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Bis(2,4-pentanedionato)phenylchromium(III). Preparation and Reactions with Organic Carbonyl Compounds and Alcohols

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A phenylchromium complex $CrPh(acac)_2$ (**1**) (acac=2,4-pentanedionato ligand) was prepared from $Cr(acac)_3$ and $AlPh_3 \cdot Et_2O$. Complex **1** reacts with acetone to give benzene, 2-phenyl-2-propanol, and mesityl oxide and is converted into a hydroxo complex $[Cr(OH)(acac)_2]_2$. The mechanism involving the insertion of the carbonyl group of acetone into the Ph–Cr bond giving an alkoxo intermediate is proposed. Reactions of **1** with esters proceed similarly to give diphenylmethanol derivatives and alkoxochromium complexes. Complex **1** reacts with ROH to give benzene and alkoxo complexes $[Cr(OR)(acac)_2]_n$ (n=1 or 2) which were characterized by means of IR spectra, elemental analyses, molecular weight measurements, magnetic susceptibilities, and chemical reactions. The reactions of **1** with β-dicarbonyl compounds yield corresponding mixed chelate complexes $Cr(\beta\text{-dic})(acac)_2$, where β-dic=diethyl malonato and 1-ethoxy-1,3-butanedionato ligands.

A number of organochromium(III) complexes having σ-alkyl or aryl bond have been prepared by treatment of chromium(III) halides with alkyl(aryl)ating agents such as Grignard reagents, organolithium and aluminium compounds.[1] Most monoalkyl or monoaryl organochromium(III) complexes thus prepared such as $CrRCl_2(thf)_n$[2,3] and its phenyl analog, $CrPhCl_2(thf)_3$[4] (thf=tetrahydrofuran), contain halogen ligands. In the course of our studies on preparation of phenyl complexes of various transition metals using triphenylaluminium as arylating agents,[5–9] we found that a new, halogen-free, monophenylchromium complex $CrPh(acac)_2$ (**1**) was prepared from the system consisted of tris(2,4-pentanedionato)chromium(III), $Cr(acac)_3$ (acac stands for 2,4-pentanedionato ligand), $AlPh_3 \cdot Et_2O$, and tetrahydrofuran. Although extensive studies have been made on the systems consisted of alkyl- and arylaluminium compounds and $Cr(acac)_3$ with special reference to its catalytic behavior towards olefin and diene polymerization,[10] no characterizable compound has been isolated from the system. Sartori and Costa[11] suggested formation of an adduct between $Cr(acac)_3$ and $AlPh_3$ in a benzene solution through IR and ESR spectroscopic studies and conductivity measurements, but the characterization is not unequivocal. The only reasonably well established organochromium(III) complex so far isolated starting from $Cr(acac)_3$ is $CrBr(\eta\text{-}C_5H_5)(acac)$, which was prepared from $Cr(acac)_3$ and $Mg(C_5H_5)Br$.[12]

Although phenylchromium(III) complex of the type $CrPhCl_2(thf)_3$ has been known,[4] the study of its reactions is limited only to the oxidation with $HgCl_2$ and I_2.[1] In view of the importance of the species possessing carbon to transition metal σ-bond in a catalytic C–C bond formation reaction, we studied the reactions of the organic carbonyl compounds with phenylchromium complexes $CrPh(acac)_2$ (**1**) and $CrPhCl_2(thf)_3$. The reactions of **1** with some organic compounds having an active hydrogen such as alcohols and β-dicarbonyl compounds were also investigated to shed light on the mechanism of the reactions of the carbonyl compounds. A part of the present study has been communicated elsewhere.[13]

Results and Discussion

Preparation and Characterization of Bis(2,4-pentanedionato)phenylchromium(III). Kurras has reported that treatment of chromium(III) chloride with triphenylaluminium etherate in tetrahydrofuran at room temperature afforded yellow-green dichlorophenyltris(tetrahydrofuran)chromium(III).[4] In contrast, when tris(2,4-pentanedionato)chromium(III) was similarly treated with $AlPh_3 \cdot Et_2O$ in tetrahydrofuran, no apparent reaction occurred at room temperature. However, on heating the system at 80 °C, a wine red solution resulted, from which brilliant red crystals deposited on allowing it to stand at −78 °C for 1 d. The crystals which appear to be $CrPh(acac)_2(thf)$ as judged from the IR spectrum, easily released the solvated tetrahydrofuran molecule and turned into an orange powder of $CrPh(acac)_2$ (**1**) on drying *in vacuo* at room temperature for 1 h (Eq. 1).

$$Cr(acac)_3 + AlPh_3 \cdot Et_2O \xrightarrow[80^\circ C]{\text{tetrahydrofuran}} \underset{\text{red crystals}}{CrPh(acac)_2(thf)} \xrightarrow{\text{drying } in\ vacuo} \underset{\text{orange powder}}{CrPh(acac)_2\ \mathbf{1}} \qquad (1)$$

A triphenylaluminium adduct of $Cr(acac)_3$, in which $AlPh_3$ was assumed to be attached to one of two oxygen of the acac ligands, has been claimed to exist in the reaction mixture consisted of $Cr(acac)_3$ and $AlPh_3$ in benzene at room temperature.[11] The higher temperature employed in the present system might have transformed this unstable adduct to the more stable phenylchromium complex **1**. A qualitative test with the use of aluminon and alizarin indicated the absence of aluminium in the product. In contrast to the arylation of $CrCl_3$ with aryl Grignard reagents, which afforded triarylchromium as well as mono- and diaryl derivatives,[1] phenylation of $Cr(acac)_3$ with $AlPh_3 \cdot Et_2O$ yielded the monophenyl derivative exclusively, as in the case of analogous alkylation with aluminium alkyls.[2,3] Addition of an equimolar amount of triphenylphosphine or tricyclohexylphosphine to the system did not alter the reaction course and the phenyl complex **1** was isolated exlusively in

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each case.

Complex **1** which is hardly soluble in diethyl ether and toluene can be recrystallized from tetrahydrofuran and is fairly inert to dry air in the solid state and even in solution. The magnetic moment of 3.52 BM, which is somewhat lower than the spin-only value of 3.88 BM for high spin Cr(III) complexes, was observed for complex **1**. Complex **1** decomposed *in vacuo* at 160—165 °C. The IR spectrum of **1** was very close to that of the parent $Cr(acac)_3$ except that there exist some additional bands due to the phenyl group at 3050 m (assignable to ν(C–H)), 675s, 695s, and 725s (π(C–H)), and 455 cm^{-1} (ν(Cr–C)). The characteristic absorptions of the acac ligand of **1** were observed as very strong bands at 1585, 1560, 1510, 1380, and 1345 cm^{-1}.

