are washed with an ethanol/water solution. Determination of carbon content of these samples gives a ratio of 0.9–1.0 mol of RNH_2/mol of $SnCl(OH)AsO_4$. Each proton in $H[SnCl(OH)AsO_4]$ is replaced by an RNH_3^+ ion or is transferred to an intercalated RNH_2 molecule. A ratio slightly below 1.0 is understandable because the chains of the monolayer require an area of 22–24 Å^2/chain, which is slightly larger than the equivalent area of 22 Å^2. Bimolecular arrangements have to be stabilized by an additional uptake of alkylamine molecules or alkylammonium ions together with gegenions.

The bilayer can also be completed by interlamellar sorption of alkanols instead of RNH_2 or RNH_3X. The spacings then increase with the alkanol chain length, as shown in Figure 6 for the dodecylammonium derivative and alkanols $C_{n_A}H_{2n_A+1}OH$, n_A = 4–16. When $n_A = n$, the spacings lie very near or on curve B for tilted bilayers. As the alkanol molecules become longer than the alkylammonium ions, the interlayer structure is determined by bilayers of the tilted alkanol molecules. The spacings with tetra- and hexadecanol thus correspond to those on line B for n = 14 and 16 (Figure 6). In case of $n_A < n$ the spacing is determined by pairs $n_A + n$.[29,30] For instance, the spacing for n = 12 and n_A = 8 agrees with the spacing of the decylammonium derivative under decanol because $n_A + n = 20 = 2 \times 10$.

It is concluded from Figure 5, in which the basal spacings of different systems are collected, that the interlayer arrangement of long-chain alkyl compounds is restricted to a few types of structures: monolayers with perpendicular chains and bilayers with chains tilted at about 56° toward the layer. The all-trans conformation of the chains seems to be preferential. A tilt angle around 56° allows an optimal formation of hydrogen bonds between the terminal NH_2 and NH_3^+ groups and surface oxygen atoms.[26,27]

Thermal Stability. When chlorotin arsenate is heated to above 60 °C, the basal spacing is slightly reduced from 7.90 to 7.63 Å, but the water monolayer is not desorbed below 200 °C. The monolayer form persists up to 320 °C along with the dehydrated form with a spacing of 6.26 Å. At 350 °C the sample becomes amorphous, and at 600 °C, formation of SnO_2 starts. The dehydrated form and the 7.63-Å form rehydrate in contact with water to give spacings of 7.86–7.92 Å (Table V).

The dehydrated forms of chlorotin arsenate and chlorotin phosphate maintain the capability of intercalating guest molecules up to dehydration temperatures of 300 °C. Even if samples are heated at 280 °C for 60 days, the intracrystalline reactivity is not lost (Table VI). After intercalation, the basal spacings of the heated and the air-dried samples are identical or very similar. Only a few compounds (e.g. NMFA in Table VI) do not expand heated samples of chlorotin phosphate.

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Supplementary Material Available: Figure 1, showing scanning electron microphotographs of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ (a) and $H[SnCl(OH)PO_4]\cdot 2H_2O$ (b), and Figure 2, showing powder diffractograms of $H[SnCl(OH)AsO_4]\cdot 2H_2O$ (a) and $H[SnCl(OH)PO_4]\cdot 2H_2O$ (2 pages). Ordering information is given on any current masthead page.

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Syntheses, X-ray Crystal Structures, and Ligand Substitution Kinetics of the Carbon-Bonded Chromium(III) Complexes *trans*-[CrR(acac)$_2$(L)] (R = CH_2Cl, $CHCl_2$; L = H_2O, CH_3OH, Pyridine)

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The alkylchromium(III) complexes *trans*-[CrR(acac)$_2$(H_2O)] (**a**) (R = $CHCl_2$, CH_2Cl; Hacac = 2,4-pentanedione) were prepared by the reaction of $[CrR(H_2O)_5]^{2+}$ with Hacac and triethylamine. Synthetic methods reported previously for $[CrR(H_2O)_5]^{2+}$ (R = $CHCl_2$, CH_2Cl) were improved to give approximately quantitative yields. The complexes *trans*-[CrR(acac)$_2$L] (L = CH_3OH, pyridine) were derived by replacing a coordinated water molecule in **a** with L. The X-ray crystal structure analyses of *trans*-[CrR(acac)$_2$(py)] (R = $CHCl_2$, CH_2Cl) have been performed. The carbon-bonded ligands $CHCl_2$ and CH_2Cl lengthen specifically the Cr–N bond trans to the Cr–C bond in *trans*-[Cr($CHCl_2$)(acac)$_2$(py)] (**b**; Cr–N = 2.154 (7) Å) as well as in *trans*-[Cr(CH_2Cl)(acac)$_2$(py)] (**c**; Cr–N = 2.201 (4) Å). The elongation of the Cr–N bonds in **b** and **c** is reflected in substantial labilization of the ligand substitution reactions at the position trans to R: *trans*-[CrR(acac)$_2$(CH_3OH)] + L ⇌ *trans*-[CrR(acac)$_2$L] + CH_3OH. The rate constants (M^{-1} s^{-1}) at 25 °C in methanol for the formation of *trans*-[CrR(acac)$_2$L] are 85 ± 2 (R = $CHCl_2$, L = py), 98 ± 1 (R = $CHCl_2$, L = 4-methylpyridine), 57 ± 1 (R = $CHCl_2$, L = isonicotinamide), and (1.2 ± 0.5) × 10^3 (R = CH_2Cl, L = py), and the rate constants (s^{-1}) for the backward reaction at 25 °C are 15 ± 1 (R = $CHCl_2$, L = py), 11 ± 1 (R = $CHCl_2$, L = 4-methylpyridine), 33 ± 1 (R = $CHCl_2$, L = isonicotinamide), and (5 ± 2) × 10^2 (R = CH_2Cl, L = py). The rate constants and the activation enthalpies and entropies are consistent with the dissociative ligand substitutions. The results may arise from the weakening of the bond trans to the alkyl group. This study has shown that the alkyl group has a strong electronic effect on the bond trans to the Cr–C bond and has presented evidence for the trans labilization that has been proposed for the rapid ligand substitution reactions of $[CrR(H_2O)_5]^{2+}$ (R = alkyl, benzyl).

