ray molecular structure and AM1 calculation for the exo adduct.



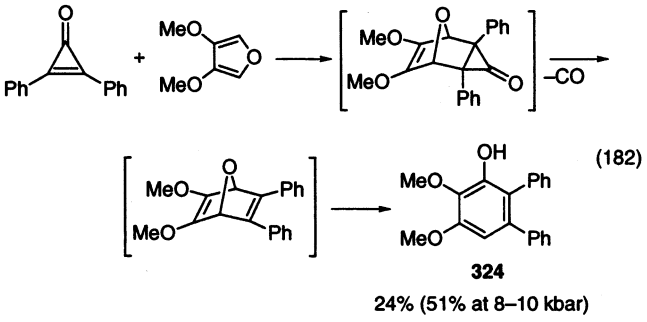
The Diels−Alder reaction between difluorocyclopropenone and 1,3-diphenylisobenzofuran produced two 1:2 adducts (**322** and **323**) in a 9:1 ratio (eq 181).[294] The attempt to observe the monoadduct



320 at low temperature by NMR was not successful, which can be understood by considering that the initially formed monoadduct **320** underwent ring opening to zwitterion **321** faster than it was formed and that **321** reacts quickly with the second molecule of diphenylisobenzofuran. This is in contrast to the reaction of the parent cyclopropenone with 1,3-diphenylisobenzofuran (eq 180), which quantitatively yielded the stable monoadduct **318**. The high reactivity of **320** was rationalized by the result of MO calculations, which indicated that the barrier to ring opening of *cis*-2,3-difluorocyclopropanone to oxyallyl [$FC^+H-C(O^-)=CHF$] is about half as large as that of the parent cyclopropanone.

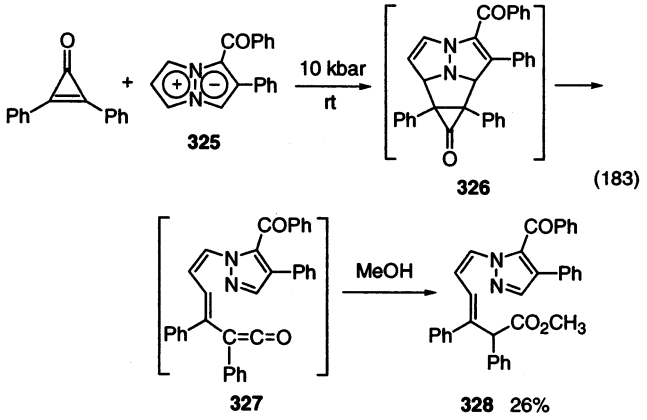
The addition of diphenylcyclopropenone to a reactive furan, 3,4-dimethoxyfuran, gave 2,3-dimethoxy-5,6-diphenylphenol **324**, which is considered to be formed via [4 + 2] addition and subsequent decarbonylation and rearrangement, in 24% yield (eq 182).[295] The formation of **324** was facilitated (51% yield) by conducting the reaction under high pressure, 8−10 kbar. Unsubstituted furan, on the other hand, did not give a cycloadduct, even at 10 kbar.

The addition of diphenylcyclopropenone to diazapentalene **325** did not proceed significantly, but the



(182)

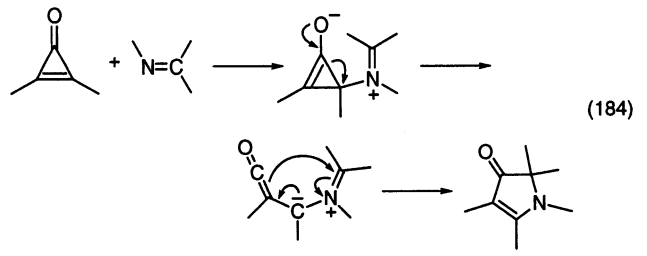
reaction at 10 kbar and subsequent treatment with methanol gave the pyrazole derivative **328**. This product can be formed by cycloaddition to give **326**, ring opening to **327**, and addition of methanol (eq 183).[296]



(183)

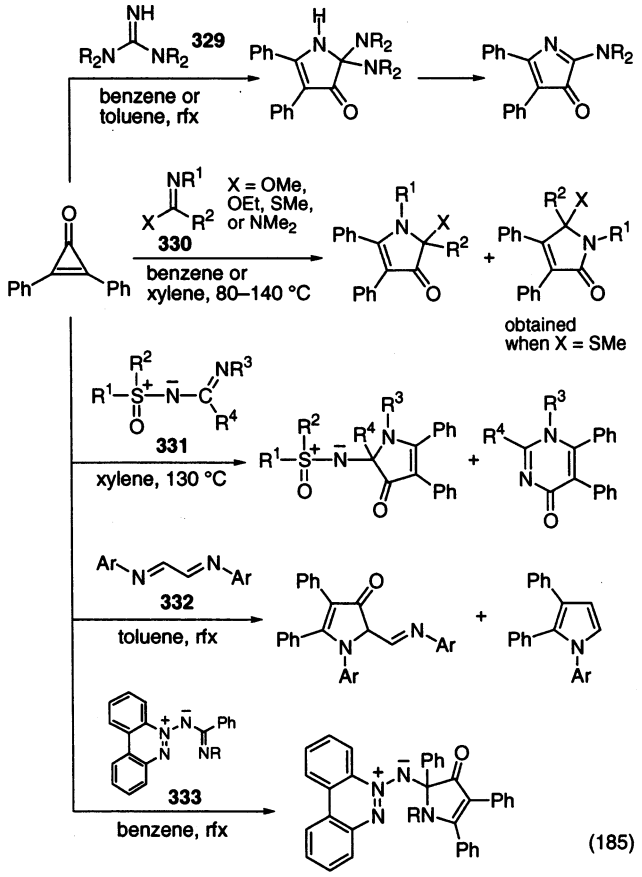
2. Addition with Cleavage of C–C Single Bond

The addition of polarized π-bonds such as C═N, C═C, N═N, C═S, C≡C, and C≡N to cyclopropenones is a well-known reaction. The C—C single bonds of the three-membered ring, which have a π character due to the ring strain, are cleaved, and the three carbon atoms, bearing the substituents and carbonyl oxygen, become a part of the larger ring in the resulting [3 + 2]-type product. Generally, the course of the reaction can be explained by the initial attack of the nucleophilic atom to C-2 of cyclopropenone followed by ring opening of the resulting Michael adduct (eq 184).



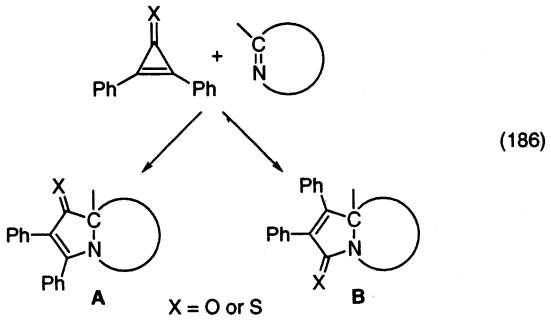
(184)

Diphenylcyclopropenone undergoes cycloaddition to the cyclopropene C—C bond with compounds containing an imine structure, such as guanidines **329**,[297] carboximidates **330** (X = OMe, OEt),[298] a carboximidothioate **330** (X = SMe),[298] amidines **330** (X = NMe_2),[298] *N*-imidoyl sulfoximide **331**,[299] 1,4-diazabutadienes **332**,[300] and benzo[*c*]cinnolinium *N*-imide **333**,[301] upon heating in solution (eq 185).



(185)

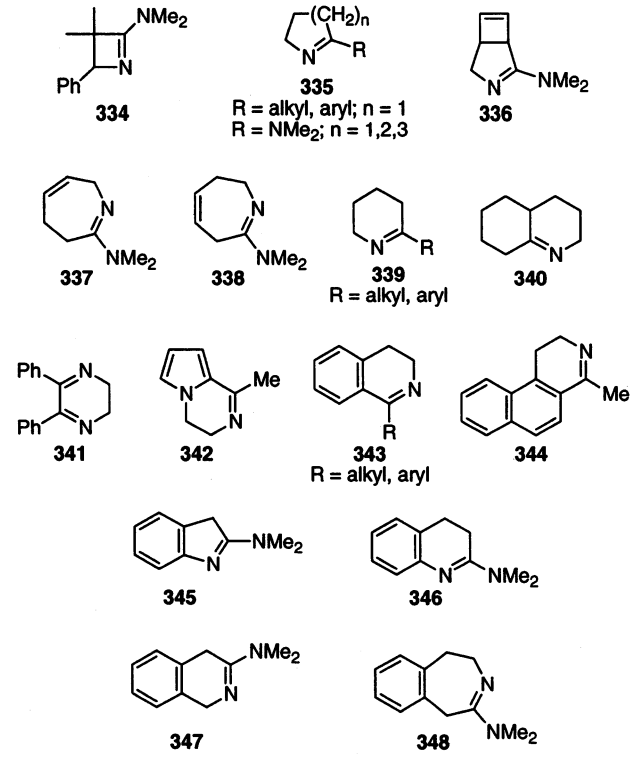
Heterocycles having a C═N double bond in the ring also form cycloadducts with cyclopropenones and their thione analogues (eq 186). Cyclic amidines



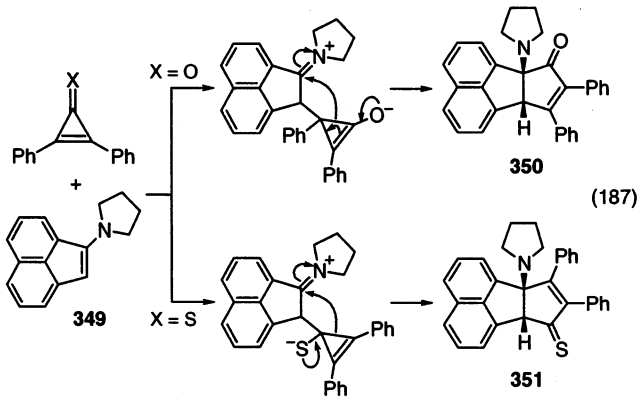
(186)

334,[302] **335** (R = NMe_2),[303] and **336**—**338**[303] and cyclic imines **335** (R = alkyl, aryl) and **339**—**344**[304] reacted in a similar fashion with diphenylcyclopropenones to yield adducts having structure **A** (X = O). Imines **343** and **344** also gave adducts of type **A** (X = S) with diphenylcyclopropenethione.[304] On the other hand, benzo-annelated amidines **345**—**348** have been reported to add to diphenylcyclopropenone in the opposite way, to give products of structure **B** (X = O).[304]

Reactions of enamines with cyclopropenones and cyclopropenethione have been shown by earlier studies to give C—N insertion products, in which the C—N bond of the enamine is divided by a ring-opened cyclopropenone (or its sulfur analogue), —C═C—(C═X)—.[4,305,306] In the reaction with 1-(1-pyrrolidin-



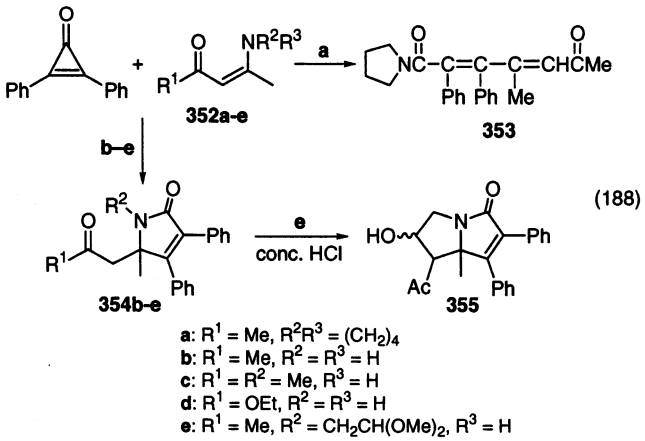
yl)acenaphthylene **349** with diphenylcyclopropenone, however, no C—N insertion was observed. Instead, the major product was cycloadduct **350** (eq 187).[307]

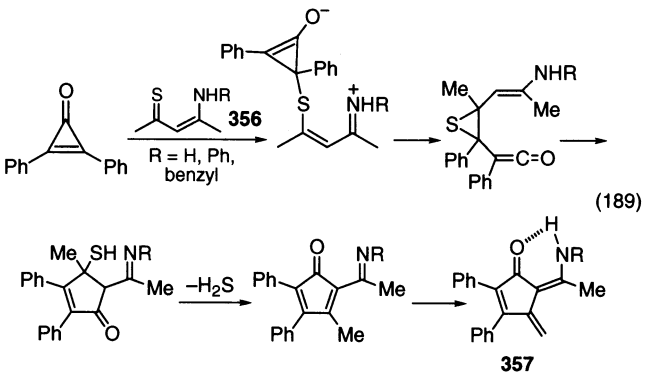


It is noteworthy that the regiochemistry of the addition was reversed to afford **351** in the reaction with diphenylcyclopropenethione. This suggests that, while initial attack of **349** occurs on C-2 of the cyclopropenone, the cyclopropenethione undergoes nucleophilic attack at the thiocarbonyl carbon.

While the reaction of tertiary enaminone **352a** with diphenylcyclopropenone gave C—N insertion product **353**, cycloadducts **354b**—**e** were obtained with secondary enaminones **352b**—**e** (eq 188).[308,309] Cycloadducts **354b**—**e** have an activated methylene group next to the acyl group, and, in the case of **354e**, a second ring was constructed by intramolecular aldol condensation, to afford **355** upon treatment with concentrated HCl.[309]

With secondary enaminethiones **356**, diphenylcyclopropenone gave 4,5-dimethylenecyclopentanone derivatives **357**. A mechanism initiated by nucleophilic attack of the sulfur atom of the thiocarbonyl group to the cyclopropenone at C-2 has been proposed (eq 189).[310] Addition of aza-analogues of **356**, *N*-benzoylacetamidine, and *N*-(methoxycarbonyl)benzamidine to diphenylcyclopropenone has been also reported.[311]



