

Group 14 Metalloles. 2. Ionic Species and Coordination Compounds

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Although silicon is a group 14 element and exhibits tetravalency like carbon, many of its properties resemble those of phosphorus. Thus, stable penta- and hexacoordinated silicon compounds are common,¹ while tricoordinated species like silenes (S=C), disilenes (Si=Si), silanimines (Si=N), silaphosphimines (Si=P), silanones (Si=O), silanethiones (Si=S), and sila-aromatic compounds are highly reactive.² Although silabenzene² have been identified spectroscopically and through their Diels-Alder adducts,³ silynes (Si≡C) and disilynes (Si≡Si) have never been observed.^{2,4} Silylenes have been observed spectroscopically and postulated as intermediates in thermolysis and photolysis reactions.⁵

Recently, however, silenes and disilenes with bulky substituents have been reported as stable and isolable compounds.⁶ The first stable silicon divalent species has been obtained by complexation with two pentamethylcyclopentadienyl ligands.⁷ The other group 14 elements are less reluctant to adopt low valency states,⁸ and their metallocenes, for instance, are well-known.⁹

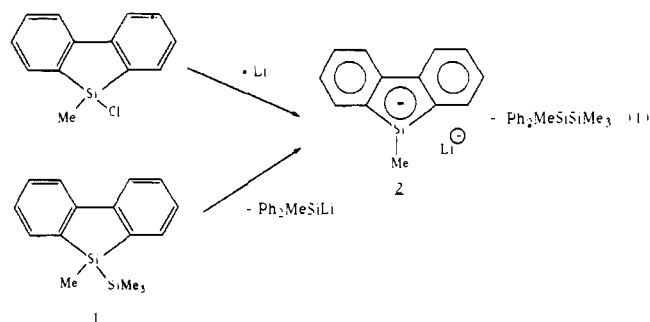
Since the first silacyclopentadiene, 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (hexaphenylsilole), was prepared in 1959 by Braye and Hübel,¹⁰ the chemistry of metalloles has developed considerably, in particular their use as ligands with transition metals.¹¹ Interest

has been directed to the similarities between cyclopentadienes and metalloles, especially with a view to the preparation of compounds containing the η^5 -metallacyclopentadienyl ligand.

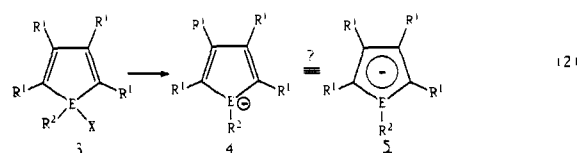
I. Sila- and Germacyclopentadienide Anions

A. Preparation and Reactivity

The first silacyclopentadienide anion was prepared by Gilman and Gorsich¹² by treatment of 1-chloro-1-methylsilafuorene with lithium (eq 1). In 1961, Benkeser and co-workers¹³ reported the silacyclopentadienide anion, but the work was later found to be irreproducible by the same group.¹⁴



Rühlmann attempted to prepare the silacyclopentadienide anion (eq 2) by treatment of 3 ($R^1 = \text{Ph}$, $R^2 = \text{Ph}$, Me , $\text{X} = \text{H}$, $\text{E} = \text{Si}$) with potassium, sodium bis-



(trimethylsilyl)amide, or phenyllithium,¹⁵ but he could not decide whether the intense red-violet colors obtained were due to the anion. This reaction was reexamined by Curtis,^{16,17} who showed that the germole ($R^1 = R^2 = \text{Ph}$, $\text{X} = \text{H}$, $\text{E} = \text{Ge}$) reacted with butyllithium to afford the anion 4, but the analogous silole gave radical anions. This last observation was confirmed by Janzen¹⁸⁻²⁰ by chemiluminescence studies and by Desy²¹ by electrochemistry.

Polarographic studies of C-phenylated 1,1-dimethylsiloles in acetonitrile containing variable amounts of water show also the formation of mono- and dianions.²² Some evidence for the formation of tetraanions in the treatment of the same siloles with lithium was also obtained.²³

Reaction of 1-chlorosiloles with alkali metals leads to unstable species that react with methyl iodide and chlorotrimethylsilane in the manner expected for 1-



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Marc Lheureux was born in 1961 in Elbeuf, Normandy, France. He obtained the diploma Maîtrise in Physical Chemistry at the Université des Sciences et Techniques du Languedoc in Montpellier (1983) and the Doctorat at the same University under the supervision of Professor R. Corriu and Dr. E. Colomer in 1988. His doctoral work involved the coordination chemistry of group 14 metalloles and the stereochemical behavior of octahedral complexes of molybdenum and tungsten with such ligands. He is now working as a post-doctoral fellow at Carl Freudenberg, Weinheim, Germany.



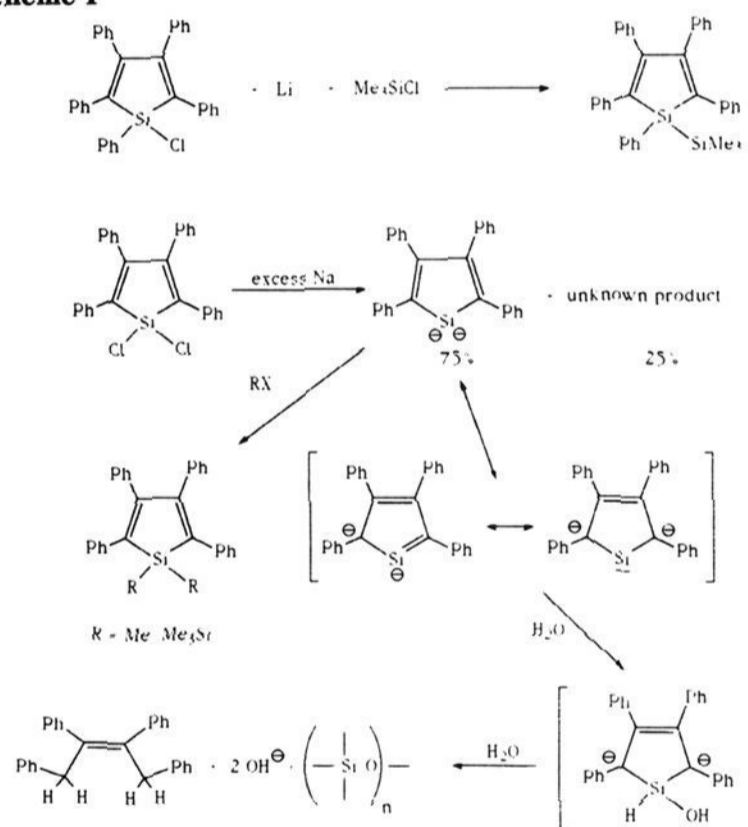
Robert Corriu was born in 1934 in Port-Vendres, Roussillon, France. He obtained the degree of Docteur ès Sciences Physiques in 1961 from the Université de Montpellier. He became Associate Professor at the Université de Poitiers in 1964 and Professor at the Université des Sciences et Techniques du Languedoc (Montpellier) in 1969. His main research interests involve organometallic chemistry: organosilicon and organogermanium compounds, transition-metal complexes, hypervalent silicon species, and organometallic polymers as precursors to new materials. He is now head of the Institut de Chimie Fine and of the Laboratoire des Précurseurs Organométalliques de Matériaux (a collaboration of the C.N.R.S., Rhône-Polenc, and the University). He has been elected Corresponding Member of the French Academy of Sciences and has obtained awards from the French Chemical Society (1969 and 1985) and from the American Chemical Society (1984).

silacyclopentadienide anions.^{24,25} The preparation of the 1,1-dianion from 1,1-dichloro-2,3,4,5-tetraphenylsilole has been reported. This species reacts with methyl iodide and Me_3SiCl but water causes ring opening; a possible mechanism is discussed for this reaction²⁵ (Scheme I).

In the C-methylated series, treatment with organolithium compounds, metallic lithium, or potassium hydride did not lead to the formation of the silacyclopentadienide ions.²⁶⁻²⁸

Silacyclopentadienide anions have been obtained by cleavage of a Si-Si bond²⁹ (eq 1) with a silyllithium

Scheme I



Scheme II

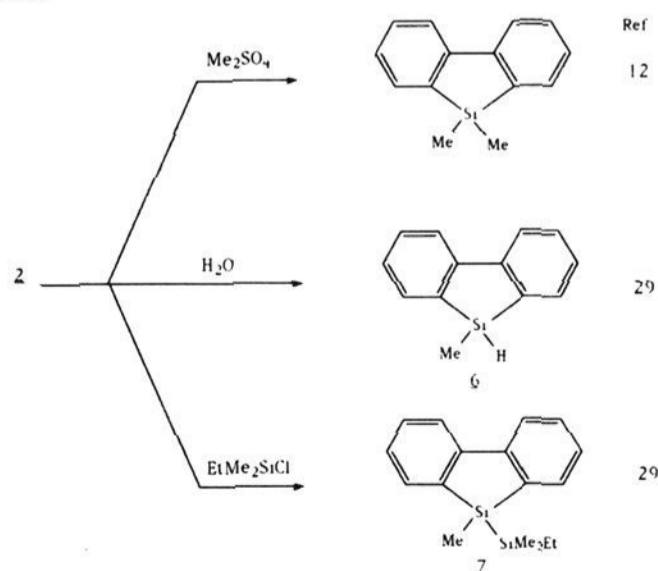
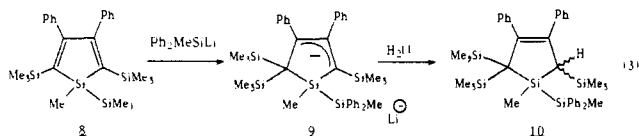


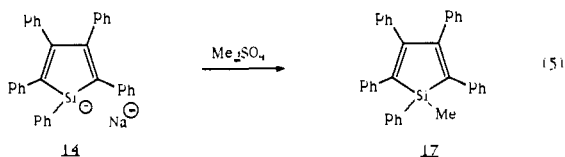
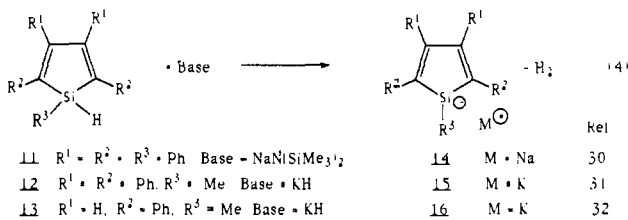


Figure 1. Conformation for the silacyclopentadienide anion. Left, planar (C_{2v}); right, pyramidal (C_s).

compound. The dibenzosilacyclopentadienide anion **2** is thus obtained and shows normal reactivity with electrophiles (Scheme II). Silole **8** (eq 3) reacts with Ph_2MeSiLi in a different manner to afford the anion **9**, which upon hydrolysis gives a mixture of the geometrical isomers **10**.



Treatment of 1-hydrosiloles with strong nonnucleophilic bases ($\text{NaN}(\text{SiMe}_3)_2$ in THF,³⁰ KH in THF with sonication,³¹ or in DME at low temperature³²) gave in good yields the expected silacyclopentadienide anions (eq 4). The anion **14** reacts with methyl sulfate to give the silole **17** (eq 5), while **16** exhibits a lack of reactivity toward electrophiles and reacts only with water (or D_2O) to regenerate the starting silole **13** (or 1-deuterated **13**). No data are available on the reactivity of **15**.



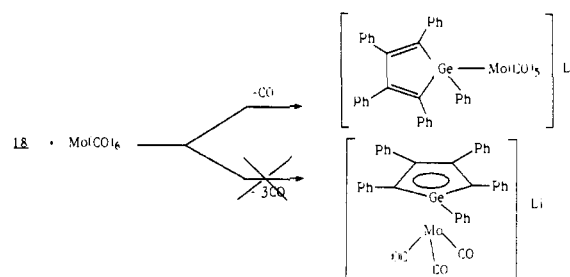
B. The Problem of Aromaticity

Spectroscopic studies support the possibility of a $d-\pi$ interaction between silicon and the π system of the molecule.^{33,34} These conclusions are not in agreement with later interpretations of the ^1H NMR results.³¹

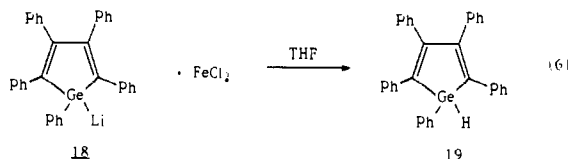
Theoretical studies on silabenzene show that its resonance energy is $2/3$ that of benzene³⁵ and that the main obstacle to the formation of the molecule is thermodynamic.³⁶ Calculations on the silacyclopentadienide anion^{37,38} predict only 3–25% of the aromaticity of the all-carbon analogue and reveal a C_s conformation³⁷ (Figure 1).

From chemical evidence, Curtis concludes that the ring structure does not confer enhanced acidity on the hydrides¹⁶ (eq 2, $\text{R}^1 = \text{R}^2 = \text{Ph}$, $\text{Y} = \text{H}$, $\text{E} = \text{Si}$, Ge) compared to Ph_3EH ($\text{E} = \text{Si}$, Ge), but further experiments show that **4** (eq 2, $\text{R}^1 = \text{R}^2 = \text{Ph}$, $\text{Y} = \text{H}$, $\text{E} = \text{Ge}$) has a $\text{p}K_a$ 6 units greater than that of Ph_3GeH .¹⁷ The final conclusion is that the corresponding anion **4** is in fact resonance stabilized (structure 5).

