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PREPARATION AND PROPERTIES OF ALKYLCHROMIUM DICHLORIDE COMPLEXES

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SUMMARY

A series of monoalkylchromium complexes, $RCrCl_2(THF)_3$ where R = methyl, ethyl, n-propyl and isobutyl and THF = tetrahydrofuran, have been prepared by reactions of chromium trichloride with organoaluminum compounds. Elemental analyses, magnetic susceptibility measurement, electronic and IR spectroscopy and chemical properties of the complexes support the above formulation. The thermal stabilities of the complexes decrease in the order $CH_3 > C_2H_5 > C_3H_9 > C_4H_9$. The effects of the alkyl groups on the rates of decomposition, and on the electronic and IR spectra of the alkylchromium complexes are discussed. The thermal decompositions of the alkylchromium complexes release alkanes, alkenes, dimeric alkanes and THF with more alkane than alkene always being formed. No evidence was obtained for chromium hydride formation in the pyrolysis. Stable pyridine-coordinated alkylchromium complexes were prepared by ligand exchange reactions of $RCrCl_2(THF)_3$ with pyridine. The alkylchromium complexes catalyse ethylene polymerization under mild conditions.

INTRODUCTION

Extensive studies have been made on the preparation, chemical and catalytic properties of alkyl- and arylchromium complexes[1-3]. Most of the studies, however, have been conducted without isolation of the alkylchromium complexes, and the terms "trialkyl" and "monoalkyl" complexes have been employed without unequivocal identification. The names have been assigned mainly on the basis of the ratio of the alkylating agent to the starting chromium compound employed in the reaction.

In a few cases the alkylchromium complexes have been isolated and characterized. The preparation of a methylchromium complex $CH_3CrCl_2(THF)_3$ (THF = tetrahydrofuran) by reaction of chromium trichloride with methylmagnesium chloride in THF has been briefly reported by Kurras[4], and other methylchromium

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complexes containing lithium have been prepared by the reaction of chromium trichloride with methyllithium[5]. Alkylcyclopentadienyldinitrosylchromium π-$C_5H_5Cr(NO)_2R$ compounds ($R=CH_3$, C_2H_5) have been also prepared and characterized[6]. Dialkylchromium chlorides have been prepared by the reaction of $CrCl_3(THF)_3$ with Grignard reagents but the complete removal of the magnesium halides from the isolated complexes is reported to be difficult[7]. The interaction of $CrCl_3$ solvates with diethylaluminum chloride have been studied and binary complexes containing both chromium and aluminum components have been prepared[8]. The isolated binary complexes have been shown to catalyze the ethylene polymerization in combination with Lewis acids. As for aryl and aralkyl complexes, triphenyl-[9], benzyl-[10] and (pyridylmethyl)chromium dichloride[11] are known.

We have now prepared several alkyl–transition metal complexes from Ziegler type mixed catalyst systems[12] and studied the reactions of various olefins with these isolated complexes[13]. These studies yielded considerable information regarding the properties of the alkyl–transition metal complexes and the mechanism of activation of the alkyl–transition metal bonds on interaction of the alkyl complexes with olefins. The extension of our efforts to isolate various alkyl–transition metal complexes and the study of their properties are mentioned in ref. 14.

RESULTS

Alkylchromium dichloride complexes having tetrahydrofuran as ligands were prepared by the reaction of $CrCl_3(THF)_3$ with organoaluminum compounds in THF.

$$CrCl_3(THF)_3 + AlR_3 \text{ (or } AlR_2OEt) \xrightarrow{THF} RCrCl_2(THF)_3 + CrCl_2(THF)_n$$

$$R=CH_3, C_2H_5, \text{n-}C_3H_7 \text{ and i-}C_4H_9 \qquad n=1 \text{ or } 2$$

The formation of the alkylchromium complex was accompanied in some cases by chromous chloride which may be formed by partial decomposition of $RCrCl_2(THF)_3$ with concomittant evolution of a gas. Table 1 summarizes representative conditions for the preparation of $RCrCl_2(THF)_3$, the yields of the alkyl complexes and of the byproducts, and the kind of gases evolved.