$CrPh(acac)_2$ (**1**) reacted with anhydrous HCl in diethyl ether to give benzene exclusively (91% of the calculated amount). The reaction of **1** with methyl iodide, allyl bromide, and acetyl chloride gave benzene (46—64%) and biphenyl. The yields of cross coupling products such as toluene, allylbenzene, or acetophenone, respectively, were very low (*ca.* 2%), indicating that the electrophilic attack of organic halogen compounds to the phenylchromium complex hardly occurred, unlike the similar reaction with phenylnickel(II) complex where certain amounts of cross coupled products have been obtained.[6] Although stable η^6-arene–chromium complexes such as $Cr(\eta^6\text{-}C_6H_6)_2$ are well known,[1,14] and formation of some η^6-arene–chromium complexes has been observed in the reaction of $CrCl_3$ with phenylmagnesium halides,[15] complex **1** is thought to have the phenyl-chromium σ-bond as is supported by the results of its reactions with organic carbonyl compounds (*vide infra*).

Reactions of $CrPh(acac)_2$ (1) with Organic Carbonyl Compounds. An orange-red heterogeneous mixture of phenylchromium complex **1** and rigorously dried acetone turned to a clear deep green solution on stirring at room temperature for 2 h. A GLC analysis of the resulting solution showed the formation of benzene, 2-phenyl-2-propanol, and 4-methyl-3-penten-2-one (mesityl oxide) in the yield listed in Table 1. Working up the system afforded a crystalline powder which was characterized as hydroxochromium complex $[Cr(OH)(acac)_2]_2$ **2** (0.84 mol/l) on the basis of IR spectrum, elemental analysis, and molecular weight measurement (*vide post*).

$$\underset{\mathbf{1}}{CrPh(acac)_2} + (CH_3)_2C{=}O \longrightarrow PhH + Ph(Me)_2COH + Me_2C{=}CHCOMe + \underset{\mathbf{2}}{[Cr(OH)(acac)_2]_2} \qquad (2)$$

The result indicates that two types of reactions, namely, protonation of the phenyl ligand and the insertion of the carbonyl group into the phenyl-chromium bond followed by protonation are taking place simultaneously in the present system. The result is in contrast to that of similar reactions of diphenylmanganese complex with acetone which afforded only benzene to give (2-oxopropyl)manganese complex indicating that protonation of the phenyl ligand with an active hydrogen of acetone was taking place exclusively.[8] On the other hand $Cr(acac)_3$ did not react with acetone upon heating under reflux for 2 h.

Formation of the hydroxochromium complex **2** and mesityl oxide indicates direct or indirect involvement of water in the reaction and it was suspected that the protonation was caused by water formed in the reaction giving mesityl oxide from 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol), the dimerization product of acetone. However, kinetic examination of the reaction as represented by Fig. 1 excludes the water as the direct proton source for giving benzene and 2-phenyl-2-propanol. Figure 1 indicates that benzene and 2-phenyl-2-propanol are formed simultaneously without any induction period. If water produced by dehydration of the diacetone alcohol is acting as the proton source, the water would be produced concomitant with mesityl oxide. It is observed, however, that the sum of benzene and 2-phenyl-2-propanol far exceeds the amount of mesityl oxide at any moment in the reaction course supporting that the dehydration of diacetone alcohol yielding mesityl oxide does not provide a sufficient amount of water to liberate benzene and 2-phenyl-2-propanol. Furthermore, addition of 2 mol of water per mol of **1** to the system

Table 1. Reactions of $CrPh(acac)_2$ **1** with organic carbonyl compounds[a)]

Compound	Reaction time (Solvent)	Products (mol/mol of **1**)			
		Alcohol	Dimer	Ketone	PhH
MeCOMe[b)]	2 h (Neat)	$Me_2(Ph)COH$ (0.71)	$Me_2C{=}CHCOMe$ (0.36)		(0.27)
MeCOPh[b)]	2 h (Et_2O)[f)]	$Me(Ph)_2COH$ (0.75)	Ph(Me)C=CHCOPh (0.91)		(0.26)
PhCOPh	1 d (Et_2O)	Ph_3COH (0.41)			(0)
MeCHO	2 h (Et_2O)[f)]	Me(Ph)CHOH (0.81)	MeCH=CHCHO (2.75)	PhCOMe (0.19)	(Trace)
EtCHO	1 d (Et_2O)	Et(Ph)CHOH (0.27)		PhCOEt (Trace)	(0.26)
PhCHO	1 d (Et_2O)		$PhCOOCH_2Ph$ (0.20)	PhCOPh (0.84)	(Trace)
MeCOOEt[c,d)]	1 h (Neat)	$Me(Ph)_2COH$ (0.03)		PhCOMe (Trace)	(0.28)
MeCOOPh[d,e)]	2 h (Neat)	$Me(Ph)_2COH$ (0.06)			(0.42)

a) Reactions were carried out under N_2 or *in vacuo* at room temperature unless otherwise stated. b) $[Cr(OH)(acac)_2]_2$ **2** was isolated from the reaction system (see text). c) $[Cr(OEt)(acac)_2]_2$ **4b** was isolated from the reaction system (see text). d) Reactions were carried out *in vacuo* at 80 °C. e) $Cr(OPh)(acac)_2$ **4i** was isolated from the reaction system (see text). f) The similar results were obtained when the reactions were carried out in the absence of solvent, diethyl ether.

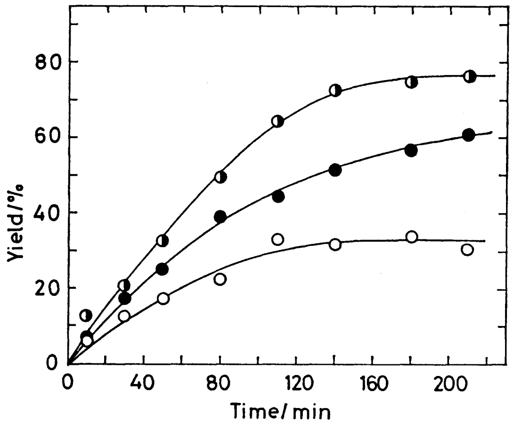
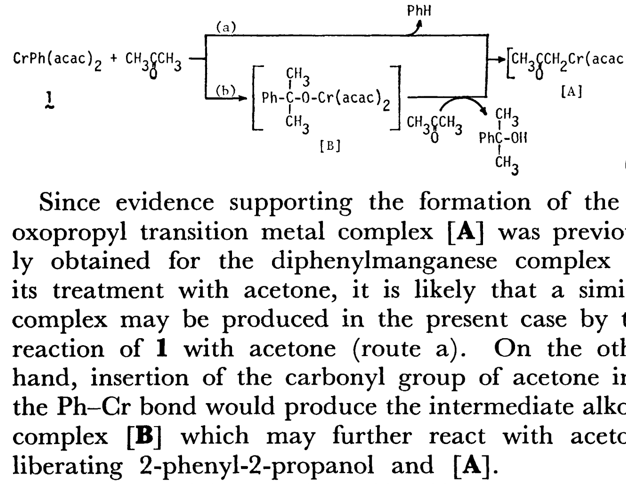