Scheme III

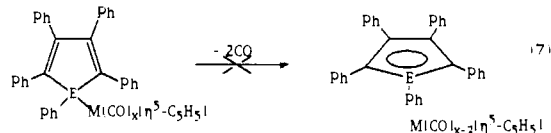


Attempts to confirm this aromaticity by η^5 -coordination to transition metals have been unsuccessful. Reaction of the germyllithium derivative **18** with iron dichloride led to the hydride **19**¹⁷ (eq 6), probably via



a series of reactions involving a one-electron transfer, giving a free germyl radical which then abstracts a hydrogen atom from the solvent. The germyllithium derivative **18** reacts with hexacarbonylmolybdenum to give a $\text{Ge}-\text{Mo}$ σ bond³⁹ (Scheme III) instead of the η^5 -germyl complex.⁴⁰

The synthesis of η^5 -complexes was attempted via complexes with silicon-transition metal (or germanium-transition metal) σ bonds, the synthesis of which will be described below (eq 7) under thermal or photochemical conditions.¹⁷ Decomposition was observed in all cases.

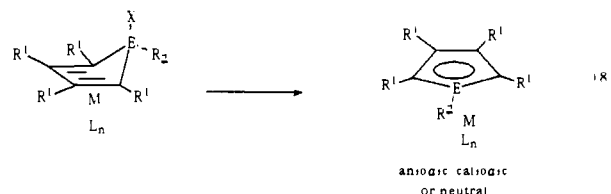


II. Sila- and Germacyclopentadienyl Cations

Recently, the preparation in solution of a silicenium cation derived from 1-methyl-2,3,4,5-tetraphenylsilole has been achieved by treatment of **12** with trityl perchlorate.⁴¹ A germacyclopentadienyl cation in which the diene moiety is coordinated to iron has been reported;⁴² its formation and structure will be discussed in section IV.A.

III. Complexation of Metalloles

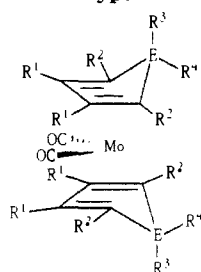
The coordination chemistry of siloles was reviewed by McMahon in 1982.¹¹ It was oriented to the transformation η^4 -metallacyclopentadiene \rightarrow η^5 -metallacyclopentadienyl-transition metal (eq 8).



A. Complexes with Group 6 Metals

The first complexes of siloles with group 6 metals were described by Abel et al.⁴³ in 1976.

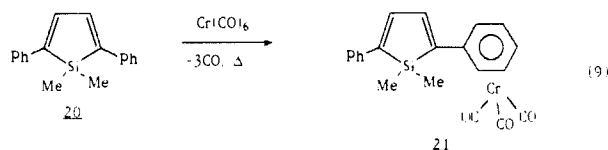
TABLE I. Complexes of the Type



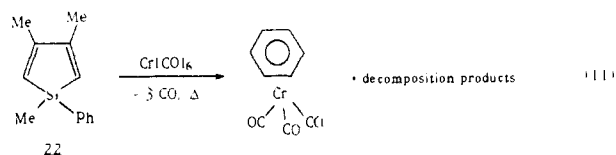
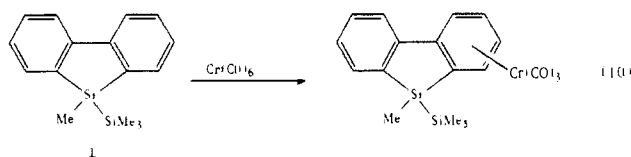
no.	E	R ¹	R ²	R ³	R ⁴	precursor ^a	yield, %	ref
38	Si	H	Ph	Me	Me	A	44	43
39	Si	H	H	Me	Me	B	43	47, 53
40	Si	Me	H	Me	Me	B	28	47
41	Ge	Me	H	Me	Me	B	20	47
42	Si	Me	H	Ph	Me	B	34	45a
43	Si	H	Ph	Fp ^b	Me	B	20	45

^aA = Mo(CO)₆, B = Mo(CO)₄(COD). ^bFp = Fe(CO)₂(η⁵-C₅H₅).

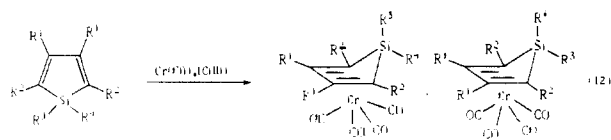
Displacement of carbonyl ligands from Cr(CO)₆ leads exclusively to the complexation of the arene in C-phenylated siloles (eq 9). This type of complexation



was also found in attempts to coordinate the silafluorene 1 with chromium⁴⁴ (eq 10). The 1-phenyl substituted silole 22 failed to give a complex with the Cr(CO)₃ moiety (eq 11). Instead, the silicon-phenyl bond was cleaved;^{45a} this cleavage has also been observed during the complexation of other arylsilanes.⁴⁶



Complexation at the diene moiety can be achieved by using tetracarbonyl(η⁴-1,5-cyclooctadiene)chromium [Cr(CO)₄(COD)] under mild conditions^{45,47-49} (eq 12).



no.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield, %	no.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield, %	Ref
21	H	H	H	H	Me	-	20	H	H	H	H	Me	-	47
24	Me	H	H	H	Me	25	31	Me	H	H	H	Me	-	47
22	Me	H	H	H	Ph	-	32a (75%)	Me	H	H	H	Ph	25	45
25	H	H	H	H	OMe	57	33	H	H	H	H	OMe	-	48
24	H	H	H	H	Me	54	34a (25%)	H	H	H	H	Me	-	49
27	H	H	H	H	Me	65	35	H	H	H	H	Me	-	49
28	H	H	H	H	OMe	48	36	H	H	H	H	OMe	-	49
29	H	H	H	H	OMe	57	37	H	H	H	H	OMe	-	49

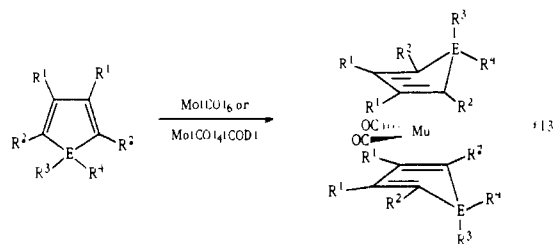
^a not isolated

^b 32a isolated in 25% yield

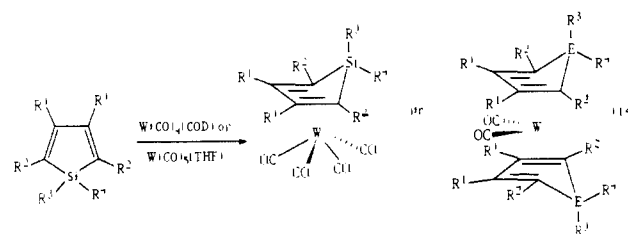
With siloles 22 and 26 a mixture of isomers 32a and 32b and 34a and 34b, respectively, is obtained; the pre-

dominant isomer bears the bulkier group in the exo position. The attributions of the stereochemistry can be made unequivocally on the basis of the results obtained by Sakurai and Hayashi,⁵⁰ who determined the range of the chemical shifts of the endo and exo methyls by ¹H NMR with lanthanide shift reagents and compared their observations to previous assignments in substituted cyclopentadienyliron tricarbonyls^{51,52} (cf. section V.E). Siloles 28 and 29 lead each to a single isomer, 36 and 37, with the isopropyl group in the exo position. Surprisingly, 27 does not give a mixture of isomers; instead 35 with the exo chlorine is obtained.

Coordination to molybdenum can be obtained with Mo(CO)₆⁴³ or better with Mo(CO)₄(COD).^{45,47,53} Complexes with two metalloles coordinated to the transition metal are thus prepared (eq 13) (Table I). It is in-



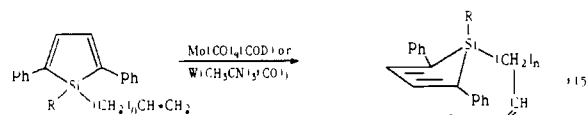
teresting to recall that 42 bears the phenyl group in the exo position exclusively. However, tungsten is more versatile than chromium and molybdenum, and, depending on the reaction conditions, mono- or bis-silole complexes can be isolated^{45a,47,49} (eq 14).



no.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield, %	no.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield, %	Ref
24	Me	H	H	H	Me	25	47	Me	H	H	H	Me	20	47
44	Me	H	H	H	CH ₂ Ph	-	48	Me	H	H	H	CH ₂ Ph	22	47
25	H	H	H	H	OMe	50	50	H	H	H	H	OMe	45	49
45	H	H	H	H	OMe	-	51	H	H	H	H	OMe	45	45

^a not isolated

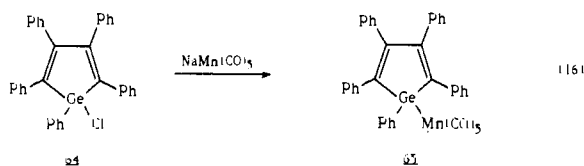
Siloles with unsaturated groups at silicon give monosubstituted complexes with the vinyl group bonded to the transition metal⁵⁴ (eq 15). Obviously, the unsaturated η² ligand is always in the endo position. With such ligands the reactivity of molybdenum and tungsten is very similar.



no.	R	n	no.	R	n	no.	R	n
52	Ph	n = 0	56	M = Mo		59	R = vinyl	n = 0
53	R = Me	n = 1	57	M = W		60	R = vinyl	n = 1
54	R = vinyl	n = 0	58	M = Mo		61	R = vinyl	n = 1
55	R = allyl	n = 1	62	M = W		63	R = vinyl	n = 1

B. Complexes with Group 7 Metals

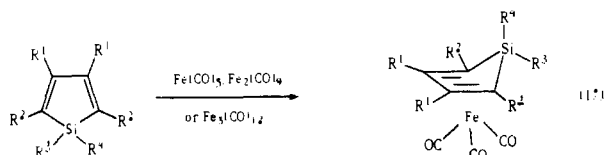
No η^4 -complexes of metalloles with manganese or rhenium are known. Reaction of 1-chlorogermole (64) with sodium pentacarbonylmanganate affords the corresponding germole with a Ge-Mn σ bond¹⁷ (eq 16).



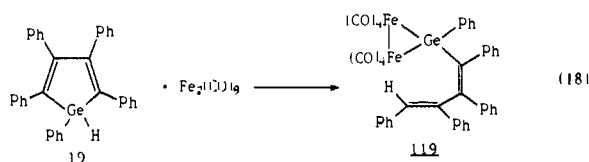
C. Complexes with Group 8 Metals

In the first complexes reported in the literature, siloles were coordinated to iron,⁵⁵ and most of the research on the coordination chemistry of metalloles has been directed to complexes bearing the $\text{Fe}(\text{CO})_3$ unit.

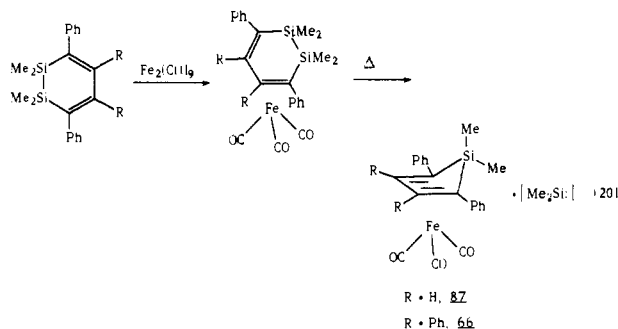
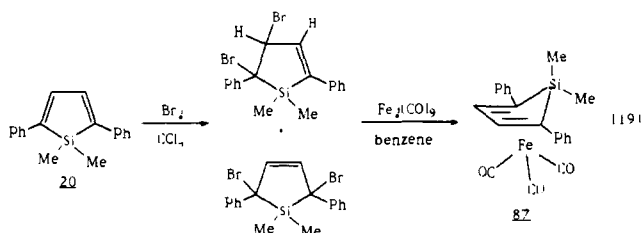
Coordination to iron can be achieved with $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, or $\text{Fe}_3(\text{CO})_{12}$, according to the general reaction shown in eq 17. The different complexes and reaction



conditions are reported in Table II. Yields are usually high except for the complexes of 1-hydridosiloles. This can be understood since $\text{Fe}(\text{CO})_5$ is a catalyst for hydrosilylation reactions,⁶⁷ and oxidative addition of silanes to iron is well-known.⁶⁸ Pentaphenylgermole reacts with $\text{Fe}_2(\text{CO})_9$ but instead of giving the expected η^4 -complex, a germanium-bridged iron dimer is obtained⁶⁹ (eq 18).

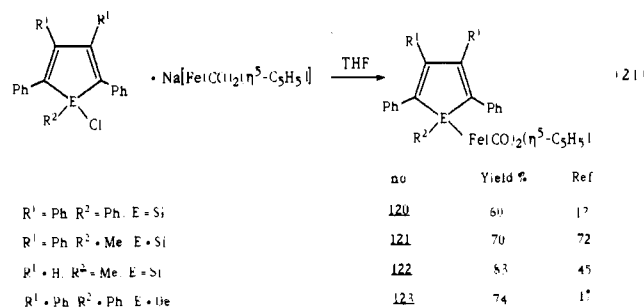


Individual syntheses have been reported but not generalized. Thus, bromination of 1,1-dimethyl-2,5-diphenylsilole and subsequent reaction of the mixture of dibromosilacyclopentenes with $\text{Fe}_2(\text{CO})_9$ gives complex 87 in medium yield⁷⁰ (eq 19), and ring contraction in tricarbonyl(η^4 -1,2-disilacyclohexadiene)iron gives the same type of complexes⁷¹ (eq 20) with expulsion of $[\text{Me}_2\text{Si}]$. In this case, when $\text{R} = \text{Ph}$, the disilacyclohexadiene complex is not stable and the reaction with $\text{Fe}_2(\text{CO})_9$ affords 66.