As the alkylaluminum compounds, either trialkylaluminums or their corresponding dialkylaluminum monoethoxides were used. Either alkylating agent may be used if the required care is taken to control the reaction temperature. For the complete conversion of the $CrCl_3(THF)_3$ to the alkyl complex, use of four to five times excess of the alkylaluminum compounds was usually necessary. The rate of reaction decreases from the methyl- to the butylaluminum compound, and the thermal instability and the solubility of the alkylchromium complex increase with increase in the length of the carbon chain of the alkyl group, so that isolation and purification of the higher alkylchromium complexes become increasingly difficult. Since both the rates of alkylation and decomposition of the alkylchromium complexes fall with decreasing temperature, a compromise is necessary in setting the reaction temperature and the reaction time to obtain the propyl and isobutyl complexes in reasonable yields, reaction times and purities. Less difficulty was encountered in getting pure methyl and ethyl complexes in high yields. The amounts of the chromous chloride formed were larger in the preparations of less stable alkylchromium, particularly

TABLE 1

PREPARATION OF $RCrCl_2(THF)_3$ FROM $CrCl_3(THF)_3$ AND ORGANOALUMINUM COMPOUNDS

Alkyl	$CrCl_3(THF)_3$ *(mmoles)*	R_3Al *(mmoles)*	R_2AlOEt *(mmoles)*	*THF (ml)*	*Reaction temp. (°C)*	*Reaction time (h)*	*Yield of* $RCrCl_2(THF)_3$ *(%)*	$CrCl_2(THF)_n$[a] *(g)*	*Gases evolved*
CH_3	25		100	150	0~23	5.5	46	2.5	CH_4
	27	125		150	−5~15	5.0	78	0	CH_4
C_2H_5	26		111	80	−5~12	18	97	0.2	C_2H_6
n-C_3H_7	26	38		100	−5~27	6.5	27	3.5	C_3H_8 and C_3H_6
i-C_4H_9	27	40		100	−14~20	70	20	2.0	i-C_4H_{10} and i-C_4H_8

[a] The value of *n* varied between 1 and 2 depending on the preparative conditions.

with longer reaction times and at higher temperatures.

The preparation of the alkylchromium complex starting from chromium(III) tris(acetylacetonate) was also attempted using triethylaluminum or diethylaluminum monoethoxide as the alkylating agent in the presence and absence of other ligands, but the chromium acetylacetonate was found to be more resistant toward alkylation and the starting materials were recovered, in contrast to the behaviour of the Group VIII transition metal compounds[12].

The isolated alkylchromium dichloride complexes and the related chromium chloride complexes are listed in Table 2 along with physical and analytical data. The composition of $RCrCl_2(THF)_3$ was determined from elemental analysis, magnetic susceptibility measurement and chemical reactions. Ethanolysis released one mole of alkane per chromium, while thermal decomposition gave alkane, alkene, and a dimeric product from the alkyl group (*vide infra*), and two moles of THF per chromium.

Displacement of the coordinated THF with pyridine yielded 3 moles of THF per chromium and pyridine-coordinated alkylchromium dichlorides, $RCrCl_2(Py)_3$, where R was methyl or ethyl groups.

The analytical and physical data of the pyridine-coordinated complexes are included in Table 2. These pyridine-coordinated alkylchromium complexes were thermally very stable; the methyl complex was not decomposed above 160°. They were less sensitive to air and moisture than the tetrahydrofuran-coordinated complexes. Higher frequency shifts (20 cm^{-1}) of the in-plane and out-of-plane ring deformations of pyridine in the pyridine coordinated complexes indicated that pyridine is coordinated with chromium through the nitrogen atom[15].

