Studies on Seven-Membered Heterocycles. XXXIV.[1] Syntheses and Reactions of 1-Benzosilepines, 1-Benzogermepines, 1-Benzophosphepines, and 1-Benzarsepines

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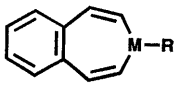
Flash vacuum pyrolysis of 2a,7b-dihydrocyclobuta[*b*]-1-benzometalloles (6a—e), prepared from the corresponding 1-benzometalloles (3) containing Si, Ge, P, or As *via* three steps, resulted in valence isomerization with ring-opening to give 1,1-dimethyl-1-benzosilepine (7a), 1-methyl-1-phenyl-1-benzosilepine (7b), 1,1-dimethyl-1-benzogermepine (7c), 1-phenyl-1-benzophosphepine 1-oxide (7d), and 1-phenyl-1-benzarsepine 1-oxide (7e). The oxides (7d, e), on treatment with trichlorosilane, underwent deoxygenation to afford 1-phenyl-1-benzophosphepine (7f) and 1-phenyl-1-benzarsepine (7g). The 1-benzometallepines (7a—g) thus obtained are hitherto unknown heterocyclic ring compounds, and their thermal stabilities and several reactions were examined.

Keywords 1-benzophosphepine; 1-benzarsepine; 1-benzogermepine; 1-benzosilepine; cyclobuta[*b*]-1-benzometallole; flash vacuum pyrolysis

Considerable attention has recently been focused on the synthesis of new fully unsaturated seven-membered heterocyclic rings (heteroepines) containing a heavier element other than nitrogen, oxygen, or sulfur (also called metallepines, due to the metallic nature of the elements) and a variety of monocyclic[2] and fused metallepines[3–8] have been prepared. With regard to benzometallepines, several 3-benzometallepines (**1**) containing Si, Sn, P, Sb, or Te are known. The silepines (**1a**)[4] and stannepines (**1b**)[5] can be prepared as relatively stable compounds, while the phosphepines (**1c**),[6] stibepines (**1d**),[7] and tellurepines (**1e**)[8] are thermolabile and gradually decompose to naphthalene by extrusion of the hetero element, even during isolation. The arsepines (**1f**)[6,7] are thermally too unstable to be isolated, although they have been detected by spectroscopy at a low temperature. However, 1-benzometallepines (**2**) have not been reported. Therefore, we were interested in the synthesis of 1-benzometallepines containing a Main Group heavier element and report here on the synthesis of the title novel metallepines containing Si, Ge, P, and As.[9]

On the other hand, we have recently shown that the tricycloheptanes[10] and tricyclooctanes[11] having a highly strained cyclopropane or cyclobutane ring undergo thermal or photochemical valence isomerization with ring-opening to give seven- and eight-membered heterocyclic rings, respectively. These results prompted us to examine the thermal behavior of dihydrocyclobuta[*b*]-1-benzometalloles, prepared from the corresponding 1-benzometalloles, with the aim of obtaining the title benzometallepines.



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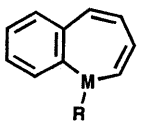

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1a : M=Si **1d : M=Sb**
1b : M=Sn **1e : M=Te**
1c : M=P **1f : M=As**

The starting 1-benzometalloles (**3a—c, f, g**) were prepared from phenyl(trimethylsilyl)acetylene *via* four steps according to the reported procedures.[12] The benzophosphole 1-oxide (**3d**) and benzarsole 1-oxide (**3e**) were obtained in high yields by treatment of **3f** and **3g** with *m*-chloroperbenzoic acid (*m*-CPBA), respectively. The benzometalloles (**3a—e**) were irradiated (400 W high-pressure Hg lamp; Pyrex filter; under N_2) with methyl acrylate in benzene in the presence of acetophenone as a sensitizer to give the tetrahydrocyclobuta[*b*]benzometalloles (**4a—e**) in 45—60% yields. The phosphole (**3f**) and arsole (**3g**) are susceptible to oxidation, being converted into their oxides (**3d**) and (**3e**), respectively, even on exposure to air. Therefore, taking into consideration that the next steps involve an oxidative reaction, the cyclobutabenzometalloles (**4f, g**) were not prepared. The intermolecular cycloaddition of **3a—e** with methyl acrylate proceeded regioselectively, but the adducts (**4**) were obtained as mixtures of two stereoisomers. Although attempts to separate the stereoisomeric mixtures (**4a—c**) containing Si or Ge by column or thin-layer chromatography (TLC) were unsuccessful, the mixtures (**4d, e**) obtained from the oxides (**3d, e**) could be separated by repeated column chromatography to give *exo*- and *endo*-isomers in ratios of *ca.* 3 : 2.

The structures of **4** including the orientation of the methoxycarbonyl group were confirmed by ^1H–^{13}C and ^{13}C–^{13}C correlation spectroscopic experiments. In the ^1H-NMR spectra of **4d, e**, the signals due to the methyl group in the 1-methoxycarbonyl group for the *endo*-isomers appeared at higher fields (δ **4d**-*endo*: 3.41; **4e**-*endo*: 3.43) than those for the *exo*-isomers (δ **4d**-*exo*: 3.80; **4e**-*exo*: 3.81), while the 1-protons of the *exo*-isomers resonate at higher fields (δ **4d**-*exo*: 3.08; **4e**-*exo*: 3.15) than those of the *endo*-isomers (δ **4d**-*endo*: 4.23; **4e**-*endo*: 3.92); these higher shifts might be a consequence of the shielding effect of the benzene ring. It is known[13] that in five-membered cyclic phosphine oxides, coupling constants for ^{31}P to the α-protons *cis* to oxygen (16—18 Hz) are greater than those

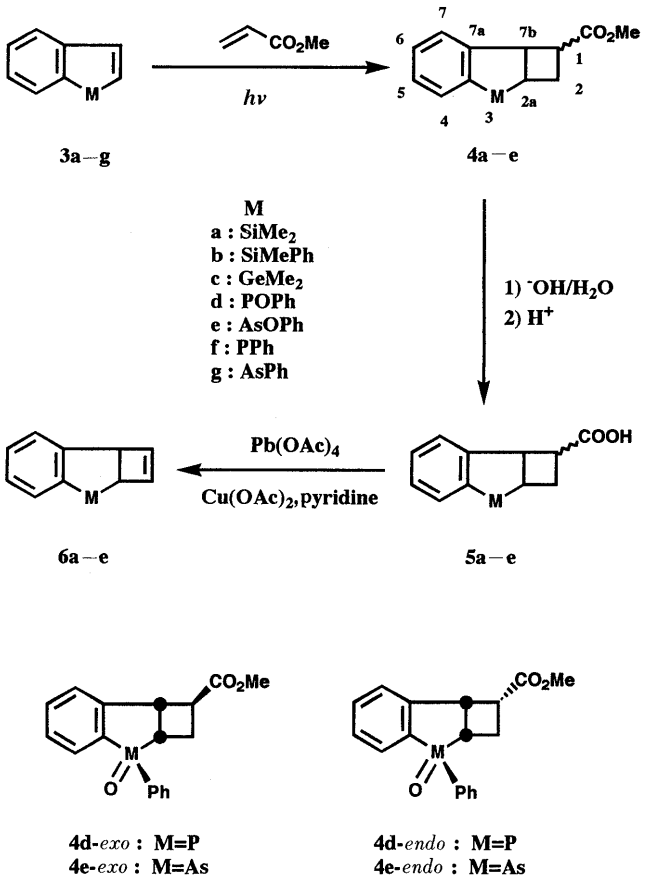


Chart 1

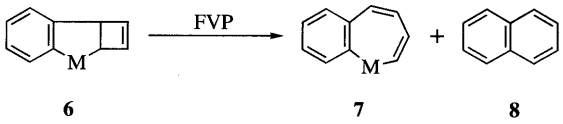
to the *trans* α-protons (8—10 Hz). Therefore, the value $J_{P,2a}=10.6$ Hz for **4d**-*exo* indicates that the 2a-proton is *trans* to the oxygen.

