

magnesium bromide.⁷ Distillation of the product mixture under reduced pressure yielded a sample of the title compound (**7e**) as the major component of the reaction mixture (about 90% pure), bp 74–76° (0.6 mm).⁸

Hydrogenation of the Olefin 7e.—The olefin was stirred under a blanket of hydrogen in methyl acetate solution with a suspension of 5% Pd/C to afford a hydrocarbon whose nmr spectrum and vpc retention time were identical with that of the equatorially methylated isomer **4e**.

Methylalumination of 5 and 6.—The olefins **5** or **6** plus 1 equiv of methanol were substituted for the tertiary alcohols in the exhaustive methylation procedure described above. A component of the reaction mixture in each case had a vpc retention time identical with that of **4e** and **7e**. The mass spectrum of this component resembled that obtained by the superposition of spectra of authentic samples of **4e** and **7e**.

4-tert-Butyl-1-(2'-hydroxyethylidene)cyclohexane (3).—Ethyl-4-tert-butylcyclohexylidene acetate⁹ was reduced in the usual

manner with LiAlH₄ in ether, giving **3**, bp 82–83° (0.4 mm), in 86.4% yield.

Anal. Calcd for C₁₂H₂₂O: C, 79.06; H, 12.16. Found: C, 78.97; H, 12.21.

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Registry No.—**1c**, 17328-78-8; **1t**, 25143-76-4; **2c**, 7103-35-7; **2t**, 7103-36-8; **3**, 41498-18-4; **4a**, 41498-76-4; **4e**, 41498-77-5; **7e**, 41498-78-6; trimethylaluminum, 75-24-1; methyl bromide, 74-83-9.

Preparation of Organometallic Complexes by Reduction of Magnesium Alkyls with Alkali Metals

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The reduction of dialkylmagnesium compounds in hydrocarbon solution by alkali metals was studied and found to yield organometallic complexes of definite stoichiometries involving magnesium and alkali metals. In most cases, the reduction appeared to occur according to the stoichiometry below, *i.e.*, a 1:1 complex was formed: $2M + 3R_2Mg \rightarrow 2R_2MgM + Mg\downarrow$. Lithium reacted to form both the 1:1 complex and a 3:1 complex, R_2MgLi_3 . Results with sodium were not so straightforward, but it appeared that this metal reduced dialkylmagnesium compounds to form a 1:2 complex (R_2Mg_2Na) as well as the 1:1 complex. Potassium, rubidium, and cesium also reduced dialkylmagnesium compounds to yield 1:1 complexes. These intermetallic reagents are viewed as complexes between alkali metal alkyls and magnesium alkyls; this complex formation solubilizes and stabilizes the alkali metal alkyls. The latter compounds, with the exception of lithium alkyls, had previously been known only as insoluble, relatively unstable species. A structure for the hydrocarbon-soluble 1:1 complexes was proposed in which a di-*sec*-butylmagnesium unit in the di-*sec*-butylmagnesium dimer is replaced by an organoalkali compound.

In 1951 Wittig,² Meyer, and Lange reported that reaction of diphenylmagnesium and phenyllithium resulted in the formation of a 1:1 complex in ether (eq 1). After the addition of xylene, the complex



precipitated as a crystalline compound, mp 212°. Recently there has been considerable interest in the preparation of additional examples of intermetallic complexes involving magnesium and alkali metals illustrated for the general case with magnesium in eq 2, where R is alkyl, aryl, or hydrogen and M is alkali metal.



The preparation of "lithium *n*-butyldimethylmagnesium" complex was reported by Coates and Heslop.³ Removal of solvent after reaction of *n*-butyllithium with dimethylmagnesium in diethyl ether yielded a viscous liquid of stoichiometry $[n-BuLi] \cdot [Me_2Mg] \cdot [OEt_2]$. Coates and Heslop also attempted to prepare alkali metal-alkylmagnesium hydride complexes analogous to $NaEt_2BeH^4$ and $NaH \cdot 2Et_2Zn$.⁵ These attempts were unsuccessful owing

to cleavage of the solvent ether by the alkali metal hydride.