Similarly, the coordinated THF of $CH_3CrCl_2(THF)_3$ was replaced by acetonitrile and 2,2′-bipyridine to give the corresponding isolable complexes. IR spectra clearly showed that all three THF ligands were replaced by these ligands. Alcoholysis of the acetonitrile- and 2,2′-bipyridine-coordinated complexes generated only methane. However, the determination of the number of the new ligands thus introduced was unsuccessful because of the difficulties in purifying the complexes. The reaction of $RCrCl_2(THF)_3$ with carbon dioxide yielded no product of insertion of CO_2 into the Cr–C bond.

The magnetic susceptibilities of these alkylchromium complexes correspond to three unpaired electrons, supporting the formulation as the trivalent chromium complexes. Of the series of the alkylchromium dichloride complexes reported here, $CH_3CrCl_2(THF)_3$ is already known[4]. The melting point and the magnetic susceptibility of our complex are in agreement with those of $CH_3CrCl_2(THF)_3$ prepared from $CrCl_3(THF)_3$ by the Grignard reaction. The higher homologs have been so far regarded unstable and difficult to isolate, but the present approach employing organoaluminum compounds as the alkylating agent provides a convenient route to a series of monoalkylchromium complexes.

Two types of chromous chloride tetrahydrofuranates were obtained along with the alkylchromium complexes, as shown in Table 2. One type had a pale green color, which turned white on drying, had the composition of $CrCl_2(THF)_2$ and a magnetic susceptibility of 5.02 B.M. at 296°K in good agreement with its formulation as the divalent chromium complex with spin-free electronic configuration. The other type was white and had the composition of $CrCl_2(THF)$. The reason why these two distinct species are produced is not clear at present.

TABLE 2

PHYSICAL AND ANALYTICAL DATA FOR ALKYLCHROMIUM DICHLORIDE AND RELATED CHROMIUM COMPLEXES

Complex	*Appearance*	*M.p.* (°C)	μ_{eff} (*B.M.*)	*Analysis found (calcd.) (%)*[a]						*RH*[b] *complex* (%)
				C	*H*	*N*	*Cl*	*Cr*	*THF*	
$CH_3CrCl_2(THF)_3$	Olive green	94 (dec.)	3.84 (289°K)	43.5	7.6		20.1	14.8	63.3	90.1
	leaflets		3.96 (297°K)	(44.1)	(7.7)		(20.0)	(14.7)	(61.1)	
$C_2H_5CrCl_2(THF)_3$	Green cubes	66 (dec.)	3.77 (291°K)	42.9	7.8		20.6	14.2	47.8	91.2
			3.98 (296°K)	(45.7)	(7.9)		(19.3)	(14.1)	(58.7)	
$n\text{-}C_3H_7CrCl_2(THF)_3$	Light green			50.0	8.2		18.5	13.2	52.9	97.1
	cubes			(47.1)	(8.2)		(18.6)	(13.6)	(56.6)	
$i\text{-}C_4H_9CrCl_2(THF)_3$	Green cubes						18.1	13.4	54.0	
				(48.5)	(8.4)		(17.9)	(13.1)	(54.6)	
$CrCl_3(THF)_3$	Violet granules		3.58 (295°K)	38.3	6.6		28.7	13.9		
				(38.7)	(6.5)		(28.6)	(14.0)		
$CrCl_2(THF)_2$	Pale green		5.02 (296°K)	33.8	5.9		27.3	19.6	53.5	
	powder			(36.0)	(6.0)		(26.6)	(19.5)	(54.0)	
$CrCl_2(THF)$	White powder			25.1	4.5		36.0	26.7	37.2	
				(24.6)	(4.1)		(36.4)	(26.7)	(36.9)	
$CH_3CrCl_2(Py)_3$	Light green			50.5	4.5	11.1	19.2	14.5		88.6
	cubes			(51.2)	(4.8)	(11.2)	(18.9)	(13.9)		
$C_2H_5CrCl_2(Py)_3$	Yellowish			53.0	5.2	10.8	18.4	13.3		68.6
	green cubes			(52.4)	(5.1)	(10.8)	(18.2)	(13.4)		

[a] The microanalysis of some chromium complexes was subject to error due to the instability of the complexes.