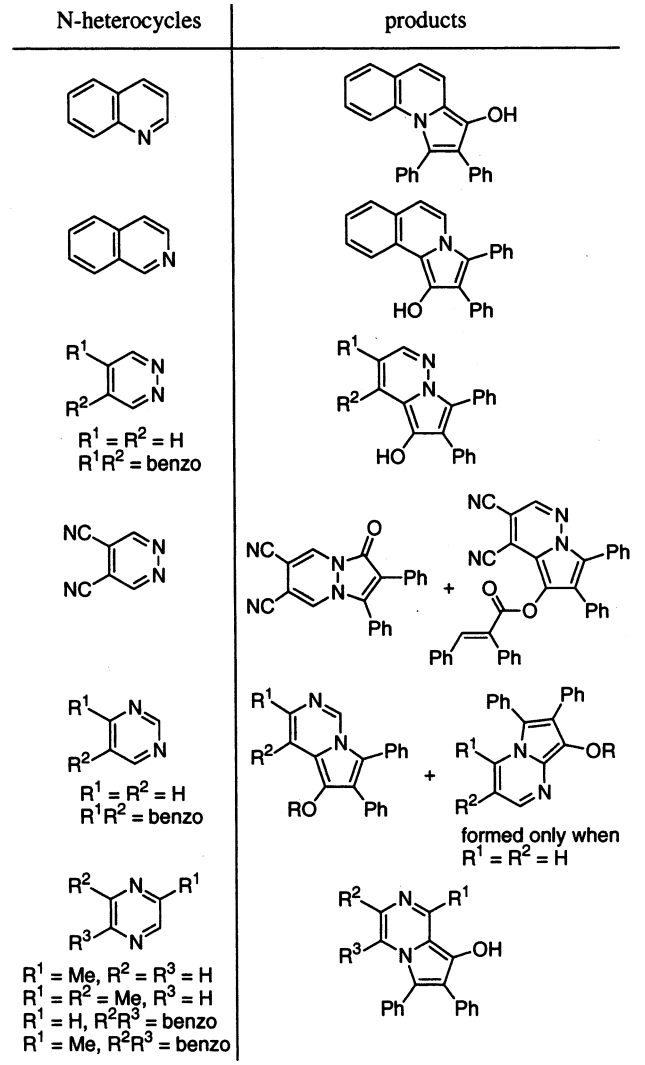


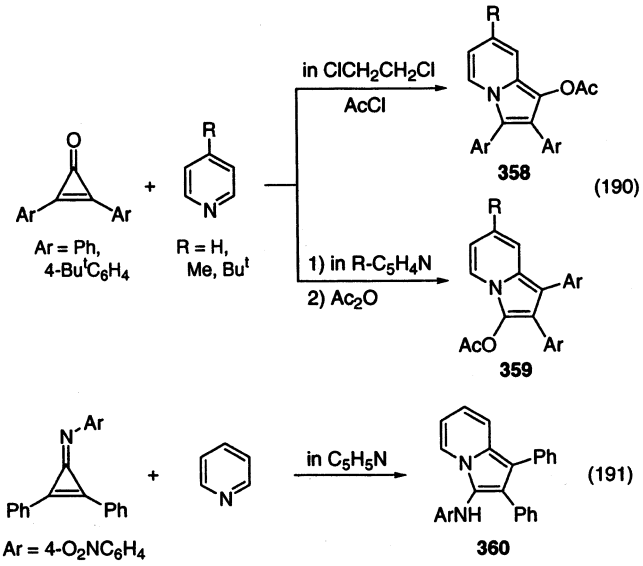
Pyridine and other nitrogen heteroaromatics effectively add to cyclopropenone and its heteroanalogues to afford a product expected from eq 186. It has been found that, while addition of unsubstituted or 4-alkylpyridines to diphenyl- and bis(4-*tert*-butylphenyl)-cyclopropenone gave the expected product **358** in inert solvents, use of the reactant pyridine as solvent inverted the regioselectivity, to form **359** as the principal product (eq 190).[312,313] A nitrogen analogue, 2,3-diphenyl-*N*-(4-nitrophenyl)cyclopropenimine, has been reported to give a similar adduct **360** with pyridine (eq 191).[38]

Diphenylcyclopropenone underwent cycloaddition at the C—C single bond with some other nitrogen heterocycles, e.g. quinoline, isoquinoline, and those having pyridazine, pyrimidine or pyrazine structural units (Table 6).[314,315] In most cases, the products of addition at a C=N bond were obtained, consistent with the reaction pathway illustrated in eq 184. Reactions with triazines have been also reported (Table 7).[316,317] In these reactions, addition occurred at an N=N bond. This can be explained by the nucleophilic attack by one of the nitrogen atoms to the C-2 of the cyclopropenone and subsequent rearrangement which is similar to that shown in eq 184.

The formation of similar adducts has been observed from compounds containing a C=S bond. Treatment

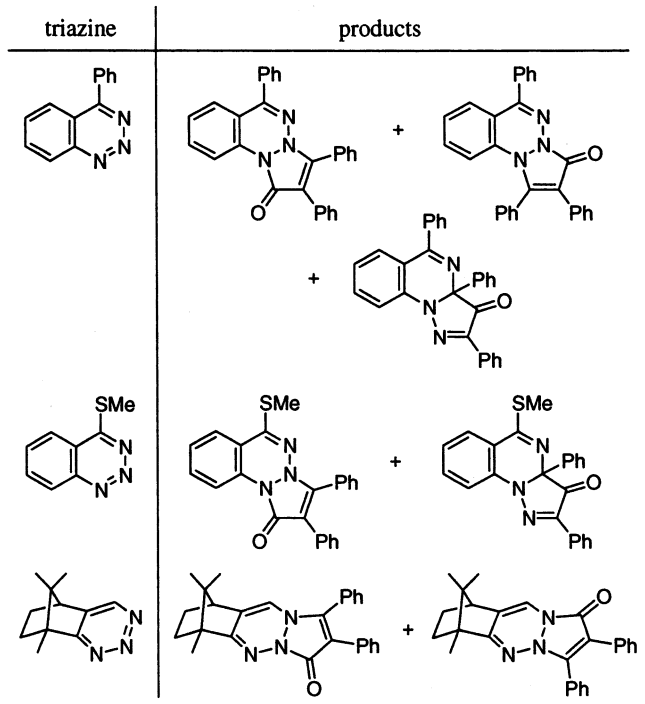
Table 6. Addition of Diphenylcyclopropenone with N-Heterocycles

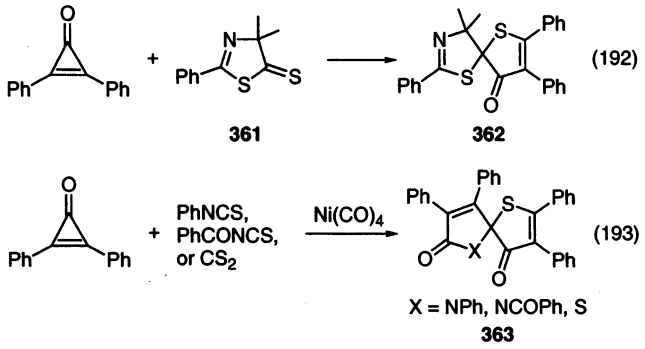




of diphenylcyclopropenone with thiazolinethione **361**, which has a thiocarbonyl group activated by an adjacent sulfur atom, gave dithiaspiro[4.4]nonadiene **362** (eq 192).[318] Isothiocyanates and carbon disulfides underwent tandem addition of two molecules of diphenylcyclopropenone in the presence of $Ni(CO)_4$ to produce heterocyclic spiro compounds **363** (eq 193).[319]

Table 7. Addition of Diphenylcyclopropenone with Triazines

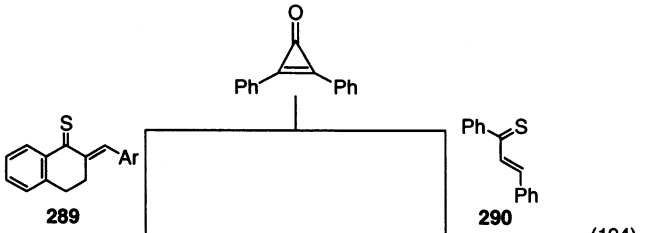




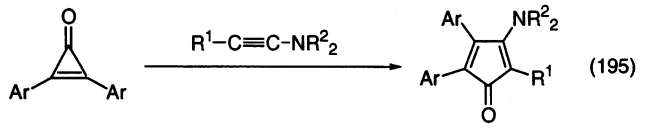
α,β-Unsaturated thiones **289** and **290** underwent [4 + 2] addition at the C−C single bond of cyclopropenone (eq 194).[276] The resulting intermediate, having a heterocyclic seven-membered ring, cleaved with a loss of arylketene (or sulfur atom) to give a thiophene (or a phenol). This is in contrast to the reactions of diphenylcyclopropenethione with **289** and **290**, which produced 1,3-dithiins by addition to the C=S bond (eq 168).

Adducts have been also obtained from diphenylcyclopropenone and its thione analogue with ynamines,[320] cyanobenzylidenephosphorane **364**,[321] dehydrodithizone **365**,[322] and pyrroloimidazole betaine **366** (eqs 195−198).[323]

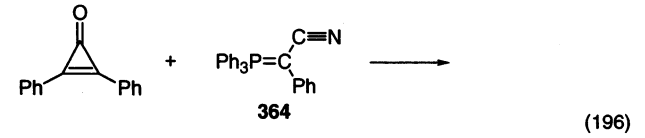
Kinetically stabilized phosphaalkyne reacted with phosphatriafulvene to form iso-1,3-diphosphinine **367** (eq 199).[260] Trimethylsilyl-substituted phosphatriafulvene gave compounds with a different π-system, 1,3-diphosphinines **368**, under similar conditions (eq 200).[324]



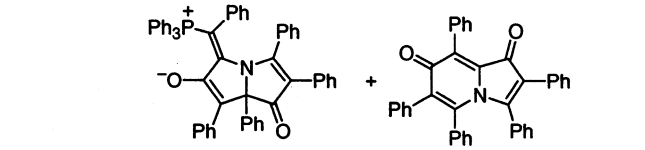
(194)



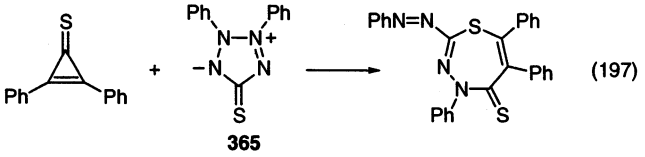
(195)

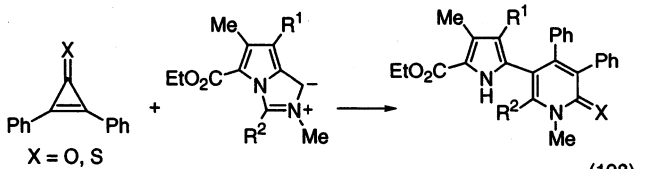


(196)

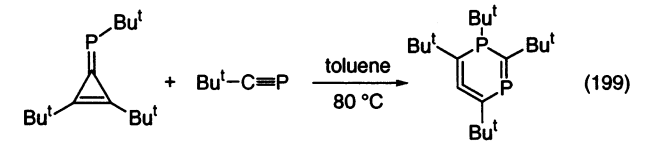


(197)

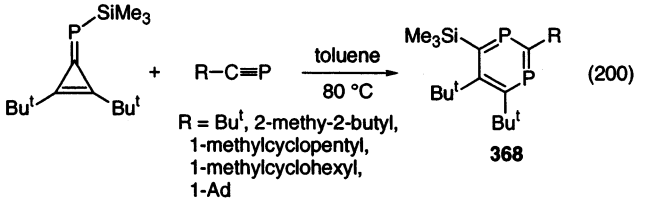




(198)



(199)

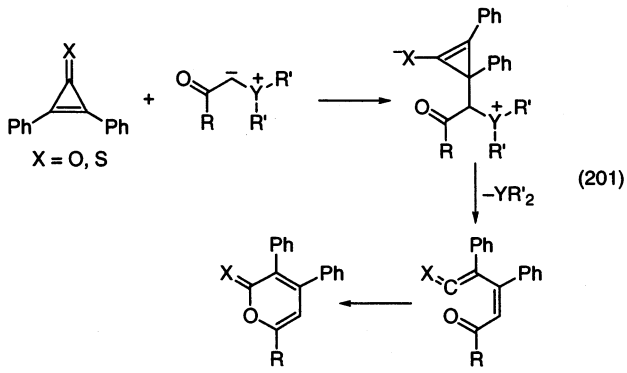


(200)

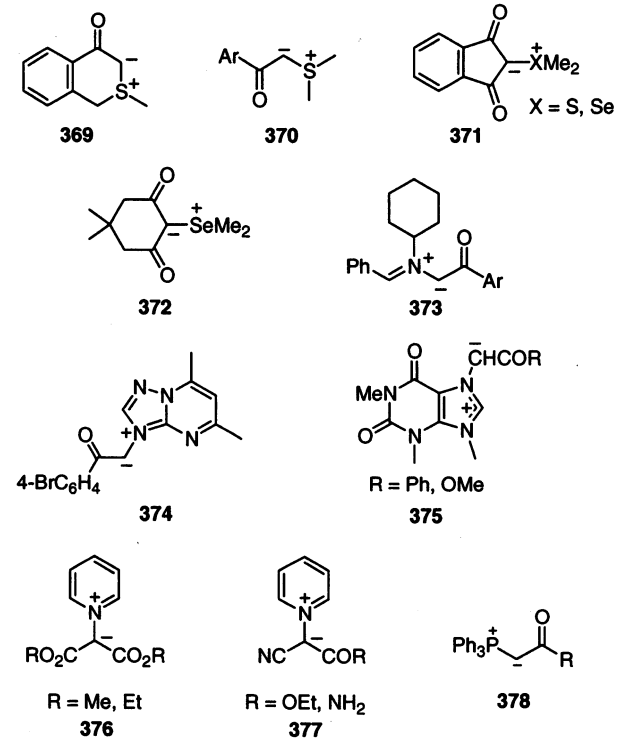
D. Reaction with Nucleophiles

1. Ring Expansion

In the reaction of cyclopropenones with ylides of type $C^-—Y^+$ (Y = S, Se, N) that are stabilized by carbonyl group(s) adjacent to the anionic carbon, formal insertion of a fragment of the ylide, —O—C=C—, to the C—C single bond of the cyclopropenone occurs to form a product with a six-membered ring. The C—Y bond of the ylide is broken, resulting in loss of the atom Y with groups attached to it. A possible reaction pathway is illustrated in eq 201. The reported examples include the reactions of cyclopropenones with sulfonium ylides **369**,[325] **370**,[326,327] and **371** (X = S),[328] selenonium ylides **371** (X = Se)[328] and **372**,[328] and ammonium ylides **373**,[329,330] **374**,[331] and **375**.[332] Diphenylcyclopropenethione is also reported to undergo similar reactions with ylides **369**,[325] **376**,[333,334] **377**,[334,335] and **378**.[336]

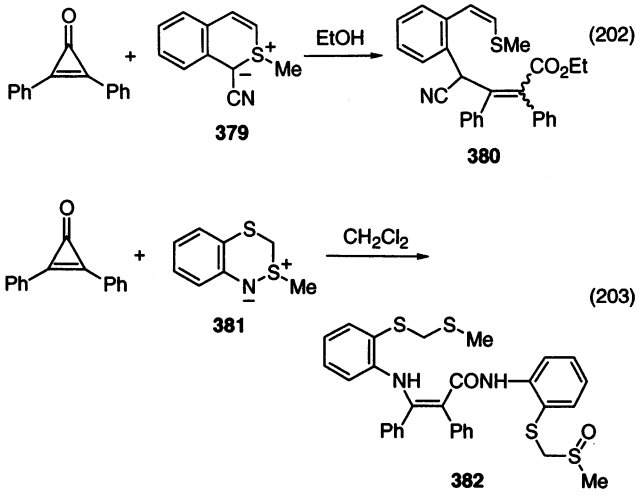


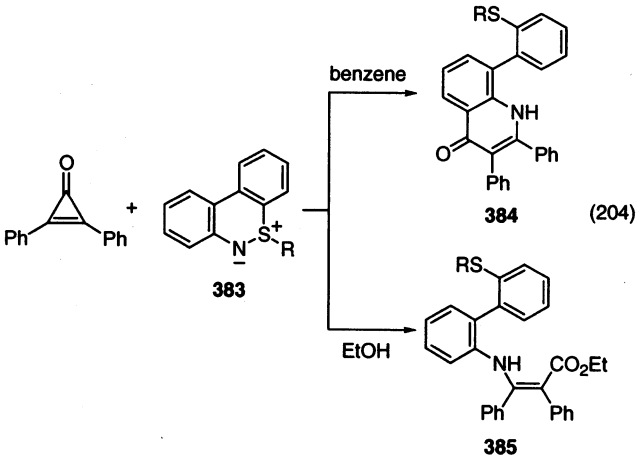
(201)



