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PHENYLBIS(ACETYLACETONATO)CHROMIUM(III). PREPARATION AND REACTIONS WITH ALDEHYDES AND KETONES

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Treatment of $Cr(acac)_3$ with $AlPh_3 \cdot Et_2O$ gave $PhCr(acac)_2$, **1**, which was characterized by IR spectrum, elemental analysis and some chemical reactions. Complex **1** reacted with aldehydes and ketones to afford phenylated alcohols and/or ketones, indicating the presence of the alkoxychromium intermediate as a result of an insertion of the carbonyl group into the Ph-Cr bond. The results were compared with the analogous reactions using the known complex, $PhCrCl_2(THF)_3$.

Extensive studies have been made on the preparation of organochromium(III) complexes having alkyl or aryl to chromium σ-bond by the interaction of chromium(III) halide and certain alkyl(aryl)ating agents such as Grignard reagent, organolithium and organoaluminium compounds.1) Although the alkylchromium complex of the type $RCrCl_2(THF)_n$ 2) and its phenyl derivative, $PhCrCl_2(THF)_3$ 3) (THF stands for tetrahydrofuran) have been prepared starting from chromium trichloride in combination with organoaluminiums in THF, all attempts to isolate the organic derivative of chromium starting from $Cr(acac)_3$ have been unsuccessful except one example, $(\eta^5\text{-}C_5H_5)CrBr(acac)$, which was prepared from $Cr(acac)_3$ and C_5H_5MgBr.4)

We now found that a new phenylchromium(III) complex, $PhCr(acac)_2$, **1**, can be prepared from the system consisting of $Cr(acac)_3$, $AlPh_3 \cdot Et_2O$, and THF. Albeit the phenylchromium(III) complex of the type $PhCrCl_2(THF)_3$, **2**, has been known3), the studies on its reactions are limited only to those with $HgCl_2$ and I_2.1) In view of the importance of the transition metal complex with carbon to metal σ-bond playing a key role in the catalytic C-C bond formation reaction of organic compounds5), the phenylation of the organic carbonyl compounds using phenylchromium complexes **1** and **2** was studied.

Preparation and characterization of $PhCr(acac)_2$ $Cr(acac)_3$ reacted with $AlPh_3 \cdot Et_2O$ in THF at 80°C to give a wine red solution. On allowing to stand at -78°C for a day, the solution deposited brilliant red crystals, which appear to be $PhCr(acac)_2(THF)$ as judged from the IR spectrum. These red crystals easily released the solvated THF molecule and turned into an orange powder of $PhCr(acac)_2$, **1**, on drying *in vacuo* at room temperature for one hr.

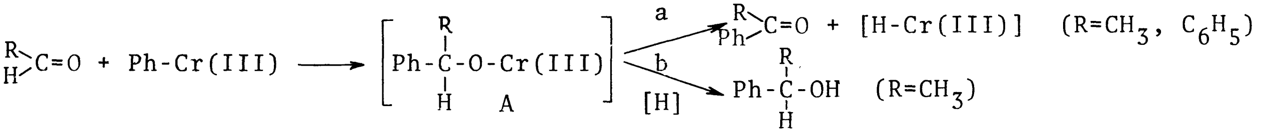
$$\underset{(Cr\ :\ Al\ =\ 1\ :\ 1)}{Cr(acac)_3 + AlPh_3 \cdot Et_2O} \xrightarrow[80^\circ C\ 8hr]{THF} \underset{\text{red crystals}}{PhCr(acac)_2(THF)} \xrightarrow{\text{drying in vacuo}} \underset{\text{orange powder}}{PhCr(acac)_2\ \mathbf{1}} \qquad (1)$$