The adduct esters (**4**: stereoisomeric mixtures) were hydrolyzed with sodium hydroxide to give the acids (**5**), which were oxidatively decarboxylated by treatment with lead tetraacetate in the presence of copper(II) acetate and pyridine, giving rise to the key starting dihydrocyclobuta[*b*]-1-benzometalloles (**6a—e**) in 35—55% yields from **4**.

Although the cyclobutabenzometalloles (**6**) were heated in solvents at 180 °C for 24 h, no reaction occurred. However, flash vacuum pyrolysis (FVP) of **6a—e** at 500—550 °C (1—6 × 10^{-5} Torr) resulted in valence isomerization with ring-opening to afford the desired 1-benzometallepines (**7a—e**), along with naphthalene (**8**) and the starting **6**. Conditions of the pyrolysis and yields of the products are summarized in Table I. In view of the high temperature required for this reaction,the ring conversion of **6** into **7** may proceed *via* homolytic cleavage of the cyclobutane ring, by analogy with the related thermal ring-opening of tricycloheptanes[10] and tricyclooctanes.[11] Thermal stabilities of the benzometallepines (**7**) thus obtained as well as the formation of naphthalene (**8**) are described later.

The deoxygenation of the metallepine 1-oxides (**7d, e**) was achieved by treatment with trichlorosilane to afford the 1-benzophosphepine (**7f**) and 1-benzarsepine (**7g**), which reverted to the oxides (**7d, e**) on oxidation with

Table I. FVP of **6a—e**



Compd. No.	M	Temp. (°C)	Press. (Torr)	Yield (%)[a]		
				7	8	Recovery
6a	$SiMe_2$	450	1.9×10^{-5}	59	Trace	40
		500	1.5×10^{-5}	84	12	2
		550	3.0×10^{-5}	77	21	—
6b	SiMePh	500	6.0×10^{-5}	82	10	5
		550	1.2×10^{-5}	68	26	—
6c	$GeMe_2$	450	5.5×10^{-5}	33	15	50
		500	4.1×10^{-5}	47	42	10
		550	5.8×10^{-5}	15	83	—
6d	POPh	530	2.6×10^{-5}	39	—	33
		550	1.5×10^{-5}	66	2	22
		580	1.2×10^{-5}	41	19	Trace
6e	AsOPh	500	1.7×10^{-5}	40	31	22
		530	2.2×10^{-5}	39	42	8
		550	1.1×10^{-5}	27	49	Trace

a) Determined by GLC analysis (3% SE-30, 3 mm × 2 m, 110—120 °C).

m-CPBA. Interestingly, although the arsepine oxide (**7e**) afforded only **7g** in 73% yield at room temperature, the phosphepine oxide (**7d**) gave the 2,5-dihydrophosphepine (**9**) as well as **7f**, and the yields of these products depended on the reaction temperature (see Table II). The dihydrophosphepine (**9**) is susceptible to air oxidation, and thus was isolated as its oxide (**10**) formed by treatment with *m*-CPBA. A possible mechanism for the reduction of **7d** is shown in Chart 3. This reduction may proceed by initial formation of the cationic intermediate (**11**), which gives **7f** *via* **12** (path a), by analogy with the deoxygenation of a variety of tertiary phosphine oxides.[14] The dihydrophosphepine (**9**) might be formed *via* the intermediate (**13**) having a P=C bond (path b). The formation of the As=C bond is predicted to be more difficult than that of the P=C bond, so the path b appears to be unfavorable for the reduction of the arsepine oxide (**7e**).

All of the 1-benzometallepines (**7a—g**) thus obtained are novel heterocyclic rings, and were characterized on the basis of their high-resolution mass spectra (HRMS) (Table III) and ^{1}H- and ^{13}C-NMR spectral data (Table IV) and of the results of some reactions.

As noted in the introductory paragraphs, 3-benzometallepines containing P, Sb, Te, or As are thermolabile, as are 1-[15] and 3-benzothiepines.[16] With regard to the present 1-benzometallepines, the silepines (**7a, b**), phosphepine 1-oxide (**7d**), and arsepine 1-oxide (**7e**) are thermally stable and remain largely unchanged even when heated at 200 °C in diphenyl ether for 24 h; they undergo thermal decomposition to naphthalene only by further FVP at 550—580 °C. The germepine (**7c**) is somewhat less stable and decomposed to napthalene (**8**) (81% yield) at 200 °C for 24 h, probably *via* the intermediate (**14**), although when it was heated at 110 °C in toluene for 20 h, no decomposition occurred. In contrast to the oxides (**7d, e**),

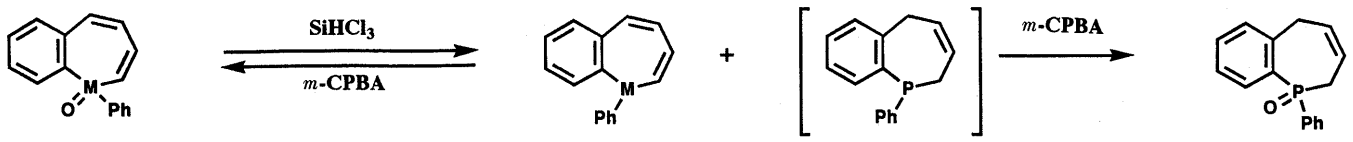


Chart 2

TABLE II. Reaction of **7d, e** with $SiHCl_3$ in Benzene

Compd. No.	Temp. (°C)	Time (h)	Yield (%)	
			7f or **7g**	**9**
7d	r.t.	48	15	56
	60	5	40 (**7f**)	27
	80	1	64	Trace
7e	r.t.	14	73 (**7g**)	—

r.t. = room temperature.

TABLE III. 1-Benzometallepines (**7**)

Compd. No.	M	mp (°C) (Solvent)	Formula	HRMS (*m/z*: M^+) Calcd (Found)
7a	$SiMe_2$	Oil	$C_{12}H_{14}Si$	186.0865 (186.0862)
7b	SiMePh	Oil	$C_{17}H_{16}Si$	248.1021 (248.1020)
7c	$GeMe_2$	Oil	$C_{12}H_{14}Ge$	232.0307 (232.0285)
7d	POPh	128—130 (Benzene)	$C_{16}H_{13}OP$	252.0704 (252.0705)
7e	AsOPh	158—159 (Benzene)	$C_{16}H_{13}AsO$	296.0182 (296.0188)
7f	PPh	84—85 (MeCN)	$C_{16}H_{13}P$	236.0755 (236.0757)
7g	AsPh	Oil	$C_{16}H_{13}As$	280.0233 (280.0226)