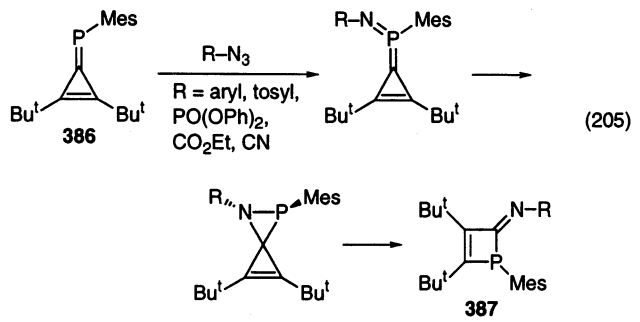
When the reaction of an ylide was carried out in a nucleophilic solvent, the ketene intermediate formed

by the collapse of the initial Michael-type adduct (eq 201) was trapped to give a ring-opened product. Reaction of diphenylcyclopropenone with thianaphthalene **379** in ethanol afforded a ring-opened ester **380** in 81% yield (eq 202).[337] In the reaction with ylide **381**, trapping of the ketene by a second molecule of **381** yielded a 1:2 adduct **382** in 11% yield (eq 203).[338] While the reaction of thiaazaphenanthrene **383** with diphenylcyclopropenone in benzene gave the cycloadduct **384**, the same reaction in ethanol afforded the ring-opened ester **385** (eq 204).[339]

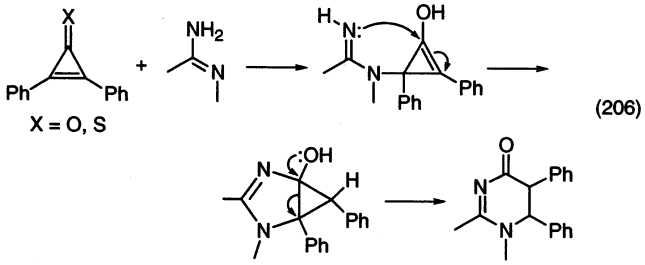




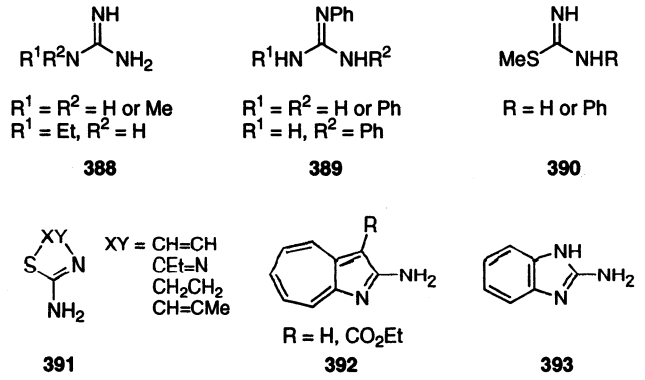
Mesitylphosphatriafulvene **386** reacted with azides to afford the ring-enlarged products **387**.[340] This reaction has been explained by the initial attachment of the R—N═ group to the phosphorus atom and subsequent 1,3-ring closure and rearrangement (eq 205).



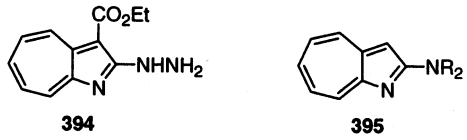
Guanidines and related compounds that have an amidine structural unit —C(═NR[1])NHR[2] add to diphenylcyclopropenone at the C—C single bond. A typical reaction pathway is given in eq 206. The



product is different from that of the aforementioned cycloadditions, in that the C═C double bond in the cyclopropene ring has been converted to a C—C single bond due to the shift of hydrogen from nitrogen to these carbon atoms. Such reactions have been reported for guanidines **388** and **389**,[297] isothioureas **390**[341] and **391**,[342] 2-amino-1-azaazulenes **392**,[343] and 2-aminobenzimidazole **393**.[342]



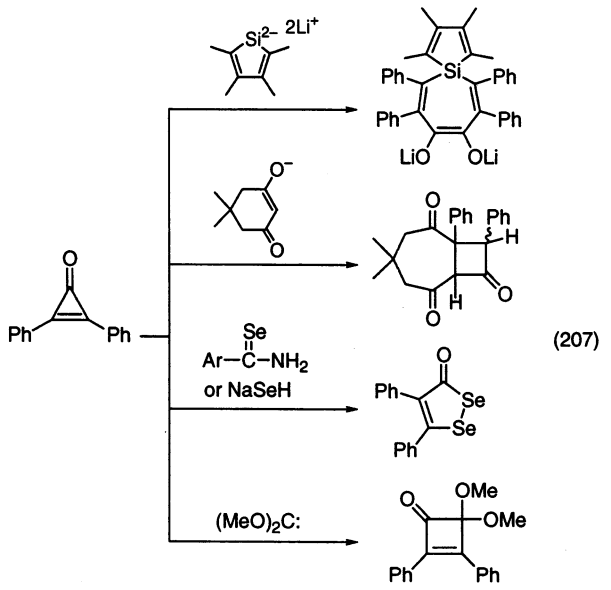
In contrast to the reaction of **392**, where initial nucleophilic attack occurs by 1-aza nitrogen (see eq 206), the reactions of closely related compounds 2-hydrazino-1-azaazulene **394**[344] and 2-(alkylamino)-1-azaazulenes **395**[345] with diphenylcyclopropenone have been reported to start with attack at different positions, the terminal hydrazine nitrogen in **394** and C-3 and C-4 of the azulene ring in **395**, to give mixtures of cycloadducts.



Other nucleophiles, such as phosphine, silole dianion,[346] the enolate ion of 1,3-diketone,[347] selenoamide,[348] and NaSeH,[348] are known to give ring expansion products (eq 207). Dimethoxycarbene is a singlet carbene that is expected to have a nucleophilic character, and this carbene is also known to react with diphenylcyclopropenone to give a ring expansion product (eq 207).[349]

2. Nucleophilic Addition with Ring Opening

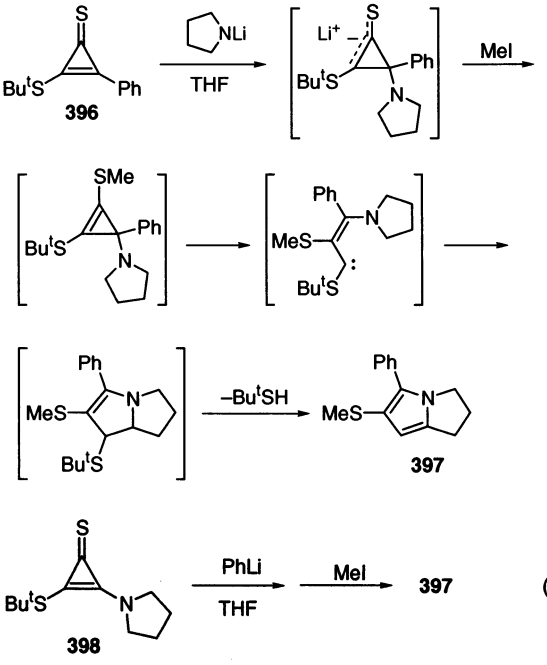
Simple C, N, P, and O nucleophiles attack at C-1 (carbonyl carbon) or C-2 (olefinic carbon). The result-



(207)

ing intermediates usually undergo CC bond cleavage to give ring-opening products, but in some exceptional cases products that retain the original three-membered ring have been obtained.

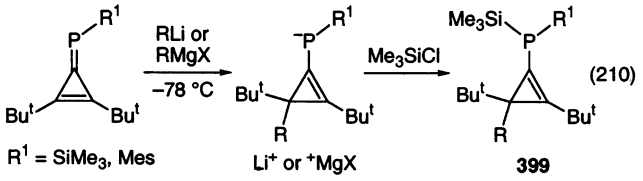
The reaction of 2-*tert*-butylthio-3-phenylcyclopropenethione **396** with lithium pyrrolidinide, followed by methylation with methyl iodide, gave the 1*H*-pyrrolidine derivative **397** (eq 208).[350,351] Similar results have been observed for *N*-lithium salts of other cyclic amines. Interestingly, the reaction of 2-*tert*-butylthio-3-(pyrrolidin-1-yl)cyclopropenethione **398** with phenyllithium also gave **397** (eq 209).[351]



(208)

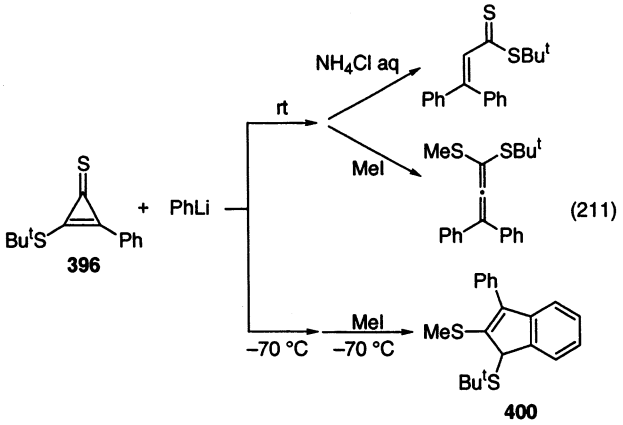
(209)

Earlier studies indicated that phenylmagnesium bromide attacks diphenylcyclopropenone at the carbonyl carbon (C-1),[36a] while phenyllithium attacks the vinylic carbon (C-2).[352] In the latter reaction, a ring-opening product, 1,2,2-triphenylpropionic acid, was obtained. Recently, the product of addition at vinylic carbon, **399**, was obtained without ring opening in the reactions of RLi or RMgX (R = Me, Bu^t, Ph) with phosphatriafulvenes (eq 210).[275]



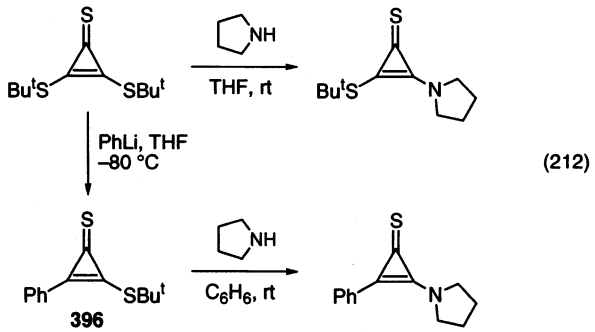
(210)

It was shown that 2-*tert*-butylthio-3-phenylcyclopropenethione **396** gives ring-opening products with phenyllithium at room temperature,[353] but the reaction at −70 °C, followed by treatment with MeI, proceeded through a pathway analogous to that shown in eq 208, to give **400** (eq 211).[351]



(211)

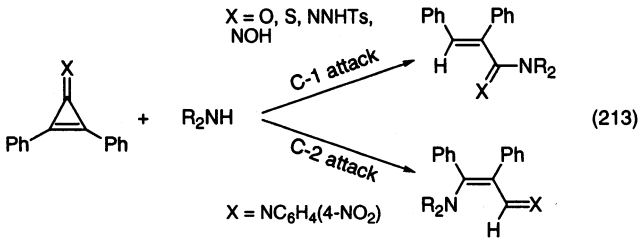
A related thione, bis(*tert*-butylthio)cyclopropenethione, underwent substitution of a Bu^{t}S group, rather than addition−ring opening, by pyrrolidine at room temperature or by phenyllithium at −80 °C (eq 212).[354] The Bu^{t}S group in thione **396** was also substituted with pyrrolidine (eq 212).[354]



(212)

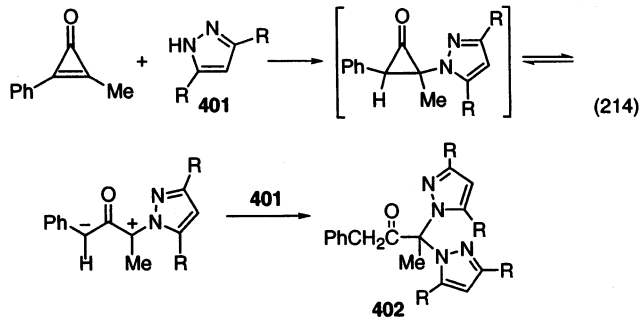
Nucleophilic attack of amines to diphenylcyclopropenone or its heteroanalogues occurs on cyclopropene ring carbons, to give the corresponding ring-opened adducts (eq 213) or compounds derived from these initial products. While the 4-nitrophenylimine with dialkylamines gave a product from the C-2 attack, other reactions in eq 213 gave products from the C-1 attack.[355]

Methylphenylcyclopropenone reacted with pyrazoles **401** to afford ketones **402**, formed by initial nucleophilic attack by N at a vinyl carbon bearing the methyl group (eq 214).[356] This was in agreement with an AM1 calculation, which indicated that attack



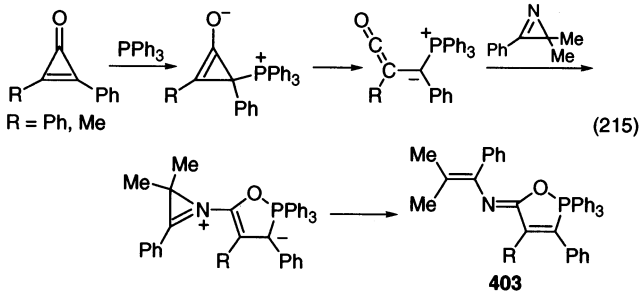
(213)

at this carbon is kinetically favored due to a higher LUMO coefficient than at the other vinylic carbon.



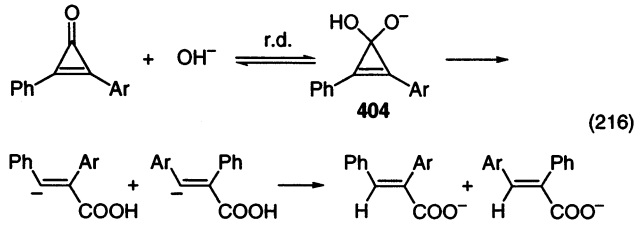
(214)

Diaryl- or alkylarylcyclopropenones underwent nucleophilic attack at the carbonyl carbon by other simple nucleophiles such as OH^-,[36a,357] MeO^-,[358] and RSH,[359] leading to ring-opening products. Cyclopropenimines have been reported to undergo ring opening by MeOH and EtOH.[38] The reaction of cyclopropenones with triphenylphosphine in the presence of dimethylphenylazirine gave the oxaphospholenes **403** as a result of the attack of PPh_3 to C-2 of the cyclopropenone, to form a ketene intermediate, and subsequent nucleophilic attack of azirine nitrogen at the electrophilic ketene carbon (eq 215).[360]



(215)

The rates of base-catalyzed ring opening of 2-phenyl-3-(2-, 3-, or 4-substituted phenyl)cyclopropenones to give the corresponding (*E*)-2,3-diphenylacrylic acids have been determined in water (eq 216).[357] The

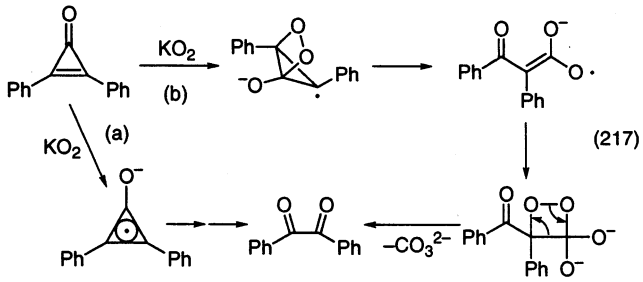


(216)

effects of meta and para substituents on the rates have been correlated using the Hammett equation to give a ρ value of 1.2. Comparison of this value with the ρ values for related reactions suggested that negative charge in the transition state resides on the carbonyl oxygen; i.e., the rate-determining step is the formation of adduct **404**.