Introduction

Organopentaaquachromium(III) complexes have covalent metal–carbon bonds and contain five water molecules. Therefore, they reveal properties of organometallic compounds as well as Werner type complexes. They have been actively studied especially from the kinetic and mechanistic viewpoints.[1] One of the characteristic properties of the organopentaaquachromium(III) complexes is that one of the five coordinated water molecules in them undergoes remarkably rapid substitutions.[2-7] Rapid in-

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corporation of anions such as Cl^-, Br^-, I^-, NCS^-, and $CH_3CO_2^-$ into the coordination sphere of $[Cr(CH_2C_6H_5)(H_2O)_5]^{2+}$ was suggested.[2] Rapid coordination of an acetate ion to $[Cr(CH_2OH)(H_2O)_5]^{2+}$ was demonstrated.[3] The reaction of $[Cr(CF_3)(H_2O)_5]^{2+}$ with a fluoride ion proceeds rapidly to form $[Cr(CF_3)(F)(H_2O)_4]^+$.[4] Kinetic studies have been made for reversible formation of $[CrR(NCS)(H_2O)_4]^+$ (R = CH_2Cl, $CHCl_2$) by the reaction between $[CrR(H_2O)_5]^{2+}$ and a thiocyanate ion.[5-7] Mechanistic studies on the reactions of $[Cr(CH_2CN)(H_2O)_5]^{2+}$ with phosphinate and several carboxylates have been made.[8] These phenomena have been recognized over two decades, and it has been postulated that labilized ligand substitutions occur at the position trans to the Cr–C bond. However, this postulate has not been directly proved because no structurally characterized organochromium(III) complex has been isolated from aqueous solution.

In this study, we have synthesized dichloromethyl and chloromethyl complexes, *trans*-$[CrR(acac)_2L]$ (R = $CHCl_2$, CH_2Cl; L = H_2O, CH_3OH, pyridine),[9] by replacing four coordinated water molecules of $[CrR(H_2O)_5]^{2+}$ with two $acac^-$ ions. The complexes, *trans*-$[CrR(acac)_2L]$ (R = $CHCl_2$, CH_2Cl; L = H_2O, CH_3OH, pyridine), provide an excellent system to investigate the trans labilization that is exerted by the Cr–C bond, since the ligand substitution reactions were found to occur only at the position trans to R. The kinetic investigation was carried out for the ligand substitution reactions

$$trans\text{-}[CrR(acac)_2(CH_3OH)] + L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[CrR(acac)_2L] + CH_3OH \quad (1)$$

where R = $CHCl_2$ and L = py, 4-methylpyridine, and isonicotinamide and where R = CH_2Cl and L = py.[9] This will be instructive to understand the trans labilization, because the CH_2Cl group is much more electron donating than the $CHCl_2$ group, as judged by their Taft's polar substituent constants, σ^*,[10] and the basicities of L range from 3.68 (isonicotinamide) to 6.04 (4-methylpyridine).[11]

Experimental Section

Methanol was purified by distillation over magnesium methoxide. Pyridine and 4-methylpyridine were dried over 4A molecular sieves. Isonicotinamide was recrystallized from diethyl ether. Other reagents were used as received.

Complexes. (a) Preparation of $[Cr(CHCl_2)(H_2O)_5]^{2+}$ (1) Solution. A solution containing 27 g (0.10 mol) of $CrCl_3 \cdot 6H_2O$, 60 g of $CHCl_3$, 8.3 mL of concentrated HCl, 10 mL of water, and 40 mL of ethanol was stirred vigorously with 50–100 g of amalgamated zinc under nitrogen at room temperature. After 2 h, the dark reddish brown solution, containing ca. 0.1 mol of $[Cr(CHCl_2)(H_2O)_5]^{2+}$, was separated from amalgamated zinc by filtration.

(b) Preparation of $[Cr(CH_2Cl)(H_2O)_5]^{2+}$ (2) Solution. A solution of $[Cr(CHCl_2)(H_2O)_5]^{2+}$ prepared by procedure a was rotary evaporated below 30 °C to remove chloroform and ethanol. To this solution were added 8.3 mL of concentrated HCl and 1.3 g of $CrCl_3 \cdot 6H_2O$, and the mixture was stirred with amalgamated zinc under nitrogen at room temperature. After 3 h, amalgamated zinc was filtered off to give a solution containing ca. 0.1 mol of $[Cr(CH_2Cl)(H_2O)_5]^{2+}$.