[b] The amount of alkane (RH) evolved on alcoholysis.

DISCUSSION

Since examples of isolation of a series of alkyl–transition metal complexes with different alkyl chain lengths are limited, the properties of the alkyl complexes were examined and the effects of the alkyl chain length on the properties of the alkyl complexes were investigated.

Thermal stability

Table 3 summarizes the results of thermal decomposition of solid $RCrCl_2(THF)_3$. The thermal stability of the alkylchromium complex decreases in the order $CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_4H_9$ as indicated by the decomposition rates and decomposition temperatures. The same trend was observed with dialkyl-2,2′-bipyridinenickel complexes, and was interpreted in terms of ligand field theory[13].

TABLE 3

THERMAL DECOMPOSITION OF ALKYLCHROMIUM COMPLEXES $RCrCl_2(THF)_3$

R	*Sample (mmole)*	*Decompn. rate at 30°* [a] *(vol. %/h)*	*Decompn. temp.*[b] *(°C)*	*Total Wt. loss (Wt %)*	*Wt. loss of (R+2 THF)*[c]	*Gaseous product distribution (mol %)*		
CH_3	0.974	1.2	85	48.0	103	CH_4 80.6	C_2H_6 18.9	C_2H_4 0.5
C_2H_5	1.038	3.7	70	44.7	95	C_2H_6 48.1	C_2H_4 8.5	C_4H_{10} 43.4
$n\text{-}C_3H_7$	0.497	28.5	40	37.8	78	C_3H_8 71.5	C_3H_6 22.9	C_6H_{14} (5.9)[d]
$i\text{-}C_4H_9$	0.561	52.0	30	32.8	65	$i\text{-}C_4H_{10}$ 77.5	$i\text{-}C_4H_8$ 22.3	C_8H_{18} trace[d]

[a] The sample was allowed to stand at 30°. for 1 h and the percentage gas evolution in this period to the total amount of the decomposition gas was taken as a crude measure of decomposition rate.

[b] The temperature at which smooth decomposition of the complex was observed.

[c] (R+2 THF) represents the calculated sum of the weight of an alkyl group and two THF ligands lost by decomposition.

[d] The value of the content of the higher hydrocarbon in the gas phase do not represent the true proportion in the total decomposition product because of the difference of solubility of the higher hydrocarbon in THF.

The methyl and ethyl complexes lost nearly the amounts of weight expected for the loss of an alkyl group and two THF ligands, whereas the amounts of gases released were smaller for the propyl and isobutyl complexes, presumably due to the prior decomposition of the unstable alkyl complexes during handling. The composition of the gas evolved from each alkylchromium complex was not substantially different from that of the gas evolved during preparation of the complex, although there were some minor differences; *e.g.*, the isobutane to isobutene ratio was greater in the decomposition experiment compared with that in the evolved gas, which contained almost equal quantities of isobutane and isobutene. It is noted that the gas from decomposition in each case contained a much greater amount of the alkane than of the alkene having the same number of carbon atoms as the original alkyl complex, and the proportion of the coupling product of the alkyl group was minor except with the ethyl complex. In the methyl complex, methane constituted the major decomposition product, and was probably formed by hydrogen abstraction from the THF ligands. This assumption was supported by the formation of mainly CH_4 accompanied by only a small amount of CH_3D on heating $CH_3CrCl_2(THF)_3$ in $CDCl_3$ at 90° for 1 h. The thermal decomposition residue heated up to 160° still contained about one mole of THF per chromium as indicated by the weight loss on heating and the IR spectrum of the residue, which is similar to those of $CrCl_2(THF)$ and $CrCl_3(THF)_3$. The formation of a chromium hydride complex has been often postulated on the basis of experiments on the isomerization of olefins by organochromium complexes prepared *in situ* in which the amount of alkanes produced by fragmentation exceeds that of alkenes[1d], but there was no indication of chromium hydride formation in our work. The IR spectra of the decomposition residue showed the absence of a Cr–H stretching band in the 2000 to 2200 cm^{-1} region, and methanolysis of the residue yielded no hydrogen. 1-Butene was not isomerized with the methyl- and ethylchromium complexes. It is thus clear that assignment of the composition of transition metal complexes solely from the gaseous decomposition products evolved during the preparation or the succeeding reactions is not always justified.

