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Synthesis of Trilithiomethane

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In 1917 the first synthesis of methyllithium was reported by Schlenk.[1] In 1955, the first synthesis of a polylithium compound, dilithiomethane, was reported by Ziegler,[2] and subsequently, tetralithiomethane was prepared in 1972 by Chung and Lagow.[3] Trilithiomethane, $(HCLi_3)_n$, is the final lithium-substituted methane to be prepared and has been synthesized by modifying the earlier procedures.[3]

Aside from utility as a reagent and historical interest, trilithiomethane is of particular interest in modern organic, inorganic, and theoretical chemistry. Hoffmann has recently discussed the requirements for stabilizing planar carbon species.[4] Schleyer and Pople[5] have discussed and predicted the low-lying energy state of *cis*-dilithiomethane and indicated that this species along with trilithiomethane and tetralithiomethane are excellent candidates for observation of the long-sought anti-Le Bel and Van't Hoff simple planar carbon species. There are some indications that the trilithiomethane monomer might be the carbon-lithium species with the greatest propensity for planarity. Of course, solid trilithiomethane is a three-dimensional polymer that reacts chemically as if it were a monomer in a manner similar to the well-known "monomeric" reactions of the methyllithium tetramer.

Trilithiomethane was prepared in 15.5% yield by cocondensing lithium vapor at 750 °C under vacuum with chloroform ($CHCl_3$) on a cryogenic surface. By use of older synthetic methods,[3] retention of the protonated site on chloroform would have been impossible. Under the previously reported reaction conditions, the exothermicity of the reaction leads to substantial vibrational excitation of the carbon-hydrogen bond and subsequently lithium substitutions, leading to perlithiated[6] products such as $(CLi_4)_n$. Milder reaction conditions were chosen to optimize preferential substitution for chlorine.

The reaction was carried out in the stainless steel reactor illustrated in Figure 1. In a 60-min reaction ca. 10 g of lithium (1.43 mol) vaporized at 750 °C was reacted with 2.5 mL of $CHCl_3$ (31.1 mol). The reactor was then opened under argon, and a black powder (still containing some metallic lithium) was removed from the cold finger.

For characterization, samples of mixtures of lithiated methanes of higher purity, which have been sieved under argon and extracted from lithium, are light tan to white. The reactive solid was slowly hydrolyzed with D_2O vapor over a 2-day period on a vacuum line. The hydrolysis gases were separated on a phenyl isocyanate/Porasil C column utilizing a temperature-programmed gas chromatographic procedure. The individual compounds were identified and quantitated by comparison of their retention times and peak areas with those of known samples. The degree of deuteration (which corresponds to lithium substitution) and identity of each species were determined by high-resolution mass spectrometry. Mass spectral intensities were used to determine the percentages of each methane species. The results are listed in Table I.

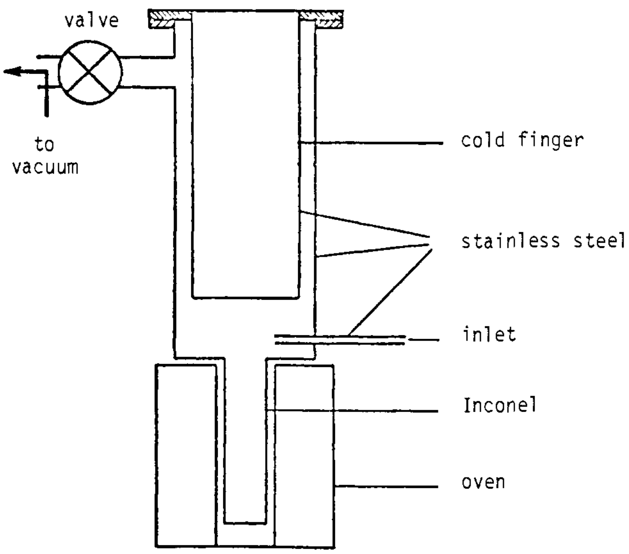

Figure 1. Basic reactor.