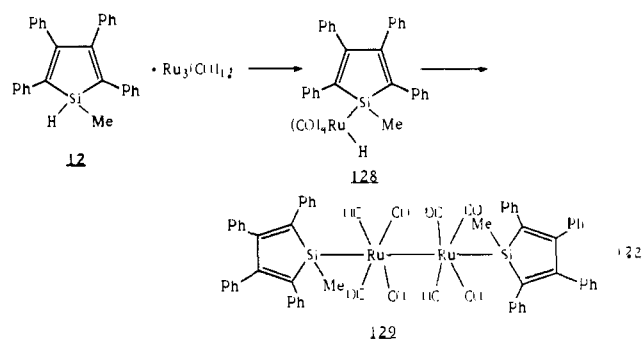


Several complexes have been prepared by reactions at silicon or at iron, starting with some of the complexes already described. Their formation will be discussed in section IV.B.3.

Compounds bearing Fe-Si or Fe-Ge σ bonds are obtained by reaction of the corresponding chlorosiloles and chlorogermoles with $\text{Na}[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ ^{17,45,72} (eq 21).

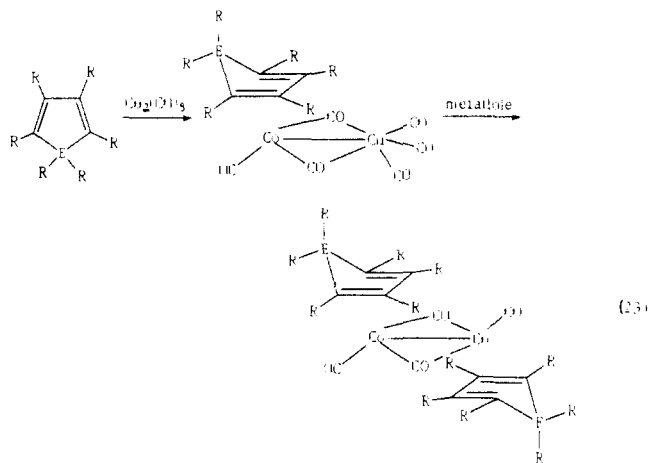


Only a few complexes with ruthenium are described. Their syntheses are analogous to those of the iron ones, starting with $\text{Ru}_3(\text{CO})_{12}$ (Table III). The formation of 126 is accompanied by ring cleavage and $\text{Me}_{12}\text{Si}_6$ is also obtained.⁴⁷ Reaction of 1-methyl-2,3,4,5-tetraphenylsilole (12)⁴³ takes place in a different way, and only the dinuclear complex 129 is obtained, probably via an unstable intermediate 128 corresponding to the oxidative addition of the Si-H bond to ruthenium (eq 22).



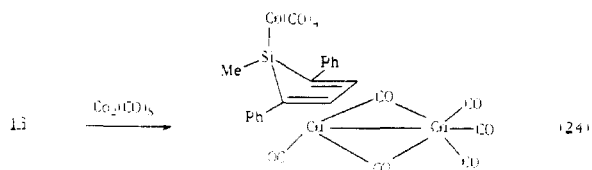
D. Complexes with Group 9 Metals

Siloles and germoles react smoothly with octacarbonyldicobalt to substitute two or four carbonyl ligands. The general reaction is shown in eq 23, and the different complexes thus obtained are reported in Table IV. The formation of type A or B complexes depends on the reaction conditions and, apparently, also on the nature of the metallole (although systematic studies have not been carried out). The most convenient method for the synthesis of type B complexes is the reaction of the monosubstituted ones (type A) with an equimolar amount of the metallole.⁴⁷ It is interesting

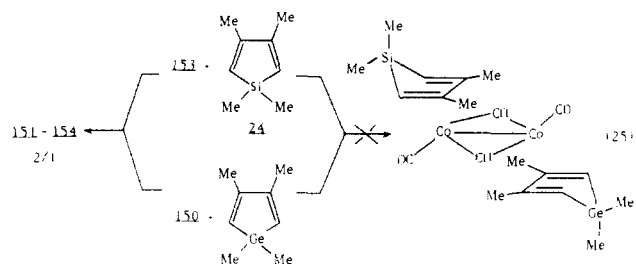


to note that in contrast to the complexation of group 6 metals, allyl and vinyl substituents do not coordinate to cobalt.

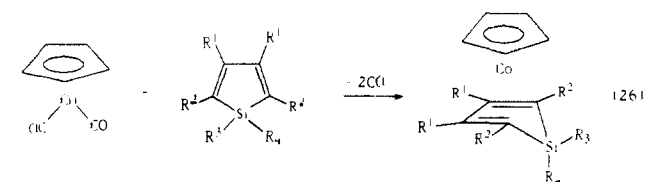
1-Ethynyl- and 1-propynyl-1-methyl-2,5-diphenylsilole can coordinate to cobalt via the diene and via the triple bond⁵⁴ (Scheme IV). 1-Methyl-2,5-diphenylsilole (13) also reacts via the diene and via the Si-H bond⁴⁹ (eq 24).



Attempts to prepare type B mixed complexes with one silole and one germole ligand have been unsuccessful⁴⁷ (eq 25), and only the homodisubstituted complexes are obtained. This result can be related to the thermal decompositions of 142 and 145 into 143 and 146, respectively.⁴⁷ Dicarbonyl(η^5 -cyclopentadienyl)-cobalt reacts with siloles with displacement of the carbonyl ligands (eq 26) to give the corresponding (η^5 -cyclopentadienyl)(η^4 -silole)cobalt complexes.^{45,49,60,73}

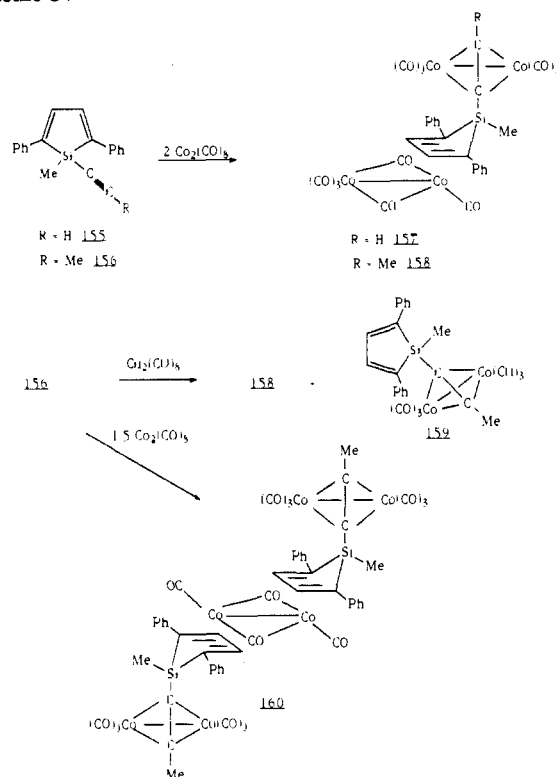


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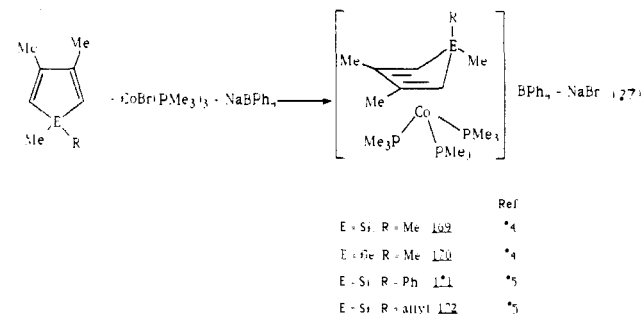


R ¹ - R ² - Ph R ³ - R ⁴ - Me		Ref
R ¹ - H R ² - Ph R ³ - R ⁴ - Me	161	73
R ¹ - H R ² - Ph R ³ - Me R ⁴ - Ph	162	60, 73
R ¹ - H R ² - Ph R ³ - Me R ⁴ - Ph	163	60
R ¹ - H R ² - Ph R ³ - Me R ⁴ - Me	164	49
R ¹ - H R ² - Ph R ³ - Me R ⁴ - Me	165	49
R ¹ - H R ² - Ph R ³ - Me R ⁴ - Me	166	49
R ¹ - H R ² - R ³ - R ⁴ - Ph	167	60
R ¹ - R ² - R ³ - Me R ⁴ - H	168	45

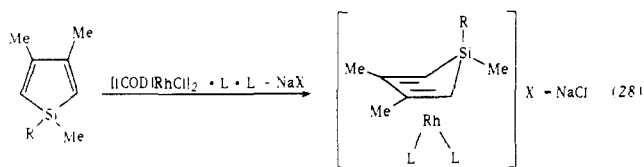
Scheme IV



Cationic complexes with cobalt have been obtained by treating $\text{CoBr}(\text{PMe}_3)_3$ with metalloles in the presence of bulky, stabilizing anions in acetone^{74,75} (eq 27). The



same group has prepared cationic rhodium complexes from $[\text{Rh}(\text{COD})\text{Cl}]_2$ by reaction with phosphines and siloles. Complexes with two different phosphines can also be obtained⁷⁵ (eq 28). Interestingly, complex 180

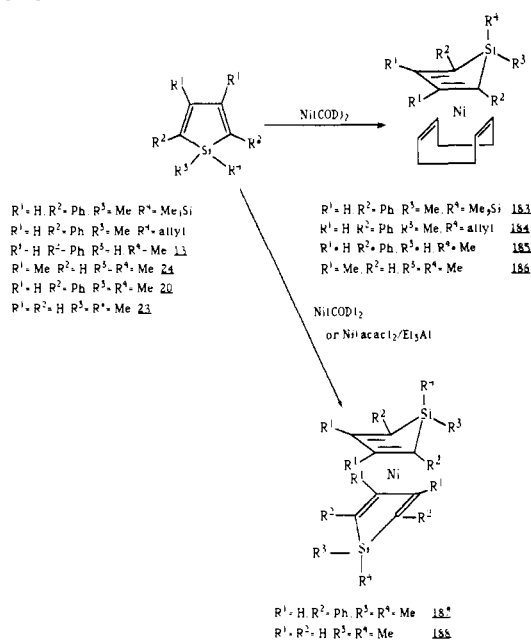


R - Me L - L - PPh ₃ X - PF ₆	173
R - Me L - L - PPh ₃ X - BF ₄	174
R - Me L - L - PPh ₃ X - SbF ₆	175
R - Ph L - L - PPh ₃ X - PF ₆	176
R - allyl L - L - PPh ₃ X - PF ₆	177
R - Me L - L - PMe ₂ Ph X - BF ₄	178
R - Me L - L - PMePh ₂ X - BF ₄	179
R - Me L - L - PPh ₃ X - BF ₄	180

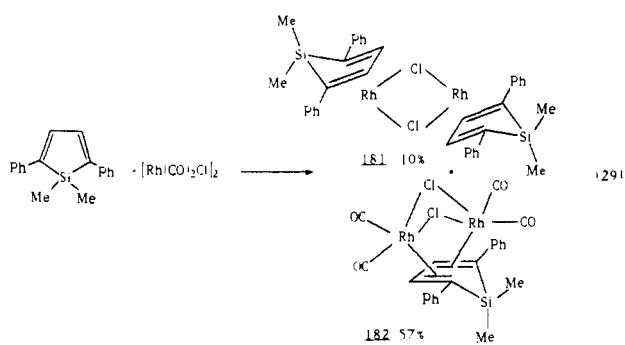
decomposes to $[\text{Rh}(\text{PMe}_3)_2(\text{PPh}_3)_2]\text{BF}_4$ when recrystallized. In all cases the bulkier substituents occupy the exo position.⁷⁵ For all these syntheses of cationic complexes, yields are close to 70%.

1,1-Dimethyl-2,5-diphenylsilole (20) leads to two different binuclear complexes upon thermal reaction in

Scheme V



boiling hexane with $[Rh(CO)_2Cl]_2$ ⁴³ (eq 29). Complexes 181 and 182 are easily isolated by fractional crystallization.



E. Complexes with Nickel

η^4 -Complexes with nickel have been obtained by complexation of siloles with $Ni(COD)_2$ ^{47,53,61} or with Ni^0 (from an in situ reduction of $Ni(acac)_2$ with Et_3Al)⁶¹ (Scheme V). It is interesting to note that treatment of **20** with $Ni(COD)_2$ or treatment of any of the other siloles studied with Ni^0 results in the formation of a nickel mirror.

Bis(1,5-cyclooctadiene)nickel leads to the monosubstitution complexes except in the case of 1,1-dimethylsilole; the sandwich type complex is then obtained. For complexes 183, 184, and 185, the exo stereochemistry for the bulkiest allyl and trimethylsilyl groups seems reasonable; however, the attributions cannot be rigorously given by ¹H NMR, since the $\Delta\delta$ of the exo and endo methyls is very small. To our knowledge, complexes with stannacyclopentadienes (stannoles) and with plumbacyclopentadienes (plumboles) have never been reported.

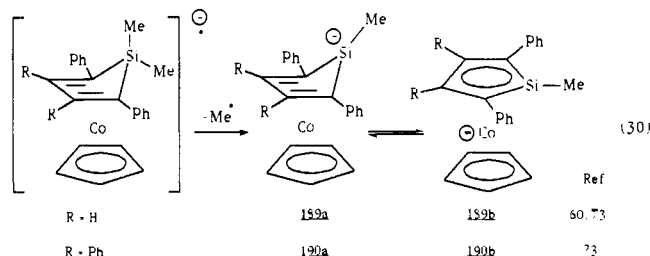
IV. Reactivity of the Metallole Complexes

As we pointed out in the introduction, the coordination chemistry of group 14 metalloles has a particular importance since η^4 -complexes are potential sources of the still unknown group 14 η^5 -metallacyclopentadienyl

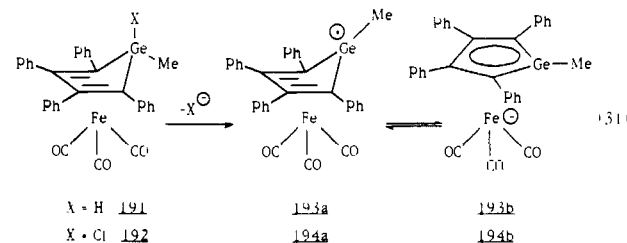
species. Thus, the study of their reactivity has been oriented toward the participation of the group 14 element in the transition-metal coordination sphere.

