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REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS

XIV*. TIN — CARBON BOND CLEAVAGE IN REACTIONS OF IODOMETHYLTRIMETHYLTIN WITH METAL CARBONYL ANIONS

R.B. KING and K.C. HODGES

Department of Chemistry, University of Athens, Georgia 30601 (U.S.A.)

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Summary

Reactions of $(CH_3)_3SnCH_2I$ with the sodium salts $NaMo(CO)_3C_5H_5$, $NaFe(CO)_2C_5H_5$, $NaMn(CO)_5$, and $NaCo(CO)_4$ in tetrahydrofuran did not give the corresponding $(CH_3)_3SnCH_2M(CO)_x(C_5H_5)_y$ derivatives but instead resulted in cleavage of a carbon—tin bond to give the corresponding trimethyltin derivatives $(CH_3)_3SnM(CO)_x(C_5H_5)_y$ ($M = Mo, x = 3, y = 1; M = Fe, x = 2, y = 1; M = Mn, x = 5, y = 0; M = Co, x = 4, y = 0$) and methyl derivatives $CH_3M(CO)_x(C_5H_5)_y$ ($M = Mo, x = 3, y = 1; M = Fe, x = 2, y = 1; M = Mn, x = 5, y = 0$).

Results

Reactions of bromomethyltrimethylsilane, $(CH_3)_3SiCH_2Br$, with various metal carbonyl anions yield trimethylsilylmethyl transition metal derivatives of the type $(CH_3)_3SiCH_2M(CO)_x(C_5H_5)_y$ in which a carbon atom is bonded both to silicon and a transition metal [2,3]. In an attempt to prepare trimethylstannylmethyl transition metal derivatives of the type $(CH_3)_3SnCH_2M(CO)_x$-$(C_5H_5)_y$, analogous reactions of the recently reported [4] iodomethyltrimethyltin with sodium salts of various metal carbonyl anions [5] were investigated. The sodium salts $NaMo(CO)_3C_5H_5$, $NaMn(CO)_5$, $NaFe(CO)_2C_5H_5$, and $NaCo(CO)_4$ were used for this study, since they represent the different basic types of metal carbonyl anions which are alkylated by appropriate alkyl halides to form transition metal alkyls with metal—carbon σ-bonds.

None of the reactions of iodomethyltrimethyltin with the four sodium salts $NaMo(CO)_3C_5H_5$, $NaMn(CO)_5$, $NaFe(CO)_2C_5H_5$, and $NaCo(CO)_4$ (Table 1) gave any evidence for formation of the desired trimethylstannylmethyl derivatives $(CH_3)_3SnCH_2M(CO)_x(C_5H_5)_y$. In all four cases the yields of identifiable organometallic products were low. In each case a major portion of the organometallic product was the corresponding trimethyltin derivative

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[*] For Part XIII see ref. 1.

TABLE 1

REACTIONS OF SODIUM SALTS OF METAL CARBONYL ANIONS WITH IODOMETHYLTRIMETHYLTIN

Sodium Salt[a,b]	Me_3SnCH_2I	Product(s)[a]	Isolation and Purification[c]	Identification[d]
$NaMo(CO)_3Cp$(7.6 mmoles)	7.35 mmoles	(1) $Me_3SnMo(CO)_3Cp$ (0.123 g., 0.30 mmoles) (2) $MeMo(CO)_3Cp$ (0.074 g., 0.28 mmoles)	Ev, E(Hex), Chr(CH_2Cl_2, Al), FS(35 - 60°/0.05 mm)	IR, NMR, MS, m.p. IR, NMR, MS, m.p.
$NaFe(CO)_2Cp$(11.4 mmoles)	11.2 mmoles	(1) $Me_3SnFe(CO)_2Cp$ (0.37 g., 1.08 mmoles)[e] (2) $MeFe(CO)_2Cp$ (0.96 g., 5.0 mmoles)[e]	Ev, E(CH_2Cl_2), Chr(Hex) D(75/0.5, VPC(160°)[e]	C, H, O: IR, NMR, MS NMR of mixture[e]
$NaMn(CO)_5$ (10.2 mmoles)	7.23 mmoles	(1) $Me_3SnMn(CO)_5$ (0.3 g., 0.84 mmoles) (2) $MeMn(CO)_5$ (trace)	Ev, E(Pent), Chr(Pent, Fl) D(40/40)	C, H, O: IR, NMR, MS IR, m.p.
$NaCo(CO)_4$ (11.0 mmoles)	9.2 mmoles	$Me_3SnCo(CO)_4$ (1.14 g., 3.4 mmoles)	Ev, E(Hex), S(38/1), Cr (Hex, −78°), S(40/1)	C, H, O, Co: IR, NMR, MS, m.p.

[a] Me = methyl; Cp = cyclopentadienyl.

[b] These sodium salts were prepared and handled in tetrahydrofuran solutions without isolation. The quantities given assume quantitative formation of the sodium salts from their precursors. The total volume of tetrahydrofuran was about 200 ml.