More recently, Ashby and Arnott⁶ have reported the preparation and characterization of several complexes between alkali metal hydrides and dialkylmagnesium compounds. Their initial attempts to prepare these species by reaction of magnesium alkyls in ether with alkali metal hydrides resulted in extensive ether cleavage, consistent with the results of earlier work by Coates and Heslop.³ However, Ashby and Arnott were able to isolate one stable complex from an ether solution by reaction of diphenylmagnesium with potassium hydride at room temperature. The complex precipitated from the ethereal reaction mixture and analysis showed it to be $KH \cdot 2Ph_2Mg$. By reaction of the hydrocarbon-soluble di-*sec*-butylmagnesium⁷ with solid potassium hydride, a relatively stable solution of a 1:1 complex was obtained which was soluble in cyclohexane and benzene. Reaction of sodium hydride with di-*sec*-butylmagnesium resulted in the formation of $[NaH] \cdot 2[sec-Bu_2Mg]$, but lithium hydride would not react.

Seitz and Brown⁸ have studied organometallic exchange reactions by lithium-7 and proton nuclear magnetic resonance, and have reported that alkyllithium

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(2) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).

(3) G. E. Coates and J. A. Heslop, *J. Chem. Soc. A*, 514 (1968).

(4) G. E. Coates and G. F. Cox, *Chem. Ind. (London)*, 269 (1962).

(5) W. E. Becker and P. Kobetz, *Inorg. Chem.*, **2**, 859 (1963).

(6) E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.*, **21**, 29 (1970).

(7) (a) C. W. Kamienski and J. F. Eastham, *J. Org. Chem.*, **34**, 1116 (1969); (b) *J. Organometal. Chem.*, **8**, 452 (1967).

(8) (a) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4140 (1966); (b) *ibid.*, **89**, 1602 (1967); (c) *ibid.*, **89**, 1607 (1967).

compounds form complexes with dialkylmagnesium compounds in ether, as in eq 3, in which $n = 1, 2,$ or 3 depending on the nature of the R groups.



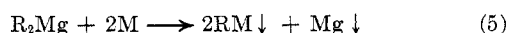
We wish to report the preparation of organometallic complexes involving alkali metal and magnesium by direct reaction of magnesium alkyls with alkali metals.

Results and Discussion

The reduction of dialkylmagnesium compounds with alkali metals has been studied. Dispersions of the alkali metals in excess were stirred with hydrocarbon solutions of di-*n*-butylmagnesium, di-*sec*-butylmagnesium, and di-*tert*-butylmagnesium; a limited amount (2-3%) of ether was present with the di-*n*-butylmagnesium reagent. Periodically the supernatant solutions were analyzed for total base, magnesium, and alkali metal. In every case it was apparent that the magnesium alkyl was being reduced; the black, amorphous metal appeared as a precipitate in the reaction mixture. However, also in every case, it appeared that this reduction either stopped or markedly slowed after an intermetallic complex of some specific stoichiometry was formed, generally with no more than one alkali metal atom per atom of magnesium, *e.g.*, as in eq 4. An organoalkali compound is a likely



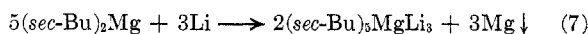
intermediate in the overall reaction, resulting from reduction or "metal-metal" exchange (eq 5). The



organoalkali compound (RM) generated *in situ* is complexed by unreacted dialkylmagnesium reagent (eq 6).