A. η^5 -Metallacyclopentadienyl Species

The observation of coordinated silacyclopentadienyl species in mass spectrometry has been reported by Sakurai⁷³ and by Fink,⁶⁰ who observed a very strong peak for masses corresponding to $(\eta^5\text{-cyclopentadienyl})(\eta^5\text{-silacyclopentadienyl})$ cobalticenium ions (eq 30). According to the results of Herberich and



co-workers⁷⁶ in the carbon series, it is reasonable to attribute these peaks to structures 189b and 190b; however, a cation with germanium and iron has actually been isolated,⁴² and spectroscopic studies (¹H and ¹³C NMR and ⁵⁷Fe Mössbauer) reveal that it should be regarded as a η^4 -diene rather than a η^5 -germacyclopentadienyl complex (eq 31). In conclusion, there is no evidence for the attribution of the η^5 structure to the peaks observed in mass spectrometry.



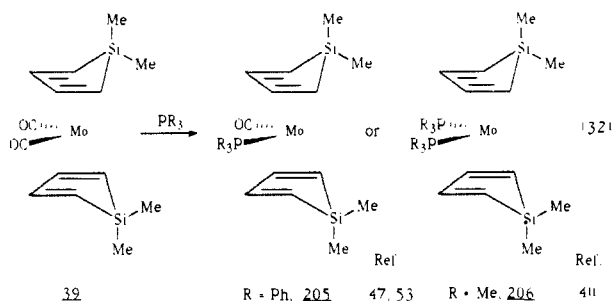
B. Types of Reaction

Reactions of these complexes can occur at three different sites: the transition-metal atom, the carbonyl ligands, and the group 14 element. Nothing is reported about the reactivity of the coordinated double bonds.

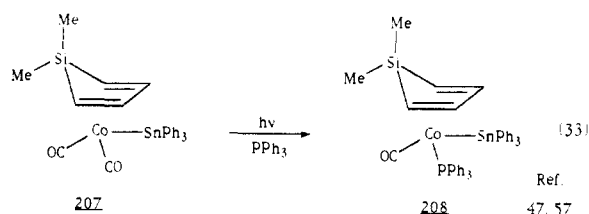
1. Reactions at the Transition Metal

Attempts at thermal substitution of a carbonyl ligand by triphenylphosphine in iron complex **66** resulted in decoordination of the η^4 -ligand⁵⁵ (Scheme VI); however, under UV irradiation, one carbonyl ligand can easily be displaced^{24,47,53,58} (Scheme VI). Decoordination has also been reported to occur on treatment of tricarbonyl- $(\eta^4\text{-1,1-dimethyl-2,3,4,5-tetraphenylgermole})$ iron (**79**) with trimethylamine oxide or with titanium tetrachloride⁵⁸ and of tricarbonyl- $(\eta^4\text{-1,1,3,4-tetramethylsilole})$ iron (**106**) with trimethylamine oxide.⁶² In bis(silole)molybdenum complexes, displacement of carbonyl ligands can only be achieved in complexes with low steric crowding; one or two carbonyls are then substituted^{47,53} (eq 32).

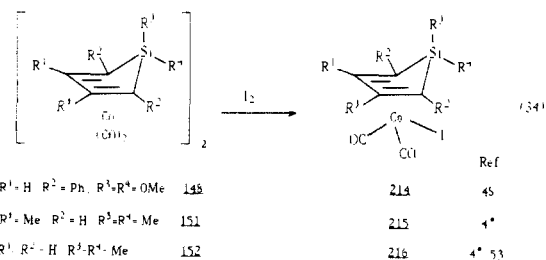
Cobalt-cobalt σ bonds are cleaved by sodium amalgam and by iodine. Reaction with sodium amalgam leads to the formation of the anion (as in most homobimetallic transition-metal complexes). These anions



react with Ph_3SnCl to give the expected complexes with Co-Sn bonds^{40,47,53,60} (Scheme VII). Yields are not easily reproduced, since the formation of the anion is irreversible (as observed by cyclic voltammetry),⁴⁷ and thus depend on the time that the complex is left on the amalgam. These anions are isostructural and isoelectronic with $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^-$ (cf. section V.B) but they do not displace halogens with RX or R_3SiX .

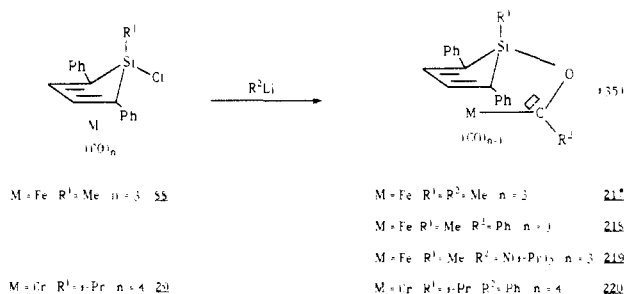


Cleavage of complexes 148, 151, and 152 with iodine leads to the corresponding ones with cobalt-iodine bonds^{47,48,53} (eq 34). This is a typical reaction of bimetallic complexes,⁷⁸ but in the case of $[\text{Co}(\text{CO})_2(\eta^4\text{-diene})]_2$ (diene = norbornadiene, isoprene, 2,3-dimethylbutadiene,⁷⁹ and 1,3-cyclohexadiene⁴⁷) the products cannot be isolated. The gain in stability seems to be due to the presence of the silicon atom in the ring rather than to the cyclic or conjugated diene.⁴⁷

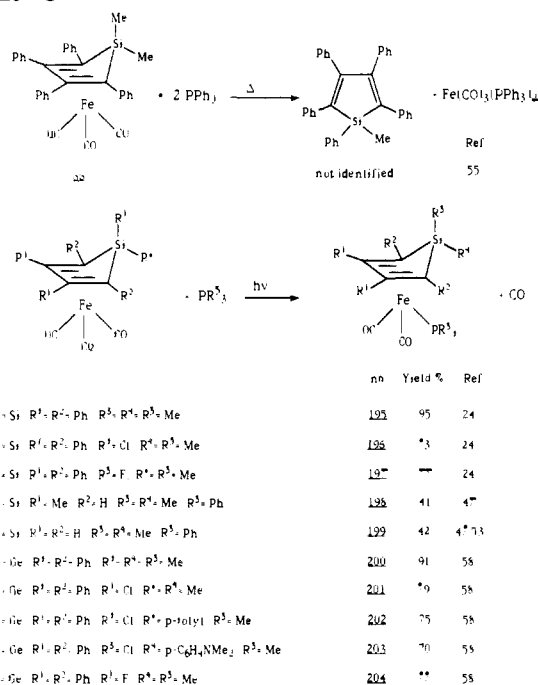


2. Reactions at Carbonyl Ligands

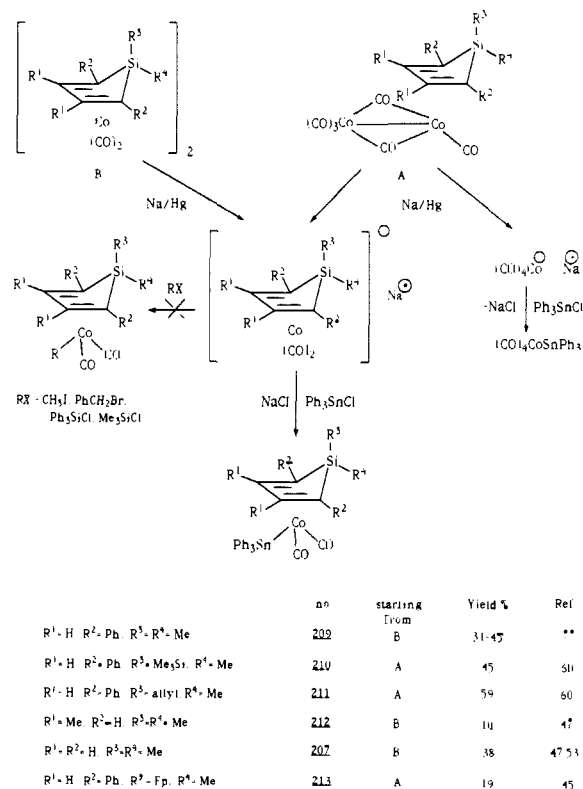
Nucleophilic attack on a carbonyl ligand by organolithium reagents leads to the formation of a carbene stabilized by the transition metal.⁸⁰⁻⁸² Carbene complexes are also obtained with silole complexes when the silicon atom bears a chloride function in the endo position⁸³ (eq 35). This reaction corresponds to retention of configuration at silicon (cf. section IV.B.3).



Scheme VI



Scheme VII

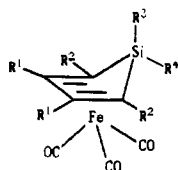


Phenyllithium reacts also with complexes having an exo chloride to give the same carbenes, with inversion of configuration;⁴⁹ this stereochemistry is unique in nucleophilic substitutions at coordinated siloles (cf. section IV.B.3). In the absence of a function at silicon, attempts to stabilize a carbene with Et_3OBF_4 or Me_3SiCl resulted in decomposition.

3. Reactions at the Group 14 Element

Reactions at silicon have developed as the most promising approach to the η^5 -silacyclopentadienyl

TABLE II. Syntheses of Complexes of the Type



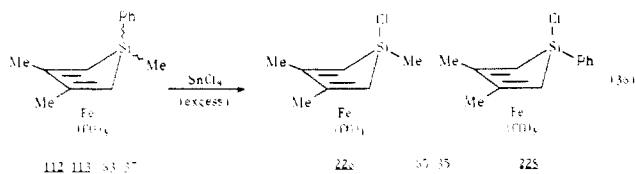
no.	E	R ¹	R ²	R ³	R ⁴	react cond ^a	temp, °C	yield, %	ref
66	Si	Ph	Ph	Me	Me	A	150	80	55, 56
66	Si	Ph	Ph	Me	Me	B	rt ^b	94	57
67	Si	Ph	Ph	Me	H	C	110	35	43
68	Si	Ph	Ph	Et	Et	A	160	70	55, 56
69	Si	Ph	Ph	Pr	Pr	A	160	75	55, 56
70	Si	Ph	Ph	<i>n</i> -Bu	<i>n</i> -Bu	A	160	65	55, 56
71	Si	Ph	Ph	Ph	Ph	A	200	80	55, 56
72	Si	Ph	Ph	<i>p</i> -tolyl	<i>p</i> -tolyl	B	rt	89	24
73	Si	Ph	Ph	PhCH ₂	PhCH ₂	A	180	80	55, 56
73	Si	Ph	Ph	PhCH ₂	PhCH ₂	B	rt	82	57
74	Si	Ph	Ph	-CH ₂ (CH ₂) ₂ CH ₂ -	-CH ₂ (CH ₂) ₂ CH ₂ -	A	180	80	55, 56
75	Si	Ph	Ph	-CH ₂ (CH ₂) ₃ CH ₂ -	-CH ₂ (CH ₂) ₃ CH ₂ -	A	190	88	55, 56
76	Si	Ph	Ph	ClCH ₂	Me	B	rt	77	57
77	Si	Ph	Ph	Me	Cl } ^f				
78	Si	Ph	Ph	Cl	Me }	B	rt	85	57
79	Ge	Ph	Ph	Me	Me	B	rt	96	57
80	Ge	Ph	Ph	PhCH ₂	PhCH ₂	B	rt	78	57
81	Ge	Ph	Ph	ClCH ₂	Me	B	rt	81	57
82	Ge	Ph	Ph	Et	Et	A/B	200 or rt	75	58
83	Ge	Ph	Ph	Ph	Ph	A/B	200 or rt	91	58
84	Ge	Ph	Ph	<i>p</i> -tolyl	<i>p</i> -tolyl	A/B	200 or rt	91	58
85	Ge	Ph	Ph	C ₆ F ₅	C ₆ F ₅	B	rt	79	58
86	Ge	Ph	Ph	<i>p</i> -C ₆ H ₄ NMe ₂	<i>p</i> -C ₆ H ₄ NMe ₂	A/B	200 or rt	93	58
87	Si	H	Ph	Me	Me	A/C	50 or 140	75-98	59, 60
88	Si	H	Ph	Me	Cl } ^d	C	50	65	49
89	Si	H	Ph	Cl	Me }				
90	Si	H	Ph	MeO	Me } ^e	C	50	54	49
91	Si	H	Ph	Me	MeO }				
92	Si	H	Ph	Et	Et	A/C	50 or 140	63	59
93	Si	H	Ph	<i>n</i> -Bu	<i>n</i> -Bu	A/C	50 or 140	61	59
94	Si	H	Ph	Me	Et } ^f	A/C	50 or 140	66	59
95	Si	H	Ph	Ph	Me } ^g	C	50	90	60
96	Si	H	Ph	Me	Ph }	C	50	4	60
97	Si	H	Ph	MeC≡C	Me	C	50	35	54
98	Si	H	Ph	Me	CH ₂ =CH	C	50	41	54
99	Si	H	Ph	Me	CH ₂ =CHCH ₂	C	50	30	61
100	Si	H	Ph	CH ₂ =CHCH ₂	CH ₂ =CHCH ₂	C	50	15	54
101	Si	H	Ph	MeO	MeO	C	50	60	48
102	Si	H	Ph	<i>i</i> -Pr	MeO	C	50	49	49
103	Si	H	Ph	<i>i</i> -Pr	Cl	C	50	57	49
104	Si	H	Ph	Me ₃ Si	Me	C	50	63	61
105	Si	H	Ph	Me	H	C	50	14	61
106	Si	Me	H	Me	Me	C	80	80	62, 63
107	Si	<i>h</i>	H	Me	Me	C	60	59	62, 63
108	Si	Me	H	<i>n</i> -Bu	Me } ⁱ	C	60		26
109	Si	Me	H	Me	<i>n</i> -Bu }				
110	Si	Me	H	<i>n</i> -Bu	<i>n</i> -Bu	C	60		26
111	Si	Me	H	Ph	Ph	C	60	42	64
112	Si	Me	H	Ph	Me }	C	40	45	45a, 64
113	Si	Me	H	Me	Ph }				
114	Si	H	H	Me	Me	C/D	60 or rt	60 or 52	53, 63, 65
115	Ge	Me	H	Me	Me	C	60	65	66
116	Ge	<i>k</i>	H	Me	Me	C	60	27	66
117	Ge	H	H	Me	Me	C	60	55	68
118	Si	H	Ph	Fp	Me	C	65	39	45

^aA, With Fe(CO)₅ in benzene, for 12-24 h, in an autoclave. B, U.V. irradiation with Fe(CO)₅ in benzene, for 100 h. C, With Fe₂(CO)₉ or Fe₃(CO)₁₂ in benzene or toluene, for 1-30 h. D, With Fe₂(CO)₉ in THF. ^brt = room temperature. ^cObtained as a mixture (77/78: 20/80). ^dObtained as a mixture (88/89: 65/35). ^eObtained as a mixture (90/91: 70/30). ^fIsomer distribution not given. ^gAlso described in ref. 61, without isomer distribution. ^h1,1,3-Trimethylsilole. ⁱObtained as a mixture (108/109: 62/38). ^jObtained as a mixture (112/113: 63/37). ^k1,1,3-Trimethylgermole.