Table I. Composition of Hydrolysis Products (%)

CH_4	2.1	CD_4	20.1
CH_3D	3.5	C_2D_2	39.7
CH_2D_2	19.1	C_2D_4	trace
CHD_3	15.5		

Flash vaporization mass spectrometry[7,8] was also utilized in characterizing the vapor species of trilithiomethane $(HCli_3)_n$. The common peaks found in the mass spectrum include $(HCLi_3)_n^+$ (n = 1-4) and $(HCLi_3)_n\mathit{Li}^+$ (n = 1-3). More details on the results, techniques, and apparatus will be the subject of another manuscript.[11]

The reactive solid was derivatized by adding chlorotrimethylsilane to a -78 °C THF solution of the reaction product, which was warmed to room temperature and then stirred over a 24-h period. Removal of the solvent by distillation yielded an oily residue, which was characterized by using a temperature-programmed gas chromatograph incorporating a 10% SE 30/chromosorb P column and low-resolution mass spectrometry. Reference samples of bis-, tris-, and tetrakis(trimethylsilyl)methanes were prepared according to methods reported by Merker and Scott.[9] Mass spectral fragmentation patterns for the monosilyl-, disilyl-, trisilyl-, and tetrasilylmethanes have been reported by Dimmel.[10] The ^1H NMR spectra of the individual chromatographed fractions were identical with those obtained by Merker and Scott[9] for bis-, tris-, and tetrakis(trimethylsilyl)methanes.

The reaction at high temperature of lithium vapor with halogenated organic compounds as a general synthesis for polylithium compounds has been reported.[3,6] Utilizing this approach, we have been able to synthesize the entire species of lithiated methanes.[11]

To purify the trilithiomethane for spectroscopic study, it will be necessary to find another synthesis that gives only $(CHLi_3)_n$ or to find a method for separation of this compound from $(CH_2Li_2)_2$ and $(CLi_4)_n$. Presently we are able to separate $(CLi_4)_n$ and $(CH_2Li_2)_n$ from lithium metal, LiCl, LiH, etc., and numerous spectroscopic studies are being undertaken.[12]

Present work is proceeding toward finding satisfactory solvents for further study of these interesting species.

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A General Homogeneous Catalytic Method for the Homologation of Methanol to Ethanol

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The direct conversion of synthesis gas to ethanol[1] and the indirect reaction of synthesis gas with methanol to yield ethanol (homologation)[2] have been studied as possible alternative processes for the production of ethanol from coal. We have discovered an unusually general catalytic method for methanol homologation occurring in methanol solutions of amines at synthesis gas pressures near 300 atm and temperatures near 200 °C. Significantly, methanol is homologated while ethanol is essentially unaffected. In each case, carbon dioxide is the oxygenated byproduct, and ethanol is formed according to the following stoichiometry:[3]

$$CH_3OH + 2CO + H_2 = CH_3CH_2OH + CO_2 \qquad (1)$$

Since our first observation of this type of reaction using $Fe(CO)_5$ catalyst,[4] we have become aware of the method's generality extending to several diverse metal centers. Table I lists reactivity characteristics of complexes that we have found to be active in amine–methanol solution. At present, we have accumulated a reasonably detailed knowledge of the mechanism for the iron carbonyl system. More important, however, a clear picture of a common pathway for all of the complexes in Table I has emerged. In general, all of the catalytic reactions use methylammonium ions as methyl carriers, transition-metal complex anions as nucleophilic methyl acceptors, and catalytic decomposition of formic acid to remove protons generated in hydrogen activation steps.

In contrast to the well-known $HCo(CO)_4$-catalyzed reaction,[2] in which methyl groups are activated by protonation of methanol, the new systems activate methyl groups via equilibria[5] of eq 2 and 3, which are established rapidly in methanol solutions of amine

$$CH_3OH + CO \overset{B}{\rightleftharpoons} HCO_2CH_3 \qquad (2)$$

$$HCO_2CH_3 + B \rightleftharpoons CH_3B^+ + HCO_2^- \qquad (3)$$

(B).[6] The method's characteristic selectivity for methanol vs. ethanol homologation arises in step 3, which generates the active methyl transfer reagent.[7] Attack (S_N2) on methyl formate by trimethylamine is preferred for steric reasons over attack on ethyl formate. In S_N2 reactions involving poor leaving groups, methyl transfers have been reported to be as much as 150 times faster than ethyl transfers.[8]

