BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 648—649 (1972)

Reactions of Grignard Reagents with Chromium(IV) *t*-Butoxide: Unstable Organochromium(IV) Intermediates

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(Received February 22, 1971)

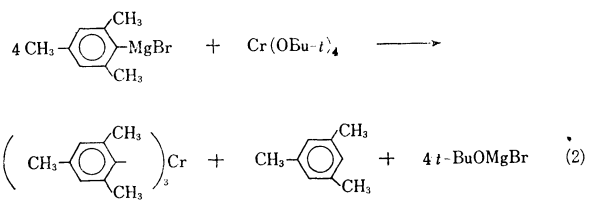
Several organochromium(III) compounds have been characterized[1] and others have been postulated as intermediates in reactions.[2] Chromium(IV) is less common and only a few compounds with this oxidation state are known.[3] We have examined the metathesis between chromium(IV) tetra-*t*-butoxide[4] [$Cr(OBu\text{-}t)_4$] and various Grignard reagents with the intention of

$$Cu^{IV}(OBu\text{-}t)_4 + nRMgX \longrightarrow \underset{\mathbf{I}}{R_nCr^{IV}(OBu\text{-}t)_{4-n}} + n\ t\text{-}BuOMgX \quad (1)$$

probing the properties and stabilities of alkyl and arylchromium(IV) species, I.

Results and Discussion

Aryl Grignard Reagents and Cr(OBu-t)$_4$. Mesityl derivatives of chromium III and II are significantly more stable than their phenyl analogs.[1a,5] The reaction between mesitylmagnesium bromide and $Cr(OBu\text{-}t)_4$ in a 4:1 molar ratio in tetrahydrofuran (THF) solution at 25°C was observed by following the disappearance of the visible absorption band of $Cr(OBu\text{-}t)_4$ at 630 nm as shown in Fig. 1. After 48 hr the visible absorption spectrum (λ_{max}=518 nm) and the electron paramagnetic resonance (EPR) spectrum ($\langle g\rangle$= 1.983) of the solution were the same as those of trimesitylchromium(III) prepared from mesitylmagnesium bromide and chromium(III) chloride.[5b] Addition of a solution of mercuric chloride in THF quantitatively converted mesitylchromium(III) and unreacted mesitylmagnesium bromide into mesitylmercuric salts,[5] which were separated and the resulting solution was analyzed. Quantitative gas chromatography indicated the presence of 1.11 mol of mesitylene per mol of $Cr(OBu\text{-}t)_4$, but only traces of bimesitylene. The partial stoichiometry of the reaction is:



The analogous reaction between phenylmagnesium bromide and $Cr(OBu\text{-}t)_4$ in a molar ratio of 4:1 produced after 2 hr a yellow-green solution whose absorption spectrum (λ_{max}=473 nm) was similar to that of a red-brown solution (λ_{max}=445 nm) of triphenylchromium(III) generated from chromium(III) chloride. The presence of other phenylchromium species derived from Ph_2Cr was suspected, but this possibility was discarded by a negative qualitative test. Thus, Ph_2Cr is unstable and is transformed to a π-arene chromium complex which on treatment with sodium tetraphenylboride after aerial oxidation should have afforded a π-arenechromium(I) salt,[6] but none was found. Excess phenylmagnesium bromide also reacted with either $CrCl_3$ or $Cr(OBu\text{-}t)_4$ to afford a solution of phenylchromium(III) species absorbing at 408 nm. On standing both reactions gave rise to dark red-brown solutions showing the same visible absorption spectrum. These differences were attributed to various phenylchromium(III) complexes containing other ligands,[5d] and not to the presence of phenylchromium(II). Analysis of the reaction mixture indicated the presence of biphenyl according to the following stoichiometry:

$$4PhMgBr + Cr(OBu\text{-}t)_4 \longrightarrow Ph_3Cr + \frac{1}{2}Ph\text{-}Ph + 4\ t\text{-}BuOMgBr \quad (3)$$