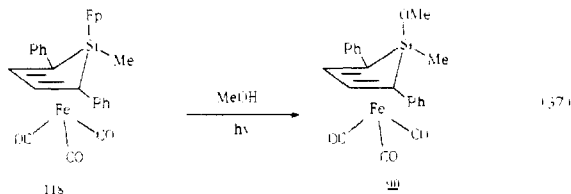
species. The most peculiar feature of these complexes is the high reactivity of substituents in the exo position. Thus, the C-Si bonds are easily cleaved under mild conditions^{24,47,51,54,57,58,73} (Scheme VIII) by SnCl₄, SbCl₅, BCl₃, ICl, SbF₅/C, or Hg(AcO)₂/HClO₄. It is interesting to note that in a mixture of 112 and 113, only the exo

substituent is cleaved^{45a} (eq 36), irrespective of its nature.

Other exo substituents, such as dicarbonyl(η⁵-cyclopentadienyl)iron are also cleaved by iodine at low temperature (Scheme IX) or by methanol under UV irradiation⁴⁵ (eq 37). The iodine derivative 229 cannot be

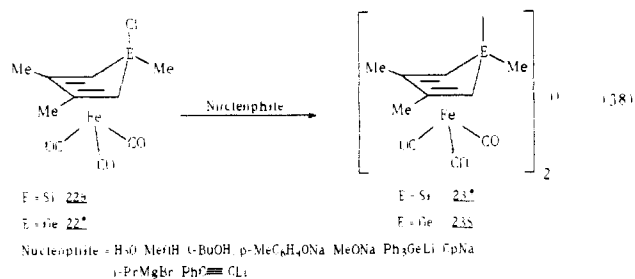


isolated and is identified by products of its further reaction. Complexes with functional silicon or germanium atoms can undergo a variety of substitutions: (a) substitution of halogen; (b) substitution of hydrogen; (c) substitution of hydroxyl or methoxyl; (d) miscellaneous reactions.



(a) *Substitution of Halogen.* The 1-halogen-substituted complexes can undergo nucleophilic substitutions (Table V). Complex 236 shows a very high reactivity and decomposes on column chromatography to the corresponding germanole complex, which in turn gives the germoxane complex during crystallization.⁴⁷

Reaction of complexes 225 or 226 with water, alcohols, alcoholates and several organometallic compounds leads to the formation of the siloxane or germoxane complex (eq 38) as the only isolable compound in yields from 100 to 50%.⁴⁷ The presence of phenyl substitution at carbon atoms leads apparently to less reactive complexes that can be isolated more easily.



When the halogen occupies the endo position, it can also be displaced, although with some difficulty (Scheme X). This shows that, unlike other cases, retention is not a consequence of the steric crowding introduced by the transition-metal moiety.

All these reactions take place with retention of configuration at silicon whatever the nucleophile,⁸⁴ in contrast to the behavior of acyclic chlorosilanes, which react with inversion of configuration.^{85,86} Retention of configuration has, however, been observed for highly strained chlorosilacyclobutanes.^{85,86}

(b) *Substitution of Hydrogen.* The exo-hydrido function is also very reactive in metallole complexes. It can be substituted by other functions or lead to hydrosilylation. The reactions are summarized in Table VI. Retention of configuration is observed in all cases; this stereochemistry is in agreement with the substitution of the Si-H in organosilanes.^{85,86}

It is interesting to note that the endo hydrogen does not lead to any substitution, and this allows exclusive substitution of the exo one in dihydrido compounds⁴⁸ (eq 39). This last type of reaction results in the formation of 1,1-unsymmetrically disubstituted siloles which, when uncomplexed, undergo fast redistribution.

TABLE III. Syntheses^a of

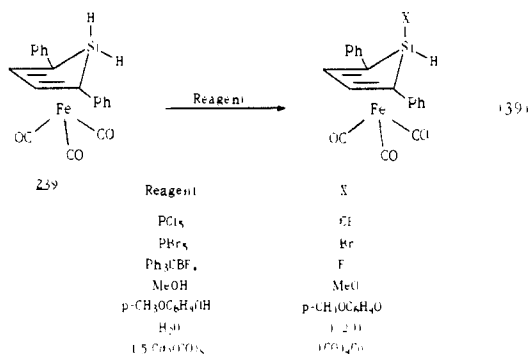
no.	R ¹	R ²	R ³	R ⁴	yield, %	ref
124	Ph	Ph	Ph	Cl	64	43
125	H	Ph	Me	Me	53	43
126	Me	H	Me	Me	40	47
127	H	Ph	Fp	Me	29	45

^a Complexations were carried out in refluxing toluene for 3–12 h.

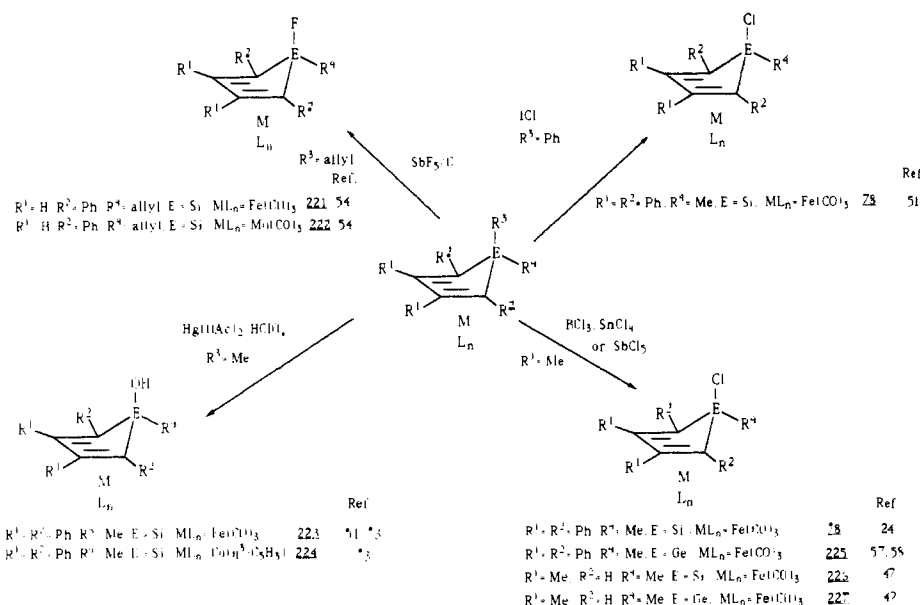
TABLE IV. Syntheses of Complexes of Type A and Type B

no.	E	R ¹	R ²	R ³	R ⁴	type	C ^a	temp, °C	yield, %	ref
130	Si	H	Ph	Me	Me	B ^c	2/1	rt ^b	52	43
131	Si	H	Ph	Me ₃ Si	Me	A	1/1	rt	63	61
132	Si	H	Ph	Me ₃ Si	Me	B	<i>d</i>	60	60	61
133	Si	H	Ph	allyl	Me	A	1/1	rt	84	61
134	Si	H	Ph	allyl	Me	B	<i>d</i>	60	60	61
135	Si	H	Ph	vinyl	Me	A	1/1	rt	56	49
136	Si	H	Ph	Me vinyl	Me					
137	Si	H	Ph	allyl	allyl	A	1/1	rt	44	54
138	Si	H	Ph	MeO	Me ^f	A	1/1	rt	60	49
139	Si	H	Ph	Me	MeO					
140	Si	H	Ph	MeO	Me	B	<i>d</i>	50	97	49
141	Si	H	Ph	Cl	Me	A	1/1	rt	92	49
142	Si	H	Ph	Cl	Me	B	<i>d</i>	50	93	49
143	Si	H	Ph	<i>i</i> -Pr	MeO	A	1/1	rt	84	49
144	Si	H	Ph	<i>i</i> -Pr	MeO	B	<i>d</i>	50	84	49
145	Si	H	Ph	<i>i</i> -Pr	Cl	A	1/1	rt	63	49
146	Si	H	Ph	<i>i</i> -Pr	Cl	B	<i>d</i>	50	93	49
147	Si	H	Ph	MeO	MeO	A	1/1	rt	77	48
148	Si	H	Ph	MeO	MeO	B	<i>d</i>	40	82	48
149	Si	H	Ph	Fp	Me	A	1/1	rt	15	45
150	Si	Me	H	Me	Me	A	1/1	-78	68	47
151	Si	Me	H	Me	Me	B	<i>d</i>	80	50	47
152	Si	H	H	Me	Me	B ^g	2/1	0	40	53
153	Ge	Me	H	Me	Me	A	1/1	-78	45	47
154	Ge	Me	H	Me	Me	B	<i>d</i>	45	35	47

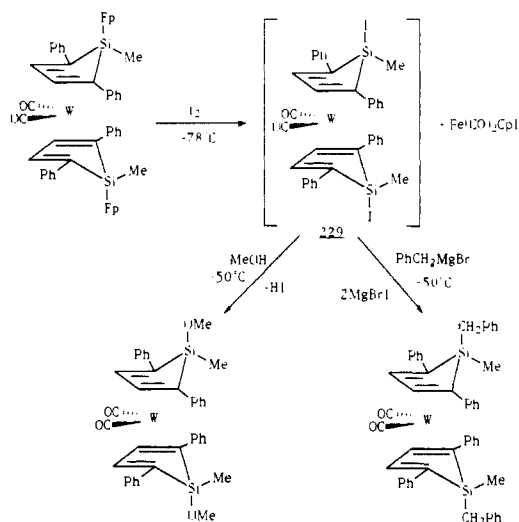
^a Metallole/cobalt carbonyl ratio. ^b rt = room temperature. ^c Type A complex is observed by IR spectroscopy. ^d Complex A is reacted with an equimolar amount of metallole. ^e Obtained as a mixture (135/136 = 1/1). ^f Obtained as a mixture (138/139 = 9/1). ^g Type A complex is observed by IR and ¹H NMR spectroscopies.



Scheme VIII



Scheme IX



Scheme X

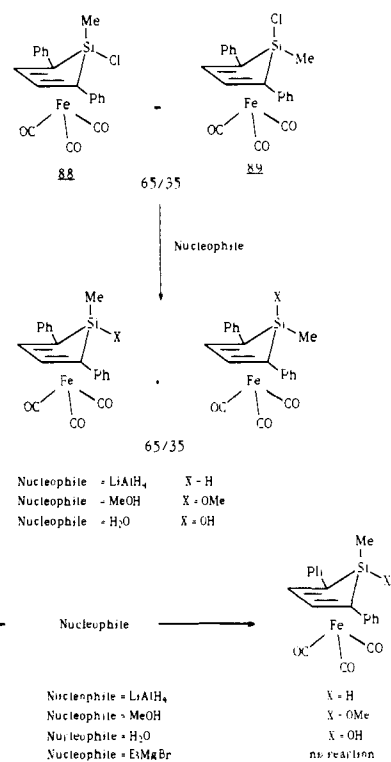
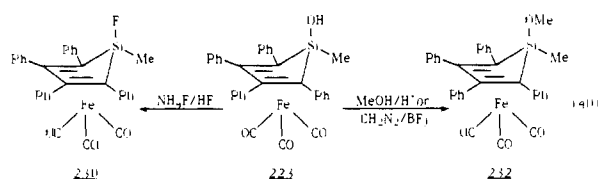


TABLE V. Nucleophilic Substitutions at Si-X

R^1	R^2	E-X	no.	nucl	E-Y	no.	ref
Ph	Ph	Si-Cl	78	LiAlH ₄	Si-H	231	51
Ph	Ph	Si-Cl	78	AgF or AgBF ₄ or AgSbF ₆	Si-F	230	24
Ph	Ph	Si-F	230	LiAlH ₄	Si-H	231	51
Ph	Ph	Ge-Cl	225	AgF	Ge-F	192	58
Ph	Ph	Ge-Cl	225	LiAlH ₄	Ge-H	191	57, 58
Ph	Ph	Ge-Cl	225	NaOMe	Ge-OMe	232	58
Ph	Ph	Ge-Cl	225	NaI	Ge-I	233	58
H	Ph	Si-Cl	89	LiAlH ₄	Si-H	231	84
H	Ph	Si-Cl	89	MeOH	Si-OMe	90	84
H	Ph	Si-Cl	89	H ₂ O	Si-OH	234	84
H	Ph	Si-Cl	89	EtMgBr	Si-Et	94	84
Me	H	Si-Cl	226	MeLi	Si-Me	106	47
Me	H	Si-Cl	226	PhLi	Si-Ph	114	47
Me	H	Si-Cl	226	MeOH/Et ₃ N	Si-OMe ^a	235	47
Me	H	Ge-Cl	227	(<i>i</i> -Bu) ₂ AlH	Ge-H ^a	236	47

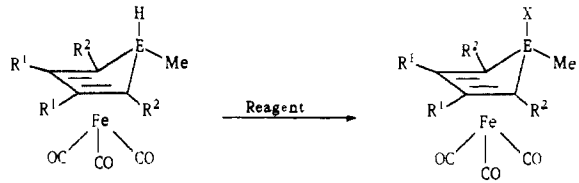
^a Identified by ¹H NMR; decomposes upon attempted isolation.

