

Short review

Novel generation of organometallic systems. Metal carbonyl complexes with silacarbacyclic π -ligands, synthetic and structural investigations¹

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Abstract

This review deals with the preparation and structure investigation of metal carbonyl (Cr, Mo, W, Fe) complexes with 9,10-disiladihydroanthracene (**I**), 9-silafluorene (**II**), 9-oxa-10-siladihydrophenanthrene (**III**), 1-silaacenaphthene (**IV**), 1-silaphenalene (**V**) and 1-silacyclohexa-2,4-diene (**VI**) π -ligands. Some questions concerning the regio- and stereo-regularities of η -coordination are considered. The most interesting properties and structural peculiarities of the new complexes are summarized: the relationship between the nature of the substituent in the sila-unit and the chemical behaviour of the complexes; the dependence of the silacycle conformation on substitution and coordination factors; the specific arrangement of $M(CO)_n$ -fragments in crystals. © 1997 Elsevier Science S.A.

Keywords: Unsaturated silacarbacycles; η^6 -, μ - η^6/η^6 -, η^4 -, η^2 -, μ - σ , σ -complexation; Transition metals; Carbonyl; Structural chemistry

1. Introduction

Silacarbacyclic compounds, the nearest analogues of cyclic hydrocarbons, are one of the most attractive classes of organosilicon derivatives. To date the central problem has been to establish the effect of the SiR_2 -unit which takes the place of the $CH=$ or CH_2- fragments in the carbacyclic skeleton and to appraise the prospects for silacyclic reagents in various aspects of organic chemistry. In this regard, the numerous papers and reviews of last two decades have been devoted to efficient synthetic methods, structural and spectral studies, as well as the dynamics and chemical reactivity of silacarbacyclic molecules [1–9].

The study of silacarbacyclic compounds involving unsaturated groupings in the capacity of π -ligands was started in our institute 20 years ago and was carried out

in cooperation with the A.N. Nesmeyanov Institute of Organoelement Compounds and Chemical Department of Moscow State University. Since most of the results were published in Russian journals, which are not readily available for foreign colleagues, it seems reasonable to present some of the results in this review, dedicated to memory of our co-author, Professor Yu.T. Struchkov.

2. Preparation of complexes

The great variety of sila-heterocyclic compounds were available in our laboratory owing to the development of efficient synthetic methods [4,5]. Starting this investigation, we chose a number of objects **I–VI** (Scheme 1), corresponding to basic types of cyclic hydrocarbon that are well known as π -ligands.

Preliminary studies of the electron structure of dibenzosilacycles **I–V** anion-radicals showed that their key peculiarity consists of a cyclic conjugation failure and in the π -electron density withdrawing effect of Si–R bonds [10–15]. The structural investigation of type **I** and **III** derivatives (**I**, $R = R_1 = Me$, $R = R_1 = Cl$ [16,17], **III**, $R = Me$, $R_1 = C_6H_4Br-p$ [18], $R = R_1 = Cl$

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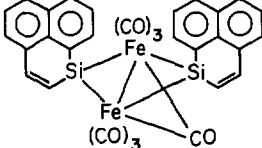
¹ Dedicated to the memory of Professor Yuri T. Struchkov, an outstanding scientist, wonderful lecturer and a person of high moral and scientific principles.

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Table 1
Metalcarbonyl complexes of silacarbacyclic ligands

No.	Compound	M.p. (°C) or b.p. (°C/mm)	Yield ^a (%)	References
1 ^b	R = R ₁ = Me, n = 0, M = Cr	132–133	95	[20–22,25,47]
2 ^b	R = R ₁ = Me, n = 1, M = M ₁ = Cr (trans-isomer)	210	35	[20–22,25,47]
3 ^b	R = R ₁ = Me, n = 1, M = M ₁ = Cr (cis-isomer)	179–181	15	[20–22,25,47]
4	R = R ₁ = OEt, n = 0, M = Cr	130	70	[23]
5 ^b	R = R ₁ = OEt, n = 1, M = M ₁ = Cr (trans-isomer)	170 (with decomp.)	51	[23,49]
6 ^b	R = Me, R ₁ = OPr ^t , n = 1, M = M ₁ = Cr (trans-, meso-)	152–154	65	[24,49]
7 ^b	R = R ₁ = Me, n = 0, M = Mo	156–158	70	[23,48]
8 ^b	R = R ₁ = Me, n = 0, M = W	174–176	65	[23,48]
9	R = R ₁ = Me, n = 1, M = M ₁ = W (trans-isomer)	200	> 10	[23]
10 ^b	R = R ₁ = Me, n = 1, M = Cr, M ₁ = W (trans-isomer)	211–212	11	[23]
11	R = R ₁ = OEt, n = 1, M = W	122–124	28	[23]
12 ^{b,c}	M = Cr, n = 0	151–153	70	[22,25,26,64]
13 ^b	M = Cr, n = 1 (trans-isomer)	240 (with decomp.)	70	[22,25,27,64]
14 ^b	M = Cr, n = 1 (cis-isomer)	176–180 (with decomp.)	6	[27,64]
15	M = Mo, n = 0	48–52	30	[23]
16 ^b	M = W, n = 0	138–141	40	[23,30]
17 ^b	n = 0, m = 1, M = Cr	128.5–130	70	[22,25,28,29]
18 ^b	n = 1, m = 0	129–130	45	[22,25,28,29]
19 ^b	n = m = 1, M = Cr	200 (with decomp.)	30	[29]
20 ^b	n = 0, m = 1, M = W	145–145.5	22	[30]
21 ^b		141–142	70	[22,25,26,61]
22 ^b	R = Me	131–132 (with decomp.)	52	[32,76]
23 ^b	R = OEt	128–129 (with decomp.)	28	[33]
24 ^b	R = R ₁ = Ph	56–58	75	[34–36]
25 ^b	R = R ₁ = Cl	36.5–37	84	[34,36,37]
26 ^d	R = Cl, R ₁ = Me	110–115/1.5	76	[36,38]
27 ^c	R = R ₁ = Me	110–112/1.5	78	[36,38]
28	R = R ₁ = OEt	120/1	53	[36,37]

Table 1 (continued)

No.	Compound	M.p. (°C) or b.p. (°C/mm)	Yield ^a (%)	References
29	R = R ₁ = OH	87–89.5	81	[36,37]
30	R = R ₁ = H	80–85/1.5	36	[36,37]
31 ^b	R = Cl	79–83	80	[39,40]
32 ^d	R = Me	38.5–40	86	[39]
33 ^b		80 (decomp.)	50	[41,74]

^a Best yields in synthetic investigations (0–200°C) are given for analytically pure samples.

^b X-ray data are available.

^c Compound was prepared in parallel work by another method [42].

^d Mixture of 1-chloro(exo)-1-methyl(endo)/1-chloro(endo)-1-methyl(exo)-isomers.

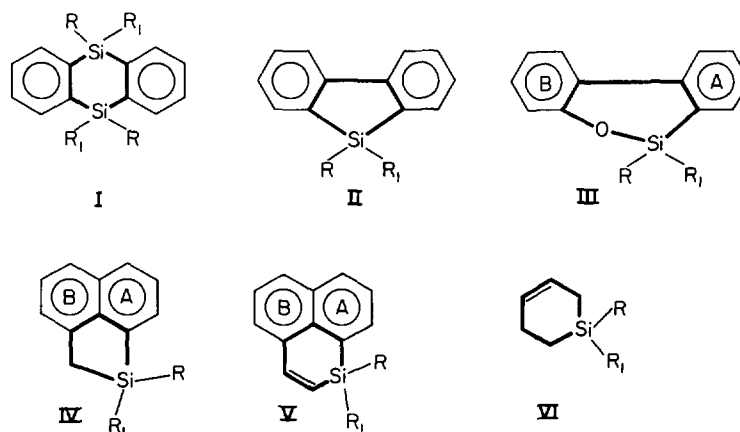
^e Compound was prepared previously by another method [43].

[19,20]) proved that electron effects of SiR₂-units are dependent on both the R-substituent nature and silacycle conformation. As early as the end of 1970s it was difficult to classify the discovered stereoelectron effects. Nevertheless, we believed that π -bonding with transition metals could be interesting for synthetic testing and, moreover, should result in unusual coordination compounds.