Fig. 1. Time dependence of the yields of benzene (○), mesityl oxide (●) and 2-phenyl-2-propanol (◑) in the reaction of $\mathrm{CrPh(acac)_2}$ **1** with excess amount of acetone at 8 °C (Eq. 2).

did not affect the yields of benzene and the alcohol, but inhibited the formation of mesityl oxide. Figure 1 shows also that the yield of mesityl oxide still increased after *ca.* 150 min when more than 95% of the phenyl complex had been consumed as reflected by leveling off of the yields of benzene and 2-phenyl-2-propanol.

These results support that the phenyl complex **1** is more susceptible to acetone than to water. Benzene and 2-phenyl-2-propanol are considered to be formed by the following parallel reactions of **1** with acetone:

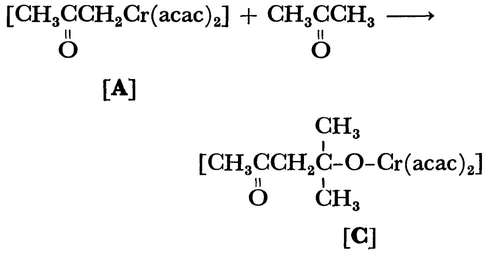


(3)

Since evidence supporting the formation of the 2-oxopropyl transition metal complex [**A**] was previously obtained for the diphenylmanganese complex on its treatment with acetone, it is likely that a similar complex may be produced in the present case by the reaction of **1** with acetone (route a). On the other hand, insertion of the carbonyl group of acetone into the Ph–Cr bond would produce the intermediate alkoxo complex [**B**] which may further react with acetone liberating 2-phenyl-2-propanol and [**A**].

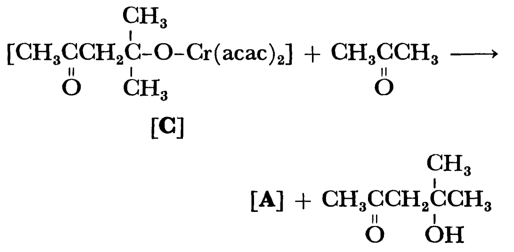
The assumed intermediate [**A**], if present, must be quite susceptible to protonation to give mesityl oxide and the hydroxo complex **2**. The exact route to produce **2** and mesityl oxide remains unclarified. Mesityl oxide may be simply formed by an aldol condensation of acetone together with water, which further attacks the intermediate [**A**] to give **2**.

However, since the reaction to form mesityl oxide and **2** proceeds very readily at room temperature in the present system and the formation of mesityl oxide is inhibited by addition of water, it is certainly reasonable to assume the intervention of a chromium complex such as [**A**] which promotes the reaction to produce mesityl oxide and is susceptible to the attack of water. A possible route is given below where the second acetone insertion into the C–Cr bond of the intermediate [**A**] is assumed.



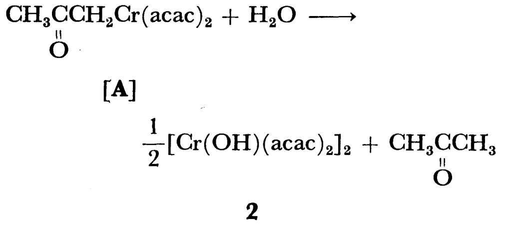
$$\underset{[\mathbf{A}]}{[\mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2Cr(acac)_2}]} + \mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_3} \longrightarrow \underset{[\mathbf{C}]}{[\mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2\underset{CH_3}{\overset{CH_3}{C}}\text{-}O\text{-}Cr(acac)_2}]} \qquad (4)$$

The intermediate [**C**] may interact further with acetone to release diacetone alcohol with regeneration of [**A**].



$$\underset{[\mathbf{C}]}{[\mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2\underset{CH_3}{\overset{CH_3}{C}}\text{-}O\text{-}Cr(acac)_2}]} + \mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_3} \longrightarrow [\mathbf{A}] + \mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2\underset{OH}{\overset{CH_3}{C}}CH_3} \qquad (5)$$

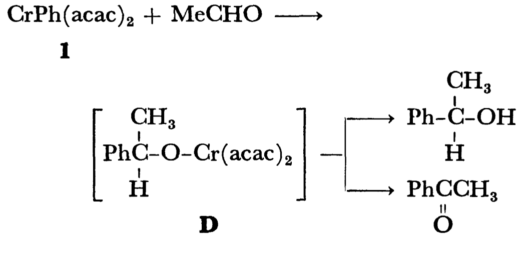
The diacetone alcohol thus produced may be dehydrated to liberate mesityl oxide and water which may readily attack [**A**] to produce the hydroxochromium complex **2**.



$$\underset{[\mathbf{A}]}{\mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2Cr(acac)_2}} + \mathrm{H_2O} \longrightarrow \underset{\mathbf{2}}{\frac{1}{2}[\mathrm{Cr(OH)(acac)_2}]_2} + \mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_3} \qquad (6)$$

Acetophenone reacted with **1** in the essentially similar fashion as did acetone to give 1,1-diphenylethanol and 1,3-diphenyl-2-buten-1-one together with benzene and the hydroxochromium complex **2** (Table 1). The reaction paths can be accounted for similarly to the reaction of **1** with acetone. In contrast, benzophenone, bearing no hydrogen attached to the carbon atom α to the carbonyl group, did not yield benzene, but gave triphenylmethanol on reaction with **1** in diethyl ether. The proton source for producing triphenylmethanol was not clarified.

Acetaldehyde reacted with **1** affording mainly the insertion product of the aldehyde into the Ph–Cr bond accompanied by formation of only a trace amount of benzene (Table 1). The formation of 1-phenylethanol (81%) and acetophenone suggests the concurrent occurrence of protonation and β-hydrogen abstraction of the intermediate 1-phenylethoxochromium complex [**D**].