$PhCr(acac)_2$, **1**, which is inert to air in the solid state and in a dry solvent, is insoluble in diethyl ether and toluene, but can be recrystallized from THF. Characterization of **1** was carried out by IR spectrum, chemical reactions and elemental analysis (Found: C, 58.4; H, 6.0%. Calcd for $C_{16}H_{19}O_2Cr$: C, 58.7; H, 5.9%. M.p. _in vacuo_, 160-5°C(dec.)). IR spectrum of **1** was very close to that of the parent $Cr(acac)_3$ except that there exist some additional bands at 3050m (νC-H of phenyl group), 675s, 695s, and 725s(δC-H(out of plane) of phenyl group), and 455m cm^{-1}(νCr-C). The characteristic bands of the acac ligand of **1** were observed as very strong signals at 1585, 1560, 1510, 1380, and 1345 cm^{-1}. Triphenylaluminium adduct of $Cr(acac)_3$, $Cr(acac\text{-}AlPh_3)_3$ in which $AlPh_3$ is assumed to be attached to one of two oxygen atoms 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.6) The higher temperature employed in the present system might have transformed this unstable adduct to the stabler phenylchromium complex **1**. The absence of the aluminium element in **1** was confirmed qualitatively by the aluminon and alizarin tests. Similarly to the other reports on the preparation of organochromium compounds using alkyl- or arylaluminium compounds,2,3,7) only mono-phenylated chromium complex was obtained in the present system.

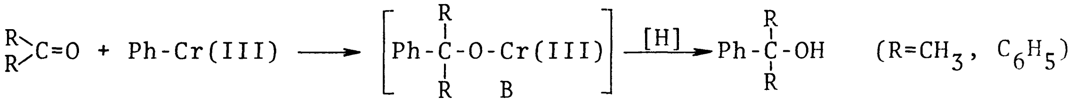
$PhCr(acac)_2$ reacted with anhydrous HCl in diethyl ether to give only benzene (91% for theoretical amount). The reactions of **1** with methyl iodide, allyl bromide, and acetyl chloride gave benzene (46-64%) and biphenyl. The yields of cross coupling products such as toluene, allyl benzene, or acetophenone, respectively, were very low (∿2%), indicating that the oxidative addition of organic halogen compounds to chromium (III) hardly occured, unlike the similar reaction with phenylnickel complex where a certain amount of cross coupled products have been obtained.8) The evidence for the σ-bonding of phenyl ligand to chromium in complex **1** was obtained from the results of its reactions with aldehydes and ketones (_vide infra_).

Reactions of $PhCr(acac)_2$ and $PhCrCl_2(THF)_3$ with aldehydes and ketones Phenylchromium complexes, $PhCr(acac)_2$, **1**, and $PhCrCl_2(THF)_3$, **2**, reacted with excess amounts of ketones and aldehydes at room temperature to give phenylated ketones and/or alcohols, together with dimerized products of aldehydes in some cases. The products distribution summarized in Table 1 indicates that the reaction product depends on the natures of both the carbonyl compounds and the complexes employed.

Acetaldehyde and propionaldehyde afforded both phenylated ketones and alcohols as phenylated organic products, (the amount of the latter predominated over the former), whereas acetone gave only tertiary alcohol, 1-methyl-1-phenylethanol. Furthermore, benzaldehyde and benzophenone yielded, respectively, benzophenone and triphenylmethanol. These results indicate that the reactions proceed _via_ an initial insertion of the carbonyl group into the phenyl-chromium σ-bond to give alkoxychromium intermediate (A and B in Eqs. 2 and 3) similarly to the known reactions of Grignard reagents with organic carbonyl compounds.



$$\overset{R}{\underset{H}{}}\!\!>\!C{=}O + \text{Ph-Cr(III)} \longrightarrow \left[\text{Ph-}\overset{R}{\underset{H}{C}}\text{-O-Cr(III)}\right]_{A} \begin{array}{l} \xrightarrow{a} \overset{R}{\underset{Ph}{}}\!\!>\!C{=}O + [\text{H-Cr(III)}] \quad (R=CH_3,\ C_6H_5) \\ \xrightarrow[{[H]}]{b} \text{Ph-}\overset{R}{\underset{H}{C}}\text{-OH} \quad (R=CH_3) \end{array} \qquad (2)$$



$$\overset{R}{\underset{R}{}}\!\!>\!C{=}O + \text{Ph-Cr(III)} \longrightarrow \left[\text{Ph-}\overset{R}{\underset{R}{C}}\text{-O-Cr(III)}\right]_{B} \xrightarrow{[H]} \text{Ph-}\overset{R}{\underset{R}{C}}\text{-OH} \quad (R=CH_3,\ C_6H_5) \qquad (3)$$

Ph-Cr(III) is either $PhCr(acac)_2$ **1** or $PhCrCl_2(THF)_3$ **2**.