Table I. Reactivity Patterns for Catalysis of Methanol Homologation in Amine–Methanol Solution[a]

expt no.	complex (mmol)	reaction time, h	C_2H_5OH,[b] mmol	CH_4, mmol	turnover freq,[c] h^{-1}
1	$Fe(CO)_5$ (16.0)	6.0	34	73	1.1
2[d,e]	RhI_3 (5.0)	2.0	42	19	6.1
3[e,f]	$Ru_3(CO)_{12}$ (5.33)	3.4	26	26	0.96
4	$Mn_2(CO)_{10}$ (11.5)	6.0	102	22	0.90
5[g]	$Mn_2(CO)_{10}$ (11.5)/ $Fe(CO)_5$ (16.0)	6.0	330	67	2.9
6[e,g,h]	$Mn_2(CO)_{10}$ (6.3)/ $Fe(CO)_5$ (60.5)	2.0	199	79	11.0

[a] In methanol solution (160 mL) containing 1-methylpiperidine (2.0 M); reaction at 200 °C and at 300 atm of 3:1 CO/H_2 with continuous gas purge of 600 mL/min. The volumes and concentrations are measurements at ambient conditions. The head gas was analyzed on a 3.5-ft spherocarb column isothermally at 80 °C, and the product solution on a 6-ft porapak Q column programmed from 50 to 220 °C at 10 °C/min. [b] Includes a small amount of $HCO_2C_2H_5$. [c] Turnover frequency = mmol of $(C_2H_5OH + CH_4)$/[(mmol of mononuclear metal)(reaction time, h)]. [d] Trimethylamine replaced 1-methylpiperidine; volume of solution = 50 mL. [e] Gas purging was not used. [f] Trimethylamine (3.2 M) replaced 1-methylpiperidine. [g] The amount of $Fe(CO)_5$ was not included in the calculation of turnover frequency. [h] Initial volume = 84 mL, temperature = 220 °C, and 1,3-bis(1-methyl-4-piperidyl)propane (1.65 M) replaced 1-methylpiperidine.

At the pressure and temperature conditions given in Table I, metal carbonyl anions[9-11] are formed according to eq 4–6. At

$$Fe(CO)_5 + H_2 + B \rightleftharpoons HFe(CO)_4^- + CO + BH^+ \qquad (4)$$

$$Ru_3(CO)_{12} + H_2 + B \rightleftharpoons HRu_3(CO)_{11}^- + CO + BH^+ \qquad (5)$$

$$Mn_2(CO)_{10} + H_2 + 2B \rightleftharpoons 2Mn(CO)_5^- + 2BH^+ \qquad (6)$$

least early in the reaction using RhI_3 as catalyst the major rhodium species was also an anion, $Rh(CO)_2I_2^-$.[12] Formate ion generated in (3) is not inert. We have observed that methanol solutions of $[N(CH_3)_3H][HCO_2]$ rapidly react according to eq 7 in the

$$BH^+ + HCO_2^- \rightarrow H_2 + CO_2 + B \qquad (7)$$

presence of $Fe(CO)_5$ under our reaction conditions. Reaction 7, which amounts to a catalytic decomposition of formic acid in basic solution, is probably initiated by the reduction of $Fe(CO)_5$ by HCO_2^- to form $HFe(CO)_4^-$. The ability to catalyze this reaction is a common property of metal carbonyls.[13-15] The effect of reaction 7 is to drive the equilibria 4–6 to the right by the removal of protons. Without formic acid decomposition the catalytic reactions in Table I would be stoichiometric in amine. Reaction 7 is the source of carbon dioxide produced in the net catalytic reaction in eq 1.

The net result of eq 2–7 is that methylammonium ions and metal carbonyl anions are both present when methanol solutions of appropriate metal carbonyl and amine are heated under CO

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(6) When methanol solutions of trimethylamine, 1-methylpiperidine, or 1,3-bis(1-methyl-4-piperidyl)propane are heated to 200 °C at 300 atm of $3CO/H_2$ pressure, (2) and (3) both reach equilibrium within 20 min and greater than 80% of each amine is converted to its methylammonium ion.

(7) Although HCO_2CH_3 is also a reasonably efficient methyl carrier, $NaHFe(CO)_4$ reacts at least 10 times faster with $N(CH_3)_4^+$.

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