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PREPARATION OF NEW ALKYLCHROMIUM COMPLEXES $RCrCl_2(BASE)_n$ ($R = CH_3, C_2H_5$) AND EFFECTS OF THE BASE ON THEIR THERMAL STABILITY

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Summary

New alkylchromium complexes of the type $RCrCl_2(Base)_n$ ($R = CH_3, C_2H_5$) have been prepared by ligand exchange reactions of $RCrCl_2(THF)_3$ (THF = tetrahydrofuran) with methylpyridines and primary amines (n-propylamine and n-butylamine); n = two for 2-methylpyridine, three for 3- and 4-methylpyridines, and four for primary amines. The thermal stability of the isolated complexes is discussed in terms of the electronic and steric effects of the coordinated bases and of ease of abstraction of hydrogen from the bases by the alkyl groups. Hydrogen abstraction from the CH_3 group attached to chromium by another CH_3 group to form methane and a carbenoid species is proposed as a possible pathway in thermolysis of the solid methylchromium complexes coordinated with THF, pyridine and methylpyridines on the basis of CH_2D_2 evolution on addition of D_2O to the thermal decomposition residues.

Introduction

The problem of the stability and reactivity of a transition metal complex with a σ-metal-to-carbon bond is one of the central themes in organotransition metal chemistry [1-3]. The number of alkyltransition metal complexes isolated has increased remarkably in the past decade and some theories concerning the thermal stability of alkyltransition metal complexes have been suggested. Some of these theories have been proposed on the basis of empirical facts that some alkyltransition metal complexes have been successfully prepared and others not. Obviously, failure in the attempted isolation of an alkyltransition metal complex does not imply that the particular complex, if prepared under more suitable reaction conditions, is thermally unstable.

The role of a "stabilizing ligand" such as a tertiary phosphine or an organic nitrogen base has been explained in terms of an electronic effect [2] and of a steric effect which blocks the site for β-elimination [1b,3]. In order to put the discussion on the stability of the alkyltransition metal compound on a more solid basis, a systematic study concerning the effects of ligands is needed. This paper describes a part of our project to study the effect of stabilizing ligands on the stability of alkyltransition metal complexes.

Previously we reported the preparation and properties of $RCrCl_2(THF)_3$ ($R = CH_3$, C_2H_5, n-C_3H_7 and i-C_4H_9; THF = tetrahydrofuran). The THF ligands in these alkylchromium complexes can be readily replaced by pyridine to give $RCrCl_2$(pyridine)$_3$ [4]. The ease of the replacement of the THF ligands by pyridine prompted us to prepare a series of alkylchromium complexes coordinated with bases and to study the effects of the bases on the stability and reactivity of the resulting alkylchromium complexes.

Experimental

Materials and general procedures

$RCrCl_2(THF)_3$ was prepared by a previously reported method [4]. Solvents and bases were dried, distilled, and stored under nitrogen. Preparation and handling of the air-sensitive alkylchromium complexes were carried out under nitrogen or in vacuum. Spectral, elemental and gas chromatographic analyses were made as previously reported [4]. Analytical and IR spectral data of the isolated alkylchromium complexes are summarized in Table 1.

Preparation of $RCrCl_2$(methylpyridine)$_n$

3-Methylpyridine (6.0 ml, 61 mmol) was added to $CH_3CrCl_2(THF)_3$ (4.0 g, 11 mmol) dispersed in 12 ml of tetrahydrofuran at —30°C. The mixture was stirred at —30°C for 4 h. The white-green cubes which were precipitated were filtered and recrystallized from a 1/1 mixture of the pyridine and tetrahydrofuran to give CH_3CrCl_2(3-methylpyridine)$_3$ in 50% yield. $C_2H_5CrCl_2$(3-methylpyridine)$_3$, $RCrCl_2$(4-methylpyridine)$_3$ and $RCrCl_2$(2-methylpyridine)$_2$ (R = Me, Et) were prepared similarly. Preparation of $RCrCl_2$(methylpyridine)$_n$ from $CrCl_3$(methylpyridine)$_3$ and AlR_3 or $AlR_2(OC_2H_5)$ was unsuccessful.

