CHROMIUM-TRICARBONYL COMPLEXES OF PHENYL-CONTAINING CYCLOSILOXANE

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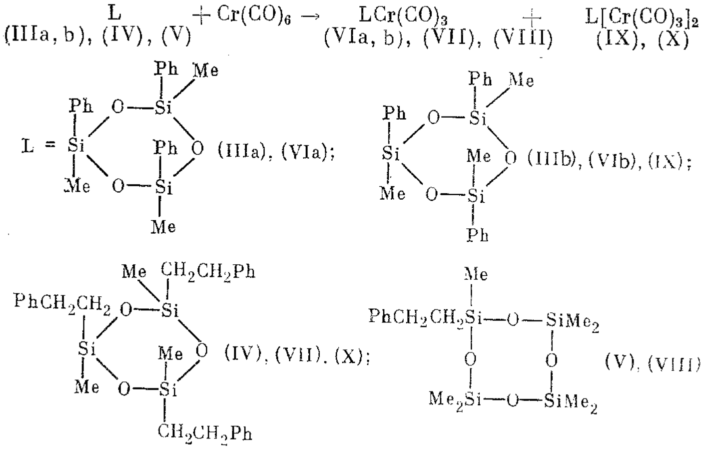
A postulation has been made in [1] on the possible aromatic character of cyclosiloxanes and cyclosilazanes, which however, has not yet been confirmed experimentally. One of the proofs of the aromaticity of the siloxane rings may be the fact that they form complexes with transition metals, similar to π-complexes. At the same time, the possibility of complexation of the crown-ether type is not excluded. In the present work, an attempt is made to verify these possibilities taking chromium carbonyl complexes as examples. We first studied siloxanes (I) and (II) containing only methyl substituents at the silicon atom $(Me_2SiO)_n$, n = 3 (I), 4 (II). We found that these siloxanes do not form complexes in reactions with $Cr(CO)_6$ or $(NH_3)_3Cr(CO)_3$. At the same time siloxanes (IIIa, b), (IV) and (V), containing phenyl or phenyl ethyl substituents, in reaction with $Cr(CO)_6$ give both mono- and binuclear (in the case of (IIIb) and (IV)) complexes with coordination at the Ph-groups.



$$\underset{(IIIa,b),\,(IV),\,(V)}{L} + Cr(CO)_6 \rightarrow \underset{(VIa,b),\,(VII),\,(VIII)}{LCr(CO)_3} + \underset{(IX),\,(X)}{L[Cr(CO)_3]_2}$$

Thus, from the cis-isomer (IIIa) only the mononuclear complex (VIa) was isolated, while from the trans-isomer (IIIb), besides the mononuclear complex (VIb), also a binuclear complex (IX) was recorded by PMR spectrum. The last compound is unstable and even during isolation, it partially splits off the second $Cr(CO)_3$ group and converts into (VIb). At the same time, from trans-(IV) a mixture of mono- and binuclear complexes is formed, which are fully stable and can be isolated in individual state. The reason for this different behavior of the ligands probably lies in the steric conditions. With a cis-orientation of the three Ph groups in (IIIa), simultaneous coordination of two $Cr(CO)_3$ groups is hindered under our reaction conditions; for the trans-isomer (IIIb) it is possible, although the product obtained is not very stable. In the case of (IV), where the Ph groups are separated from Si by two CH_2 units, the binuclear complex is completely stable.

It should be noted that all the derivatives of the trans-ligands (VIb), (IX), (VII) and (X)) are chromatographically inseparable mixtures of two isomers (of type A and B). In the PMR spectra, sets of signals of CH_3 groups and protons of coordinated Ph groups correspond to them. Taking (VIb) as an example, the isomers can be represented as follows

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TABLE 1. Characteristics of Complexes Obtained

Compound	Yield, %	mp, °C	Found/Calculated, %				Empirical formula	$\nu C\equiv O$, heptane
			C	H	Cr	Si		
(VIa)	45	121–123 (from hexane)	53,13 52,92	4,55 4,44	9,52 9,55	15,38 15,47	$C_{24}H_{24}CrO_6Si_3$	1915, 1985
(VIb)	32	59–62 (from pentane)	53,00 52,92	4,53 4,44	9,43 9,55	15,81 15,47	$C_{24}H_{24}CrO_6Si_3$	1915, 1984
(VII)	40	Oil	58,00 57,30	5,92 5,77	7,72 8,27	13,13 13,40	$C_{30}H_{36}CrO_6Si_3$	1910, 1981
(VIII)	67	57–59 (from pentane)	41,74 41,35	5,78 5,78	9,72 9,95	21,44 21,49	$C_{18}H_{30}CrO_7Si_4$	1908, 1981
(X)	38	Oil	51,51 51,82	4,83 4,74	–	–	$C_{33}H_{36}Cr_2O_9Si_3$	1911, 1980
(XII)	20	220–240 (dec.)	52,90 52,37	3,81 3,45	4,71 4,45	18,57 19,21	$C_{51}H_{40}CrO_{15}Si_8$	1912, 1989 *