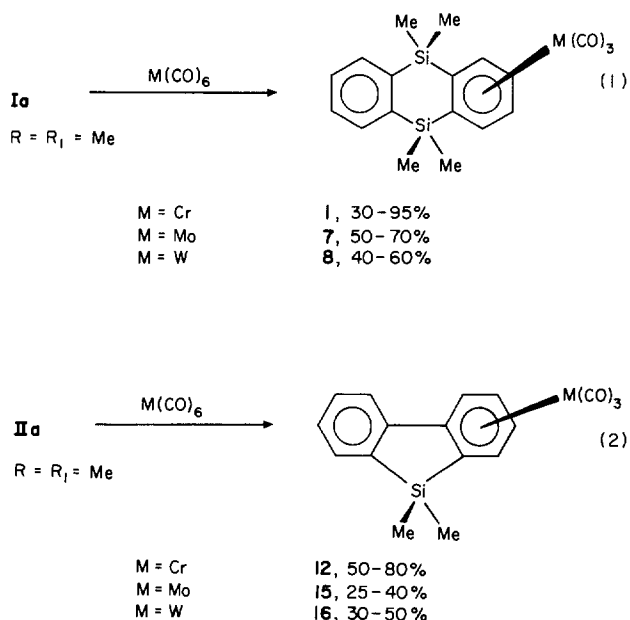
For preparation of metalcarbonyl complexes of silacycles I–VI derivatives we used ligand exchange reactions via interaction of free cycles with metalcarbonyl reagents L₃M(CO)₃ (L = CO, M = Cr, Mo, W; L = MH₃, CH₃CN, pyridine, M = Cr) or Fe_n(CO)_m (n = 2, m = 9; n = 3, m = 12).

The strategy of our work was as follows. In the first step we investigated the results of coordination of methyl-substituted dibenzosilacycles (Ia–IVa, R = R₁ = Me) in conditions, that were classic for

AreneCr(CO)₃-complex preparation, namely upon action of Cr(CO)₆ on free arene by boiling Bu₂O. All the new metalcarbonyl derivatives arising from the reaction mixtures were fixed via monitoring by PMR spectroscopy and most of them were isolated in the individual state. The data obtained were analysed carefully and were used in our further work as tentative control points. Then, in the second step, we changed the substituents R at the silicon centre, the metal carbonyl and the external conditions of complexation. Thus, an adequate appreciation of coordination possibilities of silacyclic π -ligands was obtained. From this we found that, as diarene ligands, dibenzoheterocycles of types I–III tended to coordination of two aromatic fragments. Directed synthesis of their binuclear complexes was carried out under carbonyl agent excess or by interaction of mononuclear M(CO)₃-complexes with the appropriate carbonyl agent. Furthermore, the investigation of the



Scheme 1.



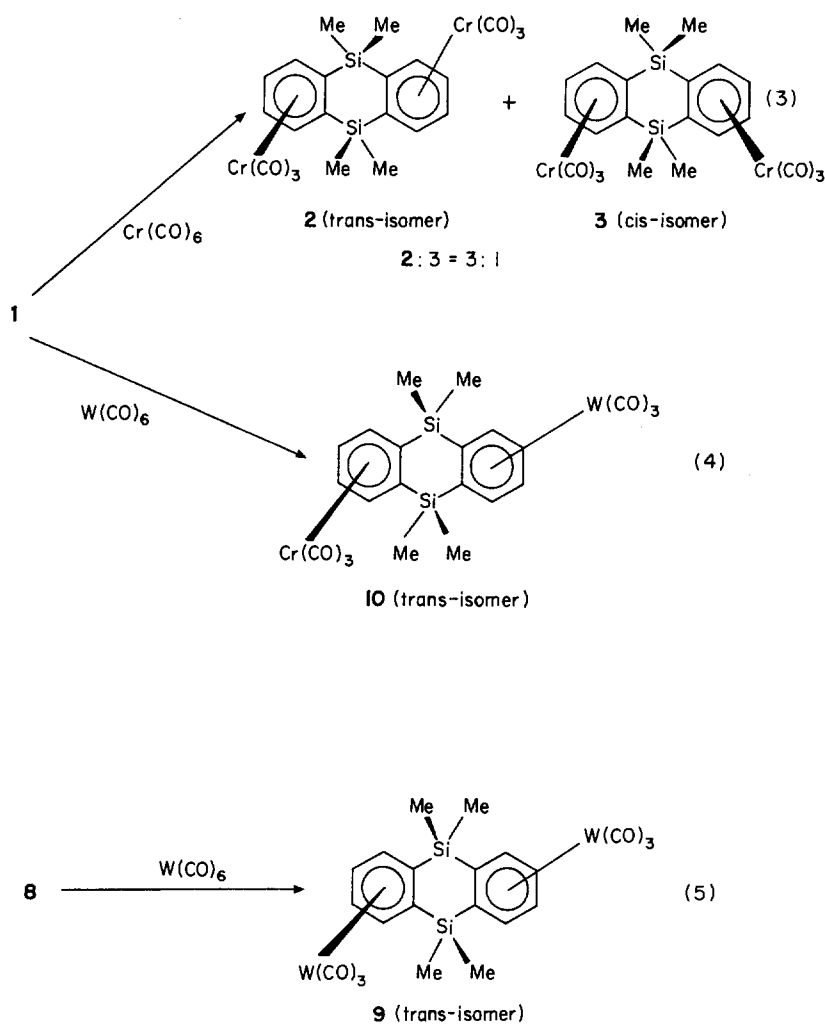
Scheme 2.

Si–R functional groups exchange in coordinated cycle **VI** ($R = R_1 = Cl$) opened an alternative efficient way to complexes with reactive substituents in the sila-unit. As a result we obtained a number of new metal carbonyl complexes, containing unsaturated silacyclic molecules in capacity of η^6 -, μ - η^6/η^6 -, η^4, η^2 - and μ - σ, σ -ligands. The structures of these complexes, listed in Table 1, were established by their total spectral data including NMR- and UR-spectra, mass-spectral analysis and X-ray investigations. The most interesting and principal peculiarities of the chemistry and structures of these complexes are considered below.

2.1. η^6 -Complexes of 9,10-disiladihydroanthracene (**I**) and 9-silafluorene (**II**) ligands

Methyl-substituted dibenzosilacycles **I** and **II** interact efficiently with $M(CO)_6$ ($M = Cr, Mo, W$), so the yields of their η^6 -complexes fluctuate from moderate to near quantitative depending on the conditions (Scheme 2).

In the course of experimental work we discovered



Scheme 3.

that bis-coordination of ligand **1a** starts in the reaction mixture from the moment when the mononuclear complex **1** accumulation approaches 30%. The best results for exhaustive coordination of **1a** were obtained when mononuclear complexes **1** or **8** were used as starting materials (see reactions (3), (4) and (5) in Scheme 3).

Investigation of the structure of separated complexes **2** and **3** resulted in unprecedented data [20,21,47]. Namely, bis-coordination of 9,9,10,10-tetramethyl-9,10-disiladihydroanthracene is not an exclusively stereospecific process and complexes with both cis- and trans-location of two $M(\text{CO})_3$ -groups are available as individual objects. Further investigation showed that this was true not only for non-rigid anthracene-like ligand **1a**, but also for the rigid and near-planar ligand **11a** (reaction (6), Scheme 4) [27]. We have also found that selectivity of poly-coordination towards trans-bi-nuclear isomers increased when methyl groups at silicon in ligand **I** were changed by alkoxy-substituents. It is especially interesting to note that the process of coordination of **1b,c** was promoted so that bi-nuclear complexes **5** and **6** were the major or single products in only 5–8 h [23,24] (Scheme 4).