(c) Synthesis of *trans*-$[Cr(CHCl_2)(acac)_2(H_2O)]$ (3). A 20-g (0.20-mol) sample of 2,4-pentanedione was added to a solution containing 0.1 mol of $[Cr(CHCl_2)(H_2O)_5]^{2+}$. The pH of the solution was adjusted between 5 and 6 during the reaction by careful addition of ethanolic 2 M triethylamine–2 M triethylammonium chloride buffer solution. Then, the reaction mixture was filtered and mixed with 30 mL of water. When the solution was concentrated under reduced pressure below 30 °C, reddish orange crystals separated.[12] The crystals were washed with a small amount of water and dissolved in 200 mL of 50% methanol containing 0.5 M $ZnCl_2$. When the solution was concentrated to small volume, an air-stable red compound, *trans*-$[Cr(CHCl_2)(acac)_2(H_2O)]$, crystallized. Yield: 7.7 g (22%). Anal. Calcd for $C_{11}H_{17}Cl_2CrO_5$: C, 37.52; H, 4.87; Cl, 20.13. Found: C, 37.72; H, 5.03; Cl, 19.70.

(d) Synthesis of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ (4). A solution of **3** (100 mg) in 2 mL of methanol was concentrated to ca. 0.5 mL. When the solution was cooled in a dry ice–acetone bath, red crystals of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ formed. Yield: 40 mg (38%). Anal. Calcd for $C_{12}H_{19}Cl_2CrO_5$: C, 39.36; H, 5.23; Cl, 19.36. Found: C, 39.15; H, 5.38; Cl, 19.09.

(e) Synthesis of *trans*-$[Cr(CHCl_2)(acac)_2(py)]$ (5). A 350-mg sample of **3** was dissolved in 100 mL of water. Upon addition of 2 mL of 1 M aqueous pyridine, orange crystals of *trans*-$[Cr(CHCl_2)(acac)_2(py)]$ precipitated immediately. The compound was recrystallized from warm methanol in the presence of a few drops of pyridine. Yield: 300 mg (73%). Anal. Calcd for $C_{16}H_{20}Cl_2CrNO_4$: C, 46.50; H, 4.88; N, 3.39; Cl, 17.16. Found: C, 46.85; H, 4.97; N, 3.25; Cl, 16.89.

(f) Synthesis of *trans*-$[Cr(CH_2Cl)(acac)_2(H_2O)]$ (6). This complex was prepared by the reaction of $[Cr(CH_2Cl)(H_2O)_5]^{2+}$ and 2,4-pentanedione by a procedure analogous to that for preparations of **3**. The yield of the reddish orange crystals of *trans*-$[Cr(CH_2Cl)(acac)_2(H_2O)]$ was 4.8 g (15%). Anal. Calcd for $C_{11}H_{18}ClCrO_5$: C, 41.59; H, 5.71; Cl, 11.16. Found: C, 41.58; H, 6.07; Cl, 11.19.

(g) Synthesis of *trans*-$[Cr(CH_2Cl)(acac)_2(py)]$ (7). A 2-mL portion of 1 M aqueous pyridine was added in small quantities to a solution containing **6** (320 mg) in 100 mL of water. Orange crystals were col-

Table I. Crystal Data for *trans*-$[Cr(R)(acac)_2(py)]$ (R = $CHCl_2$, CH_2Cl)

	trans-$[Cr(CHCl_2)(acac)_2(py)]$	*trans*-$[Cr(CH_2Cl)(acac)_2(py)]$
formula	$C_{16}H_{20}Cl_2CrNO_4$	$C_{16}H_{21}ClCrNO_4$
fw	413.24	378.80
cryst system	orthorhombic	monoclinic
space group	$A2_1ma$ (variant of No. 36)	Cm (No. 8)
syst absence	(hkl): $k + l = 2n + 1$ $(h0l)$: $h = 2n + 1$	(hkl): $h + k = 2n + 1$
a/Å	14.527 (2)	8.292 (1)
b/Å	17.198 (4)	14.076 (3)
c/Å	8.097 (1)	7.777 (1)
β/deg		92.30 (1)
V/Å^3	2022.9 (6)	907.0 (2)
Z	4	2
d_{calcd}/g cm^{-3}	1.357	1.387
d_{measd}/g cm^{-3}	1.351	1.38
cryst size/mm	0.2 × 0.3 × 0.1	0.5 × 0.3 × 0.2
radiation	Mo Kα	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite	graphite
temp	room temp	room temp
reflcn measd	h,k,l	$\pm h,k,l$
2θ range/deg	2–60	3–65
scan mode	ω–2θ	ω–2θ
ω-scan width/deg	1.3 + 0.5 tan θ	1.4 + 0.5 tan θ
bkgd (count time)/s	8.0	10.0
ω-scan rate/deg min^{-1}	4.0	4.0
no. of unique data	2287	1719
no. of data used with $\|F_o\| > 3\sigma(\|F_o\|)$	819	1481
no. of params refined	120	116
R^a	0.061	0.045
$R_w{}^b$	0.069	0.071
quality of fit indicator^c	2.41	0.64
largest shift/esd, final cycle	0.15	0.03