Preparation of $RCrCl_2$(Primary amine)$_4$

n-Butylamine (10 ml, 100 mmol) was added dropwise to a suspension of $CH_3CrCl_2(THF)_3$ (2.0 g, 5.5 mmol) in 10 ml of tetrahydrofuran at —70°C. The color of the solution immediately changed from light green to deep green and a homogeneous solution was obtained. On warming the solution to —50°C, the color turned red. At —30°C reddish crystals started to deposit. The reddish crystals obtained by allowing the reddish solution to stand at —30°C overnight were filtered, washed thrice with ether, and dried in vacuum. CH_3CrCl_2(n-butylamine)$_4$ was isolated in 90% yield. $RCrCl_2$(n-propylamine)$_4$ (R = Me, Et) was prepared similarly. The alkylchromium complexes containing the primary amines are not soluble in common organic solvents except for THF. Attempted recrystallization from THF containing the primary amine led to a complex which appears to contain both THF and the amine ligands. The analytical data for the ethyl complex was close to but not satisfactory for its formulation as $EtCrCl_2$(n-propylamine)$_4$. (Found: C, 41.6; H, 10.9; Cl, 17.0; Cr, 15.0; N, 14.3. $EtCrCl_2$(n-propylamine)$_4$

calcd.: C, 43.3; H, 10.6; Cl, 18.3; Cr, 13.4; N, 14.4%.) Ethanolysis released 75% of the calculated value of ethane.

Preparation of alkylchromium dichloride with deuterated ligands

$CH_3CrCl_2(pyridine\text{-}d_5)_3$ was prepared by adding 1 ml of pyridine-d_5 to 0.2 g of $CH_3CrCl_2(THF)_3$. The mixture of $CH_3CrCl_2(THF)_3$ and pyridine-d_5 was stirred for 3 h at room temperature and dried in vacuum. According to the IR spectrum of the isolated complex, all of the THF ligands were replaced by pyridine-d_5. $CH_3CrCl_2(THF\text{-}d_8)_3$ was obtained from a mixture of 0.3 g of $CH_3CrCl_2(THF)_3$ and 1 ml of tetrahydrofuran-d_8. The mixture of $CH_3CrCl_2(THF)_3$ and tetrahydrofuran-d_8 was stirred at —20°C for 24 h and dried in vacuum. According to the mass spectrum of the tetrahydrofuran released on thermolysis of the methylchromium complex, 70% of the tetrahydrofuran in the complex was replaced by tetrahydrofuran-d_8.

Results and discussion

Ligand exchange reaction of $RCrCl_2(THF)_3$ with bases

The THF ligands in $RCrCl_2(THF)_3$ were readily replaced by bases such as methylpyridines and primary amines below —30°C and alkylchromium complexes coordinated with the bases were isolated from the mixtures of $RCrCl_2(THF)_3$ and bases.

In the cases of 3- and 4-methylpyridines, complexes of the type $RCrCl_2(methylpyridine)_3$ were isolated. These are analogous to pyridine complexes prepared previously [4]. On the other hand, the reaction with 2-methylpyridine gave alkylchromium dichloride coordinated with only two base molecules, $RCrCl_2(2\text{-methylpyridine})_2$, probably as a result of a steric effect. Higher frequency shifts (10-40 cm^{-1}) of in-plane and out-of-plane ring deformation of the methylpyridines in the complexes indicated the coordination of the methylpyridines with chromium through the nitrogen atom [5].

Methylchromium dichloride complexes containing four molecules of primary amine, $CH_3CrCl_2(primary\ amine)_4$, were obtained by ligand exchange reactions of $CH_3CrCl_2(THF)_3$ with n-propylamine and n-butylamine. Frequency shifts of the symmetric (130 cm^{-1}) and antisymmetric (200 cm^{-1}) stretching vibrations of NH_2 of the primary amines to lower frequency were observed. The sparing solubility of the complexes in non-polar solvents such as benzene and diethyl ether may be an indication of an ionic structure such as $[CH_3CrCl(primary\ amine)_4]^+Cl^-$. Analytical and IR data for the isolated alkylchromium complexes are listed in Table 1. Considerable difficulty was encountered in the analyses of air-sensitive complexes.

In addition to the complexes tabulated in Table 1, some other base-coordinated alkylchromium complexes were prepared. The reaction of cyclohexylamine with $RCrCl_2(THF)_3$ in THF gave a light green complex of $RCrCl_2$ coordinated with cyclohexylamine as judged from the elemental analysis and the amount of alkane evolved on ethanolysis. Attempts at recrystallization, however, failed due to the lack of a suitable solvent.