E. Oxidation and Reduction

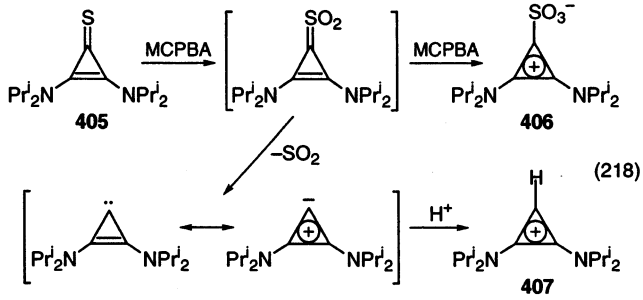
Oxidation of diphenylcyclopropenone with 2 equiv of KO_2 in benzene in the presence of dicyclohexano-18-crown-6 gave benzil. The reaction can be accounted for by (a) electron transfer to form the radical anion (eq 217a), which is eventually converted to benzil in the presence of oxygen, or (b) addition of superoxide to the C=C bond to form a dioxetane and its further transformation (eq 217b).[361]



(217)

The addition of $^1O_2$ to the C=S bond of diphenylcyclopropenethione, shown in eq 173, is another example of oxidation by activated oxygen.[282]

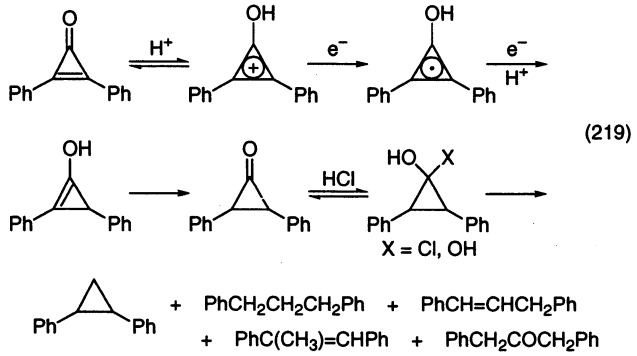
Oxidation of 1,2-bis(diisopropylamino)cyclopropenethione **405** has been studied with several oxidizing reagents.[66] While reaction of this thione with 2 equiv of *m*-chloroperbenzoic acid (MCPBA) at low temperature, followed by treatment with perchloric acid, gave diaminocyclopropenylium ion **407**, reaction with excess MCPBA gave the thione-*S*,*S*,*S*-trioxide **406** (eq 218). Cation **407** was also obtained by the oxidation of **405** with nitric acid. Oxidation of **405** with $FeCl_3$ yielded a S−S-bridged dication bis(cyclopropenyliumyl).



(218)

Early reports indicated that the reduction of diphenylcyclopropenone with metals such as Na−Hg, Mg−MgI_2, and Al−Hg in nonacidic media gave dimeric aromatized products.[362,363] Reduction with zinc amalgam in 7 M HCl or AcOH, however, gave mixtures of 1,2-diphenylcyclopropane, 1,3-diphenylpropane, diphenylpropene isomers, and dibenzyl ketone (eq 219).[364] A mechanism involving stepwise two-electron reduction to form hydroxychlorocyclopropenone, which undergoes acid-catalyzed rearrangement and further reduction by zinc, has been proposed. It is known that treatment of diphenylcy-

clopropenone with B_2H_6 also yields diphenylcyclopropane.[365]



(219)

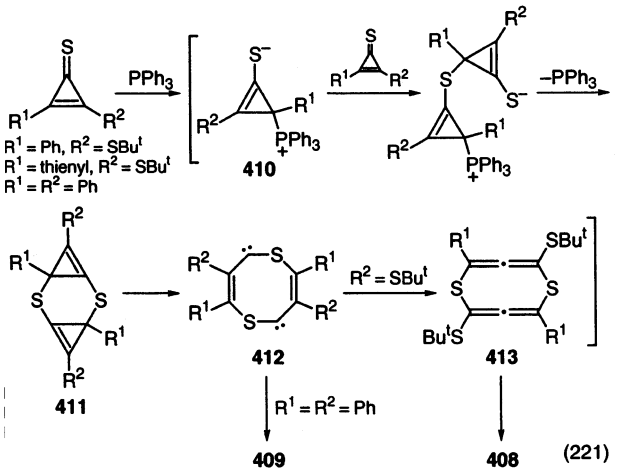
F. Rearrangement

Treatment of cyclopropenethiones with $Bu^n{}_3P$ or Ph_3P afforded a product of dimerization, thieno[3,2-*b*]thiophene **408** or thieno[3,4-*c*]thiophene **409** derivatives (eq 220).[243,366−370] In a mechanism proposed in one of these reports[370] (eq 221), triphenylphosphine attacks at the vinylic carbon of cyclopropenethiones, to form adduct **410**, which attacks another molecule of the cyclopropenethione. The resulting dimeric intermediate **411** is converted to **409** via bis(vinylcarbene) **412**, but when $R^2 = SBu^t$, **408** is formed via bisallene **413**.

(220)

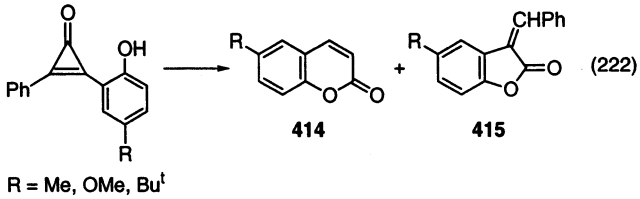
R^1	R^2	R	product (yield, %)	ref.
SBu^t	SBu^t	Bu^n	**408** (40)	366–368
SBu^t	SEt	Ph	**408** (26)	366–368
SBu^t	SMe	Ph	**408** (24)	366–368
SPr^i	SPr^i	Ph	**408** (68)	366–368
SEt	SEt	Ph	**408** (53)	368
Ph	SBu^t	Ph	**408** (46)	369,370
2-thienyl	SBu^t	Ph	**408** (21)	369,370
Ph	Ph	Ph	**409** (9)	370
Ar	Ar	Bu^n	**409** (35)	243

(Ar = 3,5-$Bu^t{}_2$-4-OHC_6H_2)



(221)

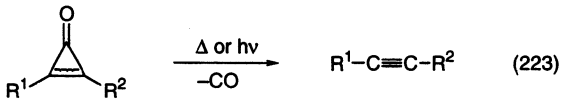
2-Phenyl-3-(2-hydroxyphenyl)cyclopropenones have been found to undergo thermal rearrangement induced by the intramolecular attack of hydroxyl oxygen to the carbonyl carbon to give lactones **414** and **415** (eq 222).[214]



(222)

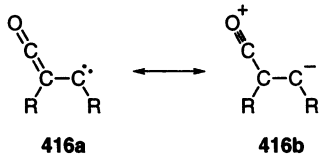
G. Decarbonylation

By photochemical and thermal decarbonylation, cyclopropenones can be converted into acetylenes and carbon monoxide (eq 223).[4]



(223)

Theoretical studies using DFT and MO calculations indicated that this reaction proceeds through a stepwise mechanism. A resonance hybrid of a semicarbene **416a** and a semi-zwitterion **416b** was suggested as an intermediate.[371]



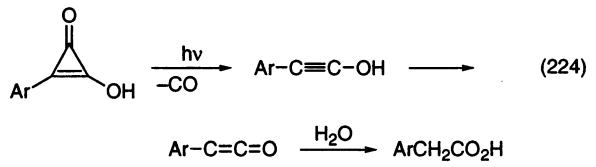
The photochemical decarbonylations are generally clean and of high yield, thus providing a synthetically useful method for the preparation of acetylene derivatives. This process was applied for the preparation of diarylcyclopropenones (eq 223; $R^1 = R^2 =$ aryl)[9,214,358] and alkoxyarylcyclopropenones (eq 223; $R^1 =$ aryl, $R^2 =$ alkoxy).[215]

Diarylcyclopropenones have also been converted to acetylenes with high efficiency by heating in 1,2-dichlorobenzene in the presence of Al_2O_3.[213] Bis(dialkylamino)acetylenes (alkyl = Me and Et) have been obtained by the vapor-phase pyrolysis of bis(dialkylamino)cyclopropenones in 80 and 85% yields, respectively.[218]

In contrast to these reactions, photolysis of diphenylcyclopropenethione did not give the corresponding acetylene, but rather afforded the products of dimerization, ring expansion, and/or ring opening.[282]

Photolysis of arylhydroxycyclopropenones also leads to decarbonylation, but the resulting hydroxy-substituted acetylenes are highly reactive, isomerizing to ketene derivatives. Laser flash photolysis studies of arylhydroxycyclopropenones have indicated that an arylhydroxyacetylene and an arylketene were formed as the primary and secondary transient species, respectively, through which the final product, arylacetic acid, was produced (eq 224).[372−374]

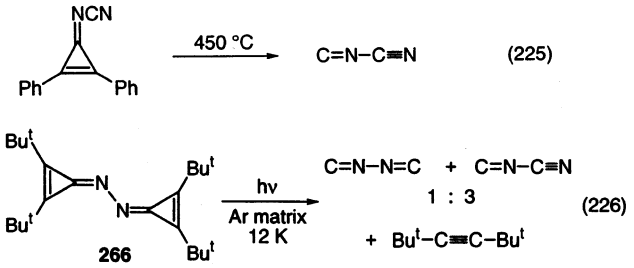
Similarly, decarbonylation of cyclopropenones having an amino substituent by flash photolysis gave



(224)

carboxylic acid amides via aminoacetylene and ketenimine intermediates.[375,376] Difluorocyclopropenone, generated by irradiation (240 nm) of difluoromaleic anhydride at 11 K in an Ar matrix (see eq 148), was decomposed by irradiation at a shorter wavelength (>185 nm) to form difluoroacetylene and carbon monoxide with a minor product, difluoropropadienone $F_2C{=}C{=}C{=}O$.[235]

Isocyanogen CNCN was produced by pyrolysis of *N*-cyano-2,3-diphenylcyclopropenimine (eq 225).[377] The molecule was identified by high-resolution IR and millimeter wave spectroscopy. Photolysis of cyclopropenonazine **266** in an Ar matrix at 12 K caused a clean fragmentation into diisocyanogen CNNC and di-*tert*-butylacetylene (eq 226).[252]



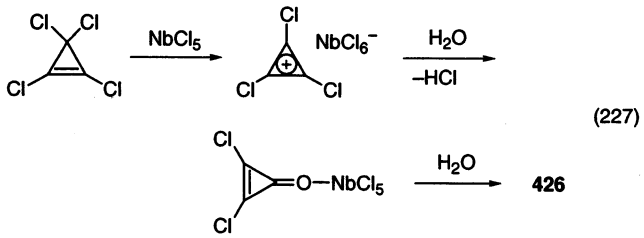
(225)

(226)

H. Formation of Metal Complexes

Cyclopropenones and their heteroanalogues form complexes with a variety of transition metals and other metals. They can act as a π-donor at a C=C bond or an n-donor at oxygen (or heteroatom). Both types of complexes are known, but due to the polarized nature of cyclopropenone ($>C^+-O^-$), most works are related to complexation at the C=X bond rather than at the C=C bond.

Coordination of the carbonyl oxygen to a metal to form a stable adduct is the simplest and most commonly observed mode of complexation. Such complexes are summarized in Table 8. Except for **426**, all the complexes were prepared by the reaction of a cyclopropenone and a metal reagent. Complex **426** was synthesized by treatment of tetrachlorocyclopropene with $NbCl_5$ and subsequent partial hydrolysis (eq 227).[390]

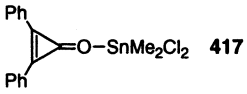
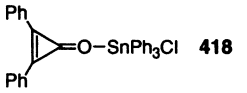
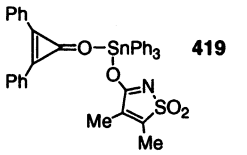
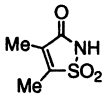
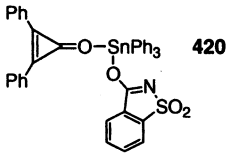
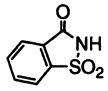
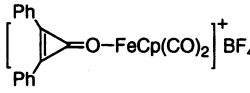
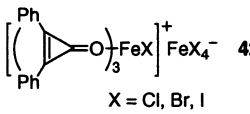
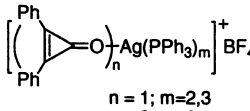
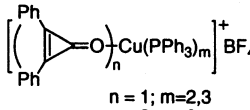
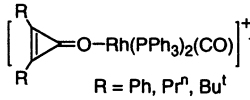
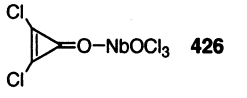
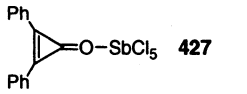


(227)

The structures of compounds **417**,[378,379] **418**,[380] **419**,[381] **420**,[381] **423** ($n = m = 2$),[386] **425** (R = Bu^t),[389] and **426**[390] were determined by X-ray single-crystal analysis. Intramolecular bridging was observed for the crystals of **417** (Figure 21) and **426** (Figure 22).

In other cases, the structure was assigned on the basis of the IR and NMR data. The most distinctive feature of this class of complexes is significant reduction (~80 Hz) in the carbonyl stretching frequency compared with that of free cyclopropenone. This indicates the contribution of the resonance $>C{=}O^+-M^- \leftrightarrow >C^+-O-M^-$ and is indicative of binding of metal through the carbonyl oxygen atom without the opening of the three-membered ring. For complex **425**, ^{31}P and ^{13}C NMR indicated equivalence

Table 8. Metal Complexes of Cyclopropenones

complex	reagent for complex formation	ref.
 **417**	Me_2SnCl_2	378, 379
 **418**	Ph_3SnCl	380
 **419**	Ph_3SnOH + 	381
 **420**	Ph_3SnOH + 	381, 382
 **421**	$[FeCp(CO)_2(H_2C{=}CMe_2)]^+ BF_4^-$	383, 384
 **422** X = Cl, Br, I	$FeCp(CO)_2X$	385
 **423** n = 1; m=2,3 n = 2; m=2	$(Ph_3P)_mAg^+ BF_4^-$	386, 387
 **424** n = 1; m=2,3 n = 2; m=2	$(Ph_3P)_mCu^+ BF_4^-$	387, 388
 **425** R = Ph, Pr^n, Bu^t	$(PPh_3)_2Rh(CO)(OTf)$	389
 **426**	see text	390
 **427**	$SbCl_5$	391

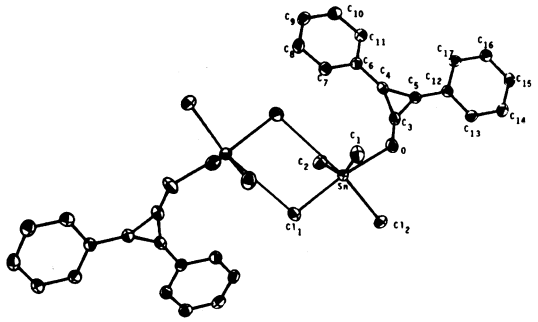


Figure 21. ORTEP drawing of complex **417**. [Reprinted with permission from ref 379. Copyright 1982 American Chemical Society.]