Alkyl Grignard Reagents and Cr(OBu-t)$_4$. Ethylmagnesium bromide and $Cr(OBu\text{-}t)_4$ were mixed in a 4:1 molar ratio in THF solution at −78°C. No reaction occurred until the temperature was raised to −55°C when the color changed abruptly from blue to brown, and a more of less equimolar mixture of ethane and ethylene (no butane) was slowly evolved. The EPR spectrum (g=1.993) of the solution taken at below −20°C was the same as that (g=1.994) of triethylchromium(III) prepared from ethylmagnesium bromide and chromium(III) chloride[1c,d,f] and shown to be relatively stable under these conditions. Approximately 1 mol of hydrocarbons was liberated from each mol of $Cr(OBu\text{-}t)_4$ between −55 and −25°C. We conclude that ethylchromium(IV) species (I, R=CH_3CH_2) are unstable between these temperatures.

$$Cr(OBu\text{-}t)_4 + 4CH_3CH_2MgBr \longrightarrow \underset{\mathbf{I}}{[CH_3CH_2Cr^{IV}]}$$

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$$I \longrightarrow (CH_3CH_2)_3Cr + [CH_3CH_3 + CH_2{=}CH_2] + 4\,t\text{-BuOMgBr} \quad (4)$$

Similarly methylmagnesium bromide and Cr(OBu-t)$_4$ reacted at less than −30°C and only methane (no ethane or ethylene) was liberated as the temperature was raised further to 25°C. The EPR spectrum (g=1.997) of the solution taken at −20°C was the same as that (g=1.995) of trimethylchromium(III) prepared for methylmagnesium bromide and chromium(III) chloride. Hydrolysis of the reaction mixture after completion produced only 65% of methane based on the methylmagnesium bromide used.

$$4CH_3MgBr + Cr(OBu\text{-}t)_4 \longrightarrow (CH_3)_3Cr + CH_4 + 4\,t\text{-BuOMgBr} \quad (5)$$

The latter reflected loss of methyl groups by attack on solvent, incontrast to the good material balance obtained withthe ethyl analog.

Organochromium(IV) Species. We conclude from these studies that alkyl and arylchromium(IV) species are rather unstable intermediates and readily converted to trialkyl and triarylchromium(III) under these conditions. During the slow conversion of Cr(OBu-t)$_4$ by mesitylmagnesium bromide shown in Fig. 1, a metastable species absorbing at approximately 600 nm could be seen after 1.5 hr. Analogous changes in the EPR spectrum of the solution were also observed. Thus, Cr(OBu-t)$_4$ showed only a weak and broad EPR spectrum (g=1.964) in THF solution. On reaction with mesitylmagnesium bromide a new species was found. The multiplet (g=1.983) absorption of this species slowly changed to one characteristic of trimesitylchromium(III). We associate both observations with an intermediate mesitylchromium(IV) species. It is, however, clear that organochromium(IV) species of the kind indicated by I are too unstable for isolation and should be compared with the recently reported trimethylsilylmethyl derivatives.[7a]