In reactions of triethylamine, dimethylbenzylamine, aniline, piperidine, triethylphosphine or tri-n-butylphosphine with $RCrCl_2(THF)_3$ in THF at —30 to

TABLE 1

ANALYTICAL AND IR DATA OF ALKYLCHROMIUM DICHLORIDE COORDINATED WITH BASES[a]

Complex[b]	Color	Analysis found (calcd.) (%)					RH[c] (%)	IR band[d] (cm^{-1})
		C	H	N	Cl	Cr		
$MeCrCl_2(4\text{-}MePy)_3$	Light green	53.4 (54.7)	5.7 (5.8)	9.8 (10.1)	17.1 (17.0)	12.9 (12.5)	100	545, 490
$MeCrCl_2(3\text{-}MePy)_3$	Yellow green	53.5 (54.7)	5.8 (5.8)	9.9 (10.1)	15.9 (17.0)	12.5 (12.5)	85	650, 640, 405
$MeCrCl_2(2\text{-}MePy)_2$	Brick red	45.1 (48.2)	5.7 (5.2)	8.1 (8.6)	22.3 (21.9)	15.4 (16.0)		
$EtCrCl_2(4\text{-}MePy)_3$	Light yellow	54.9 (55.7)	6.1 (6.0)	9.8 (9.7)	18.1 (16.5)	11.8 (12.1)	85	535, 490
$EtCrCl_2(3\text{-}MePy)_3$	Yellow green	52.6 (55.7)	6.0 (6.0)	9.3 (9.7)	17.1 (16.5)	12.1 (12.1)	75	650, 640, 410
$EtCrCl_2(2\text{-}MePy)_2$	Brick red	47.5 (49.7)	5.6 (5.6)	7.9 (8.3)	21.9 (21.0)	15.4 (15.4)	75	645, 435
$MeCrCl_2(NH_2n\text{-}C_3H_7)_4$	Pink	41.0 (41.7)	10.8 (10.4)	15.2 (15.0)	19.8 (19.0)	12.1 (13.9)	75	3200, 3080
$MeCrCl_2(NH_2n\text{-}C_4H_9)_4$	Light orange	47.5 (47.5)	11.5 (10.9)	13.4 (13.0)	20.2 (16.5)	11.7 (12.1)	80	3200, 3050

[a] Cr content was determined by the method described in the literature [7]. [b] MePy = methylpyridine. [c] The amount of alkane (RH) evolved on ethanolysis. [d] In-plane and out-of-plane ring deformation for the methylpyridine complexes and ν(N—H) for the primary amine complexes observed as KBr discs.

—70°C, color changes of the solution were observed, indicating replacement of the THF ligand by base. However, in most cases the reactions were accompanied by evolution of alkanes and alkene (ethylene from the ethyl complex), indicating cleavage of the R—Cr bond.

Less basic ligands such as thiophene, furan and triphenylphosphine did not replace the THF ligands in $RCrCl_2(THF)_3$ in a temperature range from —70 to 30°C and the changes in the visible spectrum of $RCrCl_2(THF)_3$ on addition of these bases to the THF solution were negligible in contrast to the profound change of the spectrum on addition of the primary amines and methylpyridines.

Thermal stability

Table 2 summarizes the decomposition temperature, and the compositions and amounts of evolved gases on thermolysis of the base coordinated alkylchromium complexes. If the decomposition temperature is taken as the simplest criterion for thermal stability of an alkyltransition metal complex*, several features emerge which may have some significance in the discussion of thermal stability of an alkyltransition metal complex.

(1) The methylchromium complexes containing THF, pyridine and methylpyridines show higher thermal stability than the corresponding ethyl complexes.

(2) Replacement of the THF ligands by pyridine and methylpyridines resulted in pronounced enhancement of the thermal stability of the alkylchromium complexes. The thermal stability of $RCrCl_2(base)_3$ type complexes increased

TABLE 2

THERMOLYSIS DATA FOR THE ALKYLCHROMIUM COMPLEXES

	Dec. temp.[a] (°C)	Evolved gas[b]			R/Cr[c] (%)
		CH_4/C_2H_6	$C_2H_4/C_2H_6/C_4H_{10}$	Other	
$MeCrCl_2(THF)_3$	85	3/1			60
$MeCrCl_2(Py)_3$	190	1/1			65
$MeCrCl_2(2\text{-}MePy)_2$	130	1/1			60
$MeCrCl_2(3\text{-}MePy)_3$	150	13/1			50
$MeCrCl_2(4\text{-}MePy)_3$	200	7/3			65
$EtCrCl_2(THF)_3$	60		1/6/5		50
$EtCrCl_2(Py)_3$	130		1/3/5		65
$EtCrCl_2(2\text{-}MePy)_2$	100		3/7/4		50
$EtCrCl_2(3\text{-}MePy)_3$	115		1/8/1		45
$EtCrCl_2(4\text{-}MePy)_3$	145		2/5/3		50
$MeCrCl_2(NH_2Pr)_4$	70			CH_4	90
$MeCrCl_2(NH_2Bu)_4$	75			CH_4	90
$EtCrCl_2(NH_2Pr)_4$	70			C_2H_6	90