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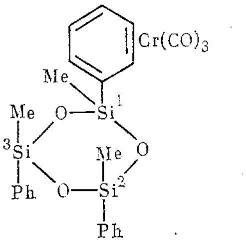
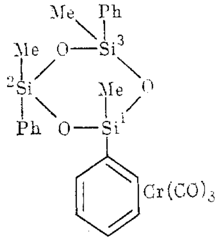
*The IR spectrum was run in heptane containing 20% of CH_2Cl_2.



(A)



(B)

Isomer A (VIb) has a plane of symmetry which is perpendicular to the plane of the siloxane ring and passes through Si^1 and an O atom at a distance from it. Therefore, the CH_3 groups at Si^2 and Si^3, and also the pairs of o- and m-H atoms of the coordinated Ph group do not differ in the PMR spectrum. Isomer B does not have elements of symmetry, and therefore all the CH_3 groups and pairs of o- and m-protons of the coordinated Ph group should differ. Isomer B can be obtained by double the number of paths, as isomer A, and therefore its content should be twice as large as that of A. Hence, in the spectrum of protons of the coordinated phenyl groups of a mixture of isomers, we should expect 8 signals with a ratio of 1:2 (p), 2:2:2 (o), 2:2:2 (m), and 5 signals of the CH_3 groups in a ratio of 1:2:2:2:2. The experimental spectrum corresponds to these considerations, which indicates an A:B = 1:2 ratio. The signals of the phenyl protons at 5.94, 5.85 (p), 5.92, 5.75, 5.65 (o); 5.52, 5.44, 5.36 ppm (m) are observed in this ratio, and 4 signals of the methyl protons are observed in the 3:2:2:2 ratio, since the signals at 0.491 ppm of $MeSi^1$ of isomer A and one of the Me groups of isomer B coincide. In a similar way, in the PMR spectrum of complex (IX), the methyl protons give 5 signals with intensity ratios of 2:1:2:2:2, which also corresponds to a mixture of type A and B isomers in a 1:2, i.e. statistical ratio.

From the cubic siloxane (XI) a chromium–tricarbonyl complex (XII) could be obtained only by the reaction with $(NH_3)_3Cr(CO)_3$ in boiling dioxane, i.e. under milder conditions [2, 3]. It should be noted that even when a large excess of $(NH_3)_3Cr(CO)_3$ is used, only the mononuclear product is formed. Complexes (VI)-(VIII) can be obtained in this way but in a lower yield than when $Cr(CO)_6$ is used.

The complexes obtained (VIa, b), (VIII) and (XII) are solid yellow substances, and (VII) and (X) are yellow oils at ~20°C. They are stable on storage in a refrigerator and are soluble in most organic solvents, whereby the solubility of complex (XII) in these solvents is much higher than that of the initial compound (XI). The characteristics and the IR spectral data of the complexes are given in Table 1, while the PMR spectral parameters are given in Table 2. In the coordination of the Ph group with $Cr(CO)_3$, there

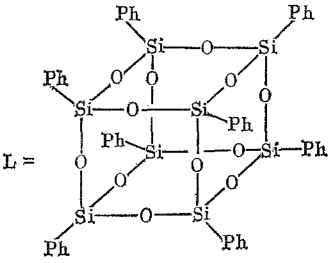
TABLE 2. Parameters of PMR Spectra (δ, ppm)

Compound	Me	CH_2—Si	CH_2—Ph	Ph (coordinated)	Ph (noncoordinated)
(IIIa)	0,59s	–	–	–	7,23–7,51m (*m*, *p*) 7,51–7,64m (*o*)
(VIa)	0,58s, 0,68s (ratio 2 :1)	–	–	5,25 t (*p*) 5,53 d(*o*) 5,75 t(*m*) *J*=6 Hz	7,20–7,47m (*m*, *p*) 7,47–7,65m (*o*)
(IIIb)	0,45s, 0,50s (ratio 1 :2)	–	–	–	7,33–7,91m
(VIb)	0,491s, 0,529s, 0,567s, 0,597s	–	–	5,22–5,98m	7,28–7,88m
(IX)	0,563s, 0,576s, 0,595s 0,616s, 0,674s	–	–	5,28–5,98m	7,28–7,88m
(IV)	0,339s, 0,346s (ratio 1 :2)	1,05–1,25m	2,84–2,99m	–	7,21–7,46m
(VII)	0,208s, 0,220s, 0,226s, 0,256s, 0,267s	0,98–1,15m	2,53–2,69m* 2.69–2,96m† (ratio 1 :2)	5,43–5,88m	7,23–7,48m
(X)	0,208s, 0,224s, 0,258s, 0,270s	0,95–1,12m	2,50–2,67 * 2,67–2,87 † (ratio 2 :1)	5,44–5,79m	7,16–7,39m
(V)	0,112s, 0,128s, 0,135s, 0,144s	0,89–1,01m	2,67–2,82m	–	7,12–7,33m
(VIII)	0,117s, 0,130s, 0,145s, 0,166s	0,87–1,02m	2,56–2,60	5,44–5,74m	–