Electronic and IR spectra of $RCrCl_2(THF)_3$

Table 4 shows the maxima in the electronic absorption bands of the series of alkylchromium dichloride complexes in THF and the molar extinction coefficients. The absorption band of the alkyl complexes in the UV region (Band I) shifts to lower frequency on going from the methyl through the ethyl to the propyl complex whereas the bands near $2.3 \times 10^4\ cm^{-1}$ (Band II) and $1.4 \times 10^4\ cm^{-1}$ (Band III) show little change with change in the alkyl group. Band I, with a large extinction coefficient, may be ascribed to a charge-transfer from a *d*-orbital of chromium to an antibonding orbital of THF in analogy with our assignment in dialkyl(2,2′-bipyridine)nickel complexes[13]. The small but significant shift of the charge-transfer band may reflect the change of the highest occupied *d*-orbital level with change in the alkyl group attached to chromium. The inductive effect of alkyl groups increases in the order of methyl <

TABLE 4

ELECTRONIC SPECTRA OF ALKYLCHROMIUM AND RELATED COMPLEXES IN TETRAHYDROFURAN

Complex	*Absorption maxima* ($10^4\ cm^{-1}$)		
	Band I ($\varepsilon \sim 2500^a$)	*Band II* ($\varepsilon \sim 300$)	*Band III* ($\varepsilon \sim 20$)
$CH_3CrCl_2(THF)_3$	3.50	2.30	1.44
$C_2H_5CrCl_2(THF)_3$	3.29	2.31	1.49
$n\text{-}C_3H_7CrCl_2(THF)_3$	3.27	2.31	1.43
$i\text{-}C_4H_9CrCl_2(THF)_3$	^{b}	2.31	1.49
$CrCl_3(THF)_3$	3.23 (sh)	1.99	
$CrCl_2(THF)_2$	3.33 (sh)		1.16
$n\text{-}C_3H_7CrCl_2(PPh_3)_2(THF)$	3.86	2.31 2.10	1.46 1.49

^{a} Molar extinction coefficient in $M^{-1}\ cm^{-1}$.
^{b} The complex was too unstable to observe this band correctly.

ethyl< propyl, and thus the energy level of the d-orbital will be raised in this order, making the excitation for the charge transfer from metal to the ligand THF easier in the same order, in agreement with our previous observations with the alkyl–nickel complexes. The absorption maxima of Band I for $RCrCl_2(THF)_3$ plotted against Taft's σ^* values, which indicate the inductive effects of the alkyl groups[16], gave a linear relationship, as shown in Fig. 1.

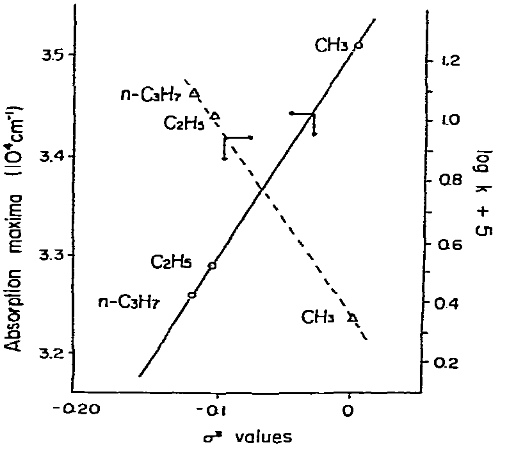

Fig. 1. The effects of alkyl groups on the UV spectra and decomposition rates of $RCrCl_2(THF)_3$. ⊙ Relationship between Taft's σ^* values and the absorption maxima of Band I. △ Relationship between the first order rate constants for decomposition of $RCrCl_2(THF)_3$ in THF and σ^* values.