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o^2]^{-1}$, where a = 0.015 for R = $CHCl_2$ and a = 0.010 for R = CH_2Cl. ^{c} Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

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(9) Abbreviations used in this paper: Hacac, 2,4-pentanedione; Hsal, salicylaldehyde; H_2acen, *N,N'*-ethylenebis(2,4-pentanedione); py, pyridine; 4-Mepy, 4-methylpyridine; ina, isonicotinamide; EDTA, ethylenediamine-*N,N,N',N'*-tetraacetic acid; HEDTA, *N'*-(2-hydroxyethyl)-ethylenediamine-*N,N,N'*-triacetic acid.
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(12) Elemental analyses are consistent with the composition $[(Cr(CHCl_2)(acac)_2)_2(acacH)] \cdot 2H_2O$. Anal. Calcd for $C_{27}H_{42}Cl_4Cr_2O_{12}$: C, 40.31; H, 5.26; Cl, 17.63. Found: C, 40.02; H, 5.54; Cl, 17.93. This compound is under investigation for further characterization.

Table II. Atomic[a] and Thermal[b] Parameters for *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)] and *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py)]

atom	x	y	z	B_{eqv}/Å^2
	trans-[Cr(CHCl$_2$)(acac)$_2$(py)]			
Cr	0	0	1609 (2)	3.5
N	901 (7)	0	3722 (12)	4.4
C(1)	−1014 (9)	0	−289 (15)	4.2
C(2)	548 (11)	0	5257 (19)	6.9
C(3)	1149 (12)	0	6617 (19)	9.0
C(4)	2066 (11)	0	6405 (19)	8.4
C(5)	2425 (11)	0	4828 (22)	6.6
C(6)	1827 (8)	0	3531 (17)	5.3
Cl	−1018 (2)	−836 (2)	−1577 (4)	6.5
O(1)	790 (4)	−797 (4)	627 (7)	5.5
O(2)	−751 (4)	−793 (3)	2688 (8)	4.5
C(7)	1542 (10)	−1990 (9)	96 (20)	10.6
C(8)	753 (8)	−1537 (7)	944 (13)	6.3
C(9)	97 (11)	−1895 (6)	1935 (14)	7.2
C(10)	−599 (7)	−1520 (6)	2727 (13)	5.7
C(11)	−1311 (10)	−1994 (8)	3695 (19)	9.3
	trans-[Cr(CH$_2$Cl)(acac)$_2$(py)]			
Cr	2500	0	5000	2.5
Cl	4229 (2)	0	1293 (2)	7.0
N	427 (5)	0	6681 (5)	2.9
C(1)	4565 (6)	0	3575 (7)	3.7
C(2)	−1107 (7)	0	6142 (7)	3.5
C(3)	−2375 (7)	0	7219 (10)	4.5
C(4)	−2040 (9)	0	8981 (11)	5.1
C(5)	−449 (9)	0	9549 (7)	4.3
C(6)	738 (6)	0	8372 (6)	3.3
O(1)	3466 (3)	967 (2)	6537 (3)	3.3
O(2)	1488 (3)	988 (2)	3550 (4)	3.4
C(7)	4520 (7)	2410 (4)	7554 (7)	4.7
C(8)	3622 (4)	1838 (3)	6198 (5)	3.3
C(9)	2997 (6)	2287 (3)	4711 (6)	4.0
C(10)	1985 (5)	1841 (3)	3474 (5)	3.3
C(11)	1381 (7)	2392 (4)	1910 (6)	4.9

[a] Atomic coordinates are multiplied by 10^4. [b] Given by the equivalent temperature factors.

lected and were recrystallized from warm methanol containing a few drops of pyridine. Yield: 280 mg (73%). Anal. Calcd for $C_{16}H_{21}ClCrNO_4$: C, 50.73; H, 5.59; N, 3.70; Cl, 9.36. Found: C, 50.44; H, 5.69; N, 3.48; Cl, 9.64.

X-ray Crystal Structure Determination of *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)] and *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py)]. Diffraction measurements were made on a Rigaku AFC-5 or a Rigaku AFC-6A four-circle diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental data are listed in Table I. The reflection data were corrected for Lorentz and polarization factors but not for absorption. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. Anisotropic temperature factors were applied for all non-hydrogen atoms. For *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py)], H atoms, except for those of the methyl groups of the 2,4-pentanedionato ligand, were included in the refinement with the fixed positions based on idealized bond geometry. For *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)], no H atoms were included in the refinement. Atomic scattering factors were taken from ref 13. The calculations were performed on a Hitachi HITAC M-200H or a Nippon Electric Co. ACOS-1000 computer using the Universal Crystallographic Computation Program System UNICS III.[14]

Kinetics. When pyridine was added in increasing concentrations to the methanolic solution of **3**, a set of visible absorption spectra was obtained with an isosbestic point at 492 nm. This indicates the occurrence of reaction 1. Kinetic measurements of reaction 1 were made in methanol solutions under psuedo-first-order conditions in the presence of excess L. Reactions were followed spectrophotometrically by using a Union-Giken RA-401 stopped-flow spectrophotometer. The observed rate constants for reaction 1 (R = CHCl$_2$; L = py) were essentially identical when **3** was used as a source of the chromium complex in place of **4** or **5**. This implies that, when **3** is dissolved in methanol, **4** is formed instantaneously. Addition of water up to 0.1 M did not affect the rate constants. We used **6** or **7** as a source of the chromium complex for reaction 1 (R = CH$_2$Cl; L = py). Both **6** and **7** gave essentially the same results.