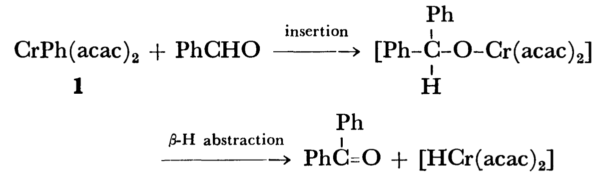


$$\underset{\mathbf{1}}{\mathrm{CrPh(acac)_2}} + \mathrm{MeCHO} \longrightarrow \underset{\mathbf{D}}{\left[\mathrm{Ph\underset{H}{\overset{CH_3}{C}}\text{-}O\text{-}Cr(acac)_2}\right]} \longrightarrow \begin{cases} \mathrm{Ph\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}OH} \\ \mathrm{Ph\underset{\overset{\|}{O}}{C}CH_3} \end{cases} \qquad (7)$$

It is noted that crotonaldehyde was formed in greater than the stoichiometric amount. A chromium complex may be promoting the aldol condensation of acetaldehyde in a manner similar to that of acetone dimerization with repetition of processes expressed by Eqs. 4 and 5. A concomitant formation of polymeric products, possibly due to the aldol condensation reaction, prohibited the isolation of the chromium complex from the reaction system.

The reaction of propionaldehyde with **1** proceeded more slowly than that of acetaldehyde to give the products shown in Table 1. In addition to the products listed in Table 1, biphenyl (0.13 mol/mol of complex) was formed, but the mechanism of its formation is not clear.

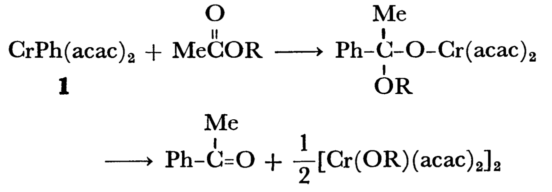
Benzaldehyde carrying no acidic hydrogen α to the carbonyl group, did not give diphenylmethanol but yielded benzophenone almost exclusively as a result of the β-H abstraction from an alkoxo intermediate which can be produced by benzaldehyde insertion into the Cr–Ph bond of **1** (Table 1).



$$\underset{\mathbf{1}}{\mathrm{CrPh(acac)_2}} + \mathrm{PhCHO} \xrightarrow{\text{insertion}} [\mathrm{Ph{-}\overset{Ph}{\underset{H}{C}}{-}O{-}Cr(acac)_2}] \xrightarrow{\beta\text{-H abstraction}} \mathrm{Ph\overset{Ph}{C}{=}O} + [\mathrm{HCr(acac)_2}] \quad (8)$$

This reaction system accompanied the formation of benzyl benzoate, the Tishtchenko type dimerization product. There are a few precedents of the Tishtchenko type reactions promoted by transition metal complexes.[8,16,17)]

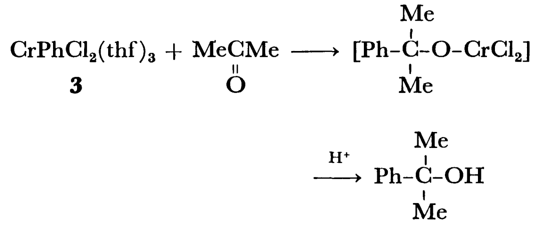
Ethyl and phenyl acetates reacted with $\mathrm{CrPh(acac)_2}$ only at elevated temperatures accompanying a color change from orange-red to deep green (Table 1). Ethoxo- and phenoxochromium complexes, $[\mathrm{Cr(OEt)(acac)_2}]_2$ and $\mathrm{Cr(OPh)(acac)_2}$, were isolated from the reaction systems. They were characterized by comparison with the ethoxo and phenoxo complexes prepared by the independent reactions of **1** with ethanol and phenol, respectively. Isolation of the alkoxochromium complexes strongly supports that the reactions proceed by the insertion of the carbonyl group of the esters into the Cr–Ph bond followed by the alkoxo group elimination as generally assumed for the reactions of Grignard reagents with carboxylic esters. Higher yields of benzene than 1,1-diphenylethanol in these reactions suggest a facile protonation of the phenyl complex with esters or acetophenone as the proton source at the elevated temperature.



$$\underset{\mathbf{1}}{\mathrm{CrPh(acac)_2}} + \mathrm{Me\overset{O}{\overset{\|}{C}}OR} \longrightarrow \mathrm{Ph{-}\overset{Me}{\underset{OR}{C}}{-}O{-}Cr(acac)_2} \longrightarrow \mathrm{Ph{-}\overset{Me}{C}{=}O} + \frac{1}{2}[\mathrm{Cr(OR)(acac)_2}]_2 \quad (9)$$

For comparing the reactivity of the phenylchromium acetylacetonate with other phenylchromium complexes reactions of $\mathrm{CrPhCl_2(thf)_3}$ (**3**) with some ketones and aldehydes were examined. The results are shown in Table 2. Although benzophenone and benzaldehyde afforded similar products to those of $\mathrm{CrPh(acac)_2}$ (**1**), the reactions of acetone and acetaldehyde with **3** gave different results from those with **1**. Thus, the yields of aldol condensates such as mesityl oxide and crotonaldehyde which were formed in relatively high yields in the case of **1** decreased, whereas considerable amounts of olefins such as α-methylstyrene and styrene were produced. Since aldol condensation is known to be accelerated by the base and the dehydration of alcohol to give olefin is catalyzed by the acid, the present results seem to reflect a stronger acidic nature of complex **3** than **1**.

The formation of 2-phenyl-2-propanol in the reaction of acetone with **3** indicates the acetone insertion into the Ph–Cr bond in **3** giving $\mathrm{Ph(Me)_2C{-}O{-}Cr}$ species which may be protonated by acetone to give the tertiary alcohol.



$$\underset{\mathbf{3}}{\mathrm{CrPhCl_2(thf)_3}} + \mathrm{Me\underset{O}{\underset{\|}{C}}Me} \longrightarrow [\mathrm{Ph{-}\overset{Me}{\underset{Me}{C}}{-}O{-}CrCl_2}] \xrightarrow{H^+} \mathrm{Ph{-}\overset{Me}{\underset{Me}{C}}{-}OH} \quad (10)$$

Dehydration of the alcohol thus formed promoted

TABLE 2. REACTIONS OF $\mathrm{CrPhCl_2(thf)_3}$ **3** WITH ORGANIC CARBONYL COMPOUNDS[a)]