Band II and III may be due to d–d transitions in the distorted octahedral complexes. The fact that the bands assigned to d–d transitions show little change from one alkyl to another suggests that there is negligible change of the ligand field strength among the alkylchromium dichloride tris(tetrahydrofuranates).

These bands are shifted when the spectra are taken in solvents other than THF, as Table 5 shows. It will be seen that the bands are shifted to higher frequencies in more basic solvents. If these bands were due do d–d transitions, such a change of

TABLE 5

SPECTRA OF $CH_3CrCl_2(THF)_3$ IN VARIOUS SOLVENTS[a]

Solvent	*Absorption maxima* ($10^4\ cm^{-1}$)
Pyridine	2.52, 1.63
Acetonitrile	2.47 (2.18), 1.52
DMF[b]	2.43 (2.30), 1.67
THF[c]	2.30, 1.49
Dioxane[c]	2.30 (2.08), 1.47
Toluene	2.24 (2.08), 1.39
Chlorobenzene	2.22 (2.04), 1.40

[a] Numbers in parentheses show the absorption maxima observed after decomposition.
[b] Dimethylformamide.
[c] Isosbestic point at 510 nm was observed in the course of the decomposition of the complex in solution.

the absorption maxima would reflect the change of the ligand field effect of the solvent.

The thermal decomposition of alkylchromium dichloride complexes in various solvents can be followed spectrophotometrically. The rate of decomposition was first order with respect to concentration of the alkyl complex, and the spectral change is usually accompanied by clear isosbestic points. Table 6 lists the first order rate constants for decomposition of $RCrCl_2(THF)_3$ in various solvents. The decomposition rate for $RCrCl_2(THF)_3$ in THF increases from the methyl through the ethyl to the n-propyl complex, as found for the decomposition of the solids. A plot of log k against the σ^* values gave a linear relationship (Fig. 1), as in the decomposition of the dialkyl-2,2'-bipyridinenickel complexes [13].

TABLE 6

SOLVENT EFFECTS ON THE DECOMPOSITION OF ALKYLCHROMIUM COMPLEXES $RCrCl_2(THF)_3$

R	*Solvent*	*Temp. (°C)*	$k^a \times 10^4$ (*sec*$^{-1}$)
CH_3	Pyridine	21.5	Too slow to measure
	Acetonitrile	18.8	0.82
	DMF	21.5	0.61
	THF	22.5	0.22
	Dioxane	21.5	1.87
	Toluene	24.0	2.10
	Chlorobenzene	21.5	1.96
	n-hexane	Insoluble	
C_2H_5	Pyridine	21.5	Too slow to measure
	DMF	21.5	0.44
	THF	7.0	0.098
	THF	23.5	1.04
	THF	28.5	1.24
	Toluene	22.5	2.12
	Chlorobenzene	22.5	2.21
n-C_3H_7	THF	29.0	1.51
	THF	22.5	1.22
i-C_4H_9	THF	30.5	3.0

[a] k, the first-order rate constants for decompositions of $RCrCl_2(THF)_3$ in various solvents.

The stabilizing effect of pyridine on the alkylchromium complex was so pronounced that no change of the spectra of $RCrCl_2$ was observed in pyridine. The reason for this remarkable stabilization is under investigation. From the temperature dependence of the rate constants for the decomposition of $C_2H_5CrCl_2(THF)_3$ in THF the activation energy for splitting the ethyl–chromium bond was evaluated as 22 kcal/mol.