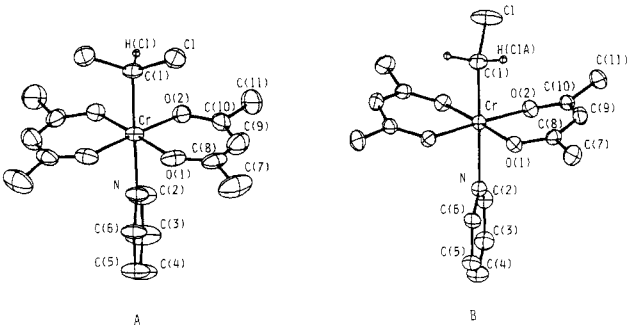

Figure 1. Perspective drawings of *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)] (A) and *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py) (B) with their atom-numbering schemes.

Table III. Bond Lengths and Angles for *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)] (**5**) and *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py)] (**7**)

	Bond Lengths/Å	
	5	**7**
Cr–N	2.154 (7)	2.201 (4)
Cr–C(1)	2.129 (8)	2.077 (6)
Cr–O(1)	1.957 (6)	1.962 (3)
Cr–O(2)	1.953 (6)	1.958 (3)
C(1)–Cl	1.776 (9)	1.785 (6)
N–C(2)	1.35 (1)	1.323 (7)
C(2)–C(3)	1.41 (2)	1.37 (1)
C(3)–C(4)	1.34 (2)	1.39 (1)
C(4)–C(5)	1.38 (2)	1.37 (1)
C(5)–C(6)	1.36 (1)	1.37 (1)
C(6)–N	1.35 (1)	1.330 (7)
O(1)–C(8)	1.30 (1)	1.261 (5)
O(2)–C(10)	1.27 (1)	1.271 (5)
C(7)–C(8)	1.55 (2)	1.501 (7)
C(8)–C(9)	1.39 (2)	1.399 (6)
C(9)–C(10)	1.36 (2)	1.400 (7)
C(10)–C(11)	1.53 (2)	1.511 (7)
	Bond Angles/deg	
	5	**7**
N–Cr–C(1)	173.6 (3)	175.8 (2)
N–Cr–O(1)	88.1 (3)	87.0 (1)
N–Cr–O(2)	89.1 (3)	90.9 (1)
C(1)–Cr–O(1)	96.5 (3)	90.0 (2)
C(1)–Cr–O(2)	86.4 (3)	92.1 (2)
O(1)–Cr–O(2)	91.2 (3)	90.7 (1)
O(1)–Cr–O(1)′[a]	88.9 (3)	87.9 (1)
O(2)–Cr–O(2)′[a]	88.6 (2)	90.5 (1)
Cr–C(1)–Cl	115.2 (4)	115.6 (3)
Cl–C(1)–Cl′[a]	108.1 (5)	
Cr–N–C(2)	120.2 (6)	125.2 (4)
Cr–N–C(6)	120.9 (5)	117.5 (3)
C(2)–N–C(6)	119.0 (8)	117.3 (5)
N–C(2)–C(3)	119.2 (9)	123.9 (6)
C(2)–C(3)–C(4)	121 (1)	118.4 (7)
C(3)–C(4)–C(5)	120 (1)	118.0 (7)
C(4)–C(5)–C(6)	118 (1)	119.4 (7)
C(5)–C(6)–N	123.0 (8)	122.9 (5)
Cr–O(1)–C(8)	125.6 (6)	126.2 (3)
Cr–O(2)–C(10)	127.0 (6)	124.4 (3)
O(1)–C(8)–C(7)	112 (1)	115.3 (4)
O(1)–C(8)–C(9)	125 (1)	125.0 (4)
O(2)–C(10)–C(9)	126 (1)	125.3 (4)
O(2)–C(10)–C(11)	114.8 (9)	115.1 (4)
C(7)–C(8)–C(9)	123 (1)	119.7 (4)
C(8)–C(9)–C(10)	125 (1)	123.9 (4)
C(9)–C(10)–C(11)	119 (1)	119.5 (4)

[a] Symmetry operation (x, $-y$, z).

Results

Crystal Structures of *trans*-[Cr(CHCl$_2$)(acac)$_2$(py)] and *trans*-[Cr(CH$_2$Cl)(acac)$_2$(py)]. Figure 1 shows the X-ray crystal

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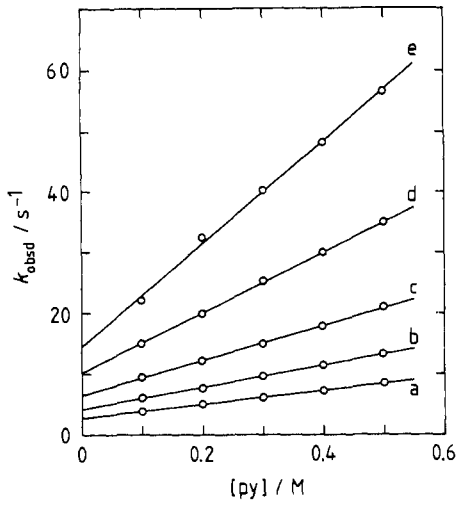


Figure 2. Pseudo-first-order rate constants for the reaction of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ with pyridine in methanol. $[Cr]_T$ = (2.0–3.0) × 10^{-3} M. Temperatures (°C): 6.5 (a); 10.7 (b); 15.0 (c); 20.0 (d); 25.0 (e).