Reaction of a large excess of lithium metal with a hydrocarbon-ether solution of di-*n*-butylmagnesium resulted in formation of a solution with a lithium:magnesium ratio of 1 and with no loss of total base, as would be expected for the 1:1 complex formation illustrated in eq 4. The lithium:magnesium ratio in the solution was unity within 9 hr of reaction at 25° and remained constant at about this value for at least 22 hr of contact with excess dispersed lithium. However, it did appear to slowly change (increase) so that after 45 hr of reaction a solution containing a 1.5:1 ratio of lithium to magnesium was produced, giving evidence that complexes with more lithium than magnesium content are formed. Better evidence for such complexes was obtained in the lithium metal reduction of di-*sec*-butylmagnesium solution, when a 3:1 ratio of the metals was formed in the solution as in eq 7.



The ratio of lithium:magnesium in the reaction of di-*sec*-butylmagnesium with lithium remained constant at 3 from 20 to 35 hr of reaction, but it also increased gradually after this time. Conceivably, a magnesium alkyl could be reduced all the way to a lithium alkyl with sufficient reaction time, but there can be little doubt that formation of specific intermetallic complexes results in a greatly reduced reactivity of the

magnesium reagent and a consequent inhibition of further reduction.

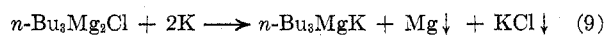
Findings made with the intermetallic complexes between the lithium and magnesium alkyls, namely, that stable solutions of complexes could be produced, were not surprising, considering the known solubility and stability of lithium reagents themselves. Greater interest in initiating this study came from considering whether stable solutions involving potassium and other alkali metal alkyls could be produced, for the organic derivatives of these metals are known to be insoluble and unstable.⁹ Thus, it was not unexpected that, in the first experiments involving treatment of cyclohexane solutions of di-*sec*-butylmagnesium with dispersions of potassium metal, all active alkyl disappeared from solution in less than 1 hr at 80°. Reduction did occur, with the typical appearance of black amorphous magnesium precipitate. The evidence suggests that a cyclohexane-insoluble 1:1 complex, tri-*sec*-butylmagnesium-potassium, was formed according to eq 8. For ex-



ample, a solution of di-*sec*-butylmagnesium was refluxed with potassium metal for 1 hr, after which essentially all total base had disappeared from solution. After removal of the cyclohexane, benzene was added and the mixture was stirred briefly. The supernatant benzene was then found to contain total base, magnesium, and potassium in the ratio 2.9:1.0:0.9. The conclusion is that the 1:1 complex is precipitated from cyclohexane, but it dissolved in benzene. Solutions of tri-*sec*-butylmagnesiumpotassium in benzene are not stable at room temperature for more than a few days. Cold storage (2-4°) inhibits the decomposition process, but even under these conditions the complex slowly decomposes owing to metalation of the solvent.

Observations with reduction of di-*n*-butylmagnesium were somewhat different, primarily owing to the presence of a small amount (approximately 2-3%) of diethyl ether necessary to keep the magnesium alkyl in cyclohexane solution. The diethyl ether tended to hold this complex in the initial cyclohexane solution, so that as reduction occurred, not all of the total base would precipitate. When the solids from one of those products were treated with a solution of benzene-diethyl ether, the resultant supernatant solution was shown to contain total base, magnesium, and potassium in the ratio 1.0:1.0:1.0.

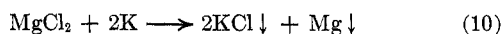
In order to make a trialkylmagnesiumpotassium reagent conveniently available for study, some effort was expended in developing a more direct synthesis of this type of compound, *i.e.*, one that did not involve prior formation of the pure magnesium alkyl. Grignard reagents, or magnesium alkyls still containing some chloride, are simpler to prepare than pure alkyls. In a preliminary experiment, a magnesium reagent solution containing the equivalent of 1 mol of Grignard reagent (*n*-BuMgCl) per mole of magnesium alkyl (*n*-Bu₂Mg), *i.e.*, the equivalent of *n*-Bu₃Mg₂Cl, was treated with potassium metal. Reduction did occur as in eq 9, yielding a solution of the tri-*n*-butyl-



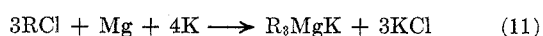
(9) G. E. Coates and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed, Methuen and Co., London, 1967, p 42.

magnesiumpotassium reagent free of chloride and with a potassium:magnesium ratio of 1.0.