Compound	Reaction time (Solvent)	Products (mol/mol of **3**) Alcohol	Dimer	Ketone	Olefin	PhX
MeCOMe	1 d (Neat)	$\mathrm{Me_2(Ph)COH}$ (0.54→0.02[c)])	$\mathrm{Me_2C{=}CHCOMe}$ (0.03→0.16[c)])		$\mathrm{Ph(Me)C{=}CH_2}$ (0.40→0.96[c)])	PhH (0.06→0.17[c)])
PhCOPh	0.5 h ($\mathrm{Et_2O}$)	$\mathrm{Ph_3COH}$ (0.17)				
MeCHO	0.5 h ($\mathrm{Et_2O}$)	Me(Ph)CHOH (0.20)	MeCH=CHCHO (Trace)	PhCOMe (Trace)	$\mathrm{PhCH{=}CH_2}$ (0.21)	PhH (0.05)
PhCHO	1 d ($\mathrm{Et_2O}$)		$\mathrm{PhCOOCH_2Ph}$ (Trace)	PhCOPh (0.88)		PhPh (0.06)

a) Reactions were carried out under N_2 at room temperature. b) Three moles of tetrahydrofuran per mole of complex were found to be present in the reaction mixture. c) After the measurement of the yields of reaction products, phenol was added to the system. The figures placed after the arrows indicate the yields after treatment with phenol.

by acid gives α-methylstyrene. In the reaction of acetone with the phenylchromium chloride liberation of HCl is also likely. The acid thus formed may also act as the dehydration agent.

A quite similar reaction sequence as discussed above may be also operative in the reaction of **3** with acetaldehyde. The assumption that the alcohol is a precursor for the olefin formation in the system utilizing complex **3** was further confirmed by the following experiment. After the completion of the reaction between **3** and acetone, a weak acid such as phenol was introduced to the system, and the reaction mixture was stirred for 1 h at room temperature. This resulted in the appreciable increase in the yield of α-methylstyrene at the expense of the alcohol (see footnote c in Table 2).

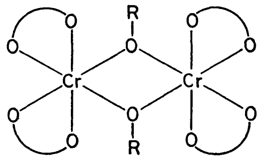
Reactions of $CrPh(acac)_2$ *(1) with Alcohols.* In view of the possible intermediacy of alkoxochromium species in the reactions of phenyl complex **1** with organic carbonyl compounds, isolation of alkoxochromium complexes *via* direct reactions of alcohols with phenyl complex **1** was attempted.

Complex **1** readily reacted with an excess of various kinds of alcohols at room temperature to give a series of green alkoxochromium complexes **4** accompanied by release of quantitative amounts of benzene.

$$\underset{\mathbf{1}}{\mathrm{CrPh(acac)_2}} + \mathrm{ROH} \longrightarrow \frac{1}{n}\underset{\mathbf{4}}{[\mathrm{Cr(OR)(acac)_2}]_n} + \mathrm{PhH} \quad (n=1 \text{ and } 2) \tag{11}$$

Although the homoleptic chromium alkoxides such as $Cr(OR)_n$ has been known,[18] complexes containing both the alkoxo- and β-diketonato ligands of the type $[Cr(OR)(\beta\text{-dik})_2]_n$ have been prepared only recently by the reactions of alcohols with $Cr(3\text{-halo-}2,4\text{-pentanedione})_2$[19,20] or of β-diketones with chromium trialkoxides under refluxing conditions.[21] The former method has a limitation that only such 2,4-pentanedionato derivatives that carries strong electronegative substituent can be replaced by alcohol, whilst the latter is inconvenient for getting complexes with an extensive series of alkoxo ligands. The present method shown in Eq. 11, albeit indirect, has an advantage that the reaction readily proceeds under mild conditions to give complexes with a variety of alkoxo ligands.

Table 3 lists analytical results of the alkoxo complexes thus obtained. Most alkoxo complexes are soluble in organic solvents such as hexane and toluene from which they were recrystallized to give green crystals. Molecular weight measurement by cryoscopy in benzene reveals that the alkoxo complexes are dimeric in solution in accordance with the observation by Mahendra *et al.*[21] and by Kasuga *et al.*[19] for $[Cr(OR)(3\text{-bromo-}2,4\text{-pentanedione})_2]_2$. Alkoxo-bridged dimeric structure in the solid state has been demonstrated for the last complex by an X-ray crystal structure analysis.[20] By analogy, most alkoxo complexes prepared in the present study may have the structure as shown below:



where O‿O represents acac ligands. The phenoxo complex $Cr(OPh)(acac)_2$ was found to be monomeric in benzene. The presence of the phenoxo group may serve to make the phenoxo oxygen less basic for formation of the bridge structure. A steric reason may be also contributing here.

Assignment of their IR bands was performed by comparing them with those of the parent complex **1**, tris(2,4-pentanedionato)chromium(III), and some other related compounds.[19,22,23] For example, methoxo complex $[Cr(OCH_3)(acac)_2]_2$ (**4a**) showed, in addi-

TABLE 3. ALKOXOCHROMIUM COMPLEXES FORMED BY THE REACTION, $n\mathrm{CrPh(acac)_2} + n\mathrm{ROH} \longrightarrow [\mathrm{Cr(OR)(acac)_2}]_n + n\mathrm{PhH}$[a]

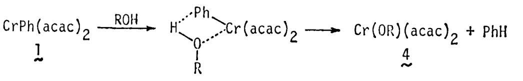
	R	Yield %	Mol wt[b]	n	μ_{eff} BM	ν(C-O) cm^{-1}	Analysis[b] (%) C	H	Cr
4a	Me	100	541(562)	2	3.52	1083	46.9(47.0)	6.2(6.1)	18.6(18.5)
4b	Et	79	c)		3.63	1054, 1092	48.4(48.8)	6.5(6.5)	17.2(17.6)
4c	n-Pr	99	c)		c)	1062	49.8(50.5)	7.0(6.8)	16.7(16.8)
4d	i-Pr	87	575(618)	2	3.41	1128	49.3(50.5)	6.7(6.8)	16.7(16.8)
4e	t-Bu	43	c)		3.35	1178	51.5(52.0)	7.3(7.2)	16.2(16.1)
4f	$PhCH_2$	99	c)		c)	1025, 1048, 1078	56.0(57.1)	6.0(5.9)	14.3(14.6)
4g	Me(Ph)CH	23	c)		c)	1100	58.4(58.2)	6.4(6.2)	c)
4h	$(Me)_2PhC$	71	732(770)	2	c)	1152	58.9(59.2)	6.6(6.5)	13.7(13.5)
4i	Ph	63	398(343)	1	3.53	1232	56.1(56.0)	5.8(5.6)	15.5(15.1)
4j	p-MeO-C_6H_4	25	c)		c)	1210	53.6(54.6)	6.0(6.7)	c)
4k	$HOCH_2CH_2$	80	c)		c)	1063	46.4(46.3)	6.4(6.2)	15.8(16.7)
2	H	99	528(534)	2	3.78	3635[d]	45.4(45.0)	5.8(5.7)	c)

a) Reactions were carried out under N_2 at room temperature without solvent for **4a**—**d** and in Et_2O and tetrahydrofuran for **4e**—**4j**, and **4k** and **2**, respectively. b) Calcd values in parentheses. c) Not measured. d) Band assignable to ν(O-H) (see text).

tion to the bands due to the acac ligand, several bands assignable to the methoxo ligand: 2925m and 2820m (ν(C–H)), 1083s (ν(C–O)), 600s, 548s, and 453s cm^{-1} (bands due to Cr–O bond). In the case of the phenoxo complex, Cr(OPh)(acac)$_2$ (**4i**), the bands arising from the phenoxo group were 3050m (ν(C–H)), 1485s (ν(C–C)), 1232s (ν(C–O)), 767s (π(C–H)), 685s (δ-(C–C)), and 600s and 480s cm^{-1} (bands due to Cr–O bond). The fairly distinctive C–O stretching bands of the alkoxo ligands are listed in Table 3.

