the filtrate. Found: C 49.16; H 5.06; Si 9.48; Cl 36.10%. $SiC_{12}H_{15}Cl_3$. Calculated: C 49.06; H 5.11; Si 9.54; Cl 36.20%. IR spectrum (ν, cm^{-1}): 495-540 (SiCl), 710-770, 3010 (C_6H_5), 800, 1260 (SiC). Proton NMR spectrum (δ, ppm): 1.2-1.5 multiplet (5H, CHSi, CH_2), 1.7-2.2 multiplet (4H, CH_2), 2.4 multiplet (1H, $\underline{C}\underline{H}C_6H_5$), 7.0-7.3 multiplet (5H, C_6H_5) mass spectrum (m/z): 292 M^+.

CONCLUSIONS

In combination with HCl or H_2O, $EtAlCl_2$ is an active catalyst for alkylation of aromatic compounds by alkenylchlorosilanes, and compounds of boron, titanium, and tin are inactive in this reaction.

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COMPLEXATION OF COPPER(II) WITH 2-DIMETHYLAMINOMETHYLPHENOL

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A series of complexes of o-aminomethylphenols with Cu^{2+} with composition of Cu^{2+} ligand = 1:1 and 1:2 were synthesized [1-3]. However, the stability constant was determined for the 1:2 complex of 2-diethylaminomethylphenol with Cu^{2+} only [3].

In aqueous solutions, o-aminomethylphenols form zwitterions and the tautomeric equilibrium constant may vary over wide limits [4]. In contrast to 2-diethylaminomethylphenol, for which the tautomeric equilibrium is shifted strongly in the direction of the zwitterionic form, 2-dimethylaminomethylphenol (I) contains a commensurate amount of the zwitterionic and neutral forms [4], i.e., in this case, the proton transfer ability is decreased. It was therefore of interest to study the complexation of (I) with Cu^{2+}.

The ionization constants of (I) in a 40% aqueous-alcoholic solution at a ionic strength of 0.1 ($NaNO_3$) were determined by potentiometric titration. They correspond to equations $H_2L^+ \rightleftarrows HL + H^+$ ($pK_a = 8.26$) and $HL \rightleftarrows L^- + H^+$ ($pK_a = 10.85$). The complexation was studied under these conditions. Addition of Cu^{2+} to the solution of (I) causes the appearance of a band with a maximum at 419 nm in the absorption spectrum. The optical density D at the maximum increases with increase in the ligand concentration. At the concentration used, the aqua-complex of Cu^{2+} and the ligand do not absorb near 419 nm.

We studied the influence of the pH of the medium on the complexation at constant Cu^{2+} ($C_{Cu^{2+}}$) and ligand (C_L) concentrations (Fig. 1a). The optical density of the solution reaches saturation at pH values lower than in the case of Cu^{2+} solutions containing 2-diethylaminomethylphenol [3]. Under these conditions (pH ∿ 7.2), the protonated form of the ligand (H_2L^+) is preferentially present in the solution.

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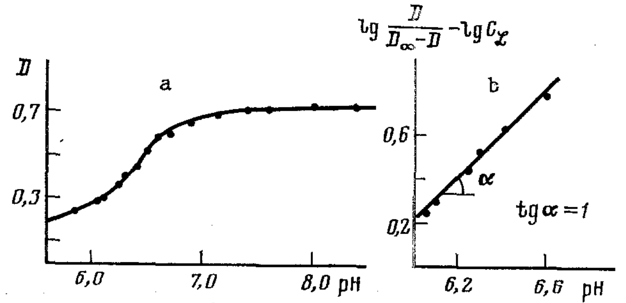

Fig. 1. Dependence of a) optical density of solution (C_L = $3.54\cdot10^{-1}$, $C_{Cu^{2+}}$ = $4.07\cdot10^{-4}$ mole/liter) at 419 nm; b) values of log D/(D∞ − D) − log C_L on pH of medium.

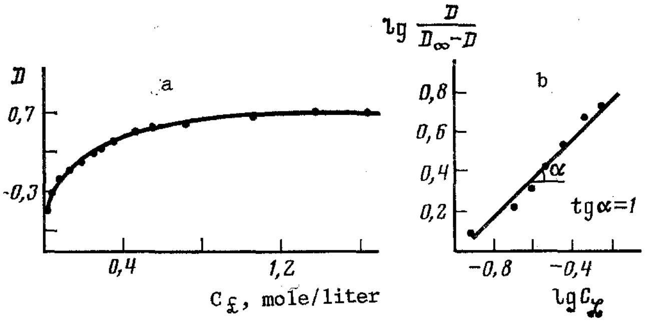

Fig. 2. Dependence of D at 419 nm on C_L (a) and the value of log D/(D∞ − D) on log C_L (b).