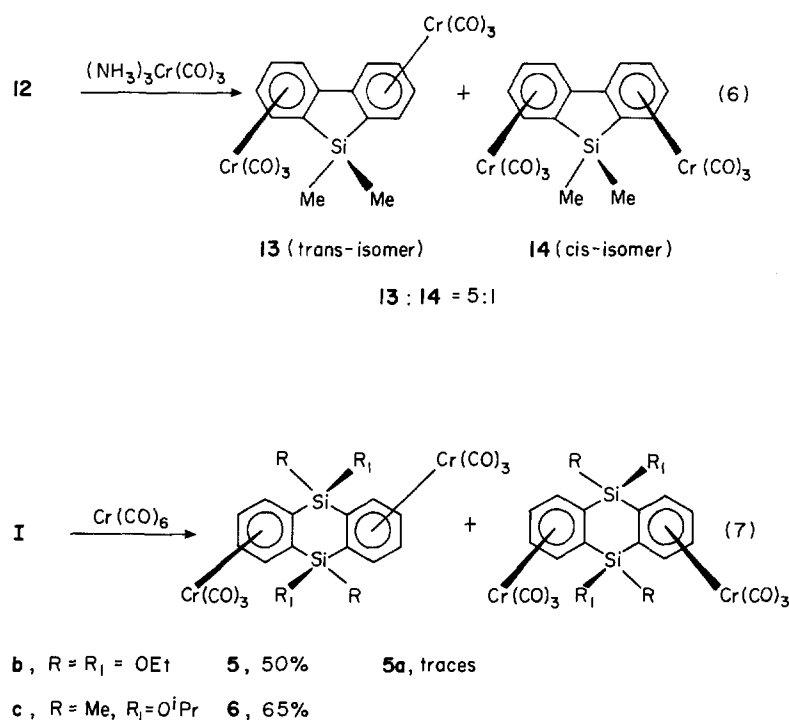
All complexes **1–16**, both of mono- and bi-nuclear structures, are crystalline substances, stable to air in the solid state and in solution. Fractional extraction and crystallization, column and thin-layer chromatography at ambient conditions were used successfully for their isolation and purification, including that of stereo-isomer separation. The only exception was complex **15**, for which a low temperature was necessary for its storage.

It is especially interesting to note here that the known chromium carbonyl η^6 -complexes of organic analogues with anthracene-like and fluorene-like skeletons are easily oxidized in solution with cleavage of a coordination bond. As a rule, carba-polycycles coordination is limited by two main factors: kinetic instability of the coordination bond and a steric barrier. The role of the latter is especially important for rigid and planar systems (for a recent review see Ref. [44]; see also Refs. [45,46]). Our results, presented in this section, show that incorporation of the sila-unit in a polycyclic framework removes some of these restrictions. In this regard, the structural chemistry of silacyclic complexes is of specific interest and the most important peculiarities of the structure are reflected in Section 3.

2.2. η^6 -Complexes with 9-oxa-10-siladihydrophenanthrene (**III**) and 1-silaacenaphthene (**IV**) ligands

Silacycles **III–V** present two distinct types of di-arene ligand constructed on the base of a biphenyl (**III**) or a fused naphthalene (**IV**) framework. At the same time the common peculiarity of the heterocycles is their unsymmetrical structure. In this regard, we looked upon these systems as the objects which allowed one to compare the coordination capacity of the arene rings A and B (see abbreviation in Scheme 1) and therefore to obtain the synthetic data about the α -sila-unit influence on complexation of diarenes with various structures.

The action of $\text{Cr}(\text{CO})_6$ on free cycles **IIIa** and **IVa** ($R = R_1 = \text{Me}$) under the same conditions that we have

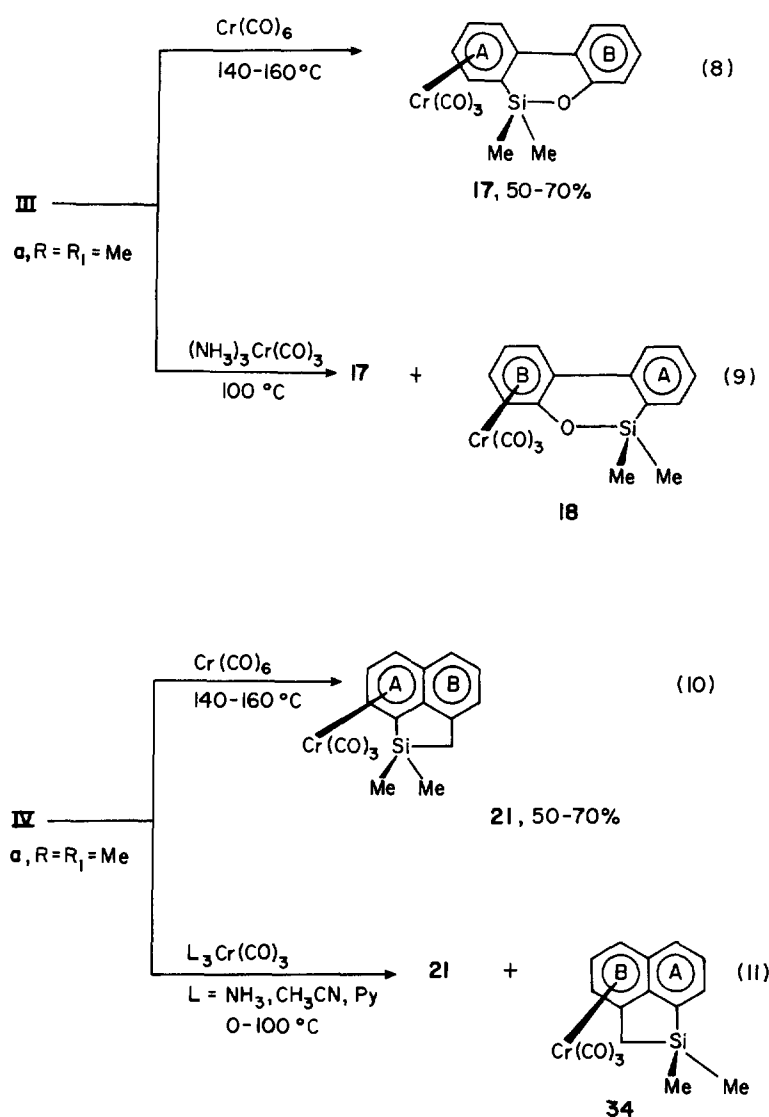
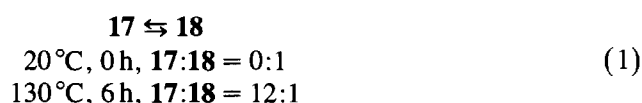


Scheme 4.

found as the most efficient for complexation of **Ia** and **IIa**, resulted in an unexpected phenomenon at first sight — regio-selective coordination of Si-substituted rings A in both of types of silacycle [25,26,28] (reaction (8) and (10) in Scheme 5). We believe [26] that regio-selectivity of coordination is really the consequence of the different stability (or different kinetic lability) of the regio-isomeric complexes. Indeed, this was confirmed in our further work.

Coordination of free ligands **IIIa** and **IVa** under mild conditions (reactions (9) and (11) in Scheme 5) resulted in mixtures of regio-isomeric pairs of the complexes. The ratio of isomers **17:18** and **21:34** changed drastically depending on reaction time or temperature. The initial complexes **18** and **34** disappeared in the course of the reactions and were replaced by complexes **17** and **21** respectively. This fact was of special interest to us in view of the intramolecular arene ligand exchange reac-

tions in the complexes of silacyclic polyarenes. Therefore, thermal transformations of **18** and **34** in solution were investigated by dynamic NMR-spectroscopy [53–55]. As a result, the ease of intramolecular $\text{Cr}(\text{CO})_3$ -group migration between rings A and B was discovered for diarenes **IIIa** and **IVa** (Eqs. (1) and (2)). An enhanced tendency to metal migration distinguishes the complexes of silacycles **IIIa** and **IVa** from the related derivatives of the biphenyl and fused systems studied in parallel or the later work on metal migration [56–59]. One exception was the complexes of 2,6(2,7)-dimethoxynaphthalenes which had extremely high rates of metal migration [60].



$34 \rightleftharpoons 21$ 20 °C, 0 h, $34:21 = 19:1$ 80 °C, 25 h, $34:21 = 1:3$ 100 °C, 6 h, $34:21 = 1:3$

(2)

One explanation may be in the participation of the sila-unit in stabilization of the Cr-ligand π -bond as in the base η^6 -, or in the transition η^{6-x} -states. It may be possible to proceed on the assumption that the endo-groups at silicon serve as intramolecular chelating ligands for stabilization of the supposed transient η^{6-x} -AreneCr(CO)₃ complexes [62–69].