[a] The temperature at which smooth decomposition of the complex was observed. [b] Evolution of trace amounts of C_2H_4 and H_2 was observed for the methyl complexes coordinated with THF, pyridines and methylpyridines. [c] The amount of $(CH_4 + 2C_2H_6)$ for methyl complexes and $(C_2H_6 + C_2H_4 + 2C_4H_{10})$ for ethyl complexes per chromium.

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* It should be noted that in some cases the variation in the decomposition temperature of a series of alkyltransition metal complexes does not parallel the variation in their activation energy for thermolysis as we observed in thermolysis of a series of alkylcopper complexes [6]. In the thermolysis of the alkylcopper complexes the activation energy of thermolysis decreased in the order of i-Bu > Pr > Et, whereas the decomposition points showed only small differences.

in the order: THF < 3-methylpyridine < pyridine < 4-methylpyridine. These results may indicate the importance of the electronic effect in determining the stability of the alkyltransition metal complexes. The trend is basically in line with our previously proposed hypothesis explaining the thermal stability of an alkyltransition metal complex in terms of an energy gap between the lowest unoccupied or half-filled *d*-orbital and a bonding alkylmetal orbital [2c,4], i.e. the coordination of a base to an alkyltransition metal complex would raise the energy of the *d*-orbital thus making the electronic promotion less easy and making the complex more stable. Alkylchromium dichloride complexes containing two 2-methylpyridine ligands showed somewhat lower stability in comparison with the 3- and 4-methylpyridine-coordinated complexes. The reason may be accounted for either by the presence of a vacant site in the 2-methylpyridine-containing complex or by interaction of the methyl group in the pyridine with the neighboring chromium-bonded alkyl group.

(3) Alkylchromium complexes containing primary amines are thermolyzed at lower temperatures than the corresponding complexes containing pyridine bases, in spite of the higher basicity of the primary amines. Examination of the thermolysis gas reveals that in the thermolysis of the primary amine-coordinated complexes about 1 mole of RH (alkanes) was evolved per mole of the alkylchromium complex and no olefin or coupling products of the alkyl groups were produced. The results differ markedly from thermolysis of the THF- and pyridine-coordinated complexes which liberated methane and ethane from the methyl complex, and ethylene, ethane and butane from the ethyl complex. The coordinated primary amines may provide a low energy pathway involving hydrogen abstraction from the coordinated amine by the chromium-bonded alkyl group. Abstraction of hydrogen in a ligand by an alkyl or an aryl group bonded to titanium has been reported [8].

In order to get further insight into the mechanism of thermolysis we prepared methylchromium dichloride complexes containing deuterated THF and pyridine ligands and examined their thermolysis gases by mass spectrometry. $MeCrCl_2$ coordinated with THF-d_8 on thermolysis at 85°C liberated CH_4 and C_2H_6 in a ratio of 3/1 with negligible amounts of H_2, CH_3D and ethylene. $MeCrCl_2$(pyridine-d_5)$_3$ on thermolysis at 190°C released methane containing less than 10% of CH_3D. On addition of D_2O to the thermolysis residue of $MeCrCl_2$(pyridine-d_5)$_3$ further evolution of methane (3 mole % based on the methylchromium complex) was observed which consisted of 80% CH_3D and 20% CH_2D_2 and a trace amount of CH_4. CH_3D is considered to be formed from the remaining methylchromium complex, resistant to thermolysis, and CH_2D_2 from a carbenoid complex formed during thermolysis. Evolution of a small amount of ethylene from the methyl complex on thermolysis also supports the formation of the carbenoid species. These results suggest that in the thermolysis of the methylchromium complex an α-elimination process provides an important decomposition pathway. Formation of a carbenoid species during pyrolysis [8a, 8c] and photolysis [9] of methyltitanium complexes and during degradation of methylchromium complexes prepared in situ in the presence of diphenylacetylene [10] has been proposed, and recently isolation of an alkylcarbene complex of tantalum has been reported [11].

In the thermolysis of the ethylchromium complex, on the other hand, disproportionation occurred and coupling products of the ethyl group were produced.

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