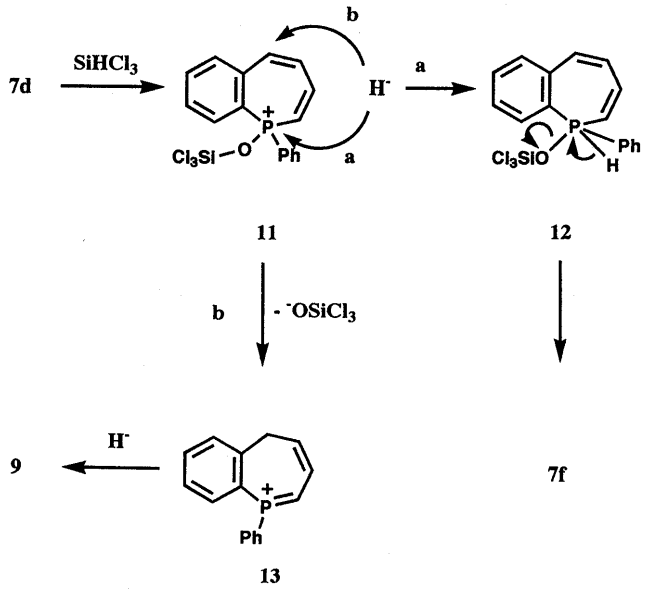


Chart 3

TABLE IV. ^1H- and ^{13}C-NMR Spectral Data for 1-Benzometallepines (**7**) (400 MHz, $CDCl_3$: δ)

Compd. No.	2-H (2-C)	3-H (3-C)	4-H (4-C)	5-H (5-C)	$J_{2,3}$	$J_{3,4}$ (Hz)	$J_{4,5}$	Me-H (Me-C)	Ar-H
7a	5.88 (132.2)	6.79 (140.6)	6.30 (129.9)	6.91 (135.3)	14.3	5.9	13.2	0.29 (−4.1)	7.3—7.5
7b	6.13 (130.2)	6.98 (142.1)	6.37 (129.3)	6.90 (130.2)	14.7	6.2	12.8	0.56 (−4.9)	7.3—7.5
7c	5.97 (133.9)	6.71 (138.7)	6.26 (130.2)	6.81 (135.2)	13.2	5.8	13.2	0.38 (−4.5)	7.3—7.4
7d	6.40 (124.6)	6.98 (138.6)	6.45 (127.6)	7.08 (136.6)	12.9	6.4	12.7[a]		7.3—8.1
7e	6.41 (125.9)	7.03 (139.5)	6.37 (128.3)	6.99 (136.9)	11.9	6.2	13.3		7.4—7.6
7f	6.07 (129.8)	6.52 (133.6)	6.55 (131.2)	7.16 (136.3)	11.4	5.5	12.1[b]		7.1—7.8
7g	6.17 (132.7)	6.66 (133.7)	6.46 (130.6)	7.05 (135.1)	11.3	5.3	12.5		6.8—7.6

a) 2-, 3-, and 4-H and 2-C are also coupled with P: $J_{2\text{-H,P}}=12.0$, $J_{3\text{-H,P}}=41.0$, $J_{4\text{-H,P}}=1.7$, $J_{2\text{-C,P}}=98.0$ Hz. *b*) 2-H, 3-H, and all ring carbons are coupled with P: $J_{2\text{-H,P}}=11.3$, $J_{3\text{-H,P}}=20.5$, $J_{2\text{-C,P}}=10.0$, $J_{3\text{-C,P}}=16.0$, $J_{4\text{-C,P}}=8.0$, $J_{5\text{-C,P}}=8.0$ Hz.

the deoxygenated phosphepine (**7f**) and arsepine (**7g**) are extremely thermolabile in solution and gradually decompose even at room temperature, whereas in pure forms they can be kept for several days in a refrigerator without decomposition. The half-lives of **7f** and **7g** estimated by ^1H-NMR spectral analysis[17] in toluene at 80 °C are about 90 and 10 min, resepctively. These thermal behaviors are similar to those of 3-phenyl-3-benzophosphepine ($t_{1/2}=$ 120 min at 80 °C),[6] 1-benzothiepine ($t_{1/2}=58$ min at 47 °C),[15] and 2-ethoxycarbonyl-3-benzothiepine ($t_{1/2}=$ 54 min at 24 °C),[16] whose oxides are also thermally stable. Therefore, the oxide group in **6d, e** is essential for the present thermal isomerization into benzophosphepines and benzarsepines; in fact, FVP of the cyclobutabenzome-

talloles (**6f, g**) having no oxide group, prepared by the reduction of **6d, e** with trichlorosilane, gave only naphthalene and no metallepines (**7f, g**).

Azepines, oxepines, and thiepines are known to undergo intramolecular photo-induced cyclization and intermolecular cycloaddition with a variety of dienophiles and dienes, as monoenes, dienes, or trienes.[18] Therefore, we examined such reactions of the novel metallepines (**7**). Irradiation (400 W high-pressure Hg lamp; Pyrex filter) of **7a, c** in benzene for 1 h afforded the starting tricyclic compounds (**6a, c**) in 70—75% yields, whereas the phosphepine (**7f**), arsepine (**7g**), and their oxides (**7d, e**), on irradiation under similar conditions, were decomposed to give no characterizable products except for naphthalene.

The metallepines (**7a, c**) were reacted with 4-phenyl-1,2,4-triazoline-3,5-dione at room temperature to give the [4+2]π cycloadducts (**15**) in moderate yields, although they did not react with maleic anhydride, dimethyl acetylenedicarboxylate, or tetracyanoethylene, and the oxides (**7d, e**) did not react even with the triazoline-3,5-dione. When the silepine (**7a**) was heated with 3,4-diphenylcyclopentadienone (**16A, B**) in refluxing benzene for 48 h, no reaction occurred. However, heating a mixture of **7a** and **16A** (R = CO_2Me) at 140 °C in xylene for 48 h gave the [2+4]π cycloadduct (**17A**) (14% yield) and the cage compound (**19A**) (21% yeild), together with the starting **7a** (30%), whereas the reaction of **7a** with **16B** (R = Me) in refluxing xylene for 70 h afforded the [4+2]π cycloadduct (**18B**) (35% yield) as well as **7a** (22%). The [2+4]π cycloadduct (**17A**) was further heated in refluxing xylene, giving rise to the cage compound (**19A**), and irradiation of the [4+2]π cycloadduct (**18B**) resulted in the formation of the cage compound (**19B**). On the contrary, the metallepine oxides (**7d, e**) did not react with the cyclopentadienones (**16**).

It is known that similar [2+4]π cycloadducts to **17A** derived from azepines,[19] 1,3-oxazepines,[20] and 1,3-diazepines[21] with cyclopentadienones readily undergo thermal [3,3]-sigmatropic rearrangement (a Cope rearrangement), giving the corresponding [4+2]π cycloadducts analogous to **18B**. On the basis of these results, the present reaction may also proceed by initial formation of the [2+4]π cycloadducts (**17**), which then undergo [3,3]-sigmatropic rearrangement to give the [4+2]π cycloadducts (**18**), although **17B** and **18A** have not been isolated. Differences between the reactions with **16A** and with **16B** may be explained as follows. The addition with **16B** required a longer time than that with **16A**, and therefore, the adduct (**17B**) initially formed might rearrange entirely to **18B** under the reaction conditions, and the photo-induced [2+2]π cycloaddition of **18A**