TABLE 1. Reactions of $PhCr(acac)_2$ (**1**) and $PhCrCl_2(THF)_3$ (**2**) with aldehydes and ketones[a)]

Aldehydes or Ketones	Complex	Reaction Time (Solvent)	Products (mol/mol of complex)[b)]					
			Alcohols	Ketones	Olefins	Dimers	PhH	PhPh
MeCHO			Ph(Me)C(H)OH	PhCOMe	$PhCH=CH_2$	MeCH=CHCHO		
	1	1 day (Et_2O)	0.78	0.09	0	1.20	trace	
	2	30min (Et_2O)	0.20	trace	0.21	trace	0.05	
EtCHO			Ph(Et)C(H)OH	PhCOEt				
	1	1 day (Et_2O)	0.27	trace			0.26	0.13
MeCOMe			$Ph(Me)_2COH$		$PhC(Me)=CH_2$	$Me_2C=CHCOMe$		
	1	1 day (neat)	0.86		0	0.36	0.14	
	2	1 day (neat)	0.54 →0.02[c)]		0.40 →0.96[c)]	0.12	0.06 →0.17[c)]	
PhCHO				PhCOPh		$PhCOOCH_2Ph$		
	1	1 day (Et_2O)		0.84		0.20	trace	0
	2	1 day (Et_2O)		0.88		trace	0	0.06
PhCOPh			Ph_3COH					
	1	1 day (Et_2O)	0.41					
	2	30min (Et_2O)	0.17					

a) Reactions were carried out under N_2 at room temperature. Two to ten times of aldehydes or ketones to the complexes were used except the reaction with acetone which was carried out in neat acetone. b) In the reactions with complex **2**, three moles of THF 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 this system. The figures placed after the arrows indicate the yields after treatment with phenol.

In the case of aldehyde, the presence of β-hydrogen atom in the intermediate A makes it possible to give ketone via a β-elimination process (path a in Eq. 2). This is the case when benzaldehyde was allowed to react with **1** or **2** in which benzophenone was the sole phenylated product. In the reaction of acetaldehyde, the majority of the intermediate A may have abstracted hydrogen from the aldehyde or solvent. The large difference in the yields of ketone and alcohol in this system makes the bimolecular hydrogen transfer mechanism (disproportionation) less probable.

In the case of ketone, the absence of β-hydrogen atom in the intermediate B leads to the exclusive formation of tertiary alcohol on the hydrogen abstraction.

It is noted in Table 1 that styrene and α-methylstyrene were formed in the reactions of acetaldehyde and acetone, respectively, only when phenylchromium complex **2** was employed. In view of the known fact that alcohols are dehydrated in the presence of acid to give olefin,[9)] it is considered that styrene and α-methylstyrene are formed by the dehydration of 1-phenylethanol and 1-methyl-1-phenylethanol, respectively. In fact, complete conversion of 1-phenylethanol to styrene was observed to take place in diethyl ether containing aqueous HCl at room temperature in 10 min. Furthermore, the assumption that the alcohol is a precursor for the olefin formation in the present system was confirmed by the following experiment. After the completion of the reaction between **2** and acetone, the weak acid such as phenol was introduced to the system and the reaction mixture was stirred for 60 min at room temperature. This resulted in the appreciable increase in the yield of α-methylstyrene at the expense of the alcohol (footnote c in Table 1). These results indicate the more acidic nature of **2** than **1**. This is in line with the observed increase in the yields of aldol condensates, crotonaldehyde and mesityl oxide in the reactions of acetaldehyde and acetone, respectively, with **1** as compared with **2**. The aldol condensation reaction is known to be accelerated in the basic conditions.$^{10)}$ In the case of benzaldehyde having no hydrogen atom on the β-carbon, the ester formation reaction similar to the known Tischchenko reaction$^{11)}$ took place to yield benzyl benzoate. Although the reactions of trialkyl(aryl)chromium complex with aldehydes or ketones to give tertiary alcohols have been known,$^{12)}$ the present results exemplify the first such reactions with monoarylchromium complex.

Despite of the high reactivities of **1** and **2** to the carbonyl compounds such as aldehydes and ketones, which can be compared with the reactivities of Grignard reagents, compounds **1** and **2** did not react with atmospheric pressure of carbon monoxide, carbon dioxide and oxygen at room temperature. Furthermore, compounds **1** and **2** were found to be inert to hydrogen at atmospheric pressure, although there has been a report on the reaction of $Li_3Cr(Ph)_6$ with hydrogen gas to give benzene and $Li_3Cr(Ph)_5(H)$.$^{13)}$

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