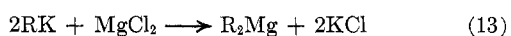
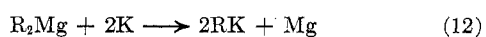
It seemed likely that even magnesium chloride should be reduced by potassium, as represented in eq 10,



so that the final technique evolved for trialkylmagnesiumpotassium preparations was the following "one-pot" synthesis. Starting with *n*-butyl chloride and magnesium in cyclohexane with a limited amount of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), a mixture of solids and supernatant was obtained containing di-*n*-butylmagnesium and magnesium chloride. Sufficient metallic potassium was then added to this mixture for reaction with both the organometallic product, as in eq 4, and the magnesium chloride, as in eq 10. The overall reaction in the vessel was thus as in eq 11.



Actually, when potassium reduces a mixture of magnesium alkyls and magnesium chloride, it is quite likely that the magnesium chloride is not being reduced directly as in eq 10, but that the following two reactions are occurring in sequence. The sum of eq 12 and 13 is eq 10. After all of the magnesium chloride



has been reduced (alkylated), the formation of RK as in eq 12 leads to complex formation as below (eq 14).



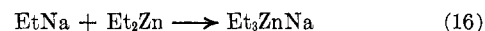
Experimental evidence consistent with the above interpretation of the reduction of a mixture of magnesium alkyl and magnesium chloride is the following. This reduction goes to completion in about 2 hr under the conditions developed, *i.e.*, at the end of that time a clear supernatant is formed containing no chloride, a maximum amount of total base, and as many gram-atoms of potassium as of magnesium. However, during the first 1.5 hr of this reduction, no potassium appears in solution, and all chloride disappears from solution. It seems likely that during this first 1.5 hr, only reactions 12 and 13 are occurring; subsequently, only 30 min are required to dissolve the potassium *via* reactions 12 and 14.

Observations with sodium metal reductions of magnesium alkyls were not so straightforward as those with lithium and potassium. With the latter, reduction appeared to go directly and rather rapidly to a 1:1 intermetallic complex and stop, and initially advantage was taken of the fact that precipitation of this complex occurred when di-*sec*-butylmagnesium was reduced in cyclohexane. With sodium the reduction was slower, precipitation did not occur (although phasing of the reduction mixtures sometimes did), and an intermediate 1:2 complex apparently formed, as in eq 15.

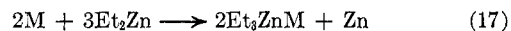


During the study of the reaction of sodium with di-*sec*-butylmagnesium in cyclohexane, a phasing of the reaction product was noted; two liquid layers formed. This peculiar phasing is not without precedent. A

similar phasing was observed in the reactions of ethylsodium with diethylzinc (eq 16), and the products



from the reaction of alkali metals on diethylzinc (eq 17). The mobile upper phase consisted of a dilute



solution of the complex in diethylzinc, and the lower viscous layer consisted of a solution of diethylzinc in the complex. The separation into layers was attributed to the formation of two phases of considerably different polarity and dielectric constant.¹⁰

The phasing observed in the present study can be interpreted similarly. The two phases after centrifuging are initially clear, but gradually each phase becomes hazy. This is probably due to a dissolution process of the complex in the upper layer. From the analyses of the upper, it appears that the di-*sec*-butylmagnesium is slowly dissolving in the lower layer, which consists mainly of *sec*-butylsodium. When sufficient *sec*-butylsodium is present to form the soluble 1:1 complex, phasing is no longer observed.