In accordance with the observation by Mahendra *et al.*,[21] magnetic moments of the present alkoxo complexes were found to be in the region of 3.35 to 3.63 BM which are less than the value of 3.88 BM calculated for the spin only system of Cr(III), suggesting occurrence of the antiferromagnetism due to super exchange through bridging alkoxo ligands.[22]

The formation of the alkoxo complexes may be explained by considering nucleophilic attack of alcohol to a vacant site of the metal center of phenylchromium complex **1** followed by formation of Cr–O bond.



(12)

The necessity of a vacant site on the metal center was demonstrated by the following additional experiment. The orange phenylchromium complex **1**, on treatment with γ-picoline in tetrahydrofuran at room temperature, turned to a yellow adduct, CrPh(acac)$_2$-(γ-picoline) (**5**), which was characterized on the basis of IR spectrum and elemental analysis. In contrast to the high reactivity of **1** toward alcohol as described above, coordinatively saturated complex **5** did not react with ethanol in tetrahydrofuran at room temperature, but reacted at 80 °C to give the alkoxo complex [Cr(OEt)(acac)$_2$]$_2$ liberating quantitative amounts of benzene and γ-picoline. This result implies that dissociation of γ-picoline ligand is a prerequisite for complex **5** to be attacked by alcohol according to Eq. 12.

The reaction of **1** with ethylene glycol in tetrahydrofuran at room temperature afforded a deep purple solution, from which a pale purple powder was obtained on working up. On treatment with hot toluene, the purple powder turned to a green powder **4k** which showed a strong IR band at 3490 cm^{-1} assignable to ν(OH). In view of the fact that the rest of the IR absorptions are quite similar to those of the other alkoxo complexes **4** and that the elemental analysis excludes the binuclear structure with a bridging $-OCH_2CH_2O-$ group, complex **4k** is tentatively formulated as a 2-hydroxyethoxo complex [Cr(OCH$_2$CH$_2$OH)(acac)$_2$]$_2$. The structure of the pale purple precursor which has no ν(OH) band is not certain.

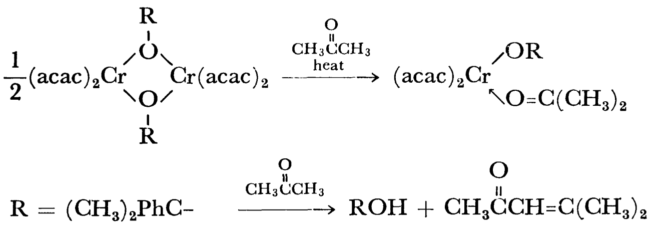
Reactions of Alkoxochromium Complexes. Alkoxobis(2,4-pentanedionato)chromium(III) complexes **4a**, **4b**, **4d**, **4i**, and **4j** reacted with acetyl chloride to give quantitvatie amounts of corresponding esters. Since the reaction takes place readily at ambient conditions, it may be applicable to the rest of the alkoxo complexes listed in Table 3 which were not examined.

$$\underset{\mathbf{4}}{[\mathrm{Cr(OR)(acac)_2}]_n} + \text{excess MeCOCl} \longrightarrow n\ \mathrm{MeCOOR} + \text{“complex”} \qquad (13)$$

All the reaction products thus obtained showed the identical IR bands with those of the reaction products between **1** and HCl (*vide supra*), at 2790m, 1695s, 1170m, and 1050m cm^{-1} in addition to those of the acac ligand. The complex is tentatively assigned to CrCl$_n$(acac)$_m$. The reaction of acetyl chloride with the alkoxo complex, [Cr(OCH$_2$CH$_2$OH)(acac)$_2$]$_2$ (**4k**), derived from ethylene glycol afforded diester, ethylene glycol diacetate, the yield of which was one mol per Cr atom.

The alkoxo complexes **4** were found to be chemically inert to most reagents other than acetyl chloride. Thus, in contrast to trialkoxochromium(III) complexes, Cr(OR)$_3$, which reportedly react with isocyanate to give insertion product, Cr(OR)$_{3-n}$\{N(Ph)COOR\}$_n$,[24] complex **4b** did not react with excess phenyl isocyanate in toluene at room temperature. Methyl iodide and phenyl acetate did not react with **4b** even on heating at 80 °C. Only a trace amount of anisole was detected in the reaction of the phenoxo complex **4i** with methyl iodide at room temperature. When the ethoxo complex **4b** in toluene was stirred at room temperature in the presence of equimolar amount of phenol for 9 h, only 2% of ethanol per **4b** was formed, indicating that the alkoxo exchange reaction of **4** with more acidic alcohol proceeds very slowly. Neither CO$_2$ (4 atm, 80 °C) nor CO (1 atm, room temperature) reacted with **4b** in toluene solution or in ethanol suspension.