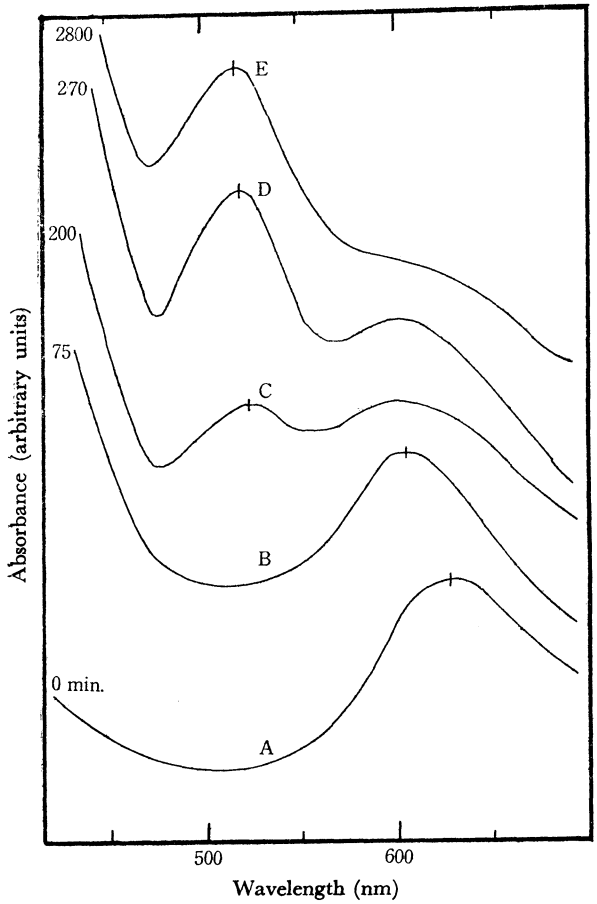

Fig. 1. Reaction of 0.039M Cr(OBu-t)$_4$ and 0.16M mesitylmagnesium bromide in THF at 25°C. A, mix; B, 75 min; C, 200 min; D, 270 min; E, 2800 min. A and E correspond to spectra of Cr(OBu-t)$_4$ and Mes$_3$Cr, respectively.

Experimental

Materials. Cr(OBu-t)$_4$ was prepared according to the reported procedure[8] from bis-benzene chromium[9] and di-t-butyl peroxide in benzene. The purity of Cr(OBu-t)$_4$ checked by iodometry was 95.0%. The Grignard reagents were synthesized under nitrogen by the conventional method. Tetrahydrofuran was refluxed and distilled over $LiAlH_4$ under nitrogen. $CrCl_3$ was used as purchased.

All operations described below were carried out under nitrogen atmosphere except the operation following the addition of $HgCl_2$.

The Reaction of Cr(OBu-t)$_4$ and Mesitylmagnesium Bromide. To the magnetically stirred solution of 4.25 ml THF containing 0.30 mmol Cr(OBu-t)$_4$ in a 100 ml flask, 0.75 ml THF solution containing 0.88 mmol mesitylmagnesium bromide was added at −78°C with a hypodermic syringe. The reaction mixture was gradually warmed to room temperature and kept at ambient temperatures for 50 hr. Of the reaction mixture, 1.80 ml was removed to a 50 ml test tube capped with a rubber septum, and 0.53 ml THF solution of 0.70 mmol $HgCl_2$ was added. After 20 hr the inorganic precipitate was removed by filtration and the resulting solution was analyzed for mesitylene by quantitative gas chromatography (6 ft DEGS on firebrick, durene as a marker).

The Reaction of Cr(OBu-t)$_4$ and Ethylmagnesium Bromide. To a 50 ml test tube capped with a rubber septum, 4.80 ml THF solution of 0.08 mmol Cr(OBu-t)$_4$ was added with a hypodermic syringe chilled to −78°C. Then 0.20 ml THF solution of 0.32 mmol ethylmagnesium bromide was added to this magnetically stirred solution, followed by the injection of 0.50 ml of methane marker gas. The reaction temperature was gradually raised by allowing the ice bath to stand at ambient temperatures. Quantitative gas chromatography analysis using a Porapak column for ethane and ethylene formation was carried out periodically at various temperatures. Standard mixtures of methane, ethane, and ethylene without substrate were calibrated under the same conditions.

EPR Spectra. EPR spectra of THF solutions of the organochromiums were obtained using a Varian E-4 spectrometer. Solutions of the organochromium species were prepared by mixing the degassed THF solutions of Cr(OBu-t)$_4$ and the Grignard reagents at the dry-ice temperature and transferring directly the resulting reaction mixture to an EPR sample tube cooled to dry-ice temperatures. g-Values were determined by calibration with DPPH powder.

We wish to thank the National Science Foundation, U. S. A. for financial support.

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