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Preliminary communication

Preparation of peralkylchromium(IV) compounds*

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SUMMARY

Tetra-t-butylchromium was prepared from $CrCl_3 \cdot 3THF$ and t-butyllithium in pentane by a disproportionation reaction or from tetra-t-butoxychromium and t-butyllithium. It was isolated by sublimation and characterized by ESR, UV, visible and IR spectra. The following compounds were not isolated but characterized in solution by their ESR spectra: tetramethylchromium, tetraisopropylchromium, tetra-sec-butylchromium, tetra-n-butylchromium, tetra-3-pentylchromium and tetrakis(cyclohexylmethyl)chromium.

INTRODUCTION

Alkyl-transition metal compounds undergo thermal decomposition, if processes such as α- or β-elimination of a metal hydride, homolysis, or coupling of ligands at the transition metal can occur[1—3]. Intramolecular transfer of hydrogen from a β-carbon to the metal is considered to be the dominant path when it can occur[4]. The recent preparations of peralkyl transition metal compounds, whose decomposition by β-hydrogen elimination is prevented by using alkyl ligands of the type $-CH_2X$, where X is an atom without a hydrogen (*e.g.*, $-C(CH_3)_3$ [5], $-Si(CH_3)_3$ [4,6], $-C_6H_5$ [7,8], 1-norbornyl[9]), show that extremely stable peralkyl transition metal compounds can be prepared, and that the presence of strong ligands such as tertiary phosphines and similar ligands is not necessary. Steric crowding also contributes to the stability of these compounds, as is particularly shown by our preparation of $t\text{-}Bu_4Cr$. Models show that four t-butyl groups fit snugly around the first row transition metals. The crowding of these bulky groups may make it difficult for them to achieve the geometry required in the transition state for β-hydrogen elimination. Steric bulk of the t-butyl group has been invoked to explain the exceptional

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stability[10] of $(h^5\text{-}C_5H_5)Fe(CO)_2$-t-Bu. Rate measurements of the decomposition of alkylmanganese compounds[16], prepared *in situ*, show that t-butylmanganese compounds decompose by orders of magnitude faster than methyl, neopentyl, and benzyl compounds. In this case the t-butyl group is not in a crowded situation and β-hydrogen elimination can occur easily. Whether the tetrahedral d^2 electron configuration of chromium(IV) also contributes to the stability of chromium(IV) peralkyls, deserves further investigation.

EXPERIMENTAL

All preparative work and handling of air-sensitive material was done in "pop bottles"[11]. The commercially unavailable alkyllithium compounds were prepared by adding 100 mmoles of the alkyl chloride to 1.4 g lithium wire (0.08% Na) in 100 ml pentane in a pop bottle. The reaction mixture was kept for 6 h at 70° under stirring (about 2 atm pressure developed), centrifuged while still warm and the supernatant liquid containing the alkyllithium separated from the insoluble portion.

t-Bu_4Cr. One equivalent $Cr(OR)_4$ [12] (R = t-butyl) was treated with four equivalents of t-butyllithium in pentane at –78°, which produced a violet precipitate. On warming to room temperature the solid disappeared and the solution became red-brown. The reaction mixture was chromatographed anaerobically on basic alumina, and the dark red t-Bu_4Cr (I), which was eluted with pentane, was sublimed at 55° under vacuum (10^{-4} mmHg). Based on $Cr(OR)_4$, the yield was 60%. (I) was also prepared from $CrCl_3 \cdot 3THF$ [13], analogous to the preparation of tetra-1-norbornylchromium[9]. One equivalent of $CrCl_3 \cdot 3THF$, suspended in pentane, was treated with four equivalents of t-butyllithium at –78°, and within a few minutes the reaction mixture became red-brown. Gaseous CO_2 was introduced at room temperature to remove excess t-butyllithium. The centrifuged supernatant liquor was evaporated and the pyrophoric solid sublimed. The yield was 10% with respect to $CrCl_3 \cdot 3THF$. (Analysis, found: Cr, 18.53%; calc.: Cr, 18.54%. M.p. 80°, dec.).

$(neo\text{-}C_5H_{11})_4Cr$ (II). (II) was prepared by disproportionation from $CrCl_3 \cdot 3THF$ and neopentyllithium in pentane in 25% yield. It was also prepared by a one-step procedure. The neopentyl chloride was added to a pentane or ether suspension of lithium pieces and $CrCl_3 \cdot 3THF$ and the reaction mixture was stirred overnight at room temperature to produce (II). Magnesium in ether can be used instead of lithium.