Table VI. Rate Constants and Activation Parameters for the Reactions of *trans*-$[CrR(acac)_2(CH_3OH)]$ (R = $CHCl_2$, CH_2Cl) with Pyridine and Pyridine Derivatives in Methanol at 25 °C

		R = $CHCl_2$		R = CH_2Cl	
L	pK_a[a]	$k_f/M^{-1}\ s^{-1}$	k_b/s^{-1}	$k_f/10^2\ M^{-1}\ s^{-1}$	$k_b/10^2\ s^{-1}$
4-Mepy	6.04	98 ± 1	11 ± 1		
py	5.42	85 ± 2	15 ± 1	12 ± 5[b]	5 ± 2[b]
ina	3.68	57 ± 1	33 ± 1		

	L = py	
	R = $CHCl_2$	R = CH_2Cl
ΔH_f^*/kJ mol^{-1}	73 ± 6	66 ± 9
ΔS_f^*/J K^{-1} mol^{-1}	37 ± 2	30 ± 30
ΔH_b^*/kJ mol^{-1}	61 ± 3	62 ± 7
ΔS_b^*/J K^{-1} mol^{-1}	−17 ± 10	20 ± 20

[a] Values in aqueous solution. [b] Extraporated value.

structures of *trans*-$[Cr(CHCl_2)(acac)_2(py)]$ and *trans*-$[Cr(CH_2Cl)(acac)_2(py)]$ with their atom-numbering schemes. The geometry around the chromium(III) center is octahedral for both complexes. The alkyl ligand, $CHCl_2$ or CH_2Cl, and pyridine take trans positions. The positional parameters are listed in Table II. Table III summarizes the relevant data of the bond lengths and bond angles.

Kinetics. Ligand substitution reactions at the position trans to the Cr–C bond (eq 1) were so rapid that the stopped-flow method was required to follow the reactions. The reactions followed single-step, pseudo-first-order kinetics, and obeyed the rate equation

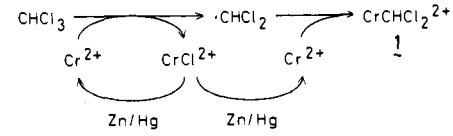
$$-d[complex]/dt = k_{obsd}[complex] \quad (2)$$

$$k_{obsd} = k_f[L] + k_b \quad (3)$$

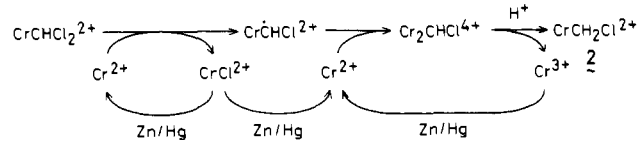
where k_{obsd} is the observed rate constant and k_f and k_b are the forward and the backward rate constants of reaction 1. Figure 2 shows the dependence of the observed rate constants, k_{obsd}, on the pyridine concentrations for the reaction of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ with pyridine. The reaction of *trans*-$[Cr(CH_2Cl)(acac)_2(CH_3OH)]$ with pyridine is much faster than the corresponding reaction with *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$, and the k_{obsd} values are listed in Table IV.[15] Kinetic data for the reactions of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ with 4-methylpyridine and isonicotinamide are listed in Table V.[15] The rate constants, k_f and k_b, and the activation parameters are summarized in Table VI.

(15) Supplementary material.

Scheme I



Scheme II



Discussion

Improved Syntheses of $[Cr(CHCl_2)(H_2O)_5]^{2+}$ and $[Cr(CH_2Cl)(H_2O)_5]^{2+}$. $[Cr(CHCl_2)(H_2O)_5]^{2+}$ (**1**) was originally prepared by the reaction of aqueous chromous ions with chloroform.[16] The reaction is believed to proceed by the scheme

$$Cr^{2+} + CHCl_3 \xrightarrow{slow} [CrCl(H_2O)_5]^{2+} + {}^{\bullet}CHCl_2 \quad (4)$$

$$Cr^{2+} + {}^{\bullet}CHCl_2 \xrightarrow{fast} [Cr(CHCl_2)(H_2O)_5]^{2+} \quad (5)$$

where 2 mol of Cr^{2+} is required to form 1 mol of $[Cr(CHCl_2)(H_2O)_5]^{2+}$. Therefore, the maximum yield of **1** is limited to only 50%, and the $[CrCl(H_2O)_5]^{2+}$ ions are always present in the reaction mixture.