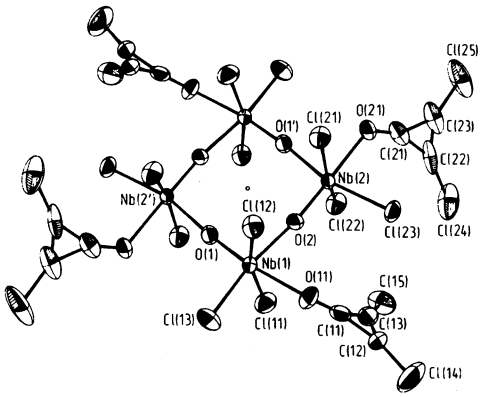
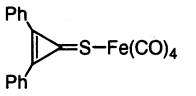
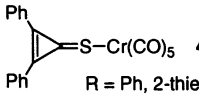
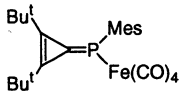
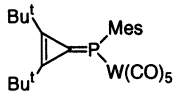


Figure 22. ORTEP drawing of complex **426**. [Reprinted with permission from ref 390. Copyright 1988 Verlag der Zeitschrift für Naturforschung.]

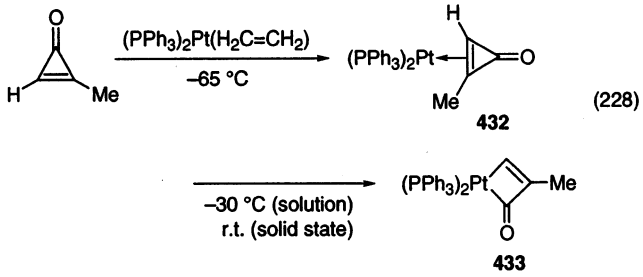
Table 9. Metal Complexes of Cyclopropenethiones and Phosphatriafulvenes

complex		reagent for complex formation	ref.
	**428**	$Fe_2(CO)_9$	392 393
 R = Ph, 2-thienyl	**429**	$Cr(CO)_3(CH_3CN)_3$	394
	**430**	$Fe_2(CO)_9$	70
	**431**	$W(CO)_5$•THF	70

of the two PPh_3 ligands, two olefinic carbons of the three-membered ring, and two alkyl groups.

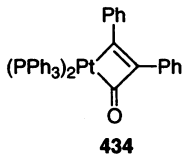
Some complexes, listed in Table 9, have been also prepared from cyclopropenethiones and phosphatriafulvenes. X-ray structural data have been obtained for complexes **428**[392] and **431**.[70]

In contrast to complexation at the carbonyl oxygen, observation of coordination at C=C double bond of cyclopropenone has been reported only for $(PPh_3)_2Pt$ complex **432**.[395] It was prepared in $CDCl_3$ at −65 °C by the ligand exchange between methylcyclopropenone and $(PPh_3)_2Pt(H_2C{=}CH_2)$ and isolated as a crystalline material (eq 228). The structure was

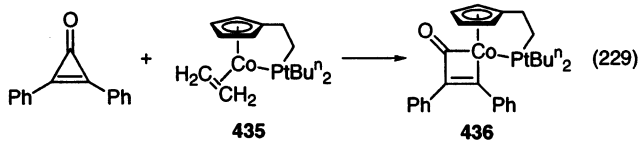


(228)

determined on the basis of $^{195}Pt-^{1}H$ and $^{31}P-^{1}H$ NMR coupling constants, which are similar to those previously observed for $(PPh_3)_2Pt$ complexes of 1,2-dimethylcyclopropene[396] and cyclic allenes.[397] Complex **432** is stable only at low temperatures; it rearranged to metallacyclobutenone **433** at −30 °C in solution or at room temperature in the solid state. The existence of Pt−metallacyclobutenone was clearly shown by the isolation and X-ray structure analysis of **434**, obtained by the reaction of diphenylcyclopropenone with $(PPh_3)_4Pt$.[398]



A metallacyclobutenone involving Co, **436**, which was formed by the reaction between diphenylcyclopropenone and cyclopentadienyl chelate **435**, could be also studied by single-crystal X-ray analysis (eq 229).[399]

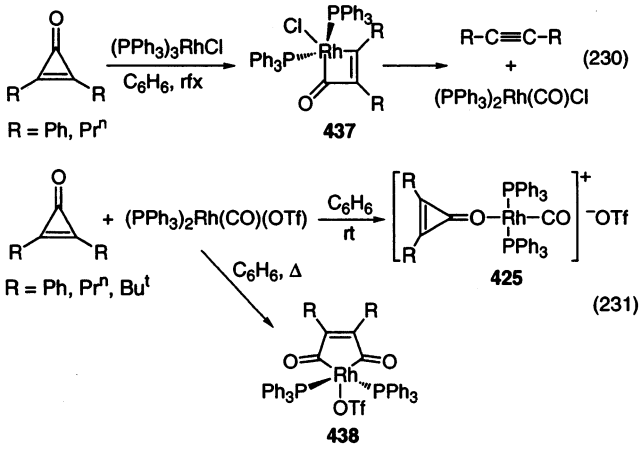


(229)

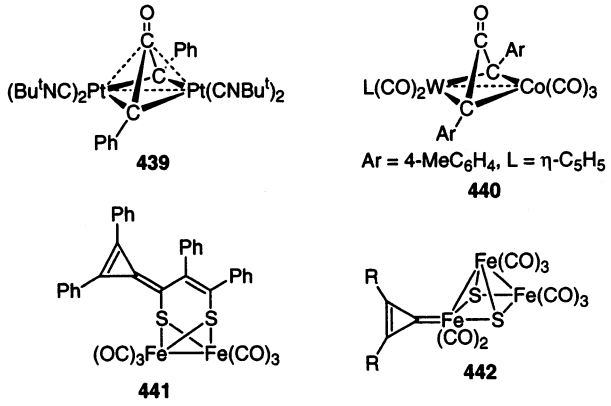
Reactions of diphenyl- or dipropylcyclopropenone with $(PPh_3)_3RhCl$ resulted in decarbonylation, for which a mechanism involving a metallacyclobutenone intermediate **437** was proposed (eq 230).[389] When allowed to react with $(Ph_3)_2Rh(CO)(OTf)$ at room temperature, however, the same cyclopropenone gave cationic complex **425** (eq 231). Reactions at 60−65 °C gave a different complex, **438**, which was considered a product of further transformation of **425** at high temperatures.[389]

Involvement of a metallacyclobutenone intermediate has been also proposed for the formation of diphenylcyclobutenones or diphenylhydroxyphenols by the reactions of cyclopropenones with Cr carbene complexes $(CO)_5Cr{=}(OMe)R$ (R = Me, cyclopropyl, Ph, 1-propenyl)[400] and dimerization of diphenyl and dipropylcyclopropenones, to form benzoquinone derivatives with bis(1,5-cyclooctadiene)nickel(0) catalyst.[401]

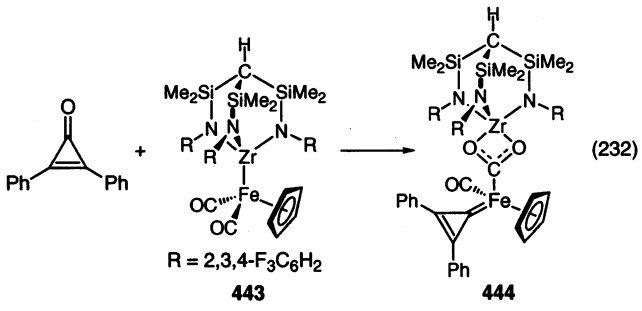
Cyclopropenones are known to give some dinuclear metal complexes and complexes with a metal-



containing cluster. When treated with $Pt_3(CNBu^t)_6$[402] and $WCo(CO)_7(\eta\text{-}C_5H_5)$,[403] diarylcyclopropenones underwent cleavage of the C=C bond, forming homo- and heterodinuclear complexes **439** and **440**, respectively. The reaction of diphenylcyclopropenethione with $Fe_2(CO)_9$ gave a complex having a triafulvene structure **441** and a carbene complex **442**.[393] The structures have been determined by X-ray analysis for complexes **439**−**442**.



Treatment of diphenylcyclopropenone with Zr−Fe dinuclear complex **443** gave a carbene complex **444**, the structure of which was determined by X-ray analysis (eq 232). The linking CO_2 unit was formed by transfer of oxygen from the cyclopropenone group to one of the CO ligands. This atom transfer was established by ^{17}O- and ^{13}C-labeling experiments.[404,405]



VI. Summary

As mentioned at the beginning of this article, cyclopropenylium cations and cyclopropenones represent the smallest ring system having the "Hückel aromaticity", which is now a rather "classical" concept, in view of various novel aromatic compounds with a variety of new structures, as demonstrated in the recent thematic issue on "Aromaticity" in this journal.[406] In accord with the recent development of theoretical calculations at high levels, renewed theoretical treatments have been made on these highly strained but stabilized systems.[407−413]

In this review, we described mainly the experimental work involving synthesis, structure, and properties, as well as reactions, of these three-membered aromatic species. As to the synthetic method, the combination techniques of C_2 and C_1 units are now well established. In addition to the all-carbon species, a trigermanium analogue of the cyclopropenylium cation and a silicon analogue of the homocyclopropenylium cation were recently synthesized, and they are included in this article. For determination of the precise structures of these species as well as the cyclopropenylium and related species, the technical development of X-ray crystallography has played a crucial role. Thus, many structural parameters for these species have been clarified, which are important in verification of the validity of theoretical calculations.

Most of the reactions of cyclopropenylium cations are those with nucleophiles to give 3-substituted cyclopropenes, which can give various types of compounds through rearrangements initiated by the cyclopropene → vinylcarbene process. On the other hand, both nucleophiles and electrophiles can react with cyclopropenones. Particularly in the past two or three decades, the synthesis and structural studies on the organometalic complexes with a three-membered ring (cyclopropenylium cation and cyclopropenone) or its rearranged system as a ligand have been developed. It is expected that the use of both cyclopropenylium cations and cyclopropenones as C_3 synthetic blocks will find more applicability in the field of synthetic chemistry in the future.

VII. References

(1) For recent reviews, see: (a) Billups, W. In *The Chemistry of the Cyclopropyl Group*; Patai, S., Rappoport, A., Eds.; Wiley Interscience: New York, 1987. (b) Komatsu, K.; Yoshida, Z. In *Methods of Organic Chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, pp 3079−3192.
(2) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318.
(3) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984.
(4) Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189.
(5) Greenberg, A.; Tomkins, R. P. T.; Dobrovolny, M.; Liebman, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 6855.
(6) Breslow, R.; Haynie, R.; Mirra, J. *J. Am. Chem. Soc.* **1959**, *81*, 247.
(7) Vol'pin, M. E.; Koreshkov, Yu. D.; Kursanov, D. N. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1959**, 560; *Chem. Abstr.* **1959**, *53*, 21799.
(8) (a) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 1459. (b) West, R.; Sado, A.; Tobey, W. *J. Am. Chem. Soc.* **1966**, *88*, 2488. (c) West, R.; Zecher, D. C.; Goyart, W. *J. Am. Chem. Soc.* **1970**, *92*, 149. (d) West, R. *Acc. Chem. Res.* **1970**, *3*, 130. (e) West, R. *Pure Appl. Chem.* **1971**, *28*, 379.
(9) Wellman, D. E.; Lassila, K. R.; West, R. *J. Org. Chem.* **1984**, *49*, 965.
(10) Bindl, J.; Seitz, P.; Seitz, U.; Salbeck, E.; Salbeck, J.; Daub, J. *Chem. Ber.* **1987**, *120*, 1747.
(11) Komatsu, K.; Tsuji, R.; Murata, Y.; Takeuchi, K. *Chem. Lett.* **1993**, 911.
(12) Musigmann, K.; Mayr, H.; de Meijere, A. *Tetrahedron Lett.* **1987**, *39*, 4517.
(13) Weiss, R.; Kölbl, H.; Schlierf, C. *J. Org. Chem.* **1976**, *41*, 2258.