(c) *Substitution of Hydroxyl and Methoxyl.* The substitution of exo hydroxyl by fluorine is effected by treatment with NH₄F/HF in sulfuric acid. The OH function can be methylated by methanol or diazomethane⁵¹ (eq 40). The exo methoxyl is reduced by



LiAlH₄ into the complex bearing an exo hydrogen, but in the presence of metal alkoxide, the complex isomerizes into the one bearing hydrogen in the endo posi-

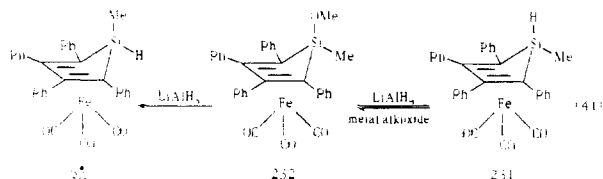
TABLE VI. Substitution of the E-H Function



R ¹	R ²	E	reagent	X	no.	ref
Ph	Ph	Si	Me ₂ CO	OCHMe ₂	240	51
Ph	Ph	Si	CCl ₄	Cl	78	51
Ph	Ph	Si	MeOH/Pd	OMe	232	51
Ph	Ph	Si	Ph ₃ CBF ₄	F	230	24, 51
Ph	Ph	Ge	CCl ₄	Cl	225	58
H	Ph	Si	H ₂ O	OH	234	49
H	Ph	Si	MeOH	OMe	90	49
H	Ph	Si	<i>p</i> -MeOC ₆ H ₄ OH	<i>p</i> -MeOC ₆ H ₄ O	241	49
H	Ph	Si	PCl ₅	Cl	89	85
H	Ph	Si	Ph ₃ CBF ₄	F	242	49
H	Ph	Si	PhCHO	PhCH ₂ O	243	49
H	Ph	Si	PhC≡CH	<i>trans</i> -PhCH=CH	244	49
H	Ph	Si	Co ₂ (CO) ₈	Co(CO) ₄	245	49
Me	H	Ge	H ₂ O	1/2O	238	47 ^a

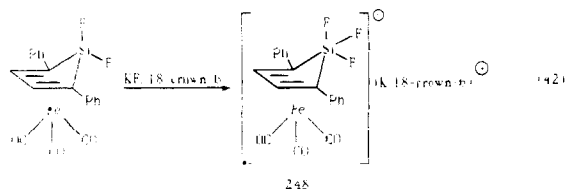
^a Cf. section IV.B.3.a.

tion⁵¹ (eq 41). The actual mechanism of this reaction is obscure.



Methoxy groups are better reduced by (*i*-Bu)₂AlH with retention of configuration but with no selectivity with respect to the exo and endo positions; tin and antimony halides can also replace MeO^{48,58} (Scheme XI). A mixture of complexes 165 and 166 is reduced by LiAlH₄ without isomerization⁴⁹ (Scheme XII). This result is in contrast to that reported by Sakurai et al.⁵¹

(d) *Miscellaneous Reactions.* Reactions at the group 14 element have been reported by Jutzi et al.⁴² (cf. Section IV.A), affording a three-coordinated germanium species. Five-coordinated silicon is obtained by treating the tricarbonyl complex of 1,1-difluoro-2,5-diphenylsilole with 18-crown-6 potassium fluoride⁸⁷ (eq 42).

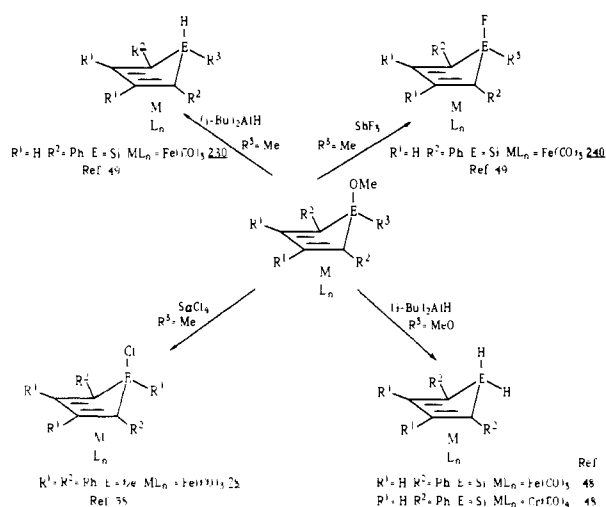


V. Structural Features

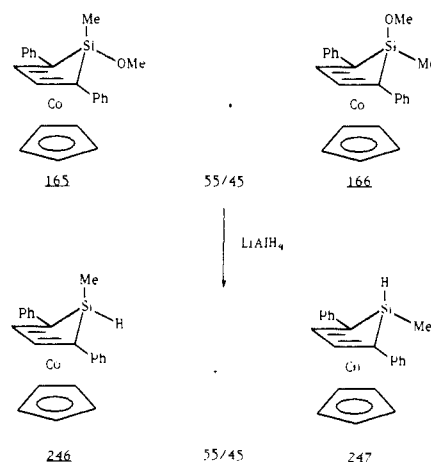
A. Crystallographic Studies

The first crystal structure of a silole complex, tricarbonyl(η^4 -1,1-dimethyl-2,5-diphenylsilole)ruthenium (125), was compared to that of the free ligand 20.⁸⁸ Silole 20 possesses an exact *C_s* symmetry; the mirror plane passes through the silicon atom and is normal to the plane of the silole ring. The bond lengths are consistent with complete localization of the double

Scheme XI



Scheme XII



bonds, and the butadiene unit is exactly planar. This finding is confirmed by the X-ray structure of 1,1-dimethyl-2,3,4,5-tetraphenylsilole,⁸⁹ the C-C (single) bond length in the diene shows also reduced delocalization of the double bonds, but the ring Si-C bonds are shorter. The author considers that this observation is consistent with partial delocalization through the silicon atom (but not through the butadiene unit) (cf. section I.B).

In complex 125 approximate *C_s* symmetry is retained. The coordination may be described as octahedral with three sites occupied by the carbonyls and the other three by C(1), C(4), and the midpoint of the C(2)-C(3) bond (isomer B, Figure 2). This structure is very similar to that of Ru(CO)₃(η^4 -C₈H₈).⁹⁰ Although the silole ring is almost planar in 20 (the dihedral angle between the plane of the diene and that defined by C(1), Si, and C(4) is 3.7°), in complex 125 this angle has a value of 32° (Figure 3). As a consequence of this angle, the Ru-Si distance is 2.992 (2) Å and excludes the possibility of a bonding interaction between them (the length of the Ru-Si covalent bond is known to be 2.43 Å⁹¹).

Some differences appear in the structure of other ML₃(η^4 -metallole) complexes. Indeed, the X-ray structures of tricarbonyl(η^4 -1-*exo*-fluoro-1-methyl-2,3,4,5-tetraphenylgermole)iron (192),⁵⁸ (η^4 -1,1,3,4-tetramethylsilole)tris(trimethylphosphine)cobalt tetraphenylborate (169),⁷⁴ and (η^4 -1,1,3,4-tetramethyl-

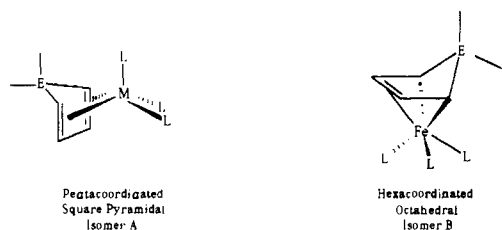


Figure 2.

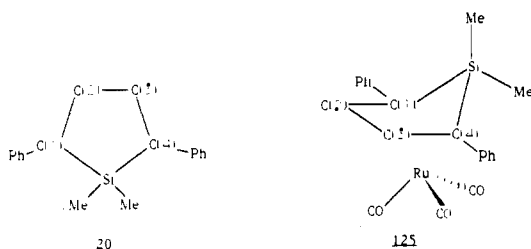


Figure 3. Dihedral angle between the plane of the diene and that defined by C(1)-Si-C(4): 3.7° for 20 and 32° for 125.

germole)tris(trimethylphosphine)cobalt tetraphenylborate (170)⁷⁴ show that in these molecules the metallole acts as a η^4 ligand (isomer A, Figure 2) and the geometry corresponds to a square pyramid with a η^1 ligand in the axial position.

Other crystal structures are reported for tetracoordinated and hexacoordinated complexes: bis(η^4 -1,1-dimethyl-2,5-diphenylsilole)nickel (187),⁶¹ tricarbonyl[η^4 -[1-*exo*-methyl(η^2 -1-*endo*-allyl)-2,5-diphenylsilole]molybdenum (58),⁵⁴ tricarbonyl[η^4 -(1-*exo*-methyl(η^2 -1-*endo*-vinyl)-2,5-diphenylsilole]molybdenum (56),⁵⁴ dicarbonyl[η^4 -(1-*exo*-methyl(η^1 -phenylmethylene)oxy)-2,5-diphenylsilole]iron (218),⁸³ *cis*-dicarbonylbis(η^4 -1,1,3,4-tetramethylsilole)molybdenum (40),⁹² and tetracarbonyl(η^4 -1,1,3,4-tetramethylsilole)chromium (31).⁹³

The molecular geometry of complex 248⁸⁷ is similar to that of acyclic $[\text{R}_2\text{SiF}_3]^-$. The silicon atom is essentially trigonal bipyramidal, with the five-membered ring occupying axial-equatorial positions. Slight interactions between the cation and the axial fluorine atom and one equatorial fluorine atom are observed; this renders the two equatorial fluorine atoms nonequivalent. This nonequivalence, however, is not observed by variable-temperature NMR experiments (cf. section VI).

The dihedral angles in the metallole ligands vary from 8.9° to 44.5° (Table VII); the reasons invoked for these changes are steric. With bulky ligands at the transition metal, the fold angle is increased (complexes 170, 169, 31, and 40) as low substitution leads to lower values (complex 187). Coordination of an *endo* substituent at silicon forces the silole ring to become more planar (complexes 218 and 56), and when the chain is longer (complex 58), the fold angle is close to that of 125 and 192 due to less steric constraint.

B. Infrared Studies

Jutzi and Karl^{24,59} report the observation of two pairs of carbonyl absorptions in the IR spectra in solution of trimethylphosphino-substituted complexes 195–197, 200, 201, and 204. The pair of bands at lower wavenumber is less intense. This is evidence for the existence of an interconversion, with a low energy barrier,

TABLE VII. Fold Angles of Coordinated Metalloles

complex	no.	angle, deg	ref
$[\text{Co}(\eta^4\text{-germole})^a(\text{PMe}_3)_3]^+$	170	44.5	74
$[\text{Co}(\eta^4\text{-silole})^b(\text{PMe}_3)_3]^+$	169	41.2	74
$\text{Cr}(\text{CO})_4(\eta^4\text{-silole})^b$	31	37.7	93
$\text{Mo}(\text{CO})_2(\eta^4\text{-silole})_2^b$	40	36.6	92
$\text{Ru}(\text{CO})_3(\eta^4\text{-silole})^c$	125	32	88
$\text{Fe}(\text{CO})_3(\eta^4\text{-germole})^d$	192	31.1	58
$\text{Fe}(\text{CO})_3(\eta^4\text{-silole})^e$	248	30.8	94
$\text{Mo}(\text{CO})_3(\eta^4, \eta^2\text{-allylsilole})^f$	58	28.0	53
$\text{Ni}(\eta^4\text{-silole})_2^c$	187	22 and 20.3	61
$\text{Fe}(\text{CO})_2(\eta^4\text{-methylene-silole})^g$	218	16.6	83
$\text{Mo}(\text{CO})_3(\eta^4, \eta^2\text{-vinylsilole})^h$	56	8.9	54

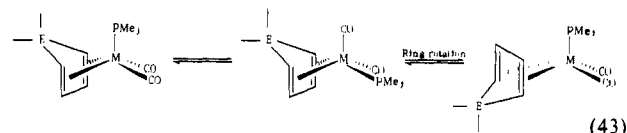
^a 1,1,3,4-Tetramethylgermole. ^b 1,1,3,4-Tetramethylsilole. ^c 1,1-Dimethyl-2,5-diphenylsilole. ^d 1-*exo*-Fluoro-1-methyl-2,3,4,5-tetraphenylgermole. ^e 1,1,1-Trifluoro-2,5-diphenylsilacyclopentadienide. ^f 1-*endo*-allyl-1-methyl-2,5-diphenylsilole. ^g 1-*exo*-Methyl-1-((phenylmethylene)oxy)-2,5-diphenylsilole. ^h 1-*exo*-Methyl-1-vinyl-2,5-diphenylsilole.