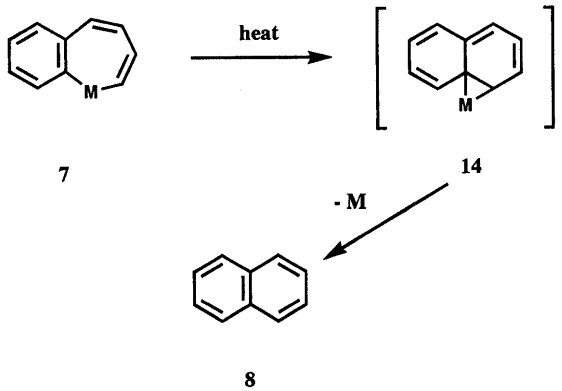


Chart 4

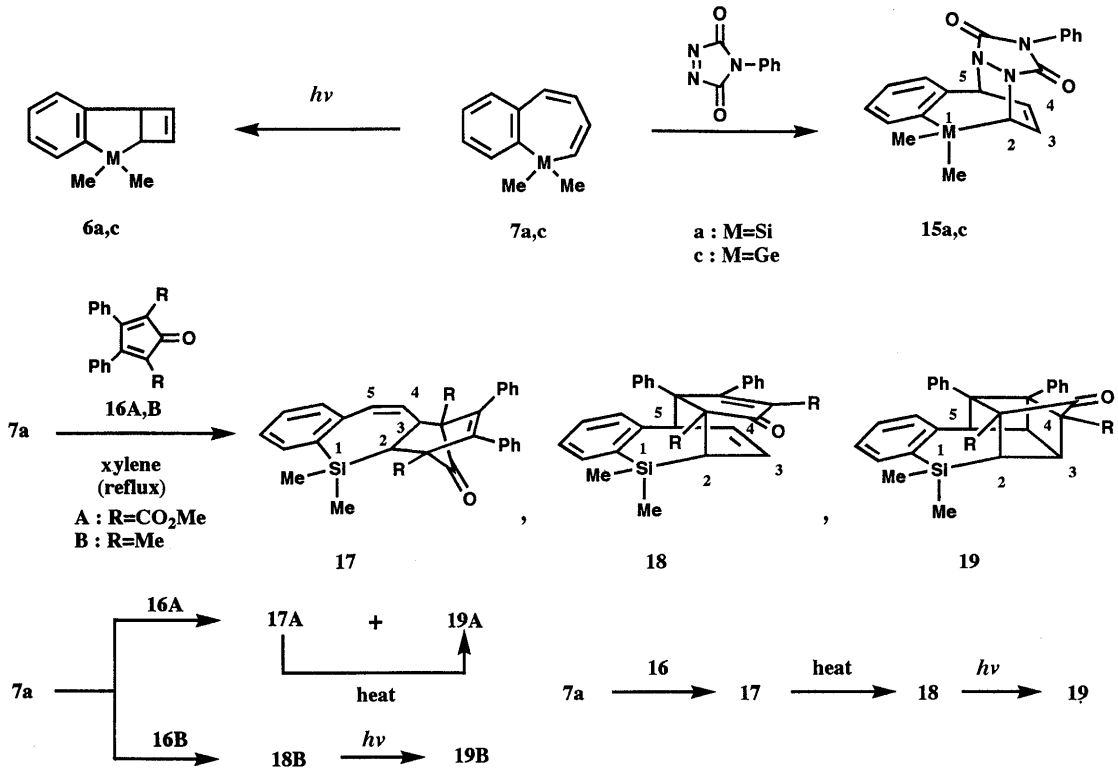


Chart 5

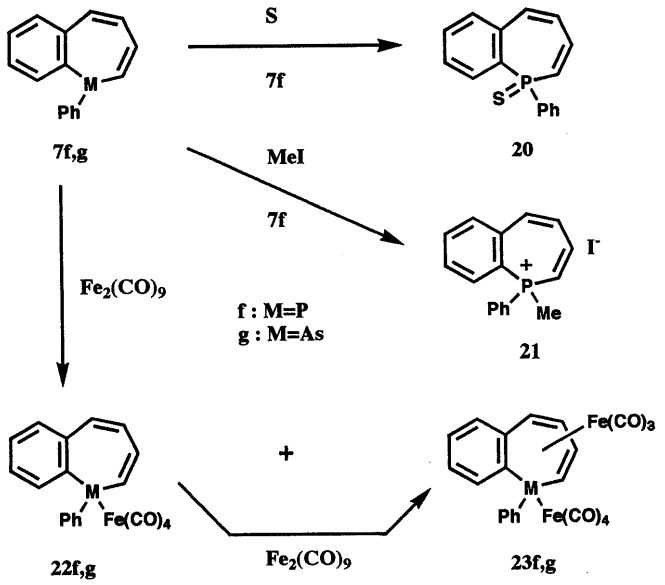


Chart 6

having an electron-withdrawing methoxycarbonyl group may take place more easily than that of **18B** having electron-donating methyl groups, even in daylight.

Finally, several reactions of the phosphepine (**7f**) and arsepine (**7g**) were examined. Treatment of **7f** with sublimed sulfur in benzene gave the sulfide (**20**) in 95% yield and treatment with methyl iodide afforded the phosphepinium iodide (**21**) in 96% yield. Thermally unstable cyclic dienes such as norcaradienes,[22] 1,2-diazepines,[23] and thiepines[24] are known to be stabilized by transition metal complexation. Therefore, the thermolabile metallepines (**7f, g**) were treated with $Fe_2(CO)_9$ (1 mol eq), resulting in P- or As-complexation to give the $Fe(CO)_4$-complexes (**22**) (**22f**: 72%; **22g**: 86% yield) together with small amounts of the $Fe(CO_4)\cdot Fe(CO)_3$-complexes (**23f, g**) (3—5% yields), which were also obtained by further treatment of **22** with $Fe_2(CO)_9$, indicating that the complexation takes place preferentially at the metal elements rather than at the dienes. Both complexes (**22** and **23**) are, as expected, thermally stable and do not decompose even when heated in refluxing benzene for 48 h.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and HRMS were recorded on a JEOL JMP-DX300 instrument. ^{1}H- and ^{13}C-NMR spectra were determined with a JEOL PMX-60-SI (60 MHz) or JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling, ^{1}H–^{13}C correlation spectroscopy (^{1}H–^{13}C COSY), ^{13}C–^{13}C COSY, and/or nuclear Overhauser effect (NOE) analyses. Microanalyses were performed in the Microanalytical Laboratory of this Faculty by Mrs. Igarashi and Miss Yakubo. Photolyses were carried out under a nitrogen atmosphere in an immersion apparatus equipped with a 400 W high-pressure Hg lamp and a Pyrex filter, which was cooled internally with running water. FVP were carried out using an apparatus prepared according to Brown.[25]

1-Benzometalloles (3a—g) 1,1-Dimethyl-1-benzosilole (**3a**), 1,1-dimethyl-1-benzogermole (**3c**), 1-phenyl-1-benzophosphole (**3f**), and 1-phenyl-1-benzarsole (**3g**) were prepared by the reported methods.[12]

1-Methyl-1-phenyl-1-benzosilole (**3b**) was synthesized from (*Z*)-β,*o*-dibromostyrene according to the procedure described for the preparation of **3a**, using $MePhSiCl_2$ instead of Me_2SiCl_2, in *ca.* 70% yield from the starting styrene. **3b**: colorless oil. ^{1}H-NMR (60 MHz) δ: 0.67 (3H, s, 1-Me), 6.47 (1H, d, J=10.4 Hz, 2-H), 7.16—7.80 (10H, m, Ph-H). HRMS *m/z*: M^+ Calcd for $C_{15}H_{14}Si$: 222.0865. Found: 222.0860.

1-Phenyl-1-benzophosphole 1-oxide (**3d**) and 1-phenyl-1-benzarsole 1-oxide (**3e**) were obtained from **3f** and **3g** by treatment with *m*-CPBA in benzene at room temperature, followed by chromatography on silica gel with CH_2Cl_2–acetone (20 : 1), respectively, in almost quantitative yields.