Observations made on the reduction of the magnesium alkyls with rubidium were similar in many respects to those with potassium. Thus, when a solution of di-*sec*-butylmagnesium in cyclohexane is treated with rubidium metal, virtually all of the active alkyl is removed from solution and the appearance of the precipitated magnesium metal is evident. Removal of the cyclohexane and addition of benzene results in a reappearance of the active alkyl in solution and equal gram-atoms of rubidium and magnesium in the solution. The conclusion is again that a 1:1 complex is formed which is cyclohexane insoluble but benzene soluble. As with the potassium reagent, tri-*sec*-butylmagnesiumrubidium in benzene is not stable to long term storage owing to the facile metalation of solvent. One to one complexes are also observed when di-*n*-butylmagnesium and di-*tert*-butylmagnesium are reduced by rubidium.

Reductions of dialkylmagnesium reagents with cesium occurred, but the intermetallic complexes formed were found to be less stable and more heat sensitive than those of the other alkali metals. Initial attempts at reducing di-*sec*-butylmagnesium in cyclohexane with cesium at reflux and room temperature resulted in extensive decomposition of the active alkyl in the reaction mixture. At lower temperatures the cesium apparently reduced the di-*sec*-butylmagnesium in the usual manner, although less cesium than magnesium went into the product. In the reduction of di-*sec*-butylmagnesium by cesium, phasing was observed in the reaction product similar to that observed in some of the sodium reductions.

In the reaction of di-*tert*-butylmagnesium with cesium, no phasing was observed but reduction did occur. The product, as in the case of the *sec*-butyl analog, precipitated from cyclohexane but dissolved in benzene. The resultant solution contained a cesium:magnesium ratio of about one.

Table I presents a summary of representative preparations of the intermetallic complexes involving magnesium and alkali metal alkyls. Since organic deriva-

(10) Reference 9, pp 44, 45.

TABLE I
 PREPARATION OF INTERMETALLIC COMPLEXES BY REDUCTION OF DIALKYLMAGNESIUM COMPOUNDS

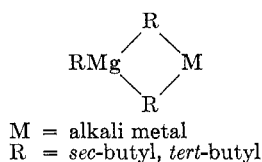
Registry no.	Compd prepared	Reactants		Reaction		Product analysis			
		R ₂ Mg amount, mol	Alkali metal amount, g-atom	Time, hr	Temp, °C	Total base, N	Mg, M	Alkali metal, M	Alkali metal/Mg
20910-20-7	<i>n</i> -Bu ₃ MgLi	0.034	0.13	22	25	1.37	0.43	0.45	1.05
39342-44-4	<i>s</i> -Bu ₃ MgLi ₃	0.033	0.13	20	25	0.93	0.16	0.50	3.12 ^a
41120-87-0	<i>s</i> -Bu ₃ MgNa	0.036	0.046	6	80	0.92	0.33	0.26	0.79
41120-88-1	<i>n</i> -Bu ₃ MgNa	0.022	0.044	2	80	1.12	0.38	0.32	0.84
39342-45-5	<i>n</i> -Bu ₃ Mg ₂ Na	0.039	0.052	4	80	1.39	0.58	0.23	0.40 ^b
41120-89-2	<i>n</i> -Bu ₃ MgK ^c	0.021	0.021	7.5	80	0.81	0.27	0.27	1.00
	<i>n</i> -Bu ₃ MgK ^d	0.035	0.200	2	80		0.20	0.20	1.00
41120-90-5	<i>s</i> -Bu ₃ MgK	0.040	0.045	1	80	1.09	0.36	0.33	0.92
41120-91-6	<i>n</i> -Bu ₃ MgRb ^c	0.012	0.012	20	25	0.83	0.28	0.29	1.04
	<i>n</i> -Bu ₃ MgRb ^d	0.065	0.059	14	25		0.34	0.34	1.00
41120-92-7	<i>s</i> -Bu ₃ MgRb	0.012	0.012	1.3	0	0.61	0.21	0.19	0.91
41120-93-8	<i>t</i> -Bu ₃ MgRb	0.006	0.012	2	0	0.19 ^e	0.06	0.07	1.17
41120-94-9	<i>s</i> -Bu ₃ MgCs	0.0075	0.0075	2.5	0	0.30	0.12	0.09	0.73
41120-95-0	<i>t</i> -Bu ₃ MgCs	0.0055	0.0075	1.5	0	0.27 ^f	0.08	0.09	1.13