TABLE VIII. Carbonyl Absorptions of $[\text{Co}(\text{CO})_2(\eta^4\text{-metallole})_2]$ and $[\text{Fe}(\text{CO})_2(\eta^4\text{-cyclopentadienyl})_2]$ in Solution

complex	no.	ν_{CO} , cm^{-1}	ref
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^a$	130	2020, 1997, 1842	43
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^b$	132	2020, 1995, 1840	61
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^c$	134	2020, 1995, 1842	61
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^d$	140	2020, 1845	49
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^e$	142	2044, 1844	49
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^f$	144	2036, 1835	49
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^g$	146	2038, 1840	49
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^h$	148	2042, 1835	49
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^i$	151	1990, 1820	47
$[\text{Co}(\text{CO})_2(\eta^4\text{-germole})_2]^j$	153	1982, 1812	47
$[\text{Co}(\text{CO})_2(\eta^4\text{-silole})_2]^k$	152	2030, 2000, 1830	47, 53
$[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$		2001, 1958, 1786	96, 97
$[\text{Fe}(\text{CO})_2(\eta^5\text{-Me}_5\text{C}_5)]_2$		1932, 1764	98

^a 1,1-Dimethyldiphenylsilole. ^b 1-*exo*-(Trimethylsilyl)-1-methyldiphenylsilole. ^c 1-*exo*-Allyl-1-methyldiphenylsilole. ^d 1-*exo*-Methoxy-1-methyldiphenylsilole. ^e 1-*exo*-Chloro-1-methyldiphenylsilole. ^f 1-*exo*-Isopropyl-1-methoxydiphenylsilole. ^g 1-*exo*-Isopropyl-1-chlorodiphenylsilole. ^h 1,1-Dimethoxy-2,5-diphenylsilole. ⁱ 1,1,3,4-Tetramethylsilole. ^j 1,1,3,4-Tetramethylgermole. ^k 1,1-Dimethylsilole.

between two diastereomers, which cannot be observed by NMR (eq 43). Another possible interpretation could



be isomerization via a rotation of the metallole ring⁹⁶ (cf. section VI). When steric crowding is present (i.e., when silicon bears a bulky *endo* substituent (*p*-tolyl or *p*-(dimethylamino)phenyl) or when a bulky phosphine is used (PPh_3)), only one pair of bands is observed (complexes 198, 199, 202, and 203).^{47,58}

The IR spectra in solution of $[\text{Co}(\text{CO})_2(\eta^4\text{-metallole})_2]$ complexes show a close similarity with those of $[\text{Fe}(\text{CO})_2(\eta^5\text{-cyclopentadienyl})_2]$ complexes;⁴⁷ both types are isoelectronic and appear also to be isostructural in solution. Table VIII shows the carbonyl absorptions of both types of complex. Indeed, when the substituents at silicon are not functional and the 3- and 4-positions are not substituted, the ν_{CO} absorptions resemble that of $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$. When the 3- and 4-positions are substituted, the complexes have a higher symmetry and their spectra resemble that of $[\text{Fe}(\text{CO})_2(\eta^5\text{-Me}_5\text{C}_5)]_2$. It is difficult, however, to rationalize the higher sym-

metry displayed when the silicon atoms bear functional groups (Cl, MeO).

C. Electrochemical Reduction of Cobalt–Cobalt Complexes

Since bimetallic metallole–cobalt and cyclopentadienyl–iron complexes are isoelectronic and isostructural when the metallole does not bear functional groups, they could possess other similar properties. The electrochemical reduction takes place at a similar value for both types of bimetallic complexes ($E_{1/2} \sim -1.5$ V;^{47,99} this value is quite different from that observed for the reduction of $\text{Co}_2(\text{CO})_8$ ($E_{1/2} = -0.3$ V)⁹⁹ and shows that the reduction potentials depend on the structure of the compounds rather than on the nature of the metals. The reduction potential of $[\text{Co}(\text{CO})_2(\eta^4\text{-}2,3\text{-dimethylbutadiene})_2]$ is $E_{1/2} = -1.63$ V⁴⁹ and shows that neither the presence of silicon nor the presence of the cyclic diene is associated with this property.

D. Electronic Structures

A comparative study of the electronic structures of tricarbonyl(η^4 -metallole)iron complexes, the parent η^4 -cyclopentadiene complex, and the free ligands reveals that the interaction between the metallole and the $\text{Fe}(\text{CO})_3$ moiety results in a clear electron transfer from iron to the ligand.⁶⁶ This system is comparable to an aromatic π system. The fold angle of the ligand (cf. section V.A) might indicate the tendency of the system to be stabilized by a metal–ligand interaction including $2n + 2$ electrons, unless it is derived from a simple steric effect.

The significant localization of the HOMO orbital of the ring predicts high reactivity for such complexes toward electrophilic reagents. The high charge density on carbon atoms α to the group 14 element (which is also revealed by a high deshielding effect in the ^1H NMR) may induce interesting electrophilic reactions.

E. NMR Spectra

Complexation of metalloles leads to great modifications of the NMR signals compared with those of the free ligands (cf. Dubac et al., part 1 (companion paper in this issue)). In the ^1H NMR three important features are observed: the presence of two exo/endo signals, a large shielding (~ 4 ppm) of the olefinic protons α to silicon or germanium (less pronounced for the β protons (~ 1 ppm)), and a great decrease of the $^3J_{\text{H,H}}$ coupling constant in the ring.⁶³

When the group 14 element bears two identical substituents, the exo/endo attributions can be easily made on the basis of the work of Sakurai and Hayashi⁵⁰ (cf. section III.A). The $\Delta\delta$ between the exo- and endo-methyl group lies in the range 1.38–0.34 ppm, with a mean value of ~ 0.7 ppm. However, with nickel complexes (185, 186, and 187), the $\Delta\delta$ is low (0 (the presence of paramagnetic impurities allows a resolution < 0.2 ppm), 0.17, and 0.26 ppm). However, in general, it is possible to determine the configuration in 1-methyl-substituted complexes (in all cases when the spectra of both isomers are available). The same features are observed in dimethoxy, diallyl, dibenzyl, dihydrido, and di-*p*-tolyl derivatives.

It is interesting to note that phenyl substitution at the 2,5-positions leads to a $\Delta\delta$ close to 1 ppm for the 1,1-dimethyl derivatives, whereas tetrasubstitution at the 2,3,4,5-positions leads to a decrease of $\Delta\delta$ (~ 0.5 ppm). In complexes of metalloles without phenyl substitution, $\Delta\delta$ lies in the range of 0.7 ppm (except for bis(metallole) sandwich type complexes, 38, 39, 40, 47, 205, and 206, for which $\Delta\delta \sim 0.4$ ppm), and the presence of phosphine and stannyl ligands enhances this value to ~ 1 ppm. The proximity of the observed proton to the group 14 metal in substituents other than methyl is important for the $\Delta\delta$ value; benzylic protons show $\Delta\delta \sim 1$ ppm, methoxy protons show $\Delta\delta \sim 0.8$ ppm, but methyl protons in *p*-tolyl substituents are only separated by 0.03–0.04 ppm.

The spectrum of the dihydridosilole complex 239 is interesting since it shows an AB system in which one of the protons is coupled to the olefinic ones with a low constant (1.2 Hz). Since in any case the exo hydrogens are not coupled with the olefinic ones, it is possible to attribute the signal to the endo hydrogen. This result confirms the previous attribution of stereochemistry for the nickel complex 185 in which $J_{\text{H,H}} = 2$ Hz.

In the ^{13}C NMR the same features are observed for the exo/endo methyl groups, the exo ones being more shielded than the endo ones. Although few data are available, $\Delta\delta$ goes from ~ 5 ppm in cationic complexes 169 and 170 to 11–12 ppm in neutral complexes 40, 106, 115, and 206.

The few reports on the ^{29}Si NMR allow the identification of exo/endo hydrido isomers. The resonance is shifted upfield (~ 3 ppm) and $J_{\text{Si,H}}$ is higher for the endo-hydrido isomer. Thus, the $J_{\text{Si,H}}$ values for 105, 231, 246, and 247 are 212, 182, 205, and 173 Hz, respectively; these values are to be compared to those of 239 (220 and 188 Hz, respectively, for the coupling constants with the endo and exo protons).^{49,100}

Table IX shows the NMR data for several complexes.

F. Mass Spectra

Although in the past few years most of the new reported complexes have been identified by means (inter alia) of mass spectrometry, few systematic studies have been carried out. In iron tricarbonyl complexes of the C-non-phenylated series⁶³ (complexes 106, 107, and 114) the parent ion is observed (8–21%). As in other metal complexes, fragments corresponding to successive decarbonylation of the molecular ion are abundant; the last one, (metallole – Fe)⁺, is the base peak.

Loss of carbonyl ligands is always observed for other complexes with Cr, Mo, W, and Co (prior to loss of phosphine in phosphine-containing complexes). Loss of methyl groups bound to silicon or germanium can precede decarbonylation and decoordination of the metallole.^{47,61,63,102}

The (metallole – Fe – CH_4)⁺ ion is abundant for 106 and 107 (56 and 59%), but not for 114 (8%).⁶³ These ions are postulated as aromatic fragments, (silabenzene – Fe)⁺ ions, already invoked in the fragmentation of tricarbonyl(η^4 -silacyclohexadiene)iron complexes.¹⁰³ The possible formation of η^5 -metallole species in mass spectrometry has been discussed in section IV.A).

An automated interpretation of the mass spectra of metallole complexes has been reported.¹⁰² However, in contrast to other organometallic complexes,¹⁰⁴ exo and

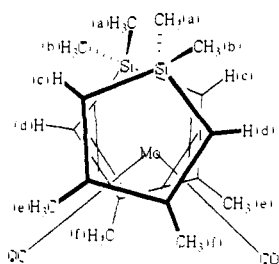


Figure 4. Schematic view of complex **40** showing the magnetic nonequivalence of protons.

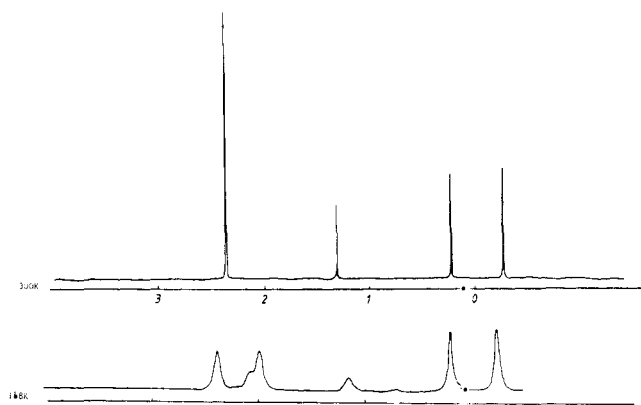


Figure 5. ^1H NMR spectra of **40**.

endo isomers give identical fragmentation patterns and they cannot be distinguished by this technique.

VI. Dynamic Stereochemistry

In connection with the observations of Jutzi and Karl (cf. section V.B), other "anomalous" IR spectra with respect to the X-ray structures are obtained in solution for *cis*-dicarbonylbis(η^4 -metallole)(group 6 metal) complexes. In fact, for all the complexes studied, four ν_{CO} absorptions are observed, instead of the predicted two; these bands appear as two pairs, with the pair at lower wavenumbers being less intense.⁹² The IR spectrum of *cis*-carbonylbis(η^4 -1,1-dimethylsilole)(triphenylphosphine)molybdenum (**205**) shows two carbonyl absorptions instead of one. These observations are in agreement with the coexistence of diastereoisomers in solution. The values of ν_{CO} absorptions are assembled in Table X. In complexes with 2,5-diphenylsiloles, the ν_{CO} absorptions are broadened; the resolution becomes $<10\text{ cm}^{-1}$ and only two are observed.

The ^1H NMR spectra of complexes **40–42**, **47**, **51**, and **206** show two different signals for the exo and endo methyls, but only one for the other types of protons which have a different environment (Figure 4). However, at low temperature, the ^1H NMR spectra show this nonequivalence (Table XI) for those complexes having two nonidentical η^1 ligands^{45,92} (Figure 5).

The NMR spectra of **205** give much information, since ^{31}P NMR shows one resonance at 278 K but two at 172 K (with different intensities: 40/60). The ^1H NMR spectrum at 173 K shows 12 signals (6 + 6) for α and β protons to silicon and 8 (4 + 4) for exo and endo methyls (Figure 6). This multiplicity indicates that only isomers *cis*- $\Delta\Delta\text{uu}$ and *trans*-*ou* are significantly present in solution (Figure 7). The isomerization is explained by a twist mechanism^{105–110} (Figure 8), but the room temperature spectrum and double-irradiation

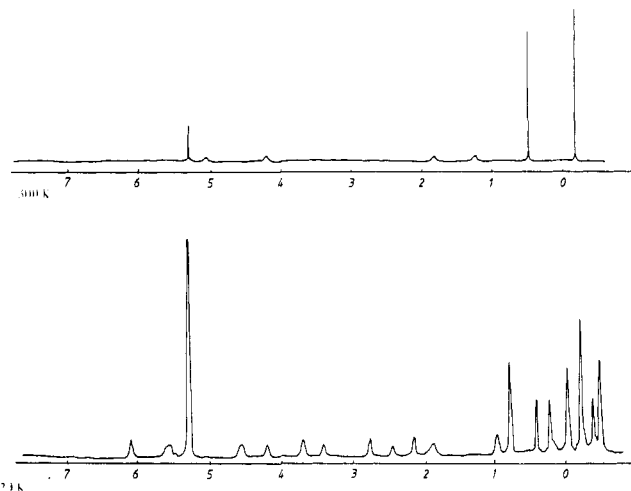


Figure 6. ^1H NMR spectra of **205**.