3d: colorless prisms (from benzene), mp 88—90 °C (lit.[26b] mp 84—88 °C).

3e: colorless prisms (from AcOEt), mp 175—177 °C. ^{1}H-NMR (60 MHz) δ: 6.81 (1H, d, J=8.2 Hz, 2-H), 7.52—7.92 (10H, m, 3- and Ph-H). *Anal.* Calcd for $C_{14}H_{11}AsO$: C, 62.24; H, 4.10. Found: C, 62.06; H, 4.07.

1-Methoxycarbonyl-1,2,2a,7b-tetrahydrocyclobuta[*b*]-1-benzometalloles (4a—e) General Procedure: A solution of **3** (2—3 g) and a large excess of methyl acrylate (20—30 mol eq) in benzene (350–400 ml) containing acetophenone (*ca.* 1.5 mol eq) as a sensitizer was irradiated. The photoreaction was followed in terms of the disappearance of the spot of the starting **3** on silica gel TLC, and was complete in 8—12 h. The reaction mixture was concentrated *in vacuo* and the residue was chromatographed on silica gel with benzene to give a mixture of **4** and acetophenone, which could not be separated by column chromatography. Therefore, in order to remove acetophenone as its reduction product, the mixture was treated with $NaBH_4$ (*ca.* 1 mol eq for acetophenone used) in MeOH with stirring at room temperature for 1—2 h and the solvent was evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 and the extract was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with benzene to give **4** as a mixture of *exo*- and *endo*-isomers.

It was difficult to separate the stereoisomeric mixtures of **4a**—**c** and thus each mixture was used in the following reaction without separation. Yields and spectral data for the mixtures (viscous oils) are given below.

4a: *exo* : *endo* = 5 : 1, 58% yield. ^{1}H-NMR (60 MHz) δ: 0.29 and 0.40 (6H × 5/6, 1 : 1, each s, $SiMe_2$ of *exo* adduct), 0.43 and 0.52 (6H × 1/6, 1 : 1, each s, $SiMe_2$ of *endo* adduct), 1.60—3.03 (5H, m, 1-, 2-, 2a- and 7b-H), 3.70 and 4.15 (3H, 1 : 5, each s, CO_2Me), 7.03—7.62 (4H, m, Ph-H). HRMS *m/z*: M^+ Calcd for $C_{14}H_{18}O_2Si$: 246.1076. Found: 246.1053.

4b: *exo* : *endo* = 2 : 3, 62% yield. ^{1}H-NMR (60 MHz) δ: 0.55 and 0.70 (3H, 2 : 3, each s, $SiMe_2$), 2.01—3.20 (5H, m, 1-, 2-, 2a-, and 7b-H), 3.40 and 3.86 (3H, 2 : 3, each s, CO_2Me), 7.15—7.76 (9H, m, Ph-H). HRMS *m/z*: M^+ Calcd for $C_{19}H_{20}O_2Si$: 308.1232. Found: 308.1235.

4c: *exo* : *endo* = 4 : 1, 45% yield. ^{1}H-NMR (60 MHz) δ: 0.43 and 0.50 (6H × 4/5, 1 : 1, each s, $GeMe_2$ of *exo* adduct), 0.52 and 0.58 (6H × 1.5, 1 : 1, each s, $GeMe_2$ of *endo* adduct), 2.03—3.36 (5H, m, 1-, 2-, 2a-, and 7b-H), 3.79 and 4.14 (3H, 1 : 4, each s, CO_2Me), 7.20—7.78 (4H, m, Ph-H). HRMS *m/z*: M^+ Calcd for $C_{14}H_{18}GeO_2$: 292.0517. Found: 292.0520.

In the case of **4d** and **4e** (*ca.* 60% yields, *exo* : *endo* = 3 : 2), the mixtures could be separated by repeated chromatography on silica gel with CH_2Cl_2–acetone (20 : 1—10 : 1) to give the *exo*- and *endo*-isomers, successively, as pure compounds.

4d-*exo*: colorless prisms (from benzene–hexane), mp 107—108 °C. IR (KBr): 1732 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 2.64 (1H, ddd, 2-H_β), 2.96 (1H, ddddd, 2-H_α), 3.08 (1H, dddd, 1-H), 3.50 (1H, ddddd, 2a-H), 3.80 (3H, s, CO_2Me), 4.30 (1H, dddd, 7b-H), 7.27—7.71 (9H, m, Ph-H), $J_{1,2\text{-}\alpha}$=9.9, $J_{1,2\text{-}\beta}$=5.8, $J_{1,2a}$=1.1, $J_{1,7b}$=4.4, $J_{2\text{-}\alpha,2\text{-}\beta}$=13.1, $J_{2\text{-}\alpha,2a}$=6.6, $J_{2\text{-}\alpha,7b}$=1.5, $J_{2\text{-}\beta,2a}$=10.3, $J_{2a,7b}$=8.1, $J_{P,2\text{-}\alpha}$=17.6, $J_{P,2\text{-}\beta}$=13.1, $J_{P,2a}$=10.6, $J_{P,7b}$=12.1 Hz. *Anal.* Calcd for $C_{18}H_{17}O_3P$: C, 69.23; H, 5.49. Found: C, 69.27; H, 5.48.

4d-*endo*: colorless viscous oil. IR (neat): 1738 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 2.30—2.44 (1H, m, 2-H_β), 2.96—3.16 (2H, m, 2-H_α and 2a-H), 3.41 (3H, s, CO_2Me), 3.72 (1H, br ddd, 7b-H), 4.23 (1H, br ddd, 1-H), 7.36—7.79 (9H, m, Ph-H), $J_{1,2\text{-}\alpha}$=8.1, $J_{1,2\text{-}\beta}$=8.1, $J_{1,7b}$=9.2, $J_{2\text{-}\beta,2a}$=9.5, $J_{2a,7b}$=9.2, $J_{P,7b}$=9.2 Hz; other coupling constants could not be determined because most of the signals were broad. HRMS *m/z*: M^+ Calcd for $C_{18}H_{17}O_3P$: 312.0915. Found: 312.0900.

4e-*exo*: colorless viscous oil. IR (neat): 1726 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 2.98 (1H, ddd, 2-H_β), 3.15 (1H, dddd, 2-H_α), 3.16 (1H, dddd, 1-H), 3.35 (1H, dddd, 2a-H), 3.81 (3H, s, CO_2Me), 4.53 (1H, ddd,

7b-H), 7.44—7.75 (9H, m, Ph-H), $J_{1,2\text{-}\alpha}=9.7$, $J_{1,2\text{-}\beta}=7.6$, $J_{1,2a}=1.1$, $J_{1,7b}=5.1$, $J_{2\text{-}\alpha,2\text{-}\beta}=13.2$, $J_{2\text{-}\alpha,2a}=5.5$, $J_{2\text{-}\alpha,7b}=1.3$, $J_{2\text{-}\beta,2a}=10.6$, $J_{2a,7b}=8.1$ Hz. HRMS *m/z*: M^+ Calcd for $C_{18}H_{17}AsO_3$: 356.0394. Found: 356.0345.