Treatment of the dependence of D on pH according to [5] shows that in the complexation one proton is eliminated (see Fig. 1b). With the dependence of D on C_L (Fig. 2a) it is possible to determine the number of ligands, which according to the slope of the log [D/D∞ −D)] vs. log C_L dependence (see Fig. 2b) is equal to unity. In accordance with the results obtained, the complexation of Cu^{2+} with (I) can be represented by equation

$$Cu^{2+} + H_2L^+ \overset{K_p}{\rightleftarrows} [CuHL]^{2+} + H^+ \qquad (1)$$

In contrast to 2-diethylaminomethylphenol [3], the composition of the complex includes a neutral form of a monodentate ligand. Thus, for the formation of the complex in the solution, a higher concentration of the ligand ($3.54\cdot10^{-1}$ mole/liter) is required than in the case of the ethyl derivative ($6.30\cdot10^{-3}$ mole/liter). The absence of polynuclear complexes in the system studied was shown in experiments with varying Cu^{2+} concentrations. Calculation of the stability constants of the complex $\beta = [CuHL]^{2+}/[Cu^{2+}][HL]$ from the D = f (pH) and D = f(C_L) dependences [5] leads to the same values of log β, equal to 2.69 ± 0.05 and 2.60 ± 0.08, respectively. The value of log K_p = −5.60 was found for the equilibrium constant of (1).

In contrast to diethylaminomethylphenol [3], compound (I) forms slightly stable charged complex with Cu^{2+} with a 1:1 composition, as determined by the characteristic features of the acid–base equilbria of these phenols [4]. The neutral form of (I) exists at lower pH (pK_a' = 8.9), while the splitting of a proton from this form is hindered (pK_a'' = 10.72) in comparison with the case of 2-diethylaminomethylphenol with pK_a' = 9.24 and pK_a'' = 10.40 [4]. The differences in the pK_a values of o-aminomethylphenols containing Me and Et substituents at the N atom, are probably due to the solvation features of their neutral and charged forms [6]. The difference in solvation should be also noticeable in the stability constants of the complexes. The solvation effects for (I) favor a higher stabilization of the charged 1:1 complex, and this also leads to its preferential formation.

EXPERIMENTAL

Chemically pure $Cu(NO_3)_2\cdot3H_2O$ and $NaNO_3$ and twice distilled water were used for the preparation of the solutions. 2-Dimethylaminomethylphenol and its phenolate were obtained according to [3].

The optical density of the solutions was measured on the "Specord UV-VIS" spectrometer in cuvettes thermostated at 20 ± 0.10°C. The potentiometric determination of pK_a was carried out by titrating the ligand and its phenolate by NaOH and HCl solutions, with pK_a values calculated according to [7]. A glass electrode was calibrated with reference to HCl solutions in a 40% aqueous–alcoholic solution.

CONCLUSIONS

With Cu^{2+} 2-dimethylaminomethylphenol forms a complex with a 1:1 composition, in which a neutral form of the liquid participates. A stability constant of the complex in the 40% aqueous—ethanol solution has been determined.

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REACTIONS OF ω-HALOALKYLBENZENECHROMIUM TRICARBONYL WITH METAL-CONTAINING NUCLEOPHILES

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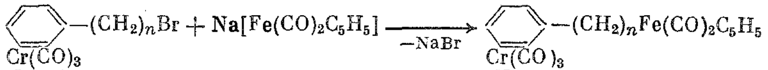
In continuation of investigations on the possiblity of synthesizing ω substituted alkylbenzenechromium carbonyls, which are potential precursors of chelate complexes with a metal—metal bond, we have studied the interaction of ω-bromo derivatives (I) with the anions. $[Fe(CO)_2C_5H_5]^-$ and $[Re(CO)_5]^-$. These anions usually react readily with alkyl halides with the formation of the corresponding σ-complexes as in [1-5].

It was shown that the expected products (II) were formed in the reactions of complexes (I) with $[Fe(CO)_2C_2H_5]^-$ at ∿20°C in THF



(Ia, b) (IIa, b)

$n = 2$ (a), 3 (b).

It should be noted that similar binuclear complexes (n = 0, 1) were obtained previously in [6] by the interaction of σ-phenyl- and σ-benzyl-π-cylcopentadienyliron dicarbonyl with $Cr(CO)_6$ under significantly more drastic conditions. These conditions are unacceptable in the present case due to the inadequate thermal stability of such compounds as $Ph(CH_2)_3Fe(CO)_2C_5H_5$ [7].

Complexes (II), which were solid yellow substances, were completely stable in air, soluble in polar and poorly soluble in nonpolar organic solvents. There were four $\nu C\equiv O$ bands in the IR spectra of (II) in cyclohexane. Two of them, which were attributed to carbonyl bonded to Fe (cf. $Ph(CH_2)_3Fe(CO)_2C_5H_5$ [7]), were appreciably weaker in comparison with the bands of carbonyl groups on a Cr atom (Table 1).

The $[Re(CO)_5]^-$ anions practically did not interact at ∿20°C with (Ib) so that even after extended stirring (8-10 h) the initial compound was recovered almost completely with insignificant contamination by the dehalogenation (reduction) product $C_6H_5C_3H_7Cr(CO)_3$. On extended heating of the reaction mixture practically none of the initial compound remained and together with significant decomposition only the dehalogenation product was detected.

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