Another approach consists of the examination of the sum of the electron effects of the α -sila-unit incorporated in the unsaturated ligand framework. The modern theory of chemical bonds considers the accepting effect of silyl groups as π -electron density transfer into σ^* -orbitals of Si–R bonds (an effect of the negative hyperconjugation [72]). The effectiveness of such hypervalent $\pi \rightarrow \sigma^*$ interactions depends firstly on the relative orientation of the π -density and the Si–R bond and

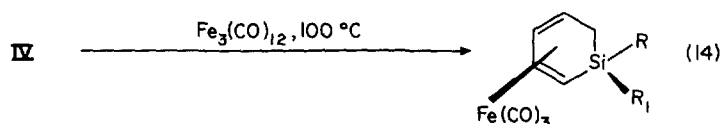
Table 2

PMR spectroscopy data (60 MHz, δ , acetone-*d*₆)

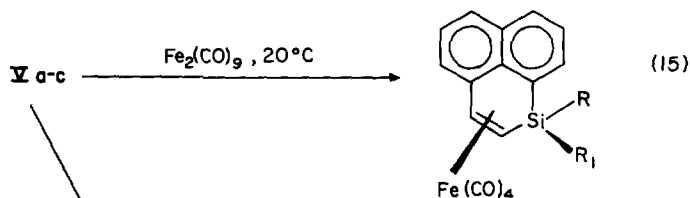
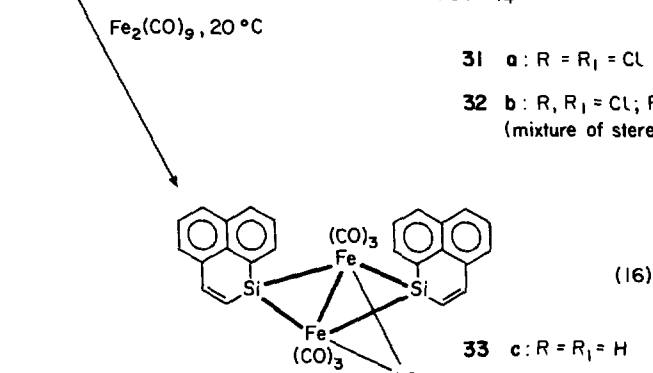
Complex	Si–Me _{exo} ^a	Si–Me _{endo} ^a	Reference
1	0.40	0.67	[21,25]
2	—	0.75	[21,25]
3	0.48	0.85	[21,25]
12	0.54	0.67	[25,26]
13	—	0.74	[27]
14	0.56	0.89	[27]
17	0.40	0.70	[28]
18	0.47	0.64	[28]
21	0.40	0.73	[26,53]
34	0.49	0.60	[26,53]

^a Relative to metal atom.

secondly on the nature of substituent R. As for coordinated π -density, a third factor is the requirement of the coordinating metal centre: namely, the role of the π -acceptor substituent is the most significant for those complexes where the balance of direct and back-dona-

24, R = R₁ = Ph25, R = R₁ = Cl26, R = Cl, R₁ = Me26a, R = Me, R₁ = Cl

26: 26a = 2:3

31 a: R = R₁ = Cl32 b: R, R₁ = Cl; R₁, R₂ = Me
(mixture of stereoisomers)

Scheme 6.

tion components of π -bonding is distorted. Such examples are the η^2 - and η^4 -bonded ironcarbonyl derivatives [70,71] or η^6 -AreneCr(CO)₃ complexes with $\eta^6 \rightarrow \eta^4$ distortions. Returning to consideration of the silacyclic complexes, note that our synthetic, spectroscopic and X-ray analysis data as a whole are in a good agreement with both aspects of possible intramolecular effects mentioned above.

So the unbonding contacts between the Si-R_{endo} substituent and the nearest CO-group appear in most of the crystals studied (see Table 1, footnote b) and are 3.39–3.80 Å. The smallest values of such contacts were established for η^2 -, η^4 - and $\eta^6 \rightarrow \eta^4$ complexes containing Si-Cl or Si-OEt substituents [33,40,75,76] (for synthesis see Section 2.3). Evidently, the effectiveness of such weak contacts increases in solution, and especially in donor solvents. In any case, the Si(Me)_{endo}...CO interactions may be the reason for the significant downfield shift of the Si-Me_{endo} proton signals in the PMR spectra of silacyclic complexes (see Ref. [52] and Table 2).

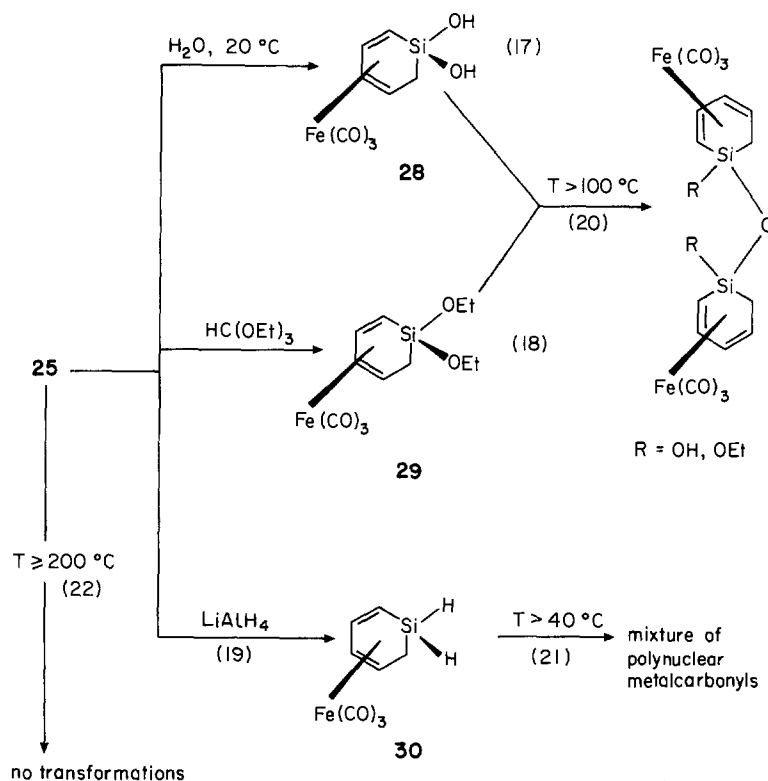
2.3. η^2 -, η^4 - and η^6 -complexes with 1-silaphenylene (V) and 1-silacyclohexa-2,4-diene (IV) ligands

We have found that the formation of the η^2 or η^4 -complexes in the reaction of free derivatives of V or

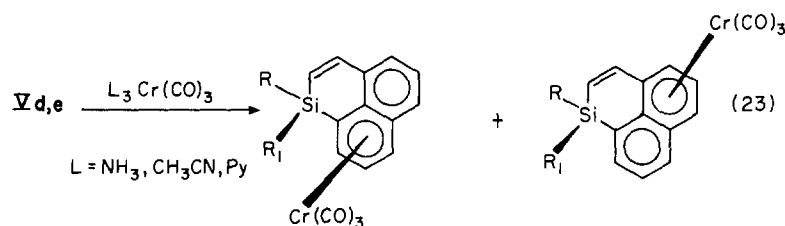
VI with iron carbonyls is strongly dependent on the nature of substituents R. So, stable complexes with good yields were obtained if substituents R were Ph or Cl groups [34–40]. In the case of R = Me, H, OH, OEt groups the process of η -coordination was complicated by secondary transformations or by the reactivity of the Si-R bonds with respect to the metal carbonyl reagent [41] (Scheme 6). Nevertheless, we found a successful way to synthesize η^4 -complexes with reactive substituents at silicon and traced some transformations of such complexes during the thermal and mass-spectral decay [36,37]. This method consists of the substitution of the Si-Cl groups in complex 25 (Scheme 7).

Conversions of complex 25 upon action of H₂O, HC(OEt)₃ and LiAlH₄ showed up the first examples of substitution of both functional groups in coordinated silacyclic ligands. We did not observe a significant difference in the reactivity of Si-Cl_{endo} and Si-Cl_{exo} bonds, as it was observed later during Si-Cl group substitutions in coordinated silole ligand [73].