4e-*endo*: colorless viscous oil. IR (neat): 1726 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 2.61 (1H, dddd, 2-H$_\beta$), 3.22 (1H, dddd, 2-H$_\alpha$), 3.43 (3H, s, CO_2Me), 3.46 (1H, ddd, 2a-H), 3.92 (1H, ddd, 1-H), 4.52 (1H, dddd, 7b-H), 7.36—7.79 (9H, m, Ph-H), $J_{1,2\text{-}\alpha}=8.8$, $J_{1,2\text{-}\beta}=9.5$, $J_{1,7b}=8.8$, $J_{2\text{-}\alpha,2\text{-}\beta}=13.2$, $J_{2\text{-}\alpha,2a}=8.8$, $J_{2\text{-}\alpha,7b}=1.1$, $J_{2\text{-}\beta,2a}=9.5$, $J_{2\text{-}\beta,7b}=1.3$, $J_{2a,7b}=8.8$ Hz. HRMS *m/z*: M^+ Calcd for $C_{18}H_{17}AsO_3$: 356.0394. Found: 356.0376.

2a,7b-Dihydrocyclobuta[*b*]-1-benzometalloles (6a—e) General Procedure: A mixture of **4** (3—5 g, a mixture of two stereoisomers), 5% NaOH (10 ml), and MeOH (100 ml) was heated at 50—60 °C with stirring for 5—6 h, and then concentrated *in vacuo*. The residue was dissolved in water (100—150 ml) and the solution was acidified with 10% HCl, and then extracted with CH_2Cl_2. The extract was washed with brine, dried, and concentrated to give the acid (**5**), which was used in the following decarboxylation reaction without purification.

A mixture of the crude **5** (2—3 g), $Pb(OAc)_4$ (1.2—1.5 mol eq), $Cu(OAc)_2$–H_2O (0.2 mol eq), pyridine (0.5—1.0 mol eq), and benzene (80—100 ml) was heated slowly to 80 °C with stirring, and then refluxed for 1—1.5 h. After the mixture had cooled, water (100 ml) and hexane (200 ml; for **5a—c**) or benzene (150 ml; for **5d, e**) were added to it with stirring in an ice bath, and the mixture was filtered through a Celite pad. The layers of the filtrate were separated and the aqueous layer was extracted with hexane or benzene (100 ml). The combined organic layer was successively washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane (for **6a—c**) or CH_2Cl_2–acetone (10 : 1) (for **6d, e**) to give **6**, as a colorless viscous oil except for **6e**. The yields were calculated from **4**.

6a: 46% yield. ^{1}H-NMR (400 MHz) δ: 0.33 and 0.40 (each 3H, s, SiMe), 2.84 (1H, d, 2a-H), 4.52 (1H, d, 7b-H), 6.28 and 6.30 (each 1H, d, 1- and 2-H), 7.32—7.60 (4H, m, Ph-H), $J_{1,2}=2.6$, $J_{2a,7b}=3.7$ Hz. HRMS *m/z*: M^+ Calcd for $C_{12}H_{14}Si$: 186.0865. Found: 186.0862.

6b: 51% yield. ^{1}H-NMR (400 MHz) δ: 0.63 (3H, s, SiMe), 3.03 (1H, d, 2a-H), 4.57 (1H, d, 7b-H), 6.30 (2H, br s, 1- and 2-H), 7.16—7.67 (9H, m, Ph-H), $J_{2a,7b}=3.5$ Hz. HRMS *m/z*: M^+ Calcd for $C_{17}H_{16}Si$: 248.1021. Found: 248.1020.

6c: 38% yield. ^{1}H-NMR (400 MHz) δ: 0.50 and 0.53 (each 3H, s, GeMe), 2.96 (1H, d, 2a-H), 4.52 (1H, d, 7b-H), 6.19 and 6.25 (each 1H, d, 1- and 2-H), $J_{1,2}=2.6$, $J_{2a,7b}=3.7$ Hz. HRMS *m/z*: M^+ Calcd for $C_{12}H_{14}Ge$: 232.0307. Found: 232.0305.

6d: 55% yield. ^{1}H-NMR (400 MHz) δ: 3.66 (1H, dd, 2a-H), 4.48 (1H, dd, 7b-H), 6.32 (1H, dd, 2-H), 6.47 (1H, d, 1-H), 7.31—7.56 (9H, m, Ph-H), $J_{1,2}=2.2$, $J_{2,2a}=0.4$, $J_{2a,7b}=3.3$, $J_{P,7b}=3.3$ Hz. HRMS *m/z*: M^+ Calcd for $C_{16}H_{13}OP$: 252.0704. Found: 252.0722.

6e: 34% yield. Colorless prisms (from AcOEt), mp 196—198 °C. ^{1}H-NMR (400 MHz) δ: 4.06 (1H, dd, 2a-H), 4.84 (1H, dd, 7b-H), 5.93 (1H, dd, 2-H), 6.52 (1H, dd, 1-H), 7.42—7.79 (9H, m, Ph-H), $J_{1,2}=2.6$, $J_{1,7b}=1.1$, $J_{2,2a}=0.9$, $J_{2a,7b}=3.5$ Hz. HRMS *m/z*: M^+ Calcd for $C_{16}H_{13}AsO$: 296.0182. Found: 296.0190.

FVP of 6: Formation of 1-Benzometallepines (7a—e) General Procedure: Compound **6** was vaporized under reduced pressure and pyrolyzed through a hotzone (quartz tube: i.d. = 1 cm, l = 20 cm) heated in a pyrolysis furnace. The pyrolyzate was collected in a trap cooled with liquid N_2 and chromatographed on silica gel with pentane (for **6a—c**) or CH_2Cl_2–acetone (20 : 1) (for **6d, e**) to give naphthalene (**8**), 1-benzometallepine (**7**), and the starting **6**, successively. Conditions of the pyrolysis and yields of the products determined by GLC are shown in Table I. Physical, analytical, and NMR spectral data are listed in Tables III and IV.

Reduction of 1-Phenyl-1-benzophosphepine 1-Oxide (7d) with Trichlorosilane General Procedure: A benzene solution of $SiHCl_3$ (1.4 M, 2—3 mol eq) was added to a solution of **7d** (0.3—0.5 g) in benzene (50 ml) and the mixture was stirred at room temperature or heated at 60 °C or 80 °C with stirring, until the starting **7d** was completely consumed (see Table II). The mixture was diluted with benzene (50 ml) and stirred with 2 N NaOH (20 ml) for 5 min in an ice bath, in order to decompose excess $SiHCl_3$. The layers were separated and the organic layer was washed, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–benzene (2 : 1) to give 1-phenyl-1-benzophosphepine (**7f**) and 1-phenyl-2,5-dihydro-1-benzophosphepine (**9**) in the yields shown in Table II. Physical and spectral data of **7f** are given in Tables III and IV.

The dihydrophosphepine (**9**) was gradually oxidized during isolation, so it was isolated and characterized as its oxide (**10**). A solution of **9** (20 mg) and *m*-CPBA (20 mg) in CH_2Cl_2 (10 ml) was stirred for 0.5 h in an ice bath, and then diluted with CH_2Cl_2 (30 ml). The solution was successively washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with CH_2Cl_2–acetone (10 : 1) to give **10**: 20 mg, 94% yield, colorless prisms (from benzene), mp 140—142 °C. ^{1}H-NMR (400 MHz) δ: 3.07 (1H, dd, 2-H), 3.41 (1H, ddd, 2′-H), 3.24 and 3.75 (each 1H, dd, 5-H and 5′-H), 5.74 (1H, dddd, 3-H), 6.35 (1H, ddd, 4-H), 7.2—7.7 (9H, m, Ph-H), $J_{2,2'}=15.0$, $J_{2,3}=7.0$, $J_{2',3}=6.6$, $J_{2',P}=15.0$, $J_{3,4}=9.5$, $J_{3,P}=12.1$, $J_{4,5}=7.0$, $J_{4,5'}=7.0$, $J_{5,5'}=15.0$ Hz. *Anal.* Calcd for $C_{16}H_{15}OP$: C, 75.58; H, 5.95. Found: C, 75.78; H, 6.00.