^a Ratio was 3.13 after 35 hr of reaction time. ^b Ratio was 0.58 after 18 hr of reaction time. ^c Complex prepared with di-*n*-butylmagnesium in cyclohexane-diethyl ether (98:2) solution. ^d Complex prepared with di-*n*-butylmagnesium in cyclohexane-TMEDA solution. ^e After 20 hr of standing at ambient temperature, solution had fallen to 0.01 N in total base. ^f After 20 hr of standing at ambient temperature, solution had fallen to 0.07 N in total base.

tives of the alkali metals (other than lithium) in the past have been observed to be unstable, insoluble species,⁹ the significance of the present work is that hydrocarbon-soluble, relatively stable derivatives of these alkali metal reagents have been obtained. In the case of the *n*-butyl reagents, some of the solutions contained ether and it is even more surprising that this ether did not cause rapid reaction (decomposition) of the potassium reagents.

Besides the analysis of the supernatants for total base, magnesium, and alkali metal, an auxiliary method for monitoring the reactions was to follow the chemical shift of the protons on the carbon α to the metal. As the reaction progressed, the chemical shift (measured from benzene internal standard) of these protons moved to higher field. For example, in one of the "one-pot" syntheses of tri-*n*-butylmagnesiumpotassium in cyclohexane-TMEDA, the chemical shift of the α -methylene protons moved from τ 10.57 initially to τ 10.74 after reaction was complete. A summary of the chemical shifts of the complexes is presented in Table II.

The species R₃MgM could be represented as salt-like in character, *i.e.*, M⁺[R₃Mg]⁻. However, the observed hydrocarbon solubilities of some of these compounds (R = *sec*-butyl and R = *tert*-butyl) seem inconsistent with this representation. Di-*sec*-butylmagnesium has been shown to exist as a dimer in cyclopentane.⁷ With this in mind, a structure is proposed in which a di-*sec*-butylmagnesium molecule is replaced by a *sec*-butylalkali compound in the original dimer of di-*sec*-butylmagnesium. The reluctance of



cesium to enter into complexes with a cesium:magnesium ratio greater than about 0.7 may have been

 TABLE II
 NMR CHEMICAL SHIFTS IN SOME SELECTED ORGANOMETALLIC SOLUTIONS

Reagent	Solvent system ^a	Chemical shift ^b of α proton(s)
<i>s</i> -Bu ₂ Mg	Cyclohexane	436
<i>n</i> -Bu ₂ Mg	Cyclohexane-DEE	449
<i>n</i> -Bu ₂ Mg	Cyclohexane-THF	446
<i>n</i> -Bu ₃ MgLi	Cyclohexane-DEE	473
<i>s</i> -Bu ₃ MgLi	Cyclohexane	447
<i>s</i> -Bu ₃ MgNa	Cyclohexane	484
<i>n</i> -Bu ₃ MgNa	Cyclohexane-DEE	477
<i>n</i> -Bu ₃ Mg ₂ Na	Cyclohexane-DEE	474
<i>s</i> -Bu ₃ MgK	Benzene	483
<i>n</i> -Bu ₃ MgK	Cyclohexane-DEE	474
<i>n</i> -Bu ₃ MgK	Benzene-DEE	479
<i>n</i> -Bu ₃ MgK	Cyclohexane-TMEDA	477
<i>s</i> -Bu ₃ MgRb	Benzene	461
<i>n</i> -Bu ₃ MgRb	Cyclohexane-TMEDA	480
<i>n</i> -Bu ₃ MgRb	Cyclohexane-DEE	482
<i>n</i> -Bu ₃ MgRb	Cyclohexane-THF	483
<i>s</i> -Bu ₃ MgCs	Benzene	458

^a Symbols: DEE, diethyl ether; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine. ^b Cycles per second upfield from benzene internal standard.

in part due to the inability of the large cesium atom to move fully into this 1:1 complex.