(14) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607.
(15) (a) West, R.; Zecher, D. C.; Tobey, S. W. *J. Am. Chem. Soc.* **1970**, *92*, 168. (b) Chicos, J. S.; Patton, E.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 1647.
(16) Eicher, T.; Huch, V.; Schneider, V.; Veith, M. *Synthesis* **1989**, 367.
(17) Maier, G.; Volz, D.; Neudert, J. *Synthesis* **1992**, 561.
(18) de Meijere, A.; Faber, D.; Noltemeyer, M.; Boese, R.; Haumann, T.; Müller, T.; Bendikov, M.; Matzner, E.; Apeloig, Y. *J. Org. Chem.* **1996**, *61*, 8564.
(19) de Meijere, A.; Faber, D.; Heinecke, U.; Walsh, R.; Müller, T.; E.; Apeloig, Y. *Eur. J. Org. Chem.* **2001**, 663.
(20) Buchholz, H. A.; Prakash, G. K. S.; Deffieux, D.; Olah, G. A. Proc. *Natl. Acad. Sci. U.S.A.* **1999**, *96*, 10003.
(21) Prakash, G. K. S.; Buchholz, H. A.; Deffieux, D.; Olah, G. A. *Synlett* **1994**, 819.
(22) Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett.* **1980**, *21*, 947.
(23) Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1980**, *21*, 1221.
(24) Moss, R. A.; Shen, S.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J.; Munjal, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 134.
(25) Kerber, R. C.; Hsu, C.-M. *J. Am. Chem. Soc.* **1973**, *95*, 3239.
(26) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.
(27) (a) Van Dine, G. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1966**, *88*, 2321. (b) Schleyer, P. v. R.; Buss, V. *J. Am. Chem. Soc.* **1969**, *91*, 5880.
(28) (a) Komatsu, K.; Arai, M.; Okamoto, K. *Tetrahedron Lett.* **1982**, *23*, 91. (b) Komatsu, K.; Arai, M.; Hattori, Y.; Fukuyama, K.; Katsube, Y.; Okamoto, K. *J. Org. Chem.* **1987**, *52*, 2183.
(29) Fischer, H.; Troll, C. *J. Chem. Soc., Chem. Commun.* **1994**, 457.
(30) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Org. Chem.* **2000**, *65*, 1422.
(31) (a) Chance, J. M.; Geiger, J. H.; Mislow, K. *J. Am. Chem. Soc.* **1989**, *111*, 2326. (b) Chance, J. M.; Geiger, J. H.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1990**, *112*, 3540.
(32) Ciabattoni, J.; Nathan, E. C., III. *Tetrahedron Lett.* **1969**, 4997.
(33) (a) Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415. (b) Craig, N. C.; Fleming, G. F.; Pranata, J. *J. Am. Chem. Soc.* **1985**, *107*, 7324.
(34) Weiss, R.; Miess, G.-E.; Haller, A.; Reinhardt, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 103.
(35) (a) Weiss, R.; Schlierf, C.; Schloter, K. *J. Am. Chem. Soc.* **1976**, *98*, 4668. (b) Yoshida, Z.; Konishi, H.; Miura, Y.; Ogoshi, H. *Tetrahedron Lett.* **1977**, 4319.
(36) (a) Breslow, R.; Eicher, T.; Krebs, A.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1320. (b) Eicher, T.; Hansen, A. M. *Chem. Ber.* **1969**, *102*, 319.
(37) (a) Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361. (b) Stang, P. J.; Maas, G.; Smith, D. L.; McCloskey, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4837. (c) Quirk, R. P.; Gambill, C. R.; Thyvelikakath, G. X. *J. Org. Chem.* **1981**, *46*, 3181.
(38) Eicher, T.; Graf, R.; Konzmann, H.; Pick, R. *Synthesis* **1987**, 887.
(39) Weber, H.-M.; Maas, G. *Synthesis* **1988**, 604.
(40) Kerber, R. C.; Reis, K. P. *J. Org. Chem.* **1989**, *54*, 3550.
(41) Prakash, G. K. S.; Rasul, G.; Olah, G. A.; Liu, R.; Tidwell, T. T. *Can. J. Chem.* **1999**, *77*, 525.
(42) Yoshida, Z.; Tawara, Y. *J. Am. Chem. Soc.* **1971**, *93*, 2573.
(43) Yoshida, Z. *Top. Curr. Chem.* **1973**, *40*, 47.
(44) Weiss, R. *Tetrahedron Lett.* **1979**, 3295.
(45) Weiss, R.; Schloter, K. *Tetrahedron Lett.* **1975**, *40*, 3491.
(46) Weiss, R.; Priesner, C.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 446.
(47) Yoshida, Z. (Mitsubishi Chemical Industries Co. Ltd.). Japan Patent 75117746, 1974/1975; *Chem. Abstr.* **1976**, *84*, 58741.
(48) Yoshida, Z. (Mitsubishi Chemical Industries Co. Ltd.). Japan Patent 75117747, 1974/1975; *Chem. Abstr.* **1976**, *84*, 43421.
(49) Gompper, R.; Wolf, U. *Liebigs Ann. Chem.* **1979**, 1406.
(50) Yoshida, Z.; Konishi, H.; Sawada, S.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 850.
(51) Yoshida, Z.; Konishi, H.; Miura, Y.; Ogoshi, H. *Tetrahedron Lett.* **1977**, 4319.
(52) Weiss, R.; Hertel, M.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 473.
(53) Weiss, R.; Wagner, K.-G.; Priesner, C.; Macheleid, J. *J. Am. Chem. Soc.* **1985**, *107*, 4491.
(54) Weiss, R.; Priesner, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 445.
(55) Clark, T.; Weiss, R. *J. Org. Chem.* **1980**, *45*, 1790.
(56) Weiss, R.; Lowack, R. H. *Bull. Soc. Chim. Belg.* **1991**, *100*, 483.
(57) Weiss, R.; Brenner, T.; Hampel, F.; Wolski, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 439.
(58) Weiss, R.; Rechinger, M.; Hampel, F.; Wolski, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 441.
(59) Weiss, R.; Schwab, O.; Hampel, F. *Chem. Eur. J.* **1999**, *5*, 968.
(60) Weiss, R.; Priesner, C.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 472.
(61) Landau, A.; Seitz, G. *Chem. Ber.* **1991**, *124*, 665.
(62) (a) Weiss, R.; Marolt, P. *Synthesis* **1980**, 225. (b) Weiss, R.; Marolt, P. *Synthesis* **1980**, 227.
(63) Gompper, R.; Guggenberger, R. *Tetrahedron* **1986**, *42*, 839.
(64) Maas, G.; Stang, P. J. *J. Org. Chem.* **1983**, *48*, 3038.
(65) Maas, G.; Singer, B. *Chem. Ber.* **1983**, *116*, 3659.
(66) Yoshida, Z.; Konishi, H.; Ogoshi, H. *Isr. J. Chem.* **1981**, *21*, 139.
(67) Kaiser, F.-J.; Offermann, G.; Seitz, G. *Chem. Ber.* **1986**, *119*, 2104.
(68) Seitz, G.; Kaiser, F.-J. *Chem. Z.* **1987**, *111*, 177.
(69) Allmann, R.; Kaiser, F.-J.; Krestel, M.; Seitz, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 183.
(70) Fuchs, E.; Breit, B.; Heydt, H.; Schoeller, W.; Busch, T.; Krüger, C.; Betz, P.; Regitz, M. *Chem. Ber.* **1991**, *124*, 2843.
(71) (a) Komatsu, K.; Masumoto, K.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1977**, 232. (b) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470.
(72) Fuchs, E.; Breit, B.; Bergsträsser, U.; Hoffmann, J.; Heydt, H.; Regitz, M. *Synthesis* **1991**, 1099.
(73) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60.
(74) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045.
(75) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida, Y. *Eur. J. Inorg. Chem.* **2000**, 1155.
(76) Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H.; Nagase, S. *J. Am. Chem. Soc.* **1995**, *117*, 8025.
(77) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **1999**, *121*, 11587.
(78) Sekiguchi, A.; Ishida, Y.; Fukaya, N.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 1158.
(79) (a) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988. (b) Curci, R.; Lucchini, V.; Moden, G.; Kocienski, P. J.; Ciabattoni, J. *J. Org. Chem.* **1973**, *38*, 3149.
(80) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250.
(81) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 12436.
(82) Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1575.
(83) Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.
(84) Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688.
(85) Borgias, B. A.; Scarrow, R. C.; Seidler, M. D.; Weiner, W. P. *Acta Crystallogr.* **1985**, *C41*, 476.
(86) Chance, J. M.; Geiger, J. H.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1990**, *112*, 3540.
(87) Boese, R.; Augart, S. *Z. Kristallogr.* **1988**, *21*, 32.
(88) Matsumura, N. *Heteroatom. Chem.* **1998**, 387.
(89) Schäfer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Crystallogr.* **1992**, *C48*, 912.
(90) Schäfer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Crystallogr.* **1992**, *C48*, 795.
(91) Radhakrishnan, T. P.; Van Engen, D.; Soos, Z. G. *Mol. Cryst. Liq. Cryst.* **1987**, *150b*, 473.
(92) Radhakrishnan, T. P.; Van Engen, D.; Soos, Z. G. *J. Phys. Chem.* **1987**, *91*, 3273.
(93) Clark, G. R.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1523.
(94) Maas, G.; Weber, H. M.; Exner, R.; Salbeck, J. *J. Phys. Org. Chem.* **1990**, *3*, 459.
(95) Clark, G. R.; Taylor, M. J.; Steele, D. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3597.
(96) (a) Morton, M. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 7005. (b) Morton, M. S.; Selegue, J. P. *J. Organomet. Chem.* **1999**, *578*, 133.
(97) (a) Arnett, E. M.; Molter, K. E. *Acc. Chem. Res.* **1985**, *18*, 339. (b) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels* **1987**, *1*, 17. (c) Arnett, E. M.; Flowers, R. A., II. *Chem. Soc. Rev.* **1993**, 9. (d) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938. (e) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993.
(98) Padwa, A.; Goldstein, S. I.; Rosenthal, R. J. *J. Org. Chem.* **1987**, *52*, 3278. The authors of this paper claim the Dewar benzene product to be the 2,6-dimethyl derivative, but the correct structure must be the 2,5-dimethyl derivative according to the mechanistic consideration.
(99) Hemond, R. C.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1988**, 319.
(100) Padwa, A.; Pulwer, M. J.; Rosenthal, R. J. *J. Org. Chem.* **1984**, *49*, 856.
(101) Himbert, G.; Giesa, R. *Liebigs Ann. Chem.* **1986**, 292.
(102) Kojima, H.; Yamamoto, K.; Kinoshita, Y.; Inoue, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1674.
(103) (a) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 4446. (b) Padwa, A. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2671. (c) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Org. Chem.* **1984**, *49*, 1353. (d) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1710. (e) Zimmerman, H. E.;

Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539. (f) Zimmerman, H. E.; Wilson, D. *J. Org. Chem.* **1995**, *60*, 692.
(104) (a) Padwa, A.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481. (b) Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743. (c) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1980**, *102*, 5648. (d) Padwa, A.; Blacklock, T. J.; Loza, R.; Ploniaszek, R. *J. Org. Chem.* **1980**, *45*, 2181. (e) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2797. (f) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 7202. (g) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1981**, *103*, 3057.
(105) Yoshida, H.; Kato, M.; Ogata, T.; Matsumoto, K. *J. Org. Chem.* **1985**, *50*, 1145.
(106) Yoshida, H.; Sano, H.; Kato, M.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2833.
(107) Yoshida, H.; Sano, H.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4341.
(108) Maier, G.; Wolf, R.; Kalinowski, H.-O.; Boese, R. *Chem. Ber.* **1994**, *127*, 191.
(109) Maier, G.; Wolf, R.; Kalinowski, H.-O. *Chem. Ber.* **1994**, *127*, 201.
(110) Maier, G.; Fleischer, F.; Kalinowski, H.-O. *Liebigs Ann.* **1995**, 173.
(111) Maier, G.; Reuter, K. A.; Franz, L.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 1845.
(112) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1675.
(113) Maier, G.; Neudert, J.; Wolf, O. *Angew. Chem., Int. Ed.* **2001**, *40*, 1674.
(114) Maier, G.; Emrich, R.; Malsch, K.-D.; Schneider, K.-A.; Nixdorf, M.; Irngartinger, H. *Chem. Ber.* **1985**, *118*, 2798.
(115) Maier, G.; Emrich, R.; Kalinowski, H.-O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 429.
(116) Maier, G.; Euler, K.; Emrich, R. *Tetrahedron Lett.* **1986**, *27*, 3607.
(117) Maier, G.; Bauer, I.; Born, D.; Kalinowski, H.-O. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1093.
(118) Chai, S.; Neuenschwander, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 973.
(119) (a) Miyano, H.; Nitta, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 839. (b) Miyano, H.; Nitta, M. *Tetrahedron Lett.* **1988**, *29*, 4723.
(120) Takahashi, K.; Ogiyama, M. *Chem. Lett.* **1991**, 129.
(121) (a) Zecher, D. C.; West, R. *J. Am. Chem. Soc.* **1967**, *89*, 153. (b) West, R.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 155. (c) West, R.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 161. (d) West, R.; Zecher, D. C.; Koster, S. K.; Eggerding, D. *J. Org. Chem.* **1975**, *40*, 2295. (e) Koster, S. K.; West, R. *J. Org. Chem.* **1975**, *40*, 2300. (f) Komatsu, K.; West, R.; Beyer, D. *J. Am. Chem. Soc.* **1977**, *99*, 6290.
(122) Takahashi, K.; Namekata, N.; Takase, K.; Takeuchi, A. *Tetrahedron Lett.* **1987**, *28*, 5683.
(123) Yoshida, Z.; Shibata, M.; Sakai, A.; Sugimoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 6383.
(124) (a) Yoneda, S.; Shibata, M.; Kida, S.; Yoshida, Z.; Kai, Y.; Miki, K.; Kasai, N. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 63. (b) Sugimoto, T.; Shibata, M.; Yoneda, S.; Yoshida, Z.; Kai, Y.; Miki, K.; Kasai, N.; Kobayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 7032.
(125) (a) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115.
(126) Tamm, M.; Bannenberg, T.; Grzegorzewski, A.; Fröhlich, R. *J. Organomet. Chem.* **2001**, *617*−*618*, 640.
(127) Agranat, I.; Aharon-Shalom, E. *J. Org. Chem.* **1976**, *41*, 2379.
(128) Kuhn, R.; Rewicki, D. *Angew. Chem.* **1967**, *79*, 648.
(129) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173.
(130) (a) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Miyabo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 923. (b) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J. Org. Chem.* **1990**, *55*, 996.
(131) (a) Takeuchi, K.; Kitagawa, T.; Miyabo, A.; Hori, H.; Komatsu, K. *J. Org. Chem.* **1993**, *58*, 5802. (b) Miyabo, A.; Takeuchi, K.; Komatsu, K.; Toshikazu, K. *Chem. Lett.* **1992**, 683.
(132) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011.
(133) (a) Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172. (b) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.* **1983**, *24*, 3299.
(134) (a) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 344. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J. P. *Science* **1990**, *247*, 423.
(135) Fagan, P.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.
(136) Tanaka, T.; Kitagawa, T.; Komatsu, K.; Takeuchi, K. *J. Am. Chem. Soc.* **1997**, *119*, 9313.
(137) (a) Kitagawa, T.; Tanaka, T.; Murakita, H.; Nishikawa, A.; Takeuchi, K. *Tetrahedron* **2001**, *57*, 3537. (b) Kitagawa, T.; Tanaka, T.; Murakita, H.; Takeuchi, K. *J. Org. Chem.* **1999**, *64*, 2.
(138) Ciabattoni, J.; Nathan, E. C., III. *J. Am. Chem. Soc.* **1969**, *91*, 4766.
(139) Gunasekaran, A.; Boyer, J. H. *Heteroat. Chem.* **1992**, *3*, 611.
(140) Hashmi, S. M.; Prasanna, S.; Radhakrishnan, T. P. *Synth. Met.* **1992**, *48*, 39.
(141) Maas, G.; Weber, H. M.; Exner, R.; Salbeck, J. *J. Phys. Org. Chem.* **1990**, *3*, 459.
(142) (a) Föhlisch, B.; Bürgle, P. *Liebigs Ann. Chem.* **1967**, *705*, 164. (b) Föhlisch, B.; Bürgle, P. *Liebigs Ann. Chem.* **1967**, *701*, 58.
(143) Yoshida, Z.; Konishi, H.; Tawara, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1973**, *95*, 3043.
(144) Yoshida, Z.; Konishi, H.; Tawara, Y.; Nishikawa, K.; Ogoshi, H. *Tetrahedron Lett.* **1973**, 2619.
(145) Yoshida, H.; Yagi, K.; Tamai, T.; Sano, H.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1073.
(146) (a) Curci, R.; Lucchini, V.; Kocienski, P. J.; Evans, G. T.; Ciabattoni, J. *Tetrahedron Lett.* **1972**, 3293. (b) Neunhoeffer, H.; Vötter, H.-D.; Ohl, H. *Chem. Ber.* **1972**, *105*, 3695.
(147) Jones, W. M.; Kobzina, J. W. *J. Org. Chem.* **1965**, *30*, 4389.
(148) Cheer, C. J.; Bernstein, D.; Greenberg, A.; Lyu, P.-C. *J. Am. Chem. Soc.* **1988**, *110*, 226.
(149) (a) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 81. (b) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 900. (c) Allen, F. H. *Tetrahedron* **1982**, *38*, 645.
(150) (a) Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinoski, H.-O. *Helv. Chim. Acta* **1982**, *65*, 137. (b) Schenk, H.; Benci, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 538. (c) Beintema, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1631.
(151) Kojima, H.; Ozaki, K.; Matsumura, N.; Inoue, H. *J. Chem. Res. (S)* **1991**, 324.
(152) Heim, U.; Pritzkow, H.; Fleischer, U.; Grützmacher, H.; Sanchez, M.; Réau, R.; Bertrand, G. *Chem. Eur. J.* **1996**, *2*, 68.
(153) Zurmühlen, F.; Regitz, M. *J. Organomet. Chem.* **1987**, *332*, C1.
(154) (a) Puranik, D. B.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 770. (b) Fink, M. J.; Puranik, D. B. *Organometallics* **1987**, *6*, 1809.
(155) Chandross, E. A.; Smolinsky, G. *Tetrahedron Lett.* **1960**, 19.
(156) Yoneda, S.; Hirai, H.; Yoshida, Z. *Chem. Lett.* **1976**, 1051.
(157) Eicher, T.; Lerch, D. *Tetrahedron Lett.* **1980**, *21*, 3751.
(158) Yoneda, S.; Hirai, H.; Yoshida, Z. *Heterocycles* **1981**, *15*, 865.
(159) Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K.; Acheson, R. M.; Wallis, J. D. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3015.
(160) Yoshida, H.; Tamai, T.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2891.
(161) Yoshida, H.; Takahashi, Y.; Kinoshita, H.; Ukishima, S.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3565.
(162) Yoshida, H.; Utsumi, F.; Suzuki, H.; Ito, S.; Sakashita, S.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 698.
(163) Yoshida, Z.; Hirai, H.; Miki, S.; Yoneda, S. *Tetrahedron* **1989**, *45*, 3217.
(164) Kojima, H.; Yamamoto, K.; Nakamura, K.; Inoue, H. *J. Heterocycl. Chem.* **1996**, *33*, 1417.
(165) Kojima, H.; Nakamura, K.; Yamamoto, K.; Inoue, H. *Synthesis* **1996**, 1193.
(166) Kojima, H.; Ozaki, K.; Matsumura, N.; Inoue, H. *Chem. Lett.* **1989**, 1499.
(167) Kojima, H.; Matsumura, N.; Inoue, H. *Can. J. Chem.* **1992**, *70*, 1.
(168) Kojima, H.; Kinoshita, Y.; Matsumura, N.; Inoue, H. *J. Heterocycl. Chem.* **1991**, *28*, 2059.
(169) Kojima, H.; Yamamoto, K.; Kinoshita, Y.; Inoue, H. *J. Heterocycl. Chem.* **1992**, *29*, 1473.
(170) Kojima, H.; Ozaki, K.; Matsumura, N.; Inoue, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2298.
(171) Bartmann, E.; Mengel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 225.
(172) Yoneda, S.; Kojima, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1793.
(173) Kojima, H.; Yamamoto, K.; Kinoshita, Y.; Inoue, H. *J. Heterocycl. Chem.* **1993**, *30*, 1691.
(174) (a) Heydt, H.; Eisenbarth, P.; Feith, K.; Regitz, M. *J. Heterocycl. Chem.* **1986**, *23*, 385. (b) Heydt, H.; Eisenbarth, P.; Feith, K.; Urgast, K.; Maas, G.; Regitz, M. *Isr. J. Chem.* **1986**, *27*, 96.
(175) Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 734.
(176) Kojima, H.; Ozaki, K.; Matsumura, N.; Inoue, H. *J. Heterocycl. Chem.* **1990**, *27*, 1845.
(177) Matsumura, N.; Shimizu, Y.; Yagyu, Y.; Inoue, H.; Mizuno, K.; Adachi, T. *Sulfur Lett.* **1997**, *20*, 199.
(178) Yagyu, Y.; Matsumura, N.; Tanaka, H.; Maeda, Z.; Inoue, H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 117.
(179) Breslow, R.; Gal, P. *J. Am. Chem. Soc.* **1959**, *81*, 4747.
(180) Breslow, R.; Crispino, G. A. *Tetrahedron Lett.* **1991**, *32*, 601.