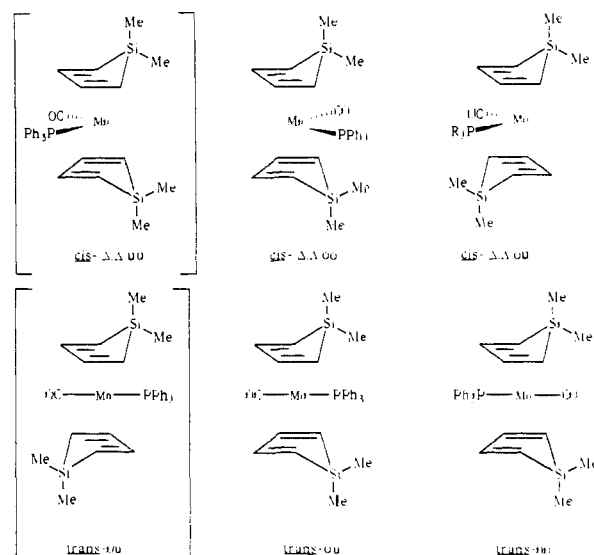


Figure 7. Possible diastereoisomers of complex **205**. Isomers observed by ^1H NMR at low temperature are shown in brackets.

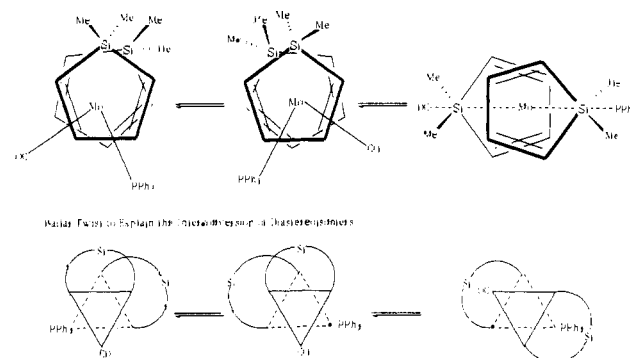


Figure 8.

experiments show that a ring rotation mechanism coexists. The twist explains the *cis*- $\Delta\Delta\text{uu} \rightleftharpoons \text{trans-ou}$ equilibrium while the ring rotation explains the *cis*- $\Delta\text{uu} \rightleftharpoons \text{cis-}\Delta\text{uu}$ equilibrium (Figure 9). The former is slow and the latter fast on the proton relaxation time scale.⁹²

The existence of the *trans-ou* isomer is easily understood since CO and phosphines are complementary ligands (in other terms, CO is a good electron acceptor, whereas phosphines are good electron donors) and they will readily adopt a *trans* disposition. For complexes with two identical η^1 ligands (the electronic effects of

TABLE IX. Selected NMR Data for Metallole Complexes

no.	¹ H NMR		¹³ C NMR		²⁹ Si NMR	
	Δδ for exo/endo protons	ref	Δδ for exo/endo carbons	ref	δ	ref
30	0.76 ^a	47				
31	0.75 ^a	47				
33	0.72 ^a	48				
38	1.16 ^b	43				
39	0.48 ^a	47, 53				
40	0.40 ^a	47	12.0	47		
41	0.34 ^a	47				
46	0.58 ^a	47				
47	0.44 ^a	47				
50	0.53 ^b	48, 49				
66	0.53 ^c	57			17.7	101
72	0.03 ^{c,d}	24				
73	1.26 ^{c,e}	57				
79	0.41 ^c	57				
80	1.20 ^{c,e}	57				
84	0.04 ^{c,d}	58				
87	0.85 ^a	60			8.8	101
88					16.3	100
89					-13.4	100
100	0.50 ^{b,f}	54				
101	0.90 ^a	48				
105					-14.9	100
106	0.68 ^a	63	11.1	74		
107	0.72 ^a	63				
114	0.74 ^a	63, 65				
115	0.63 ^g	66	11.1	74		
116	0.70 ^a	66				
125	0.90 ^b	43			15.2	101
126	0.57 ^a	47				
130	1.10 ^b	43				
137	1.30 ^{a,f}	54				
147	0.78 ^a	48				
148	0.70 ^a	48				
150	0.87 ^a	47				
151	0.76 ^a	47				
152	0.73 ^a	47, 53				
153	0.69 ^a	47				
154	0.73 ^a	47				
161	1.03 ^c	73				
162	1.20 ^a , 1.38 ^c	60, 73				
164	0.90 ^a	49				
168	0.93 ^a	45a				
169	0.61 ^h	74	5.6	74		
170	0.45 ⁱ	74	4.3	74		
181	1.25 ^b	43				
182	1.06 ^b	43				
186	0 ^{a,j}	47				
187	0.17 ^a	61				
188	0.26 ^a	47, 53				
195	0.52 ^k	24				
198	0.84 ^a	47				
199	0.89 ^a	47, 53				
200	0.50 ^k	24				
205	0.55 ^a	47, 53				
206	0.37 ^a	40	11.9	40		
207	0.83 ^a	47, 53				
208	1.06 ^a	47, 53				
209	0.88 ^a	77				
212	0.66 ^a	47				
215	0.76 ^a	47				
216	0.78 ^a	47, 53				
230					-12.1	100
239	0.47 ^a (J = 24 Hz)	100			-39.2	100
246					-35.1	49
247					-31.6	49

^aC₆D₆. ^bCDCl₃. ^cCS₂. ^dp-CH₃ protons. ^eBenzylic protons. ^fAllylic protons. ^gCCl₄. ^h(CD₃)₂CO. ⁱCD₂Cl₂. ^jLow resolution due to the presence of paramagnetic impurities. ^kCS₂/CH₂Cl₂.

which are in completion) the trans isomer will not be favored (the ν_{CO} absorption bands are in agreement with the presence of cis isomers¹¹¹).

TABLE X. Carbonyl Absorption Bands for M(CO)(L)(η⁴-metallole)₂ Complexes

complex	no.	ν _{CO} , cm ⁻¹	solvent
Mo(CO) ₂ (η ⁴ -silole) ₂ ^a	40	1978, 1919; 1972, 1912	hexane
W(CO) ₂ (η ⁴ -silole) ₂ ^a	47	1976, 1917; 1970, 1908	hexane
Mo(CO) ₂ (η ⁴ -germole) ₂ ^b	41	1970, 1917; 1963, 1905	hexane
Mo(CO) ₂ (η ⁴ -silole) ₂ ^c	39	2000, 1955; 1990, 1940	cyclohexane
Mo(CO)(PPh ₃)(η ⁴ -silole) ₂ ^c	205	1916, 1890	cyclohexane
Mo(CO) ₂ (η ⁴ -silole) ₂ ^d	42	1975, 1918; 1972, 1912	hexane

^a1,1,3,4-Tetramethylsilole. ^b1,1,3,4-tetramethylgermole. ^c1,1-Dimethylsilole. ^d1,3,4-Trimethyl-1-*exo*-phenylsilole.

TABLE XI. Variable-Temperature Data for Compounds 40-43, 47, 51, and 206

no.	T, K	=CCH ₃	=CH ^a	endo CH ₃	exo CH ₃
40	300	2.31	1.71	0.31	-0.14
40	168	2.43, 2.08	2.12, 1.19	0.21	-0.24
41	300	2.40	2.02	0.52	0.06
41	183	2.49, 2.09	2.42, 1.39	0.39	-0.03
42	300	2.37	1.96	0.69	
42	173	2.55, 2.11	2.38, 1.36	0.63	
47	300	2.49	1.44	0.34	-0.14
47	168	2.54, 2.26	1.74, 0.92	0.22	-0.23
43	300	5.10 ^b		1.29	
43	163	5.30, 4.64		1.20	
51	300	4.87 ^b		1.31	
51	168	5.13, 4.40		1.21	
206	343	4.62 ^b	1.22	0.66	0.39
206	280	5.34, 3.91	2.22, -0.22	0.71	0.46

^aOlefinic protons α to silicon. ^bOlefinic protons β to silicon.

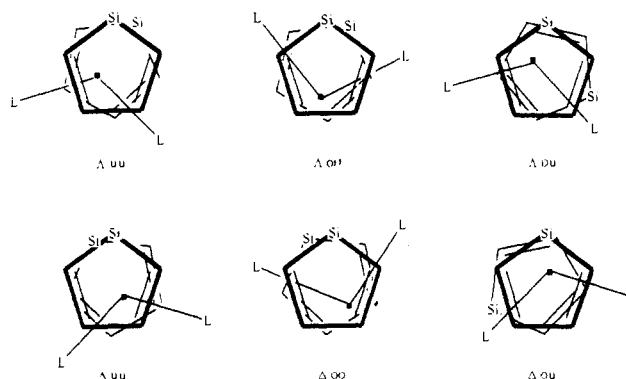
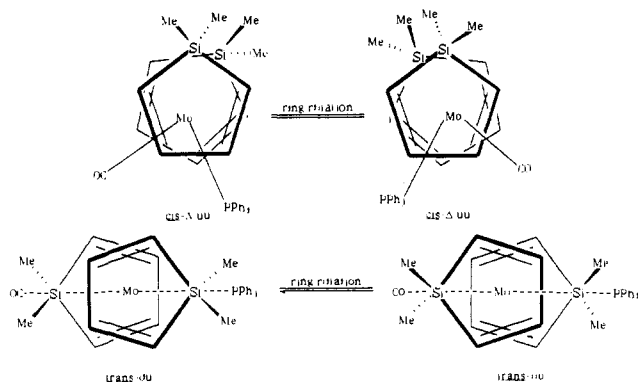
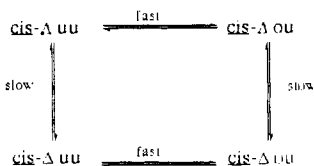
Figure 9. Cis isomers for M(CO)₂(η⁴-silole)₂.

Figure 10. Ring rotation is faster than the twist and explains the racemization cis-Δuu ⇌ cis-Δou. This mechanism also plays a role in the trans-ou isomer.

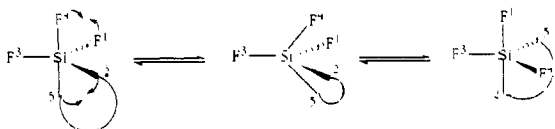
The proposed explanation is that two cis isomers (Figure 10) coexist in rapid equilibrium and they are observed in the ¹H and ¹³C NMR (³¹P NMR of 206 does not show the coexistence of diastereoisomers) as a virtual single isomer in slow equilibrium with their enantiomers (also observed as a virtual single isomer)⁴⁵

SCHEME XIII. Mechanism for the Isomerization of $ML_2(\eta^4\text{-metallole})_2^a$



^a Isomer *cis*-ΔΔ oo could be present instead of *cis*-ΔΔ uu.

Pseudorotation: high energy barrier



Turnstile: low energy barrier

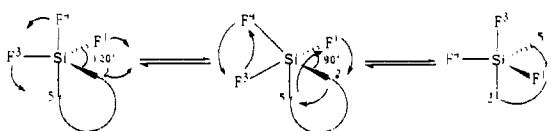


Figure 11.

(Scheme XIII). The ΔG^* values at the coalescence temperature are $\sim 30 \text{ kJ mol}^{-1}$ for the dicarbonyl complexes ($\sim 60 \text{ kJ mol}^{-1}$ for 206) and also $\sim 30 \text{ kJ mol}^{-1}$ for the *cis*,*trans* equilibrium in complex 205.

The situation can be different for complexes of 2,5-diphenylsiloles; indeed, as we pointed out above, the IR spectra show only two, not four, ν_{CO} absorptions. Thus, it is not possible to ascertain that diastereoisomers are also present in these cases, and the ^1H NMR variable-temperature observations might be due to an interconversion of the *cis*- $\Delta\Delta$ uu enantiomers.⁴⁰

The crystallographic study of complex 248⁸⁷ (cf. section V.A) showed the nonequivalence of the two equatorial fluorine atoms; this could not be confirmed by variable-temperature ^{19}F NMR. Even at 168 K only one resonance is observed for the three fluorine atoms, showing that the energy of activation is very low, and this suggests a permutational equilibrium which is best explained by a turnstile mechanism rather than a pseudorotation⁸⁷ (Figure 11).

VII. Conclusion and Perspectives

Silacyclopentadienide anions are not easily obtained, contrarily to germacyclopentadienide anions. In spite of the enhanced acidity of the germacyclopentadienide anion, compared to other germyl anions, they do not appear to be resonance stabilized.

Siloles and germales are very efficient η^4 -ligands; the presence of the group 14 element confers to the complexes a higher stability than that of other parent η^4 -diene ligands. In some aspects the behavior of the η^4 -ligand resembles that of η^5 -cyclopentadienyl.

Three sites of attack are present in these complexes: the transition metal, the carbonyl ligands, and the group 14 element. Reactions at silicon or germanium seem the more interesting, since functionalization is required in order to attain the η^5 -species. The *exo* substituent is highly reactive and substitution occurs always with retention of configuration. However, the formation of complexes with Si-O-Si or Ge-O-Ge bonds is difficult

to rationalize, although siloxanes have been obtained in reactions involving chlorosilanes and metal carbonyls.¹¹² The η^5 -silacyclopentadienyl species has not yet been obtained; however, in the C-non-phenylated series, this species might be more favored, as observed for the cyclopentadienyl ring.^{113,114} The peculiar reactivity of the *exo*-SiH bond makes possible the preparation of a variety of functionalized siloles which are unstable as free ligands.

The fluxional behavior of complexes with two η^4 -metallole ligands is very interesting since, besides the well-known ring rotations observed for other η^4 -diene complexes, a twisting mechanism is evidenced for the first time in complexes other than those with chelate ligands (e.g., acetylacetonate).

The reactivity of coordinated siloles allows the synthesis of functional complexes which, after decoordination, may yield the free ligand (the synthesis of which cannot be obtained directly). Also new η^5 -metallacyclopentadienyl complexes appear now as a possible development of this chemistry.

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