*In coordinated Ph.

†In noncoordinated Ph.

$$\underset{(XI)}{L + (NH_3)_3Cr(CO)_3} \rightarrow \underset{(XII)}{LCr(CO)_3}$$



is the usual 1.5-2 ppm shift of the aromatic proton signals into the stronger field in the PMR spectra, and the signals of the neighboring CH_2 group in complexes (VII), (VIII) and (X) are shifted in the same direction (by 0.2-0.3 ppm).

Experimental

All the operations in the synthesis and isolation of the compounds studied were carried out in an argon atmosphere using absolute solvents. The IR spectra were run on an IKS-29 spectrophotometer in heptane and the PMR spectra on a Bruker WP-200SY spectrometer (200 MHz) in CD_3COCD_3. Ligands (I)-(III) and (XI) were obtained by standard methods, (IV), according to [4], and (V) according to [5].

Preparation of Complexes (VI)-(X). A mixture of 0.5 g of $Cr(CO)_6$ 2-3 g (excess) of ligand, 50 ml of diglyme and 10 ml of heptane was boiled for 5-6 h. After filtration, the solvent was removed in vacuo, and the residue was chromatographed on a column with silica gel in 10:1 petroleum ether–CH_2Cl_2 mixture. The yellow zone was eluted with a pure CH_2Cl_2, and the solvent was evaporated in vacuo. In the separation of mono- and binuclear complexes, in the case of (VIb) and (IX), (VII) and (X), preparative TLC on silica gel in a 2:1 benzene–petroleum ether mixture was used. The characteristics of the compounds are given in Table 1.

Preparation of Complex (XII). A mixture of 0.5 g of (XI) and 0.2 g (twofold excess) of $(NH_3)_3Cr(CO)_3$ was boiled for 7 h in 50 ml of dioxane. After filtration, the solvent was removed in vacuo, and the product was isolated by preparative TLC on Al_2O_3 in a 2:1 benzene—petroleum ether mixture. The pale-yellow zone was collected, giving 0.12 g (20%) of complex (XII), which was reprecipitated from CH_2Cl_2 by heptane (see Table 1).

Conclusions

The reaction of different cyclosiloxanes with chromium-carbonyls was studied. Mono- and binuclear chromium-tricarbonyl complexes of phenyl-containing cyclosiloxanes were obtained for the first time.

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EFFECT OF BRIDGING LIGANDS ON THE BASICITY OF TRIGONAL OSMIUM CLUSTERS

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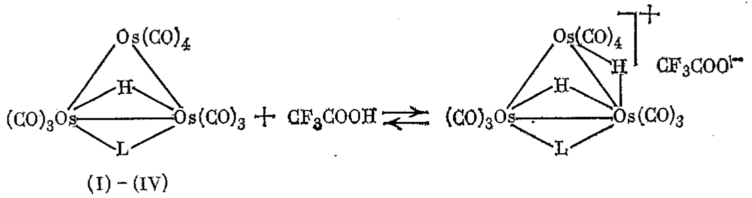
The reactivity of polynuclear metal complexes toward addition of a proton in the form of a bridging hydride ligand upon treatment with acids can be used as an excellent measure of the basicity of the complex. However, only two alternatives have been studied thus far concerning the protonation reactivity of cluster compounds: either the cluster adds a proton upon dissolution in concentrated H_2SO_4 or CF_3COOH, or, due to its low basicity, the complex does not add a proton [1, 2]. This research approach does not make it possible, first of all, to evaluate quantitatively the effects of ligands on the basicity of cluster compounds, and, second, to follow the dynamics of the protonation process.

In the present paper we have investigated using PMR spectroscopy the reactivity of trigonal osmium clusters (I)-(IV), containing various three-electron bridging ligands, with respect to proton addition to give a bridging hydride ligand upon treatment with CF_3COOH in CH_2Cl_2. By varying the concentration of CF_3COOH it was possible to determine the equilibrium concentration ratio of salt and cluster starting material in reaction (1) for all of the clusters under consideration.



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