The high reactivity of complex 25 in the sila-unit is combined with the largest stability of that complex for thermal decay. The structure of 25 is remarkable for numerous nonvalent contacts in the environment of the heteroatoms [75] (see Fig. 6). Another peculiarity of structure 25 is the shortened Si-C_{sp²} bond length up to 1.804 Å. It may be supposed that in this molecule both



Scheme 7.



d ,	R = R ₁ = Me	22	22a
	100 °C	22 : 22a = 1:0	
	0 °C	22 : 22a = 2:3	
e ,	R = R ₁ = OEt	23	23a
	0–100 °C	23 : 23a = 1:0	

Scheme 8.

of Si–Cl substituents participate in hypervalent interactions: the Cl_{endo} atom via donor–acceptor bonding with the carbon atom of the apical CO-group and the Si–Cl_{exo} bond via a $\pi \rightarrow \sigma^*$ accepting action. Consequently, combination of these effects is responsible for both the stability and reactivity of complex **25**.

By interaction of derivatives of 1-silaphenylene **V** with chromium carbonyls we obtained η^6 -complexes and found that the regio-selectivity of η^6 -bonding was the same as that observed for silacycles **IIIa** and **IVa** [32,33] (see Scheme 8).

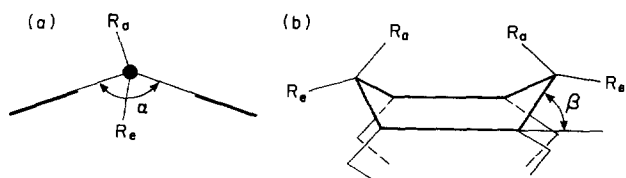
In contrast to **IVa**, ligand **Vd** does not provide for reversible metal migration between A and the B rings. We observed only **23a** \rightarrow **23** transformation in solution [32] and we failed to identify the complex **23a** in reactions mixtures (see Scheme 8). At the same time, complex **23** was black-violet in colour, was easier to prepare, purify and crystallize than the red complex **22**. We noted that the properties of the complexes **1–5** with

ligands **I** (R = R₁ = Me, OEt) changed in the opposite tendency.

3. Some aspects of structural chemistry of π -complexes with silacyclic ligands

3.1. The conformation of coordinated silacyclic molecules

It is a well established fact that silacyclic molecules show a more flexible conformation than their carba-analogues [1,51]. We have found that π -coordination by the transition metal does not change this remarkable property. So disiladihydroanthracene derivatives exhibit the butterfly conformation (Scheme 9(a)) with the middle disilacyclohexadiene fragment in boat conformation (Scheme 9(b)). The values of the butterfly bending angle α and the boat bending angle β depend on the nature of substituent R; for free molecule **Ia** (R = R₁ = Me) these values are $\alpha = 155^\circ$, $\beta = 25^\circ$ [17]. We inves-



Compound no.	Conformation of disilacyclohexadiene fragment	α°	β°
Ia	boat	155	25
1,7,8	boat	144–145	29
2,3,5	flattened boat	160	14–17
6	flattened chair	160	6

Scheme 9.

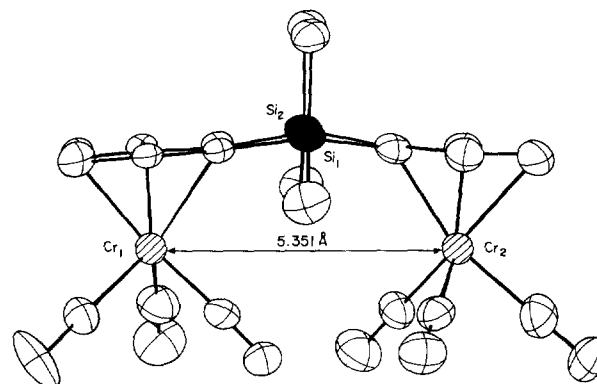
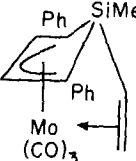
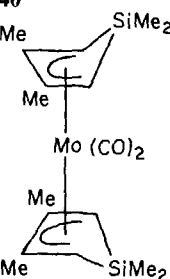
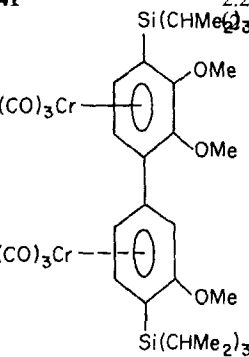
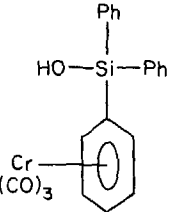
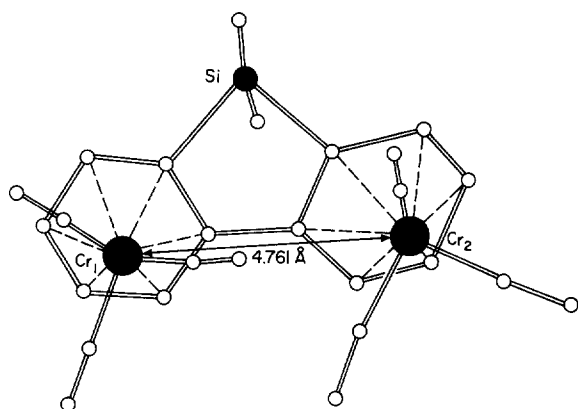
Fig. 1. Structure of complex **3**.

Table 3
Selected geometric parameters of complexes with organosilicon ligands

Complex	The average M–C bond length with the dispersion interval (Å)	The average M···Si distance (Å)	The orientation of M(CO) ₃ groups	The average C–C bond length (coord.) (Å)	The average C–C bond length (uncoord.) (Å)	The bending angle (deg) in the hetero-cycle and other peculiarities	The average Si–C (sp ²) bond length (Å)	The average Si–C (R) bond length (Å)	Ref.
1	2.222(4) (2.204(4)–2.244(3))	3.769	staggered(exo)	1.404(6)	1.387(6)	145.2	1.875(4)	1.850(5)	[47]
2 (trans-isomer)	2.220(4) (2.196(4)–2.246(4))	3.758	staggered(endo)	1.413(6)		160.0	1.854(6)	1.863(6)	[47]
3 (cis-isomer)	2.216(5) (2.185(5)–2.228(5))(5)	3.797	nearly eclipsed	1.407(7)		160.7	1.882(5)	1.879(4)	[47]
5 (trans-isomer)	2.215(8) (2.187(8)–2.244(8))	3.778	staggered(endo)	1.41(1)		160.0		1.863(8)	[49]
6 (trans-isomer)	2.217(5) (2.201(5)–2.233(8))	3.765	nearly eclipsed	1.41(1)		6.5° for two Si-atoms in the opposite direction	1.878(5)	1.843(6)	[49]
7	2.373(6) (2.366(6)–2.382(6))	3.845	staggered (exo)	1.423(9)	1.40(1)	144.4	1.869(8)	1.866(8)	[48]
8	2.353(7) (2.339(6)–2.362(6))	3.833	staggered (exo)	1.42(1)	1.43(1)	144.3 towards to the M atom	1.872(8)	1.867(8)	[48]
12	2.217(7)	3.71	nearly staggered (exo); nearly eclipsed	1.41(1)	1.38(1)	0°	1.876(7)	1.856(8)	[26,64]
(2 independent molecules)	(2.195(7)–2.239(6))								
13 (trans-isomer)	2.217(6)	3.70	nearly eclipsed (Cr1); nearly staggered (endo) (Cr2)	1.410(8)		0°	1.889(6)	1.850(7)	[64]
14 (cis-isomer)	(2.202(6)–2.232(5)) 2.232(5)	3.787	nearly staggered (endo (Cr1) exo Cr2))	1.415(7)		4° for the Si atom towards the M atom	1.878(5)	1.858(6)	[27]