(181) Maier, G.; Schick, A.; Bauer, I.; Boese, R.; Nussbaumer, M. *Chem. Ber.* **1992**, *125*, 2111.
(182) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.
(183) Li, H.; Ren, K.; Neckers, D. C. *J. Org. Chem.* **2001**, *66*, 8556.
(184) Gerson, F.; Plattner, G.; Yoshida, Z. *Mol. Phys.* **1971**, *21*, 1027.
(185) Weiss, R.; Grimmeiss, A. M. H. *Z. Naturforsch.* **1989**, *44b*, 1447.
(186) Weiss, R.; Grimmeiss, A. M. H. *Z. Naturforsch.* **1991**, *46b*, 104.
(187) Weiss, R.; Priesner, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 457.
(188) (a) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456. (b) Gompper, R.; Bartmann, E. *Liebigs Ann. Chem.* **1979**, 229.
(189) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 209.
(190) Löwe, C.; Shklover, V.; Berke, H. *Organometallics* **1991**, *10*, 3396.
(191) Tamm, M.; Grzegorzewski, A.; Hahn, F. E. *J. Organomet. Chem.* **1995**, *501*, 309.
(192) Schumann, H.; Glanz, M.; Girgsdies, F.; Hahn, F. E.; Tamm, M.; Grzegorzewski, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2332.
(193) Kirchgässner, U.; Piana, H.; Schubert, U. *J. Am. Chem. Soc.* **1991**, *113*, 2228.
(194) Miki, S.; Ohno, T.; Iwasaki, H.; Yoshida, Z. *J. Phys. Org. Chem.* **1988**, *1*, 333.
(195) (a) Clark, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2027. (b) Goddard, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2025.
(196) Re, N.; Sgamellotti, A.; Floriani, C. *Organometallics* **1996**, *15*, 5330.
(197) Dehmlow, E. V.; Zeisberg, R.; Dehmlow, S. S. *Org. Magn. Reson.* **1975**, *7*, 418.
(198) (a) Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* **1979**, *112*, 218. (b) For the reaction with $[Co(CO)_4]^-$, see: Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846.
(199) Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 862.
(200) Hughes, R.; Lambert, J. M. J.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L. *Organometallics* **1986**, *5*, 789.
(201) Hughes, R.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1754.
(202) Hughes, R.; Kläui, W.; Reisch, J. W.; Müller, A. *Organometallics* **1985**, *4*, 1761.
(203) Ditchfield, R.; Hughes, R. P.; Tucker, D. S.; Bierwagen, E. P.; Robbins, J.; Robinson, D. J.; Zakutansky, J. A. *Organometallics* **1993**, *12*, 2258.
(204) (a)Hughes, R.; Tucker, D. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3069. (b) Lichtenberger, D. L.; Hoppe, M. L.; Subramanian, L.; Kober, E. M.; Hughes, R. P.; Hubbard, J. L.; Tucker, D. S. *Organometallics* **1993**, *12*, 2025.
(205) Blunden, R. B.; Cloke, F. G. N.; Hitchcock, P. B.; Scott, P. *Organometallics* **1994**, *13*, 2917.
(206) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1109.
(207) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 833.
(208) Broadley, K.; Connelly, N. G.; Graham, P. G.; Howard, J. A. K.; Risse, W.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1985**, 777.
(209) Hughes, R. P.; Lambert, J. M. J.; Rheingold, A. L. *Organometallics* **1985**, *4*, 2055.
(210) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 4215.
(211) Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett.* **1978**, 803.
(212) Agranat, I.; Barak, A.; Pick, M. R. *J. Org. Chem.* **1973**, *38*, 3064.
(213) Wadsworth, D. H.; Donatelli, B. A. *Synthesis* **1981**, 285.
(214) Eicher, T.; Schneider, V. *Synthesis* **1989**, 372.
(215) Weidner, C. H.; Wadsworth, D. H.; Knop, C. S.; Oyefesso, A. I.; Hafer, B. L.; Hartman, R. J.; Mehlenbacher, R. C.; Hogan, S. C. *J. Org. Chem.* **1994**, *59*, 4319.
(216) Bauer, C. B.; LeGoff, E. *Synthesis* **1970**, 544.
(217) White, J. M.; Bromley, M. K. *Tetrahedron Lett.* **1993**, *34*, 4091.
(218) Wilcox, C.; Breslow, R. *Tetrahedron Lett.* **1980**, *21*, 3241.
(219) Krebs, A.; Güntner, A.; Versteylen, S.; Schulz, S. *Tetrahedron Lett.* **1984**, *25*, 2333.
(220) Musigmann, K.; Mayr, H.; de Meijere, A. *Tetrahedron Lett.* **1990**, *31*, 1261.
(221) Isaka, M.; Ejiri, S.; Nakamura, E. *Tetrahedron* **1992**, *48*, 2045.
(222) Branan, B. M.; Wang, X.; Jankowski, P.; Wicha, J.; Paquette, L. A. *J. Org. Chem.* **1994**, *59*, 6874.
(223) Eicher, T.; Pielartzik, H.; Zacheus, P. *Tetrahedron Lett.* **1984**, *25*, 4495.
(224) Netland, K. A.; Gundersen, L.-L.; Rise, F. *Synth. Commun.* **2000**, *30*, 1767.
(225) Gleiter, R.; Merger, M. *Synthesis* **1995**, 969.
(226) Pericás, M. A.; Serratosa, F. *Tetrahedron Lett.* **1977**, 4437.
(227) Dehmlow, E. V.; Winterfeldt, A. *Tetrahedron* **1989**, *45*, 2925.
(228) Eggerding, D.; West, R. *J. Am. Chem. Soc.* **1975**, *97*, 207.
(229) Eggerding, D.; West, R. *J. Am. Chem. Soc.* **1976**, *98*, 3641.
(230) Dehmlow, E. V.; Neuhaus, R.; Schell, H. G. *Chem. Ber.* **1988**, *121*, 569.
(231) Semmingsen, D.; Groth, P. *J. Am. Chem. Soc.* **1987**, *109*, 7238.
(232) Gelb, R. I.; Schwartz, L. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 930.
(233) West, R. *Isr. J. Chem.* **1980**, *20*, 300.
(234) Jacobs, C. A.; Brahms, J. C.; Dailey, W. P.; Beran, K.; Harmony, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 115.
(235) Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8940.
(236) Dailey, W. P. *J. Org. Chem.* **1995**, *60*, 6737.
(237) Arndt, G.; Seitz, G.; Kaempchen, T. *Chem. Ber.* **1981**, *114*, 660.
(238) Yoshida, Z.; Konishi, H.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1975**, 359.
(239) Yoshida, Z.; Shibata, M.; Kida, S.; Miki, S.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1984**, *25*, 345.
(240) Baum, G.; Kaiser, F. J.; Massa, W.; Seitz, G. *Angew. Chem.* **1987**, *99*, 1199.
(241) Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1973.
(242) Yoshida, H.; Nakajima, M.; Ogata, T. *Synthesis* **1981**, 36.
(243) Sugimoto, T.; Nagatomi, T.; Ando, H.; Yoshida, Z. *Angew. Chem.* **1988**, *100*, 597.
(244) Dehmlow, S. S.; Dehmlow, E. V. *Z. Naturforsch.* **1975**, *30b*, 404.
(245) Krebs, A.; Güntner, A.; Senning, A.; Moltzen, E. K.; Klabunde, K. J.; Kramer, M. P. *Angew. Chem.* **1984**, *96*, 691.
(246) Weber, H. M.; Maas, G. *Chem. Ber.* **1988**, *121*, 1791.
(247) Gompper, R.; Schönafinger, K. *Chem. Ber.* **1979**, *112*, 1514.
(248) Landau, A.; Offermann, G.; Seitz, G. *Synthesis* **1984**, 686.
(249) Seitz, G.; Kaiser, G. *Chem. Z.* **1981**, *105*, 60.
(250) Weiss, R.; Hertel, M. *J. Chem. Soc., Chem. Commun.* **1980**, 223.
(251) Toda, T.; Yoshida, M.; Katayama, T.; Minabe, M. *Heterocycles* **1987**, *25*, 79.
(252) Maier, G.; Reisenauer, H. P.; Eckwert, J.; Sierakowski, C.; Stumpf, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1218.
(253) Yoshida, H.; Ohtsuka, H.; Ogata, T.; Matsumoto, K. *Chem. Lett.* **1987**, 659.
(254) Yoshida, H.; Ohtsuka, H.; Yoshida, K.; Totani, Y.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4347.
(255) Paquette, L. A.; Barton, T. J.; Horton, N. *Tetrahedron Lett.* **1967**, *50*, 5039.
(256) Boberg, F.; Kirchner, U.; Garming, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *66*, 177.
(257) Fuchs, E. P. O.; Heydt, H.; Regitz, M.; Schoeller, W. W.; Busch, T. *Tetrahedron Lett.* **1989**, *30*, 5111.
(258) Eisfeld, W.; Fuchs, E.; Regitz, M. *Synth. Methods Organomet. Inorg. Chem.* **1996**, *3*, 44.
(259) Breit, B.; Memmesheimer, H.; Boese, R.; Regitz, M. *Chem. Ber.* **1992**, *125*, 729.
(260) Hofmann, M. A.; Bergstrasser, U.; Reiss, G. J.; Nyulaszi, L.; Regitz, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1261.
(261) Gerecht, B.; Offermann, G.; Seitz, G. *Synthesis* **1982**, 726.
(262) Seitz, G.; Offermann, G. *Synthesis* **1984**, 752.
(263) Köhler, K.; Piers, W. E. *Can. J. Chem.* **1998**, *76*, 1249.
(264) Yoshida, H.; Nakajima, M.; Ogata, T.; Matsumoto, K.; Acheson, R. M.; Wallis, J. D. *Chem. Lett.* **1983**, 155.
(265) Yoshida, H.; Yoshida, K.; Totani, H.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3579.
(266) Gunasekaran, A.; Zhu, N.; Stevens, E. D.; Boyer, J. H. *Chem. Lett.* **1992**, 1367.
(267) Dahn, H.; My-Ngoc. U.-T. *Helv. Chim. Acta* **1987**, *70*, 2130.
(268) Breslow, R.; Oda, M.; Pecoraro, J. *Tetrahedron Lett.* **1972**, 4415.
(269) Breslow, R.; Altman, L. J. *J. Am. Chem. Soc.* **1966**, *88*, 504.
(270) Toda, F.; Kataoka, T.; Akagi, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 244.
(271) Ciabattoni, J.; Berchtold, G. A. *J. Org. Chem.* **1966**, *31*, 1336.
(272) Farnum, D. G.; Chickos, J.; Thurston, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 3075.
(273) West, R.; Chickos, J.; Osawa, E. *J. Am. Chem. Soc.* **1968**, *90*, 3885.
(274) Fink, J.; Guembel, H.; Eisenbarth, P.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1027.
(275) Fuchs, E.; Krebs, F.; Heydt, H.; Regitz, M. *Tetrahedron* **1994**, *50*, 759.
(276) Karakasa, T.; Takeda, S.; Saito, T.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3279.
(277) Neidlein, R.; Kraemer, B.; Krieger, C. *Z. Naturforsch., B: Chem. Sci.* **1990**, *45*, 1577.
(278) Neidlein, R.; Krämer, B. *Chem. Ber.* **1991**, *124*, 353.
(279) Ando, W.; Kumamoto, Y.; Ishizuka, H.; Tokito, N. *Tetrahedron Lett.* **1987**, *28*, 4707.
(280) Yoshida, H.; Kinoshita, H.; Kato, T.; Kanehira, N.; Ogata, T.; Matsumoto, K. *Synthesis* **1987**, 393.
(281) Sakamoto, K.; Ogasawara, J.; Kon, Y.; Sunagawa, T.; Kabuto, C.; Kira, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1402.
(282) Singh, S.; Bhadbhade, M. M.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 3550.
(283) Reichardt, C.; Herget, B. V.; Schulz, M.; Massa, W.; Peschel, S. *Tetrahedron Lett.* **1989**, *30*, 3521.
(284) Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355.