In our improved synthesis of **1**, all the inorganic chromium species present in solution are converted to **1** in the presence of large excess chloroform as shown in Scheme I. The $[CrCl(H_2O)_5]^{2+}$ produced by reaction 4 is reduced to Cr^{2+} by amalgamated zinc and reused for the formation of ${}^{\bullet}CHCl_2$ and $[Cr(CHCl_2)(H_2O)_5]^{2+}$. Also, Cr^{2+} is generated in situ by reduction of $CrCl_3 \cdot 6H_2O$ with amalgamated zinc, which provides convenience in preparation, because it is not necessary to make chromous solutions separately.

Preparation of $[Cr(CH_2Cl)(H_2O)_5]^{2+}$ (**2**) has also been greatly improved in our new procedure. The literature method[17] for the preparation of **2** consists of the reaction between Cr^{2+} and chloroform with more than a 4:1 mole ratio:

$$4Cr^{2+} + CHCl_3 \xrightarrow{H^+} [Cr(CH_2Cl)(H_2O)_5]^{2+} + 2[CrCl(H_2O)_5]^{2+} + Cr^{3+} \quad (6)$$

In reaction 6, it is thought that $[Cr(CHCl_2)(H_2O)_5]^{2+}$ is formed first according to eq 4 and 5 and reacts further with Cr^{2+} by the steps

$$[Cr(CHCl_2)(H_2O)_5]^{2+} + Cr^{2+} \rightarrow [Cr({}^{\bullet}CHCl)(H_2O)_5]^{2+} + [CrCl(H_2O)_5]^{2+} \quad (7)$$

$$[Cr({}^{\bullet}CHCl)(H_2O)_5]^{2+} + Cr^{2+} \rightarrow [((H_2O)_5Cr)_2CHCl]^{4+} \quad (8)$$

$$[((H_2O)_5Cr)_2CHCl]^{4+} \xrightarrow{H^+} [Cr(CH_2Cl)(H_2O)_5]^{2+} + Cr^{3+} \quad (9)$$

In the presently improved method, $[Cr(CHCl_2)(H_2O)_5]^{2+}$ is allowed to react with small amount of Cr^{2+} in the presence of amalgamated zinc, and both $[CrCl(H_2O)_5]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ ions produced by reactions 7 and 9 are reduced by amalgamated zinc to Cr^{2+}. The reaction sequence can be illustrated by Scheme II. Only a catalytic amount of Cr^{2+} is necessary to convert **1** into **2**, and the product solution contains **2** almost exclusively.

Syntheses of *trans*-$[CrR(acac)_2L]$ (R = $CHCl_2$, CH_2Cl; L = H_2O, CH_3OH, Pyridine). Alkylpentaaquachromium(III) complexes have not been considered as useful starting materials for the mixed-ligand organochromium(III) complexes, because of the supposed substitution inertness of the $[CrR(H_2O)_5]^{2+}$.[18] Thus,

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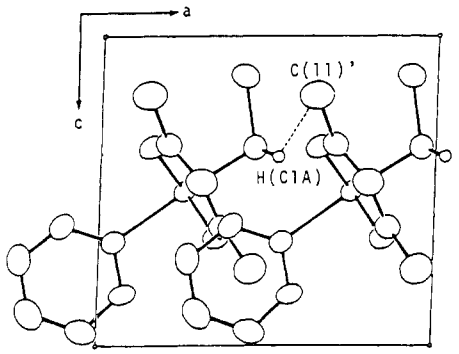

Figure 3. Projection of the crystal lattice of *trans*-$[Cr(CH_2Cl)(acac)_2(py)]$ viewed from the *b* axis.

organochromium(III) complexes of the type $[CrR_F(L\text{-}L)(py)]$ (R_F = perfluoroalkyl groups; L-L = $(acac^-)_2$, $(sal^-)_2$, $acen^{2-}$, etc.) were prepared by the reaction of $[CrR_FCl_2(CH_3CN)_3]$ with bidentate or quadridentate ligand L-L followed by the treatment with pyridine.[18]

However, the present approach to isolate organochromium(III) complexes in aqueous solution by replacing coordinated water molecules with $acac^-$ was successful: We have found that relatively rapid reaction occurs between $[CrR(H_2O)_5]^{2+}$ (R = $CHCl_2$, CH_2Cl) and two $acac^-$ ligands to give *trans*-$[CrR(acac)_2(H_2O)]$. The water molecule trans to R can be easily replaced by other ligands including CH_3OH and pyridine. Our preparative method, with convenient procedures and reasonable yields of desired complexes, opens up a new way to prepare new mixed-ligand organochromium(III) complexes. Thus, it has been found that Hsal also reacts with $[Cr(CHCl_2)(H_2O)_5]^{2+}$ in the presence of Et_3N to give a new complex, $[Cr(CHCl_2)(sal)_2(H_2O)]$, which further reacts with methanol or pyridine to give $[Cr(CHCl_2)(sal)_2L]$ (L = CH_3OH, py).[19]

Crystal Structures of *trans*-$[Cr(CHCl_2)(acac)_2(py)]$ and *trans*-$[Cr(CH_2Cl)(acac)_2(py)]$. The crystal structures of **5** and **7** have shown that the Cr–C bond in **7** (2.077 (6) Å) is shorter than that in **5** (2.129 (8) Å). These values indicate that the Cr–CH_2Cl bond in **7** is stronger than the Cr–$CHCl_2$ bond in **5**, which can be attributed to the difference in electron-donating properties between the CH_2Cl and $CHCl_2$ groups. The Cr–C bond lengths reported for the alkyl- and arylchromium(III) complexes range from 2.01 to 2.11 Å.[20-22] The Cr–C bond in **5** is slightly longer than those reported values. This may be due to the low electron-donating property and the bulkiness of the $CHCl_2$ group. The wider Cr–C–Cl angle (115.2 (4)°) for **5** than that for the sp^3 carbon (109.5°) may also arise from the bulkiness of the $CHCl_2$ group.