16	2.35(1)	3.785	nearly staggered (exo); nearly eclipsed	1.41(2)	1.41(2)	0°	1.88(1)	1.85(2)	[30]
(2 independent molecules)	(2.30(2)–2.39(2))								
17	2.221(6)	3.677	nearly eclipsed	1.406(2)	1.383(2)	the relative rotation of Ph cycles of 20.4°	1.865(4)	1.834(6)	[29]
18	(2.197(6)–2.249(4)) 2.236(4)	3.309 (Cr ··· O)	nearly staggered (exo)	1.409(2)	1.388(2)	the relative rotation of Ph cycles of 15.5°	1.857(3)	1.834(6)	[29]
20	(2.208(3)–2.280(3)) 2.35(2)	3.757	nearly eclipsed	1.42(2)	1.39(2)	the relative rotation of Ph cycles 18.6	1.84(2)	1.86(2)	[30]
21 (monoclinic)	(2.33(2)–2.38(2)) 2.249(5)	3.73	nearly eclipsed; staggered (endo)	1.411(7)	1.402(7)	0°	1.886(5)	1.845(6)	[26]
(2 independent molecules)	(2.202(5)–2.328(4))					11° for the Si atom from the M atom			
21 (orthorhombic)	2.25(1)	3.78	staggered (endo)	1.421(1)	1.41(1)	16°	1.89(1)	1.84(1)	[61]
22	(2.21(1)–2.33(1)) 2.27(1)	3.74	staggered (endo)	1.43(2)	1.44(3)	11° for the Si atom from the M atom	1.89(1)	1.91(1)	[76]
23	(2.25(1)–2.32(1)) 2.241(5)	3.67	staggered (endo)	1.414(8)	1.398(8)	5° for the Si atom from the M atom	1.837(5)		[33]
25	(2.205(5)–2.293(5)) 2.093(6)	3.132		1.429(9)		38.5° for the Si and C atoms from the M atom	1.826(7)	2.050(2) (Si–Cl)	[75]
31 (orthorhombic and triclinic forms)	(2.052(6)–2.137(6)) 2.15(1)	3.352		1.44		6.4° for the Si atoms from the M atoms	1.83(2)	2.083(6) (Si–Cl)	[40]
33	(2.12(1)–2.16(1))	2.352			1.35(2)	0°	1.85(1)		[74]

<p>39</p> 	2.402 (2.331–2.500)	2.803		8.9° for the Si atom from the M atom	1.882	1.879	[82]
<p>40</p> 	2.349 (2.265–2.454)	3.128		36.6° for the Si atom from the M atom	1.863	1.884	[83]
<p>41</p> 	2.239(6) 2.194(6)–2.292(6)	nearly eclipsed	1.414	the relative rotation of Ph cycles of 34°	1.905	1.889	[87]
<p>(Ph₃SiOH)[Cr(CO)₃]_n</p> 	n = 1 (42) n = 2 (43) n = 3 (44)	42 intermed.; 43 intermed.; 44 eclipsed					[89]

Fig. 2. Structure of complex **14**.

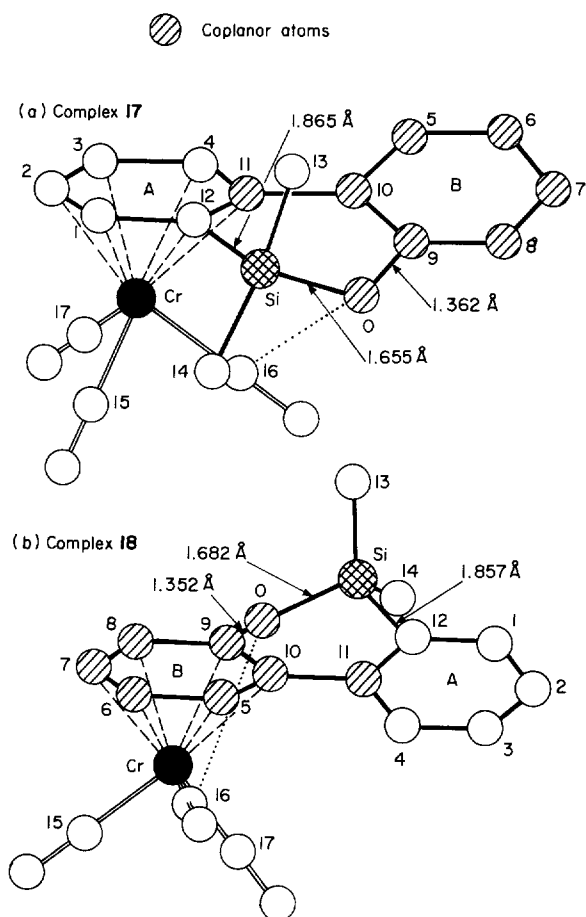
tigated the structures of seven of the 11 disilaanthracene complexes obtained. Conformation of the coordinated silacycle **I** is dependent not only on the nature of substituent **R** but also on the number of π -bonded metallic atoms and their positions. As can be seen from Table 3, where the bending angles are listed, the conformation of coordinated cycle **I** may vary towards more bending or to the planar compared with the free molecule **Ia**. These variations are evidently demonstrated in the series of complexes **1–8** (Scheme 9).

The molecule of complex **3** is presented at Fig. 1. It is especially interesting to note that two $\text{Cr}(\text{CO})_3$ -groups in the cis-complex **3** have an anti-location [45] (both groups are located under a 'house roof' [47]).

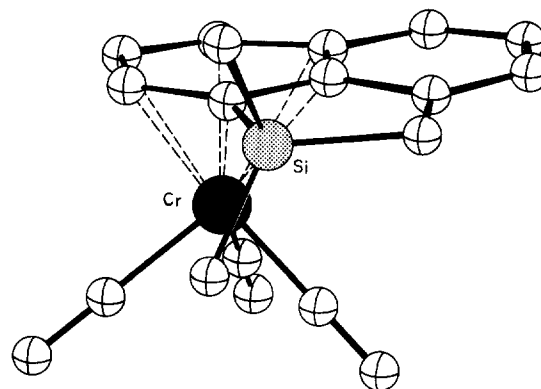
Four silafluorene complexes **12**, **13**, **14** and **16** were studied by X-ray investigation. The conformation of the rigid and planar 9-silafluorene ligand is also dependent on the number and position of π -bonded metallic atoms. The planar conformation of the silafluorene ligand is established in the isostructural mononuclear complexes **12** and **16** as well as in the trans-binuclear complex **13** [26,64]. Cis-coordination of two $\text{Cr}(\text{CO})_3$ -groups gave the remarkable ligand distortion from planar to horseshoe-shape. The middle silole fragment in **14** has a planar envelope conformation with the silicon deviating by 4.0° towards the metallic atoms [27]. The structure of complex **14** is shown in Fig. 2. In this molecule both $\text{Cr}(\text{CO})_3$ -groups have a syn-location [45] (both metallic atoms are located over the 'horseshoe').

Two regio-isomeric complexes **17** and **18** with the 9-oxa-10-siladihydrophenanthrene ligand are shown in Fig. 3. In both cases the tricyclic system of the ligand **IIIa** is nonplanar with the strongly distorted central heterocycle. The conformation of the latter is similar in both molecules. The O and C(11) atoms are coplanar with the benzene ring B. The Si and C(12) atoms are displaced out of this plane away from the metal atom [29].

Unprecedented results were obtained by the X-ray investigation of the two crystal forms of the silaace-naphthene complex **21**, that were obtained via different

Fig. 3. Structures of two regio-isomeric complexes **17** and **18**.

synthetic routes (see reactions (9) and (11) in Scheme 5). The planar conformation of the polycyclic ligand is established in the first independent molecule of the monoclinic form **21** (Fig. 4). The silacyclic fragment of the ligand has an envelope conformation with the Si atom deviating by 10.5° from the Cr atom in the second independent molecule [26]. An envelope conformation is established in the orthorhombic form **21** [61]. Moreover, the three molecules **21** have different geometric parameters (see Table 3); this reflects the dynamic

Fig. 4. Structure of complex **21**.

behaviour of this complex in solution. The additional difference between monoclinic and orthorhombic forms consists of $\eta^6 \rightarrow \eta^4$ transformation of metal coordination in the former form and $\eta^6 \rightarrow \eta^5$ transformation in the latter [61]. Such a difference is well correlated with the theoretical calculations showing that the fused systems have more than one energetic minimum for η -bonding with transition metal [56,63].

The varied conformation due to the nature of substituents in the sila-unit is established in complexes **22** and **23** with the 1-silaphenylene ligand. Coordinated 1,1-dimethyl-1-silaphenylene in **22** is a 'trihedral house roof' with a ring-junction central carbon atom in the vertex [76]. The Cr atom is situated in the anti-position and the silicon atom is bent from the other five coplanar atoms of the heterocyclic fragment away from the Cr atom by 11.0° . A nearly planar conformation of the tricyclic system **V** is established in complex **23** where 1,1-diethoxy-1-silaphenylene is coordinated.