It is rather surprising that even the alkoxo complex **4h**, derived according to Eq. 12 from **1** and 2-phenyl-2-propanol, which was thought to be a possible reaction intermediate between **1** and acetone as shown in Eq. 3, was found to be inert to further reaction with acetone at room temperature. Heating **4h** in acetone under reflux yielded only a small amount of mesityl oxide and 2-phenyl-2-propanol. The result conflicts with the mechanism presented for the reaction between the phenyl complex **1** and acetone in which mesityl oxide was formed by room temperature *via* a postulated alkoxo intermediate **4h**. Tentatively, we elucidate this inconsistency by supposing a significant difference in the reactivity of **4h** toward acetone between monomeric and dimeric forms. As shown in the preceding section, most alkoxochromium complexes once isolated were found to be dimeric in solution, which are chemically inert. On the other hand, the pentacoordinated alkoxo intermediate [**B**] in Eq. 3 formed *in situ* by the reaction of phenyl complex **1** and excess acetone may exist as a monomer, since excess acetone, behaving as a Lewis base, may occupy the vacant coordination site of chromium which is necessary for the dimerization of alkoxide. The monomeric alkoxide may have a potential to react further with excess acetone. The formation of 2-phenyl-2-propanol and mesityl oxide by the reaction of **4h** with acetone at refluxing temperature suggests that the dissociation of dimeric alkoxide may take place at the elevated temperature in the presence of acetone.



$$\frac{1}{2}(\mathrm{acac})_2\mathrm{Cr}(\mu\text{-OR})_2\mathrm{Cr}(\mathrm{acac})_2 \xrightarrow[\text{heat}]{\mathrm{CH_3C(O)CH_3}} (\mathrm{acac})_2\mathrm{Cr}(\mathrm{OR})(\mathrm{O{=}C(CH_3)_2})$$

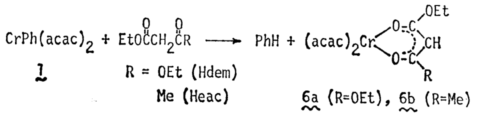
$$\mathrm{R} = \mathrm{(CH_3)_2PhC\text{-}} \xrightarrow{\mathrm{CH_3C(O)CH_3}} \mathrm{ROH} + \mathrm{CH_3C(O)CH{=}C(CH_3)_2} \quad (14)$$

*Reaction of CrPh(acac)$_2$ (**1**) with Water.* Complex **1** reacted slowly with an excess of water in the tetrahydrofuran solution at room temperature to afford benzene quantitatively and give purple crystals which were analyzed as dimeric hydroxo complex **2** on the basis of IR spectrum, elemental analysis, and magnetic susceptibility as well as molecular weight measurements. The analytical results are included in Table 3. IR spectrum of **2** showed a characteristically

$$\underset{\mathbf{1}}{2\,\mathrm{CrPh(acac)_2}} + 2\,\mathrm{H_2O} \xrightarrow[\text{room temp}]{\text{tetrahydrofuran}} 2\,\mathrm{PhH} + \underset{\mathbf{2}}{[\mathrm{Cr(OH)(acac)_2}]_2} \quad (15)$$

sharp ν(OH) band at 3635 cm^{-1} and bridging δ(OH) band at 820 cm^{-1}.[23] These bands shifted to 2665 (ν(OD)/ν(OH)=1.37) and 620 cm^{-1} (δ(CD)/δ(OH)=1.32), respectively in the deuterio analog [Cr(OD)(acac)$_2$]$_2$, which was similarly prepared from **1** according to Eq. 15 using D$_2$O in place of H$_2$O. The binuclear complexes bridged with the hydroxo group(s) have been reported for Cu,[25] Fe,[26] Co,[26] Ru,[27] and Pt,[28] as well as Cr(III) of the type [(L-L)$_2$Cr(OH)]$_2$X$_4$ (L-L=2,2′-bipyridine and 1,10-phenanthroline) and K$_4$[(C$_2$O$_4$)$_2$Cr(OH)]$_2$.[26]

*Reactions of CrPh(acac)$_2$ (**1**) with β-Dicarbonyl Compounds.* Phenyl complex **1** reacted with β-dicarbonyl compounds such as diethyl malonate (Hdem) and ethyl acetoacetate (Heac) at room temperature to give corresponding mixed chelate complexes **6** with accompanying release of quantitative amounts of benzene. Purple needles of **6a** had IR absorptions at



1

6a (R=OEt), **6b** (R=Me)

(17)

1620, 1143, and 1076 cm^{-1} assignable to the ester groups of dem ligand in addition to the bands due to acac ligands. Similarly, the IR bands due to the ester group in eac ligand in **6b** were observed at 1610, 1090, and 1058 cm^{-1}. Replacement of metal alkyls with nucleophiles such as β-dicarbonyl anion to give chelate complex has been reported for methylcopper and dimethylnickel complexes.[29] It has also been reported that Pt(acac){CH(COCH$_3$)$_2$}(PPh$_3$) reacted with dimethyl malonate (Hdmm) and Heac to replace central carbon bonded acac ligand {CH(COCH$_3$)$_2$} with dmm and eac which were also bonded to Pt through their central carbon atoms.[30] Absence of the ester carbonyl bands above 1700 cm^{-1} in the IR spectra of **6a** and **6b** indicates that dem and eac ligands are not attached unidentately through central carbon atom but chelated through two oxygens.

Experimental

Most reactions and manipulations were carried out either under dry, oxygen-free nitrogen or argon, or *in vacuo* using Schlenk-type flasks.

Solvents were dried, purified in the usual manner, and stored under an atmosphere of nitrogen. Commercial acetone was dried by Drierite, distilled under nitrogen, and stored with added molecular sieve 3A. Acetone thus purified was found to contain less than 1.5×10^{-3} M of water on the basis of GLC analysis. Acetaldehyde was dried over molecular sieve 3A, distilled under nitrogen, and stored in the presence of molecular sieve 3A. The other ketones, aldehydes, and esters were purified appropriately. Methanol was dried with Drierite, distilled under nitrogen, and distilled again over calcium hydride *in vacuo*. Commercial phenol, 2-phenyl-2-propanol, 1-phenylethanol, and *p*-methoxyphenol were used without further purification. Other alcohols were dried over anhydrous sodium sulfate. Acetyl chloride was distilled and stored under nitrogen in the presence of molecular sieve 3A. AlPh$_3$·Et$_2$O was prepared from PhMgBr and AlCl$_3$ according to the reported method.[31] Tris(2,4-pentanedionato)chromium(III) (Tokyo Kasei Industrial Co.) was used as purchased without further purification. CrPhCl$_2$(thf)$_3$ (**3**) was prepared by the literature method.[4]

Infrared spectra were recorded on a Hitachi model 295 spectrometer using KBr disks prepared under inert atmosphere. The magnetic susceptibility was measured by Gouy method using Shimadzu MB-100 apparatus at 23 °C and the diamagnetic corrections for the coordinated ligands were made on the basis of the Pascal's constants.[32] Molecular weight was measured cryoscopically in benzene solution. The organic products formed in the reactions were quantitatively analyzed by GLC using internal standard. GLC was recorded on a Shimadzu GC-3BT or GC-6A gas chromatography using SDC-550, SDC-410, and/or PEG-20M columns and helium as a carrier gas. Micro analyses (C and H) were carried out by Mr. T. Saito of our laboratory using Yanagimoto CHN Autocorder Type MT-2. Analysis of the chromium content was performed by a colorimetric method using diphenylcarbazide as a color-producing agent.[33]

*Preparation of CrPh(acac)$_2$ (**1**).* Tris(2,4-pentanedionato)chromium(III) (2.8 g, 8.0 mmol) and AlPh$_3$·Et$_2$O (2.9 g, 8.4 mmol) in 20 cm^3 of tetrahydrofuran was heated under reflux for 8 h. The original deep purple solution changed to wine red in the initial 1 h. On allowing to stand the solution at −78 °C overnight, brilliant red crystals deposited, which were filtered, washed with tetrahydrofuran, and dried *in vacuo*. Orange powdery CrPh(acac)$_2$ thus obtained weighed 1.64 g (yield, 63% based on Cr(acac)$_3$ used) and was crystallized from hot tetrahydrofuran. Found: C, 58.4; H, 6.0%. Calcd for C$_{16}$H$_{19}$O$_4$Cr: C, 58.7, H, 5.9%.