The effect of change of the alkyl groups σ-bonded with chromium on the shift of the C–O–C stretching bands of THF coordinated with chromium was also studied, as shown in Table 7. The symmetric and antisymmetric ν(C–O–C) bands of free THF shifts to lower frequencies on coordination with chromium complexes, the largest shift being observed in $CrCl_3(THF)_3$. The magnitude of the shift, $\Delta\nu$, decreases in the order $CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_4H_9$ in the alkylchromium complexes,

TABLE 7

FREQUENCY SHIFTS OF THE ν(C–O–C) BANDS OF THF ON COORDINATION WITH CHROMIUM COMPLEXES

Complex	$\Delta\nu_{as}$ (*cm*$^{-1}$)[a]	$\Delta\nu_{s}$ (*cm*$^{-1}$)[b]
$CrCl_3(THF)_3$	31, 61	60
$CH_3CrCl_2(THF)_3$	37, 58	56
$C_2H_5CrCl_2(THF)_3$	28, 53	51
n-$C_3H_7CrCl_2(THF)_3$	27[c], 55	49
i-$C_4H_9CrCl_2(THF)_3$	29[c], 57	46
$CrCl_2(THF)_2$	36	32
$CrCl_2(THF)$	29, 55	37

[a] Frequency shift of antisymmetric C–O–C stretching vibration from that of free THF.
[b] Frequency shift of symmetric C–O–C stretching vibration from that of free THF.
[c] Additional band was observed in the higher frequency side at 1063 cm^{-1}.

TABLE 8

IR BANDS SENSITIVE TO THE CHANGE OF THE ALKYL GROUPS σ-BONDED WITH CHROMIUM[a]

	Absorption bands (*cm*$^{-1}$)
$CH_3CrCl_2(THF)_3$	2790, 623, 492
$C_2H_5CrCl_2(THF)_3$	2798, 1115, 610, 465
n-$C_3H_7CrCl_2(THF)_3$	2795, 1104, 608
$CH_3CrCl_2(Py)_3$	2805, 1121, 646

[a] These bands disappear on thermal decomposition of the alkylchromium complexes except those of $CH_3CrCl_2(Py)_3$.

the tendency being especially clear in the shift of the symmetric ν(C–O–C) band. This tendency is again compatible with the trend in the inductive effects of the alkyl groups bonded to chromium.

The other IR bands sensitive to the change of the alkyl group bonded with chromium are listed in Table 8. The bands in the Table around 2800 cm^{-1} may be assigned to the ν(C–H) bands of the alkyl groups, but for the assignments of other bands further study is required. It is noteworthy that the bands in the region of 600 to 650 cm^{-1} appear to reflect the stabilities of the alkyl complexes.

Catalytic activity of $RCrCl_2(THF)_3$

Wilke briefly reported the catalytic acitivity of tris(π-allyl)chromium for ethylene polymerization[17] and Arakawa reported that dialkylchromium chloride is an effective catalyst for ethylene polymerization when used in combination with Lewis acids[8]. The present aluminum-free alkylchromium dichloride complexes isolated from the Ziegler type catalyst mixtures catalyze the ethylene polymerization at room temperature and reduced pressure. The catalytic activities of the alkyl complexes decreases in the order: methyl > ethyl > isobutyl. Detailed studies of the reactions of the alkylchromium complexes with olefins will be described separately.

EXPERIMENTAL

General

All reactions and manipulations of air-sensitive compounds were carried out under nitrogen or in vacuum.

Analyses

IR spectra in the 4000 to 400 cm^{-1} region were recorded on a Hitachi Model EP-G3 grating spectrophotometer using KBr discs prepared with exclusion of air. The measurements of visible and UV spectra were carried out with a Shimadzu Model SV-50A automatic recording spectrometer using a special cell in which the solution of air-sensitive complex for spectral measurement can be made up in the absence of air.

Magnetic susceptibility measurements were made with a Gouy balance. Gas chromatographic analyses were carried out with a Shimadzu Model 3A-H using appropriate columns.