Arrangement of the metalcarbonyl fragment in complexes with mono- and poly-cyclic silicon-containing ligands is a fundamental characteristic of their structures. The main geometric parameters of complexes studied combined into groups according to the ligand type are listed in Table 3. Independently of the ligand type, the substitution of the Cr atom by Mo and W atoms with close atomic radii [77,78] do not result in marked changes in the coordination geometry. As can be seen from Table 3, these complexes are isostructural.

3.2. The η^6 -complexes $[C_6H_4(SiR_2)_2C_6H_4][M(CO)_3]_n$ ($M = Cr, Mo, W; n = 1,2$) with disiladihydroanthracene ligands

In the molecules **1–3** and **5–8** the $M-C_{\text{arene}}$ distances lie in the standard range of values for most of the known $\text{AreneCr}(\text{CO})_3$ complexes. A detailed analysis shows that these distances are not equivalent and the elongated $M-C_{\text{arene}}$ bonds belong to the Si-substituted ring atoms. A similar picture is also observed in the complexes with exo-cyclic silyl substituents, for example in complexes **35** [79] and **36** [80] (Table 3). In our case, this may be connected with the σ -donor influence of the silyl groups and with the enhanced ability of the $\text{Si}-C_{\text{arene}}$ bond to π -accepting action on π -bonded density. The latter effect provides for repulsion between the Cr centre and the $\text{Si}-C_{\text{arene}}$ bond. The $M \cdots \text{Si}$ distances do not exceed 3.85 \AA . This is smaller than the sum of the van der Waals radii of the elements [77,78]. As seen from Table 3, there are complexes with shorter $M \cdots \text{Si}$ contacts, for example silole complexes **37** [81], **38**, **39** [82] and **40** [83], where the Si atom is significantly bent from the M atoms.

As a rule, the active substituents in the arene ring not only affect the M atom position, but they also determine the orientation of the $\text{M}(\text{CO})_3$ group relative to the

coordinated ring [84,85]. We found a staggered orientation of the $\text{M}(\text{CO})_3$ groups in complexes **1**, **2**, **5**, **7** and **8**.

The $\text{M}(\text{CO})_3$ groups are rotated until they adopt a sterically optimal nearly eclipsed orientation in the binuclear cis-complex **3** and in the trans-complex **6**. The rotation of the $\text{M}(\text{CO})_3$ groups and the $\text{Cr} \cdots \text{Cr}$ distance (5.351 \AA , Fig. 1), which is considerably greater than the double covalent radius of the Cr atom [77,78], are evidence for the absence of additional interactions in the cis-complex **3**.

It is noteworthy that the $\text{M}(\text{CO})_3$ groups have an endo-staggered orientation in the molecule of the binuclear trans-complexes **2** and **5**, where the $\text{M}-\text{CO}$ bonds are projected on the heterocycle and are directed towards each other. Mononuclear complexes **1**, **7** and **8** have an exo-staggered orientation: the $\text{M}-\text{CO}$ bonds are projected outside the heterocycle.

The C–C bond lengths in the coordinated arene rings alternate. The longer C–C bond is projected on the $\text{M}-\text{CO}$ bond in the complexes with the staggered orientation. This correlates with the results of the investigation of the density difference plots [86] relative to elongation of the C–C bonds eclipsed by carbonyl and similar ligands. Another tendency is observed in the mononuclear complexes **1**, **7** and **8**: C–C bonds in the coordinated aromatic ring are elongated compared with noncoordinated ones (see Table 3).

3.3. The η^6 -complexes $[C_6H_4(SiMe_2)C_6H_4][M(CO)_3]_n$ ($M = Cr, W, n = 1,2$) with silafluorene ligand

The $\text{M}-C_{\text{arene}}$ bond lengths and the $\text{M} \cdots \text{Si}$ distances in the metal-carbonyl complexes with the silafluorene ligands are close to the values found in disiladihydroanthracene complexes, the elongated $\text{M}-\text{C}$ bonds belong to the atoms of the central heterocycle. The most remarkable differences in the $\text{Cr}-C_{\text{arene}}$ bond lengths are established in the cis-complex **14** (Fig. 2), where the Cr atom is essentially displaced in a direction towards the outer ligand border. On the contrary, the Cr atom is displaced in the direction of the central $C_{\text{arene}}-C_{\text{arene}}$ bond of the polysubstituted diphenyl ligand in molecule **41** [87]; the longest $\text{Cr}-C_{\text{arene}}$ bonds are found for the carbon atoms bearing silyl substituents (see Table 3).

Complexes **12–14** and **16** include a compact planar ligand similar to the biphenylene, unlike the disiladihydroanthracene complexes with a nonrigid conformation of the ligand (capability of change in the bending angle of the $\text{Si} \cdots \text{Si}$ line). Evidently, the effect of the silyl group is more pronounced in the silafluorene complexes, which is evidenced by a shortening of the $\text{M} \cdots \text{Si}$ distances (see Table 3). The $\text{M}(\text{CO})_3$ group has a varied orientation relative to the coordinated aromatic ring. We found different orientations for two

independent molecules in the mononuclear complexes **12** and **16**. At the same time, at least one of the M atoms has the endo-staggered orientation in the binuclear complexes **13** and **14**; the same orientation is established in the mononuclear $\text{Cr}(\text{CO})_3$ complex with the related biphenylene ligand [88].

3.4. The η^6 -complexes $[\text{C}_6\text{H}_4(\text{OSiMe}_2)\text{C}_6\text{H}_4][\text{M}(\text{CO})_3]$ ($M = \text{Cr}, \text{W}$) with silaoxadihydrophenanthrene ligand

The $\text{M}(\text{CO})_3$ complexes with the silaoxaphenanthrene ligand are the most interesting since they include a ligand with two heteroatoms related to biphenyl. A more pronounced difference than that in the disiladihydroanthracene and silafluorene complexes was found in the $\text{M}-\text{C}_{\text{arene}}$ bond lengths for complexes **17**, **18** and **20**. It is noteworthy that the displacement of the Cr atom is greater in complex **18** than in complexes **17** and **20**. It may be supposed that the effect of the shift of the Cr atom away from the ring-junction carbon atoms reflects a different influence of the Si or O heteroatoms on the coordinated aromatic ring.

The shorter $\text{M} \cdots \text{Si}$ distances in complexes **17** and **20**, compared with other characterized complexes, as well as the intramolecular $\text{Cr} \cdots \text{O}$ contact in **18**, indicate a steric strain in these complexes. Apparently, this causes variations in the orientation of the $\text{M}(\text{CO})_3$ groups relative to the aromatic rings; in fact, there is a nearly eclipsed orientation in **17** and **20** and a nearly endo-staggered orientation in **18**. We found a noncoplanarity of the phenyl rings usually typical for the biphenyl complexes (for example, **41**). The dihedral angles between the coordinated and noncoordinated aromatic rings are 20.4° , 15.5° and 18.6° in complexes **17**, **18** and **20** respectively. Moreover, one of the CO groups is rotated towards the oxygen atom, as in the triphenylsilanol complexes **42**, **43** and **44** [89]. The value of the short intramolecular $\text{O}(\text{H}) \cdots \text{C}(\text{O})$ contact of 3.2 \AA in **49**, where a weak hydrogen bond is proposed, coincides with the $\text{O} \cdots \text{C}(16)$ distance of 3.21 \AA in **18** containing the coordinated oxygen-substituted fragment (see

Fig. 3). The intramolecular $\text{O} \cdots \text{C}(16)$ contact in complex **17** containing a coordinated silicon-substituted fragment (Fig. 3) is equal to 3.59 \AA . The oxygen atom is coplanar with the bonded benzene ring in **17**, **18** and **20**.