Experimental Section

Reagents.—Di-*sec*-butylmagnesium and di-*tert*-butylmagnesium were prepared in hydrocarbon solutions by alkylation of an "activated" magnesium chloride with *sec*-butyllithium and *tert*-butyllithium, respectively, according to the general procedure given by Kamienski and Eastham.⁷ Di-*n*-butylmagnesium was prepared in the following manner. A solution consisting of 0.20 mol of *n*-butyl chloride, 30 ml of cyclohexane, and 0.025 mol of diethyl ether was added dropwise to a slurry of 0.24 g-atom of magnesium powder in 60 ml of cyclohexane at 80°. The mixture was refluxed for an additional 1 hr, then filtered while hot, and the solids were washed with cyclohexane to give an initially clear solution which gradually became hazy owing to precipitation of *n*-Bu₂Mg. Another equivalent (0.025 mol) of diethyl ether was added. The resultant clear, colorless solution was analyzed and found to be 1.45 N in total base, 0.75

M in magnesium, and 0.05 *M* in chloride. The nmr of this solution showed the characteristic triplet of the methylene group at τ 10.15. The yields of *n*-Bu₂Mg *via* this method ranged from 70 to 80%.¹¹ *sec*-Butyllithium was obtained from Foote Mineral Co. *tert*-Butyllithium was obtained from Lithium Corporation of America. Lithium powder was obtained from Lithium Corporation of America as a 30 wt % suspension in mineral oil. Rubidium and cesium were obtained in vials from MSA Research Corp. Magnesium powder (200 mesh) was obtained from the Reade Manufacturing Co.

Anhydrous diethyl ether was dried over sodium wire before use. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was obtained from the Rohm and Haas Co. and was distilled from lithium aluminum hydride and stored over Linde 4A Molecular Sieves. Reagent grade *n*-butyl chloride was distilled and stored over Linde 4A Molecular Sieves. Hydrocarbon solvents were reagent grade and were refluxed overnight over lithium aluminum hydride and then distilled and stored over Linde 4A Molecular Sieves. All reactions and manipulations were carried out under an atmospheric pressure of dry nitrogen.

Instrumentation and Analytical Techniques.—Hydrocarbon solutions of organomagnesium reagents were analyzed by hydrolysis and analysis of the aqueous solutions for total base, chloride, and magnesium and other metal ions. Usually 1 or 2 ml of the initial organometallic solution was sufficient for the analyses. Chloride analyses were carried out using an absorption indicator method (Fajan's procedure) with dichlorofluorescein as indicator. Magnesium analyses were conducted using the standard ethylenediaminetetraacetic acid disodium salt (EDTA) method, with "calmagite" from Matheson Coleman and Bell as indicator. Analyses for total base were conducted by using an excess amount of standard aqueous acid solution in the initial hydrolysis of the organometallic solution and then back-titrating with standard base using phenolphthalein as indicator.

Lithium, sodium, and potassium were determined by flame photometry on a Perkin-Elmer Model 52C flame photometer. Rubidium and cesium were determined by atomic absorption at the laboratories of Lithium Corporation of America, Bessemer City, N. C. Samples for analysis by flame photometry and atomic absorption were prepared in the following manner. An accurately measured sample (usually 1 or 2 ml) of organometallic solution was hydrolyzed in *ca.* 100 ml of distilled water. The resultant hydrolysate was acidified by the addition of concentrated hydrochloric acid, and the hydrocarbon phase was evaporated by gently heating the solution on a hot plate. The aqueous solution was transferred quantitatively to a volumetric flask, diluted to the mark with distilled water, and analyzed for alkali metal. Nuclear magnetic resonance spectra were obtained at ambient temperature with a Varian A-60 nmr spectrometer using benzene as internal standard for measuring chemical shifts.