[c] The isolation and purification techniques are abbreviated as follows: Ev = evaporation (at 25°/35 mm.), E = extraction (solvent in parentheses), Chr = column chromatography (solvent and solid phase in parentheses), *FS = fractional* sublimation, D = distillation (°C/mm.), S = sublimation (°C/mm.), VPC = vapor phase chromatography (temperature in parentheses), Cr = crystallization (solvent, temperature to which solution cooled), Hex = hexane, Pent = pentane, Al = alumina, Fl = florisil.

[d] The elements for which satisfactory analyses were obtained by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, are listed followed by physical and spectroscopic identification techniques abbreviated as *follows: IR* = infrared spectrum in ν(CO) region, NMR = proton n.m.r., MS = mass spectrum including molecular ion, m.p. = melting point in capillaries.

[e] The indicated quantities of $Me_3SnFe(CO)_2Cp$ and $MeFe(CO)_2Cp$ were only obtained as an inseparable mixture analyzed by proton NMR. Vapor phase chromatography of this mixture at 160° resulted in complete decomposition of the $MeFe(CO)_2Cp$ but isolation of pure $Me_3SnFe(CO)_2Cp$.

$(CH_3)_3SnM(CO)_x(C_5H_5)_y$ [6]. Formation of the corresponding methyl derivative $CH_3M(CO)_x(C_5H_5)_y$ was also demonstrated in three of the four reactions (Table 1); however, the methylcobalt derivative $CH_3Co(CO)_4$ was not detected in the reaction of $NaCo(CO)_4$ with iodomethyltrimethyltin, since $CH_3Co(CO)_4$ decomposes [7] above −35°. Since all of the trimethyltin and methyl transition metal carbonyl derivatives are well-known compounds, details of the characterization and identification of these products are not given.

The formation of the trimethyl derivatives $(CH_3)_3SnM(CO)_x(C_5H_5)_y$ from metal carbonyl anions and iodomethyltrimethyltin necessarily must involve cleavage of a tin—carbon bond according to the following equation:

$$(CH_3)_3SnCH_2I + Na[M(CO)_x(C_5H_5)_y \rightarrow (CH_3)_3SnM(CO)_x(C_5H_5)_y + \text{“}NaCH_2I\text{”}$$

The concurrently formed methyl transition metal derivative can arise from further reaction of the unstable "$NaCH_2I$" involving additional metal carbonyl anion.

Analogous reactions of halomethyltrimethylsilanes with metal carbonyl anions to give mixtures of the corresponding trimethylsilyl derivatives $(CH_3)_3SiM(CO)_x(C_5H_5)_y$ and methyl derivatives $CH_3M(CO)_x(C_5H_5)_y$ have been reported [3] but these do not occur to the exclusion of the normal nucleophilic substitution of halomethyltrimethylsilanes with metal carbonyl anions to form the trimethylsilylmethyl derivatives $(CH_3)_3SiCH_2M(CO)_x(C_5H_5)_y$ as is found in this work with the corresponding tin compounds. The lower chemical stability of carbon—tin bonds relative to carbon—silicon bonds can account for this difference.

This work also inadvertently provided a new demonstration of the greater thermal stability of transition metal bonds to silicon or tin relative to similar transition metal σ-bonds to carbon. Vapor phase chromatography of a mixture of the derivative $(CH_3)_3SnFe(CO)_2C_5H_5$ with an iron—tin σ-bond and the derivative $CH_3Fe(CO)_2C_5H_5$ with an iron—carbon σ-bond at 160° resulted in the complete thermal decomposition of $CH_3Fe(CO)_2C_5H_5$ but the recovery of much of the $(CH_3)_3SnFe(CO)_2C_5H_5$.

Experimental

Iodomethyltrimethyltin was prepared from trimethyltin chloride, diiodomethane, and zinc—copper couple according to the previously [5] described procedure. The product was distilled and its purity checked by proton NMR before use. The sodium salts $NaMo(CO)_3C_5H_5$ [8,9], $NaFe(CO)_2C_5H_5$ [8,9], $NaMn(CO)_5$ [10], and $NaCo(CO)_4$ [7] were prepared by the cited procedures. Reactions were run in tetrahydrofuran and products isolated and purified as summarized in Table 1. The products $(CH_3)_3SnMo(CO)_3C_5H_5$ [6], $CH_3Mo(CO)_3C_5H_5$ [8], $(CH_3)_3SnFe(CO)_2C_5H_5$ [11], $CH_3Fe(CO)_2C_5H_5$ [8], $(CH_3)_3SnMn(CO)_5$ [12], $CH_3Mn(CO)_5$ [13] and $(CH_3)_3SnCo(CO)_4$ [14] are all well-known compounds and were identified by comparison of their indicated properties (Table 1) with those given in the cited references or with those of authentic samples prepared in our laboratory by the cited procedures. Details of the spectroscopic techniques [1,15] are the same as in previous work.

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