The Si–O bonds of 1.655 \AA , 1.682 \AA and 1.65 \AA , in complexes **17**, **18** and **20** respectively, are elongated compared with the 1.62 \AA in the free molecule 10,10-dichloro-10-sila-9-oxa-9,10-dihydrophenanthrene [19] and with the 1.622 \AA in complex **6** and 1.616 \AA in $(\text{Ph}_3\text{Si})_2\text{O}$ [90]. These parameters, together with the shortening of the $\text{C}_{\text{arene}}-\text{O}$ bond lengths to 1.363 \AA in **17**, 1.352 \AA in **18**, 1.35 \AA in **20** and the coplanarity of the oxygen atoms with the bonded benzene ring, show that the conjugation of the oxygen atom with the aromatic ring is more pronounced in complex **18**. As seen from Table 3, the elongation of the C–C bond lengths in the coordinated ring, compared with uncoordinated ones, is more pronounced in complexes **17**, **18** and **20**.

3.5. Metalcarbonyl complexes with organosilicon ligands containing the naphthalene fragment

The silaacenaphthene complex **21** is the most interesting among the $\text{M}(\text{CO})_3\text{L}$ complexes where L is a polycyclic organosilicon ligand with a fused benzene cycle. The Cr atom is displaced from the ring-junction atom of the naphthalene fragment. Moreover, the greatest displacement of the Cr atom is established in the orthorhombic form **21**. Apparently, the naphthalene system not only causes the differences in the $\text{Cr}-\text{C}_{\text{arene}}$ bond lengths, but also affects the orientation of the $\text{Cr}(\text{CO})_3$ groups relative to the coordinated ring. We found an endo-staggered orientation in four out of the five molecules studied with naphthalene-containing silacycles (see Table 3). One of the Cr–CO bonds is projected on the elongated C–C bond of the coordinated ring. The $\text{C}_{\text{arene}}-\text{C}_{\text{arene}}$ bonds in the coordinated fragment alternate, like those in the noncoordinated one. A marked elongation of the C–C bonds due to the coordination is observed in all cases with the coordinated naphthalene fragment.

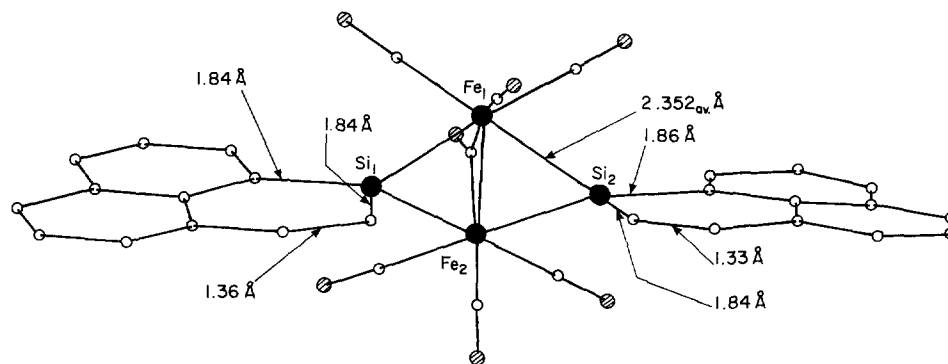
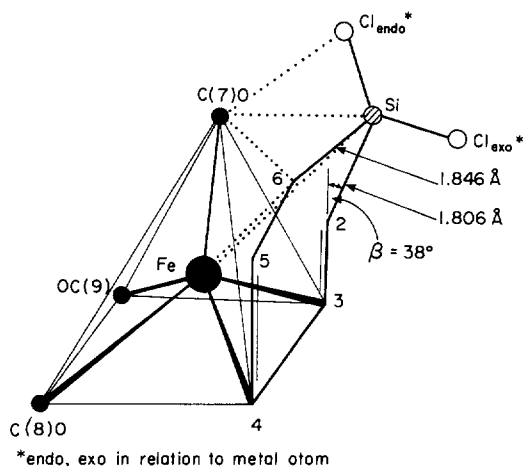


Fig. 5. Structure of complex **33**.

Fig. 6. Structure of complex **25**.

Two other coordination possibilities of the 1-silaphenylene system are present in complexes **31** (with an η^2 -coordinated ligand) and **33** (with μ - σ , σ -coordination). In molecule **31** the iron atom has tetragonal-pyramidal coordination where the olefin bond of the 1,2-dichloro-1-silaphenylene ligand is situated in an equatorial position [40]. Nonvalent contacts arise between the Cl_{endo} atom and carbon atoms of the two CO-groups: the values of these contacts are 3.61 and 3.48 Å. The smaller contact belongs to the apical Fe-CO group. The nonbonding Fe \cdots Si distance is 3.352 Å.

The central fragment of the binuclear complex **33** is the four-membered cluster Fe_2Si_2 with an Fe-Fe bond of 2.620 Å (Fig. 5). The bridging silaphenylene ligands have a planar conformation. The average length of the Fe-Si bonds is 2.352 Å, which is smaller than the sum of the covalent radii of the elements (2.37 Å [77,78]).

3.6. η^4 -Complex with 1-silacyclohexa-2,4-diene ligand

Complex **25** (Fig. 6) has a monocyclic Si-containing diene ligand, coordinated via an η^4 -type by the Fe atom. The ligand is bent along the $\text{C}_2 \cdots \text{C}_5$ line so that the Si-containing fragment deviates away from the

$\text{Fe}(\text{CO})_3$ moiety by an angle of 38° . The $\text{Fe}(\text{CO})_3$ group has a nearly staggered orientation relative to the planar π -butadiene fragment of the ligand. Deviation of the apical CO-group towards the noncoordinated endocyclic Si-C₆ bond results in the short intramolecular $\text{C}_7 \cdots \text{Si}$, $\text{C}_7 \cdots \text{Cl}_{\text{endo}}$ and $\text{C}_7 \cdots \text{C}_6$ contacts (3.334 Å, 3.444 Å and 3.196 Å respectively). The nonvalent distances Fe \cdots Si and Fe \cdots C₆ are 3.132 Å and 3.196 Å.

It is especially interesting to compare the structural regularities determined by us in the series of coordination derivatives of I–VI ligands with the results obtained by Corriu and co-workers of an investigation of the silole series of complexes [8]. In Scheme 10, the two complexes of most significance to our discussion are presented: the sterically constrained η^4 -complex **45** [90] and complex **46** [91] with five-coordinate silicon in the monocyclic π -diene ligand.

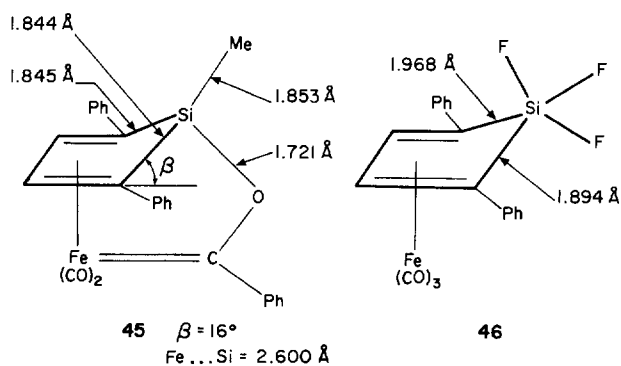
It is a general rule for the four-coordinate silicon that shortening of the $\text{R}_3\text{Si}-\text{CX}$ bond appears in cases of electron-attractive substituents R [92], incorporation of a Si-atom in the three–five-membered carbocyclic skeleton [50] or in the case of stereoelectron interactions between groups X and R [72]. The latter effect, in turn, causes elongation of the accepting Si-R bonds [72]. The elongation of the Si-C bonds also accompanies the $\text{Si}^{\text{IV}} \rightarrow \text{Si}^{\text{V}}$ transformation [31]. In both cases the elongation is connected with the occupation of the unbinding σ^* (Si-C) orbitals [72,93,92].

The Si-C_{sp²} bond transformations in the silole cycle are evidently seen in the structures **45** and **46**. As for the coordinated dibenzoheterocycles studied in our work, because of the general regularity of their structure the Si-C(Me) exo-cyclic bonds are shorter (1.85–1.86 Å) than in free ligands (1.88–1.90 Å). The opposite tendency occurs on changing to the endo-cyclic bonds Si-C_{arene} or Si-C(CH₂): these are elongated in the complexes up to 1.87–1.91 Å. In addition, the elongation of the silicon bonds correlates with the conformation of the cycles, namely with the value of the bending angle β .

It should be concluded that the structural regularities and peculiarities drawn from the detailed analysis of X-ray data for silacyclic derivatives are an adequate reflection of the intramolecular nonclassical electron effects in these molecules.

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Scheme 10.

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