Reduction of 1-Phenyl-1-benzarsepine 1-Oxide (7e) with Trichlorosilane A $SiHCl_3$ benzene solution (1.4 M, 1.6 ml, 2.2 mmol) was added to a solution of **7e** (250 mg, 0.85 mmol) in benzene (80 ml) and the mixture was stirred at room temperature for 14 h. It was then stirred with 2 N NaOH (10 ml) for 5 min in an ice bath. The benzene layer was washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–benzene (2 : 1) to give 1-phenyl-1-benzarsepine (**7g**): 156 mg, 73% yield. Physical and spectral data of **7g** are given in Tables III and IV.

Oxidation of 7f, g *m*-CPBA (1.5 mol eq) was added to a stirred solution of **7** (50 mg) in CH_2Cl_2 (5 ml) in an ice bath and the mixture was stirred at room temperature for 0.5 h, and then diluted with CH_2Cl_2 (50 ml). It was successively washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated. The residue was chromatographed on silica gel with CH_2Cl_2–acetone (20 : 1) to give the benzometallepine oxides (**7d, e**); **7d**: 48 mg, 90% yield; **7e**: 46 mg, 87% yield.

Irradiation of 7a, c—e A solution of **7a, c** (60 mg) in benzene (80 ml) was irradiated with stirring for 1 h, and then concentrated *in vacuo*. The residue was chromatographed on silica gel with pentane to give the cyclobutabenzometallole (**6**); **6a**: 41 mg, 69% yield; **6c**: 44 mg, 74% yield. However, irradiation of **7d, e** under similar conditions resulted only in decomposition to give no characterizable products.

Reaction of 7a, c—e with 4-Phenyl-1,2,4-triazoline-3,5-dione A solution of **7** (**7a**: 42 mg; **7c**: 38 mg) and 4-phenyl-1,2,4-triazoline-3,5-dione (1.5 mol eq) in benzene (5 ml) was stirred at room temperature for 12—15 h, and then concentrated *in vacuo*. The residue was chromatographed on silica gel with CH_2Cl_2–AcOEt (50 : 1) to give the adduct (**15**).

15a: 47 mg, 57% yield, colorless needles (from hexane), mp 226—228 °C. IR (KBr): 1706 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.38 and 0.44 (each 3H, s, SiMe), 4.77 (1H, d, 2-H), 5.66 (1H, d, 5-H), 6.42 (1H, dd, 3-H), 6.56 (1H, dd, 4-H), 7.25—7.53 (9H, m, Ph-H), $J_{2,3}=7.3$, $J_{3,4}=9.2$, $J_{4,5}=7.0$ Hz. MS *m/z*: 361 (M^+). *Anal.* Calcd for $C_{10}H_{19}N_3O_2Si$: C, 66.46; H, 5.30; N, 11.63. Found: C, 66.73; H, 5.17; N, 11.56.

15c: 46 mg, 78% yield, colorless needles (from hexane), mp 207—210 °C. IR (KBr): 1696 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.56 and 0.60 (each 3H, s, GeMe), 5.00 (1H, d, 2-H), 5.67 (1H, d, 5-H), 6.50 (1H, dd, 3-H), 6.57 (1H, dd, 4-H), 7.33—7.70 (9H, m, Ph-H), $J_{2,3}=7.4$, $J_{3,4}=9.4$, $J_{4,5}=7.2$ Hz. MS *m/z*: 407 (M^+). *Anal.* Calcd for $C_{20}H_{19}GeN_3O_2$: C, 58.97; H, 4.66; N, 10.31. Found: C, 58.72; H, 4.52; N, 10.29.

However, when a solution of **7d, e** and the dienophile in benzene was stirred at room temperature for 3 d, no reaction occurred and **7d, e** were recovered unchanged.

Reaction of 7a with 2,5-Di(methoxycarbonyl)-3,4-diphenylcyclopentadienone (16A) A solution of **7a** (98 mg) and **16**A (270 mg, 1.5 mol eq) in xylene (3 ml) was heated under reflux for 2 d. After cooling, the solution was subjected to chromatography on silica gel with hexane to give the starting **7a** (28 mg, 30%). Further elution with CH_2Cl_2 gave the [2+4]π cycloadduct (**17**A) and the cage compound (**19**A), successively.

17A: 37 mg, 14% yield, colorless needles (from hexane), mp 119—122 °C. IR (KBr): 1802, 1742 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.45 and 0.81 (each 3H, s, SiMe), 3.63 and 3.65 (each 3H, s, CO_2Me), 2.12 (1H, d, 2-H), 3.00 (1H, ddd, 3-H), 5.89 (1H, dd, 4-H), 7.01 (1H, dd, 5-H), 7.03—7.69 (14H, m, Ph-H), $J_{2,3}=11.4$, $J_{3,4}=5.9$, $J_{3,5}=1.8$, $J_{4,5}=11.4$ Hz. MS *m/z*: 534 (M^+). *Anal.* Calcd for $C_{33}H_{30}O_5Si$: C, 74.15; H, 5.62. Found: C, 73.92; H, 5.51.

19A: 57 mg, 21% yield, colorless needles (from hexane), mp 120—122 °C. IR (KBr): 1820, 1740 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.27 and 0.50 (each 3H, s, SiMe), 3.67 and 3.74 (each 3H, s, CO_2Me),

1.89 (1H, dd, 2-H), 2.76 (1H, dd, 4-H), 2.89 (1H, dd, 3-H), 3.82 (1H, dd, 5-H), 6.99—7.60 (14H, m, Ph-H), $J_{2,3}=5.5$, $J_{2,5}=8.8$, $J_{3,4}=8.4$, $J_{4,5}=2.9$ Hz, MS *m/z*: 534 (M^+). *Anal.* Calcd for $C_{33}H_{30}O_5Si$: C, 74.15; H, 5.62. Found: C, 73.87; H, 5.59.

Isomerization of 17A into 19A A solution of **17A** (20 mg) in xylene (3 ml) was refluxed for 3 d, and then subjected to chromatography on silical gel with CH_2Cl_2 to afford **17A** (3 mg, 15%) and **19A** (14 mg, 70% yield).

Reaction of 7a with 2,5-Dimethyl-3,4-diphenylcyclopentadienone (16B) A solution of **7a** (130 mg) and **16B** (275 mg, 1.1 mol eq) in xylene (5 ml) was heated under reflux for 3 d. After cooling, the solution was subjected to chromatography on silica gel with hexane to give the starting **7a** (30 mg, 22%). Further elution with hexane–CH_2Cl_2 (5 : 1) gave the $[4+2]\pi$ cycloadduct (**18B**): 108 mg, 35% yield, colorless prisms (from hexane–Et_2O), mp 213—214 °C. IR (KBr): 1692 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.12 and 0.53 (each 3H, s, SiMe), 0.82 (3H, s, Me), 1.96 (3H, s, Me), 2.16 (1H, d, 2-H), 3.73 (1H, d, 5-H), 5.92 (1H, dd, 4-H), 6.00 (1H, dd, 3-H), 7.00—7.42 (14H, m, Ph-H), $J_{2,3}=7.3$, $J_{3,4}=8.8$ $J_{4,5}=7.7$ Hz. MS *m/z*: 446 (M^+). *Anal.* Calcd for $C_{31}H_{30}OSi$: C, 83.41; H, 6.73. Found: C, 83.32; H, 6.51.