Other peralkylchromium(IV) compounds. A wide variety of peralkylchromium(IV) compounds, more or less stable between –78° and room temperature, were prepared by the reaction of $(t\text{-}BuO)_4Cr$ with the corresponding alkyllithiums in pentane at –78°. The following compounds were not isolated but were characterized in solution by their ESR signals[14]: Me_4Cr, i-Pr_4Cr, s-Bu_4Cr, n-Bu_4Cr, $(3\text{-}C_5H_{11})_4Cr$, tetrakis(cyclohexylmethyl)chromiun (cyclohexylmethyl)chromium. Whereas the Me_4Cr starts decomposing above –78°, tetrakis(cyclohexylmethyl)chromium and n-Bu_4Cr are stable for several hours at 0° in solution. These compounds could not be prepared by disproportionation of chromium(III).

By increasing the bulkiness of the alkyl group, we hoped to prepare stable peralkyl chromium(III) compounds. However, the ESR spectra showed that even the very bulky neophyllithium and $(C_2H_5)_3CCH_2Li$ yielded the peralkylchromium(IV) compounds from $CrCl_3 \cdot 3THF$ by disproportionation in pentane suspension. These disproportionation reactions occur in hydrocarbons and ether. They do not occur when THF is used as the solvent because the greater basicity of THF apparently stabilizes chromium(III) in an octahedral, hexacoordinate form.

Physical chemical measurements

The magnetic susceptibilities of 0.3 *M* heptane solutions of (I) and (II) were measured by the Gouy method. For (I), the magnetic moment, μ_{eff}' was 2.6 B.M. and for (II) it was 2.9 B.M. These values approximate those expected for two unpaired electrons in low-lying e_g orbitals. The ESR spectra agreed with those of tetravalent chromium[14].

The IR spectrum of (I) in heptane showed weak absorptions at 572, 500, 428, and 408 cm^{-1} which probably result from skeletal vibrations. A medium intensity band at 385 cm^{-1} may be assigned to the Cr—C stretching frequency. (II) showed medium intensity bands at 590, 555, 515, 445, and 375 cm^{-1}.

The electronic spectra showed peaks for (I) at 487 nm ($\alpha = 800$) with a shoulder at 640 nm ($\alpha = 200$) and for (II) at 485 nm ($\alpha = 850$), shoulder at 640 nm ($\alpha = 240$). These data indicate that the t-butyl and neopentyl groups are strong field ligands. The higher extinction coefficient[15] as compared with octahedral $[Cr(CH_3)_6]^{3-}$ is expected for a tetrahedral species having no symmetry center. In the UV region (to 250 nm), (I) had a strong charge transfer band at 290 nm ($\alpha = 2.2 \cdot 10^4$) and (II) at 287 nm ($\alpha = 3.3 \cdot 10^4$) and 256 nm ($\alpha = 3.9 \cdot 10^4$). Mass spectral measurements were performed with a Du Pont CEC-21-110 mass spectrometer using probe introduction. When the electron impact technique was used at 70eV, the mass spectra of (I) and (II) exhibited extensive fragmentation. No parent mass peak ($m/e = 280$) was observed for (I), but 0.39% of the base peak ($m/e = 107$) was observed at $m/e = 223$ corresponding to the $t\text{-}Bu_3Cr^+$ ion. (II) showed the parent mass peak at $m/e = 336$ (1% of base peak $m/e = 108$) and 1.7% $m/e = 265$ corresponding to $(neo\text{-}C_5H_{11})Cr^+$. When the field ionization technique was used,(II) gave only the parent peak at $m/e = 336$ whereas no parent peak of (I) was observed.

Thermal decomposition experiments

No significant decomposition of (II) was observed after several days in heptane solution at 80°. The half-life for thermal decomposition of (I) in heptane at 70° was 4.5 min as measured by first order plots of the decrease of the mid field chromium(IV) ESR signal. Over the range of 55 to 80°, the energy of activation (E_a) was 29 ± 3 kcal/mole. The main decomposition products at 80° were isobutane and isobutylene in a ratio of 6.5/1. Small amounts of methane, ethane, and propane were also detected. The black precipitate consisted mostly of chromium metal, but contained 5% carbon. Thermal decomposition of σ-alkylcopper compounds under mild conditions does not involve free alkyl radicals. It appears that the intense reactivity of the intermediate decomposition products, *e.g.*, R_3Cr, R_2Cr, can lead to a complicated product mixture.

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