Chromium and chlorine contents were analyzed by the method described in the literature[8] with a slight modification. Microanalyses of carbon, hydrogen and nitrogen were performed by Mr. T. Saito of our laboratory. The THF contents in the complexes were determined by gas chromatographic analysis of the displaced THF by pyridine using toluene as the internal standard.

Reagents

Solvents were purified and dried by the usual procedures and stored under nitrogen. Chromium trichloride tris(tetrahydrofuranate) was prepared from sublimed $CrCl_3$ (Riedel. De Haen A.G.) according to the method described by Zeiss[18]. The complex thus prepared proved sufficiently pure for the reactions and was used without further recrystallization. (Found: C, 38.3; H, 6.6; Cl, 28.7; Cr, 13.4. $C_{12}H_{24}Cl_3CrO_3$ calcd.: C, 38.7; H, 6.5; Cl, 28.6; Cr, 14.0%.)

Dialkylaluminum monoethoxides were prepared from trialkylaluminum and ethanol[12].

Preparations of alkylchromium dichloride tris(tetrahydrofuranate)

The preparations of the series of alkylchromium complexes were mainly carried out in the same way but with some modifications depending on the particular alkyl group present. As a typical example the preparation of $CH_3CrCl_2(THF)_3$ will be given below, and comments made on the modifications required for preparing the other alkylchromium homologs.

To a suspension of $CrCl_3(THF)_3$ (25 mmoles) in 150 ml of THF kept at $-5°$ trimethylaluminum (125 mmoles) was added dropwise during 30 min. During addition of the trimethylaluminum evolution of methane was observed. The reaction mixture was stirred for 1 h at $-5°$ and then allowed to warm to room temperature. The color changed from the initial bluish purple to brown and then dark green. After 5 h the green crystals formed were filtered and washed three times with 20 ml of THF. The filtrate and the washings were combined and cooled at $-25°$ for 2 days to give further crops of green crystals. The green crystals were combined and recrystallized from THF. The complex thus obtained was dried below $-5°$ *in vacuo* for 8 h and olive green leaflets were obtained. The complex is very sensitive to air and moisture, soluble in ethers, ketones, fairly soluble in aromatic hydrocarbons, and insoluble in aliphatic hydrocarbons. The production of the green complex was sometimes accompanied by formation of chromous dichloride, which is less soluble in THF and can be removed by dissolving the alkyl complex in THF and filtering off the chromous dichloride.

In the case of preparation of the propyl or isobutyl complex the higher solubility of the alkyl complex necessitated special precautions and procedures. When the solution had turned brown in the reaction of $CrCl_3(THF)_3$ with the alkylaluminum compound, the reaction was stopped without waiting for the color to change to green, and the insoluble precipitate containing the unreacted $CrCl_3$ and $CrCl_2$ complexes was separated from the solution at about 0°. The solution was concentrated and some hexane was added, the insoluble matters were removed by filtration, and the filtrate was cooled to −78° overnight to give green crystals. These crystals were washed at the temperature and then recrystallized from the 1/1 mixture of n-hexane and THF. The green complex thus obtained was dried at −20° for 20 h. The propyl and isobutyl complexes are very soluble in THF. The alkyl complexes are moderately stable in THF solutions and can be handled at room temperature, but in the solid state and in the absence of excess THF the complexes are less stable and must be handled at low temperatures.

Ligand exchange reaction

Methylchromium dichloride tris(tetrahydrofuranate) (2.91 mmoles) was mixed at −20° with pyridine (20 mmoles) and was allowed to react at room temperature overnight. The mixture was concentrated, and cooled to −20°. The dark green cubes precipitated were filtered and recrystallized from pyridine (10 ml), and dried below 15° for 20 h *in vacuo*. The yellowish green cubes were isolated in 70% yield. The ethyl homolog was prepared in 45% yield in a similar manner except that a pyridine/n-hexane mixture was used instead of pyridine.

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