Conversion of the 18B into the Cage Compound (19B) A solution of **18B** (30 mg) in benzene was irradiated for 30 min, and then concentrated *in vacuo*. the residue was chromatographed on silica gel with hexane–CH_2Cl_2 (5 : 2) to give **19B**: 19 mg, 63% yield, colorless needles (from hexane), mp 197—200 °C. IR (KBr): 1744 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz) δ: 0.21 and 0.43 (each 3H, s, SiMe), 0.91 and 1.17 (each 3H, s, Me), 1.63 (1H, d, 2-H), 2.81 (1H, dd, 3-H), 3.93 (1H, dd, 4-H), 4.37 (1H, d, 5-H), 6.91—7.56 (14H, m, Ph-H), $J_{2,3}=4.0$, $J_{3,4}=7.0$, $J_{4,5}=4.8$ Hz. MS *m/z*: 446 (M^+). *Anal.* Calcd for $C_{31}H_{30}OSi$: C, 83.41; H, 6.73. Found: C, 83.30; H, 6.71.

Reaction of 7f with Sulfur A mixture of **7f** (72 mg), sulfur (sublimed, 12 mg, 1.1 mol eq), and benzene (3 ml) was vigorously stirred at room temperature for 1 h, and then concentrated *in vacuo*. The residue was chromatographed on silica gel with benzene to give 1-phenyl-1-benzophosphepine 1-sulfide (**20**): 79 mg, 95% yield, colorless prisms (from benzene), mp 198—200 °C. ^{1}H-NMR (400 MHz) δ: 6.32 (1H, dd, 2-H), 6.45 (1H, ddd, 4-H), 6.92 (1H, ddd, 3-H), 7.09 (1H, d, 5-H), 7.26—8.27 (9H, m, Ph-H), $J_{2,3}=12.5$, $J_{2,P}=18.3$, $J_{3,4}=6.2$, $J_{3,P}=41.4$, $J_{4,5}=12.8$, $J_{4,P}=2.2$ Hz. MS *m/z*: 268 (M^+). *Anal.* Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88. Found: C, 71.56; H, 4.84.

Reaction of 7f with Methyl Iodide A solution of **7f** (85 mg) and MeI (95%, 0.52 ml, 2 mol eq) in benzene (5 ml) was stirred at room temperatue for 5 h under a nitrogen atmosphere, and then concentrated to dryness *in vacuo*. The solid residue was recrystallized from acetonitrile to give 1-methyl-1-phenyl-1-benzophosphepinium iodide (**21**): 130 mg, 96% yield, colorless needles, mp 183—187 °C. ^{1}H-NMR (60 MHz) (CD_3OD) δ: 2.73 (3H, d, $J_{Me,P}=14.3$ Hz, 1-Me), 6.59 (1H, br, 2-H), 6.81 (1H, br, 4-H), 7.41—8.00 (11H, m, 3-, 5-,and Ph-H). *Anal.* Calcd for $C_{17}H_{16}IP$: C, 53.99; H, 4.26. Found: C, 53.88; H, 4.27.

Reaction of 7f, g with $Fe_2(CO)_9$ A mixture of **7** (**7f**: 70 mg; **7g**: 48 mg), $Fe_2(CO)_9$ (110 mg for **7f**; 65 mg for **7g**; *ca.* 1 mol eq), and dry benzene (10 ml) was vigorously stirred at room temperature under a nitrogen atmosphere for *ca.* 15 h. The reaction mixture was filtered and the filterate was concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane–benzene (3 : 1) to give the $Fe(CO)_4$-complex (**22**) (**22f**: 86 mg, 72% yield; **22g**, 66 mg, 86% yield) and the $Fe(CO)_4 \cdot Fe(CO)_3$-complex (**23**) (**23f**: 8 mg, 5% yield; **23g**: 3 mg, 3% yield), successively.

The $Fe(CO)_4$-complex (**22**) (40 mg) was further treated with $Fe_2(CO)_9$ (*ca.* 2 mol eq) in benzene for 30 h and worked up in a similar manner to that described above to give **23** (**23f**: 29 mg, 55% yield; **23g**: 25 mg, 48% yield).

22f: yellow viscous oil. IR (neat): 2052, 1926 (CO) cm^{-1}. ^{1}H-NMR (400 MHz) (C_6D_6) δ: 6.37 (1H, dd, 2-H), 6.14 (1H, ddd, 3-H), 6.37 (1H, d, 5-H), 5.72 (1H, ddd, 4-H), 6.63—7.57 (8H, m, Ph-H), 8.42 (1H, dd, 9-H), $J_{2,3}=11.7$, $J_{2,P}=32.2$, $J_{3,4}=6.0$, $J_{3,P}=32.4$, $J_{4,5}=12.5$, $J_{4,P}=11.2$, $J_{8,9}=7.9$, $J_{9,P}=16.0$ Hz. HRMS *m/z*: M^+ Calcd for $C_{20}H_{13}FeO_4P$: 403.9901. Found: 403.9959.

22g: brown viscous oil. IR (neat): 2052, 1948 (CO) cm^{-1}. ^{1}H-NMR (400 MHz) (C_6D_6) δ: 5.70 (1H, dd, 4-H), 5.87 (1H, d, 2-H), 6.20 (1H, dd, 3-H), 6.36 (1H, d, 5-H), 6.90—7.20 (8H, m, Ph-H), 7.89 (1H, d, 9-H), $J_{2,3}=11.2$, $J_{3,4}=5.9$, $J_{4,5}=13.1$, $J_{8,9}=7.6$ Hz. HRMS *m/z*: M^+ Calcd for $C_{20}H_{13}AsFeO_4$: 447.9379. Found: 447.9407.

23f: yellow needles (from hexane–Et_2O), mp 161—163 °C. IR (KBr): 2072, 2052, 2008, 1978, 1928 (CO) cm^{-1}. ^{1}H-NMR (400 MHz) (C_6D_6) δ: 3.08 (1H, ddd, 2-H), 3.32 (1H, d, 5-H), 4.41 (1H, ddd, 4-H), 4.68 (1H, ddd, 3-H), 6.72—7.35 (8H, m, Ph-H), 7.87 (1H, dd, 9-H), $J_{2,3}=7.7$, $J_{2,P}=15.0$, $J_{2,4}=1.1$, $J_{3,4}=4.8$, $J_{3,P}=8.8$, $J_{4,5}=8.4$, $J_{8,9}=5.1$, $J_{9,P}=16.1$ Hz. *Anal.* Calcd for $C_{23}H_{13}Fe_2O_7P$: C, 50.78; H, 2.41. Found: C, 50.73; H, 2.40.

23g: brown viscous oil. IR (neat): 2072, 2052, 2000, 1930 (CO) cm^{-1}. ^{1}H-NMR (400 MHz) (C_6D_6) δ: 3.02 (1H, d, 2-H), 3.40 (1H, d, 5-H), 4.42 (1H, dd, 4-H), 4.75 (1H, dd, 3-H), 6.78—7.22 (8H, m, Ph-H), 7.68 (1H, d, 9-H), $J_{2,3}=7.3$, $J_{3,4}=4.8$, $J_{4,5}=8.4$, $J_{8,9}=6.9$ Hz. HRMS *m/z*: M^+ Calcd for $C_{23}H_{13}AsFe_2O_7$: 587.8576. Found: 587.8578.

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