*Reaction of CrPh(acac)$_2$ (**1**) with Acetone.* To a flask containing CrPh(acac)$_2$ (0.406 g, 1.24 mmol), 3 cm^3 of acetone was added by means of a trap-to-trap method. On stirring the mixture at room temperature for 2 h a dark green solution resulted, the GLC analysis of which using toluene as an internal reference showed the formation of benzene (0.335 mmol), 3-phenyl-2-propanol (0.880 mmol), 4-methyl-3-penten-2-one (mesityl oxide) (0.446 mmol), and 2,6-dimethyl-2,5-heptadien-4-one (0.062 mmol). Volatile liquid materials were evaporated from the solution to leave a dark colored solid. The resulting solid was successively washed at −10 °C with diethyl ether and hexane to give a purple powder which was analyzed as $[Cr(OH)(acac)_2]_2$ (0.279 g, 84% based on **1** used).

The time-course of the yields of the organic products in the reaction of **1** and acetone (Fig. 1) was followed by submitting the aliquot of the reaction mixture maintained at 8 °C to GLC analysis at regular intervals.

The reactions of **1** with other ketones, aldehydes, and esters were carried out essentially in a similar fashion as described above, except that in some experiments diethyl ether was used as solvent and the reaction mixture was heated appropriately as shown in Table 1.

Reaction of $CrPhCl_2(thf)_3$ (3) with Acetone. Acetone (2 cm^3) was condensed into a flask containing 0.114 g (0.273 mmol) of $CrPhCl_2(thf)_3$ by the trap-to-trap method. On stirring the mixture at room temperature for 10 min, a purple solution resulted. After being stirred overnight, the solution was analyzed by means of GLC to confirm the presence of benzene (0.016 mmol), styrene (0.109 mmol), 2-phenyl-2-propanol (0.147 mmol), mesityl oxide (0.007 mmol), and tetrahydrofuran (0.811 mmol). Addition of phenol to the solution changed the product distribution to benzene (0.046 mmol), styrene (0.261 mmol), 2-phenyl-2-propanol (0.005 mmol), and mesityl oxide (0.045 mmol) (Table 2).

The reactions of **3** and benzophenone, acetaldehyde, and benzaldehyde were carried out similarly except that diethyl ether was used as solvent.

Reaction of $CrPh(acac)_2$ (1) with Alcohols. Since the method is general the reaction of **1** with methanol is described as a representative example, and reaction conditions, yields, and analytical data are listed in Table 3.

To the flask containing 1.127 g (3.44 mmol) of **1** was added 5 cm^3 of methanol by the trap-to-trap method. After being stirred at room temperature for 6 h, the volatile liquid was evaporated off *in vacuo* to leave 0.834 g (86%) of a green powder of $[Cr(OMe)(acac)_2]_2$ **4a**. The powder was crystallized from 8 cm^3 of hot toluene.

In the reaction with less volatile alcohols, solvents such as diethyl ether and tetrahydrofuran were employed and freshly distilled alcohols were added to the mixture using a syringe (see Table 3).

Reactions of the Alkoxo Complexes (4) with Acetyl Chloride. To the flask containing 44.4 mg (0.079 mmol) of $[Cr(OMe)(acac)_2]_2$ (**4a**) and 2 cm^3 of toluene, *ca.* 0.5 cm^3 of acetyl chloride was added by means of the trap-to-trap method. After being stirred at room temperature for 30 min, the solution was analyzed by GLC using benzene as an internal reference to reveal the formation of 0.131 mmol (0.83 mol/Cr) of methyl acetate.

Similarly carried out were the reactions of acetyl chloride with $[Cr(OEt)(acac)_2]_2$ (**4b**) (the yield of ester was 0.99 mol/Cr), $[Cr(O\text{-}i\text{-}Pr)(acac)_2]_2$ (**4d**) (1.00 mol/Cr), $Cr(OPh)(acac)_2$ (**4i**) (0.97 mol/Cr), $[Cr(OC_6H_4\text{-}p\text{-}OMe)(acac)_2]_2$ (**4j**) (1.00 mol/Cr), and $[Cr(OCH_2CH_2OH)(acac)_2]_2$ (**4k**) (1.00 mol/Cr).

Reaction of $CrPh(acac)_2$ with Water. Stirring the mixture of 0.725 g (2.20 mmol) of $CrPh(acac)_2$ (**1**), 5 cm^3 of tetrahydrofuran, and 0.2 cm^3 (11.1 mmol) of water at room temperature for 2.5 h afforded a purple solution. Evaporating off the volatile liquid gave 0.529 g (90%) of a purple powder which was crystallized from hot toluene. The product was analyzed as $[Cr(OH)(acac)_2]_2$ (**2**) on the basis of IR spectrum, elemental analysis, and molecular weight measurement (Table 3). GLC analysis of the volatile liquid showed the formation of benzene in the yield of 1 mol per mol of complex.

Reaction of $CrPh(acac)_2$ (1) with Diethyl Malonate. To the flask containing 0.726 g (2.21 mmol) of $CrPh(acac)_2$ (**1**), 3 cm^3 of diethyl malonate was condensed under high vacuum. The mixture was stirred at room temperature for 2 d and a reddish orange suspension turned to purple solution. GLC analysis of the resulting solution indicated the formation of 1.00 mol of benzene per mol of **1**. Evaporating off the volatile liquid from the system gave a purple solid of $Cr(dem)(acac)_2$ (**6b**) (0.448 g, yield 50% on the basis of **1**). The solid was recrystallized from toluene–hexane to give purple crystals. Found: C, 48.9; H, 5.9; Cr, 12.5%. Calcd for $C_{17}H_{25}O_8Cr$: C, 49.9; H, 6.2; Cr, 12.7%.

Reaction of **1** with ethyl acetoacetate to give $Cr(eac)(acac)_2$ (**6a**) was carried out similarly.

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