The most notable point in the structures of **5** and **7** is that the Cr–N bonds in both complexes are obviously elongated compared to the average Cr–N(pyridine) bond length (2.10 Å) in *mer*-$[Cr(CF_3CO_2)_3(py)_3]$,[23] which has no Cr–C bond. The longer Cr–N bond (2.201 (4) Å) in **7** compared to the bond (2.154 (7) Å) in **5** indicates that the bond weakening is more pronounced in **7** than in **5**. This may be associated with the difference in the Cr–C bond lengths between **5** and **7**.

The Cr–O($acac^-$) bond lengths in **5** (1.953 (6) and 1.957 (6) Å) and **7** (1.958 (3) and 1.962 (3) Å) are, on the other hand, essentially the same as the average Cr–O bond lengths of $[Cr(acac)_3]$ (1.95 Å)[24] and of $[Cr(acac)_2]_2(\mu\text{-}OCH_3)_2$ (1.965 Å).[25] Therefore, the Cr–C bond specifically lengthens the bond trans to the Cr–C bond, while the distances of the Cr–ligand bonds cis to the Cr–C remain unaffected.

Although two $acac^-$ ligands and the chromium center are nearly coplanar in **5**, two $acac^-$ chelate rings in **7** are slightly bent toward the CH_2Cl group. This seems to originate in the repulsion between molecules in a crystal lattice rather than the factors within a molecule: As shown in Figure 3, the distance between H(C1A) and C(11)′ is 3.320 (6) Å, which is close to the sum of the van der Waals radii for the hydrogen and methyl groups (3.2 Å).

Correlation between Molecular Structures and Substitution Rates of Reaction 1. The elongation of the Cr–N bond and the difference of the Cr–N lengths in **5** and **7** are reflected in the rate constants of the ligand substitution reaction (1) (Table VI). Both forward and backward reactions proceed on the stopped-flow time scale, which is behavior quite different from that of the usually known "substitution-inert" chromium(III) complexes. The reaction between **7** and pyridine is one of the fastest ligand substitution reactions of chromium(III) complexes so far studied. The labilized ligand substitution is most likely the result of the weakening of the Cr–ligand bond trans to the Cr–C bond. The reaction of the chloromethyl complex is much faster than that of the dichloromethyl complex, which can be reasonably attributed to the greater extent of the bond weakening at the position trans to the Cr–C bond in **7** compared to that in **5**. The activation enthalpies and entropies of the reactions of *trans*-$[CrR(acac)_2(CH_3OH)]$ with pyridine for both the chloromethyl and the dichloromethyl complexes are similar to each other: relatively small activation enthalpies and close to zero activation entropies. These values suggest that the ligand substitutions are dissociative. This is again consistent with the bond weakening at the position trans to the Cr–C bond. In the reaction of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ with L, the k_f values are rather insensitive to the basicities of ligand L (Table VI). This is in accord with the dissociative substitution.

The structural and kinetic results have revealed that the Cr–C bond has a strong electronic effect specifically on the trans position, resulting in the bond weakening and, in consequence, the great labilization at the trans position.

It is interesting that two $acac^-$ ions replace four water molecules in $[CrR(H_2O)_5]^{2+}$ rapidly. Rapid coordination of an oxygen atom of an $acac^-$ ion is likely to occur at the position trans to the Cr–C bond at first, which is followed by the chelation with migration of the $acac^-$ to the sites cis to the Cr–C bond. The second $acac^-$ may coordinate similarly. Relatively easy incorporation of bidentate and multidentate ligands has been also found in the reaction of $[Cr(CH_2OH)(H_2O)_5]^{2+}$ with EDTA,[26] that of $[Cr(CHCl_2)(H_2O)_5]^{2+}$ with HEDTRA,[27] and those of $[Cr(CH_2CN)(H_2O)_5]^{2+}$ with phosphinate, oxalate, and methyloxalate ions.[8] These examples indicate that a wide variety of ligands may be employed to form mixed-ligand complexes.

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Registry No. **1**, 17477-10-0; **2**, 17477-09-7; **3**, 108111-19-9; **4**, 108111-20-2; **5**, 108111-21-3; **6**, 108969-70-6; **7**, 108969-71-7; $CrCl_3 \cdot 6H_2O$, 10060-12-5.

Supplementary Material Available: Listings of anisotropic temperature factors for **5** and **7**, atomic parameters for hydrogen atoms of **5**, and observed rate constants for the reaction of *trans*-$[Cr(CH_2Cl)(acac)_2(CH_3OH)]$ with pyridine (Table IV) and for the reaction of *trans*-$[Cr(CHCl_2)(acac)_2(CH_3OH)]$ with 4-methylpyridine and isonicotinamide (Table V) (4 pages); listings of observed and calculated structure factors of **5** and **7** (13 pages). Ordering information is given on any current masthead page.

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