(285) Takahashi, K.; Tarutani, S. *J. Chem. Soc., Chem. Commun.* **1994**, 519.
(286) Takahashi, K.; Tarutani, S. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1997**, *296*, 145.
(287) Tarutani, S.; Mori, T.; Mori, H.; Tanaka, S.; Takahashi, K. *Chem. Lett.* **1997**, 627.
(288) Kascheres, A.; Rodrigues, J. A. R.; Pilli, R. *Heterocycles* **1984**, *22*, 1709.
(289) Pilli, R. A.; Rodrigues, J. A. R.; Kascheres, A. *J. Org. Chem.* **1983**, *48*, 1084.
(290) Sasaki, T.; Kanematsu, K.; Kahei, A. *J. Org. Chem.* **1971**, *36*, 2451.
(291) Breslow, R.; Oda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4787.
(292) Oda, M.; Breslow, R. *Tetrahedron Lett.* **1972**, 4419.
(293) Cordes, M. H. J.; de Gala, S.; Berson, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11161.
(294) Jacobs, C. A.; Dailey, W. P. *J. Org. Chem.* **1995**, *60*, 7747.
(295) Matsumoto, K.; Ikemi, Y.; Hashimoto, S.; Lee, H. S.; Okamoto, Y. *J. Org. Chem.* **1986**, *51*, 3729.
(296) Matsumoto, K.; Hashimoto, S.; Uchida, T.; Acheson, R. M. *Heterocycles* **1982**, *19*, 1483.
(297) Eicher, T.; Franke, G. *Liebigs Ann. Chem.* **1981**, 1337.
(298) Yoshida, H.; Sogame, S.; Bando, S.; Nakajima, S.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3849.
(299) Yoshida, H.; Sogame, S.; Takishita, Y.; Ogata, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2438.
(300) Takahashi, M.; Funaki, T.; Honda, H.; Yokoyama, Y.; Takimoto, H. *Heterocycles* **1982**, *19*, 1921.
(301) Barr, J. J.; Storr, R. C.; Tandon, V. K. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1147.
(302) Stierli, F.; Prewo, R.; Bieri, J. H.; Heimgartner, H. *Helv. Chim. Acta* **1983**, *66*, 1366.
(303) Eicher, T.; Rohde, R. *Synthesis* **1985**, 619.
(304) Eicher, T.; Krause, D. *Synthesis* **1986**, 899.
(305) Bilinski, V.; Steinfels, M. A.; Dreiding, A. S. *Helv. Chim. Acta* **1972**, *55*, 1075.
(306) Eicher, T.; Böhm, S. *Tetrahedron Lett.* **1972**, 2603.
(307) Tsuge, O.; Okita, S.; Noguchi, M.; Watanabe, H. *Chem. Lett.* **1981**, 1439.
(308) Kascheres, C.; Kascheres, A.; Pilli, P. S. H. *J. Org. Chem.* **1980**, *45*, 5340.
(309) Kascheres, A.; Schumacher, H. C.; Rodrigues, R. A. F. *J. Heterocycl. Chem.* **1997**, *34*, 757.
(310) Kascheres, A.; Kascheres, C.; Braga, A. C. H. *J. Org. Chem.* **1993**, *58*, 1702.
(311) Cunha, S.; Kascheres, A. *J. Braz. Chem. Soc.* **2001**, *12*, 481.
(312) Wadsworth, D. H.; Bender, S. L.; Smith, D. L.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 3569.
(313) Wadsworth, D. H.; Bender, S. L.; Smith, D. L.; Luss, H. R.; Weidner, C. H. *J. Org. Chem.* **1986**, *51*, 4639.
(314) Weidner, C. H.; Michaels, F. M.; Beltman, D. J.; Montgomery, C. J.; Wadsworth, D. H.; Briggs, B. T.; Picone, M. L. *J. Org. Chem.* **1991**, *56*, 5594.
(315) Turchi, S.; Giomi, D.; Capaccioli, C.; Nesi, R. *Tetrahedron* **1997**, *53*, 11711.
(316) Davies, D. E.; Reeves, D. L. R.; Storr, R. C.; Rees, C. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 808.
(317) Nagai, S.-I.; Ueda, T. *J. Heterocycl. Chem.* **2000**, *37*, 1663.
(318) Jenny, C.; Obrecht, D.; Heimgartner, H. *Tetrahedron Lett.* **1982**, *23*, 3059.
(319) Ohshiro, Y.; Nanimoto, H.; Tanaka, H.; Komatsu, M.; Agawa, T.; Yasuoka, N.; Kai, Y.; Kasai, N. *Tetrahedron Lett.* **1985**, *26*, 3015.
(320) Eicher, T.; Urban, M. *Chem. Ber.* **1980**, *113*, 408.
(321) Eicher, T.; Sebold, U.; Stegmann, U. *Tetrahedron Lett.* **1983**, *24*, 2977.
(322) Potts, K. T.; Elliott, A. J.; Titus, G. R.; Al-Hilal, D.; Lindley, P. F.; Boyd, G. V.; Norris, T. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2692.
(323) Musicki, B. *J. Org. Chem.* **1991**, *56*, 110.
(324) Hofmann, M. A.; Heydt, H.; Regitz, M. *Synthesis* **2001**, 463.
(325) Tanaka, K.; Hayashi, J.; Kaji, A. *Phosphorus Sulfur* **1983**, *16*, 201.
(326) Hirano, K.; Minakata, S.; Komatsu, M. *Chem. Lett.* **2001**, 8.
(327) Hirano, K.; Minakata, S.; Komatsu, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1567.
(328) Magdesieva, N. N.; Gordeev, M. F.; Kyandzhetsian, R. A. *Zh. Org. Khim.* **1983**, *19*, 2433.
(329) Matsumoto, K.; Ikemi, Y.; Kakehi, A.; Shigihara, A.; Lown, J. W. *Tetrahedron Lett.* **1995**, *36*, 5295.
(330) Matsumoto, K.; Ikemi, Y.; Toda, M.; Kakehi, A.; Uchida, T.; Lowen, J. W. *Tetrahedron Lett.* **1995**, *36*, 3011.
(331) Hori, M.; Kataoka, T.; Shimizu, H.; Imai, E.; Tanaka, K.; Kimura, K.; Hashimoto, Y.; Inagaki, S.; Goto, N.; Kido, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2531.
(332) Hori, M.; Kataoka, T.; Shimizu, H.; Imai, E.; Matsumoto, Y.; Kawachi, M.; Kuratani, K.; Yokomoto, M. *Chem. Pharm. Bull.* **1986**, *34*, 1328.
(333) Matsumoto, K.; Uchida, T.; Yagi, Y.; Tahara, H.; Acheson, R. M. *Heterocycles* **1985**, *23*, 2041.
(334) Matsumoto, K.; Ikemi, Y. *Heterocycles* **1980**, *14*, 1445.
(335) Ikemi, Y. *J. Heterocycl. Chem.* **1990**, *27*, 1597.
(336) Yoshida, H.; Shimizu, J.; Ogata, T.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2445.
(337) Hori, M.; Kataoka, T.; Shimizu, H.; Narita, K.; Ohno, S.; Ogura, H.; Takayanagi, H.; Iitaka, Y.; Koyama, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1885.
(338) Shimizu, H.; Sugimoto, A.; Kataoka, T.; Hori, M. *Heteroat. Chem.* **1995**, *6*, 167.
(339) Shimizu, H.; Ozawa, M.; Matsuda, T.; Ikedo, K.; Kataoka, T.; Hori, M.; Kobayashi, K.; Tada, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1709.
(340) Eisfeld, W.; Slany, M.; Bergstrasser, U.; Regitz, M. *Tetrahedron Lett.* **1994**, *35*, 1527.
(341) Kascheres, A.; Kascheres, C.; Augusto, J.; Rodrigues, R. *Synth. Commun.* **1984**, *14*, 905.
(342) Kascheres, A.; Reyes R., J. L.; Fonseca, S. M. *Heterocycles* **1984**, *22*, 2529.
(343) Abe, N.; Kakehi, A. *Heterocycles* **1993**, *36*, 1961.
(344) Abe, N.; Kakehi, A. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2487.
(345) Abe, N.; Murafuji, T.; Sugihara, Y.; Kakehi, A. *Heterocycles* **1995**, *41*, 2289.
(346) Sohn, H.; Merritt, J.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5133.
(347) Bilinski, V.; Dreiding, A. S. *Helv. Chim. Acta* **1985**, *68*, 2140.
(348) Takahashi, M.; Watanabe, S.; Kasai, T. *Heterocycles* **1980**, *14*, 1921.
(349) Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 1194.
(350) Yagyu, Y.; Ito, M.; Matsumura, N.; Inoue, H.; Mizuno, K.; Adachi, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1175.
(351) Matsumura, N.; Yagyu, Y.; Ito, M.; Adachi, T.; Mizuno, K. *J. Org. Chem.* **2000**, *65*, 3341.
(352) Ciabattoni, J.; Kocienski, P. J.; Melloni, G. *Tetrahedron Lett.* **1969**, 1883.
(353) Yagyu, Y.; Matsumura, N.; Tanaka, H.; Inoue, H.; Yasui, M.; Iwasaki, F. *J. Chem. Res., Synop.* **1996**, 272.
(354) Yagyu, Y.; Matsumura, N.; Tanaka, H.; Maeda, Z.; Inoue, H. *J. Chem. Res., Synop.* **1995**, 420.
(355) Eicher, T.; Boehm, S.; Ehrhardt, H.; Harth, R.; Lerch, D. *Liebigs Ann. Chem.* **1981**, 765.
(356) Kascheres, A.; Correa Filho, J.; Cunha, S. *Tetrahedron* **1992**, *49*, 381.
(357) Bowden, K.; Burgess, E. J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1594.
(358) Becker, H. D.; Andersson, K. *J. Org. Chem.* **1987**, *52*, 5205.
(359) Yoshida, H.; Ogata, T. *Nippon Kagaku Kaishi* **1982**, 534; *Chem. Abstr.* **1982**, *97*, 6263.
(360) Kascheres, A.; Joussef, A. C.; Duarte, H. C. *Tetrahedron Lett.* **1983**, *24*, 1837.
(361) Neckers, D. C.; Hauck, G. *J. Org. Chem.* **1983**, *48*, 4691.
(362) Toshima, N.; Moritani, I.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1245.
(363) Harrison, E. A., Jr. *J. Chem. Soc., Chem. Commun.* **1970**, 982.
(364) Di Vona, M. L.; Rosnati, V. *Tetrahedron* **1993**, *49*, 10925.
(365) Dunkelblum, E. *Tetrahedron* **1972**, *28*, 3879.
(366) Yoneda, S.; Ozaki, K.; Inoue, T.; Sugimoto, A.; Yanagi, K.; Minobe, M. *J. Am. Chem. Soc.* **1985**, *107*, 5801.
(367) Yoneda, S.; Tsubouchi, A.; Ozaki, K. *Nippon Kagaku Kaishi* **1987**, 1328.
(368) Yoneda, S.; Ozaki, K.; Tsubouchi, A.; Kojima, H.; Yanagi, K. *J. Heterocycl. Chem.* **1988**, *25*, 559.
(369) Matsumura, N.; Yagyu, Y.; Tanaka, H.; Inoue, H.; Takada, K.; Yasui, M.; Iwasaki, F. *Chem. Lett.* **1996**, 421.
(370) Matsumura, N.; Tanaka, H.; Yagyu, Y.; Mizuno, K.; Inoue, H.; Takada, K.; Yasui, M.; Iwasaki, F. *J. Org. Chem.* **1998**, *63*, 163.
(371) Nguyen, L. T.; De Proft, F.; Nguyen, M. T.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **2001**, 898.
(372) Chiang, Y.; Kresge, A. J.; Hochstrasser, R.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 2355.
(373) Wagner, B. D.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1994**, *116*, 6433.
(374) Chiang, Y.; Kresge, A. J.; Popik, V. V. *J. Am. Chem. Soc.* **1995**, *117*, 9165.
(375) Chiang, Y.; Grant, A. S.; Kresge, A. J.; Pruszynski, P.; Schepp, N. P.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1356.
(376) Chiang, Y.; Grant, A. S.; Guo, H.-X.; Kresge, A. J.; Paine, S. W. *J. Org. Chem.* **1997**, *62*, 5363.
(377) Yamada, K. M. T.; Markus, M. W.; Winnewisser, G.; Joentgen, W.; Kock, R.; Vogel, E.; Altenbach, H. J. *Chem. Phys. Lett.* **1989**, *160*, 113.
(378) Ng, S.-W.; Zuckerman, J. J. *J. Chem. Soc., Chem. Commun.* **1982**, 475.
(379) Ng, S. W.; Barnes, C. L.; Hossain, M. B.; Van der Helm, D.; Zuckerman, J. J.; Kumar Das, V. G. *J. Am. Chem. Soc.* **1982**, *104*, 5359.
(380) Ng, S. W.; Das, V. G. K. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 929.

(381) Ng, S. W.; Kumar Das, V. G.; Yip, W.-H.; Mak, T. C. W. *J. Organomet. Chem.* **1993**, *456*, 181.
(382) Ng, S. W.; Kuthubutheen, A. J.; Arifin, Z.; Wei, C.; Das, V. G. K.; Schulze, B.; Molly, K. C.; Yip, W.-H.; Mak, T. C. W. *J. Organomet. Chem.* **1991**, *403*, 101.
(383) Woell, J. B.; Boudjouk, P. *Angew. Chem.* **1981**, *93*, 412.
(384) Boudjouk, P.; Woell, J. B.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 582.
(385) Brown, D. A.; Lyons, H. J.; Hussein, F. M.; Munir, C. *J. Indian Chem. Soc.* **1982**, *59*, 139.
(386) Lin, C.-J.; Lin, S.; Lee, G.-H.; Wang, Y. *J. Organomet. Chem.* **1997**, *535*, 149.
(387) Chen, Y.-H.; Lin, C.-C.; Lin, S. *J. Chin. Chem. Soc. (Taipei)* **2001**, *48*, 855.
(388) Lin, S.; Lin, C.-J.; Cheng, S.-T.; Wen, Y.-S.; Liu, L.-K. *Inorg. Chim. Acta* **1997**, *256*, 35.
(389) Song, L.; Arif, A. M.; Stang, P. J. *Organometallics* **1990**, *9*, 2792.
(390) Patt-Siebel, U.; Thullen, H.; Mueller, U.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 795.
(391) Yoshida, Z.; Miyahara, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3219.
(392) Dettlaf, G.; Hübener, P.; Weiss, E. *J. Organomet. Chem.* **1978**, *152*, 95.
(393) Dettlaf, G.; Huebener, P.; Klimes, J.; Weiss, E. *J. Organomet. Chem.* **1982**, *229*, 63.
(394) Edelmann, F.; Klimes, J.; Weiss, E. *J. Organomet. Chem.* **1982**, *224*, C31.
(395) Visser, J. P.; Ramakers-Blom, J. E. *J. Organomet. Chem.* **1972**, *44*, C63.
(396) Visser, J. P.; Schipperijn, A. J.; Lukas, J.; Bright, D.; de Boer, J. J. *J. Chem. Soc., Chem. Commun.* **1971**, 1266.
(397) Visser, J. P.; Leliveld, C. G.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1972**, 178.
(398) Wong, W.; Singer, J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672.
(399) Foerstner, J.; Kakoschke, A.; Wartchow, R.; Butenschoen, H. *Organometallics* **2000**, *19*, 2108.
(400) Zora, M.; Herndon, J. W. *Organometallics* **1994**, *13*, 3370.
(401) Noyori, R.; Umeda, I.; Takaya, H. *Chem. Lett.* **1972**, 1189.
(402) Carroll, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1472.
(403) Hart, I. J.; Jardin, A. E.; Jeffery, J. C.; Stone, F. G. A. *J. Organomet. Chem.* **1988**, *341*, 391.
(404) Gade, L. H.; Memmler, H.; Kauper, U.; Schneider, A.; Fabre, S.; Bezougli, I.; Lutz, M.; Galka, C.; Scowen, I. J.; McPartlin, M. *Chem. Eur. J.* **2000**, *6*, 692.
(405) Lutz, M.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. *Organometallics* **2001**, *20*, 2631.
(406) *Chem. Rev.* **2001**, *101*, issue no. 5.
(407) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **1999**, *468*, 171.
(408) Abboud, J.-L. M.; Castaño, O.; Herreros, M.; Leito, I.; Notario, R.; Sak, K. *J. Org. Chem.* **1998**, *63*, 8995.
(409) Mo, Y.; Jiao, H.; Lin, Z.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1998**, *289*, 383.
(410) Glukhotsev, M. N. *J. Chem. Educ.* **1997**, *74*, 132.
(411) Li, W.-K.; Riggs, N. V. *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 189.
(412) Byun, Y.-G.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689.
(413) Hopkinson, A. C.; Lien, M. H. *J. Am. Chem. Soc.* **1986**, *108*, 2843.

CR010011Q