Preparation of Complexes. A. Reaction of Lithium with Di-*n*-butylmagnesium.—To a 100-ml three-neck round-bottom flask equipped with a reflux condenser and two rubber septum caps was added a vial containing 0.90 g (0.13 g atom) of lithium powder in a mineral oil suspension. The vial was broken under a nitrogen atmosphere in the reaction flask. To this was added 49 ml (0.034 mol) of 0.70 *M* di-*n*-butylmagnesium in the cyclohexane-diethyl ether (approximately 98:2). After stirring for 3 hr at room temperature an aliquot was removed and centrifuged, and the supernatant was analyzed to show 1.31 *N* in total base, 0.51 *M* in magnesium, and 0.30 *M* in lithium. After a total of 9 hr of stirring, analysis of another centrifuged aliquot showed 1.32 *N* in total base, 0.43 *M* in magnesium, and 0.40 *M* in lithium. After a total of 22 hr of stirring the supernatant was found to be 1.37 *N* in total base, 0.43 *M* in magnesium, and 0.45 *M* in lithium. After a total of 45 hr, the supernatant was found to be 0.35 *M* magnesium and 0.49 *M* lithium.

B. Reaction of Sodium with Di-*sec*-butylmagnesium.—To a 200-ml three-neck round-bottom flask equipped with a reflux condenser and two rubber septum caps was added 1.05 g (0.046 g-atom) of lump sodium. Enough methylcyclohexane was added to cover the sodium, which was dispersed by stirring and refluxing the methylcyclohexane overnight. The supernatant hydrocarbon was removed from the sodium with syringe and 75 ml (0.036 mol) of 0.48 *M* di-*sec*-butylmagnesium was added. This mixture was refluxed with vigorous stirring for 1 hr, after which

it was cooled and a sample of the hazy supernatant was removed and centrifuged for analysis. The supernatant separated into an upper mobile phase and a smaller lower viscous phase. These layers were clear immediately after centrifuging, but both gradually became hazy. Further centrifuging caused each layer to become clear again, but the haziness subsequently reappeared. Samples from the upper layer were hydrolyzed for analysis while the layer was clear and found to be 0.80 *N* in total base, 0.39 *M* in magnesium, and 0.03 *M* in sodium. The reaction mixture was heated to reflux for an additional 1 hr and a sample was removed for analysis. Once again phasing was observed, but there was considerably more of the lower layer than after 1 hr of reflux. The upper layer was 0.64 *N* in total base, 0.30 *M* in magnesium, and 0.05 *M* in sodium. After a total of 4 hr of reflux, the supernatant no longer separated into two phases and analysis showed it to be 0.92 *N* in total base, 0.33 *M* in magnesium, and 0.26 *M* in sodium. An nmr spectrum of this solution showed the characteristic multiplet of the methine proton from the *sec*-butyl group at τ 10.68.

C. Reaction of Potassium with Di-*sec*-butylmagnesium.—To a 200-ml three-neck round-bottom flask was added 1.75 g (0.045 g-atom) of potassium. Enough cyclohexane to cover the lumps of potassium was added and the potassium was dispersed. The supernatant hydrocarbon was removed, 84 ml (0.040 mol) of 0.48 *M* di-*sec*-butylmagnesium was added, and the mixture was refluxed for 1 hr with vigorous stirring. The total base concentration in the supernatant had fallen to 0.01 *N*. The supernatant was removed by syringe and the solids were washed with two 20-ml portions of cyclohexane. To the solids was added 60 ml of dry benzene and the mixture was stirred for several minutes. The solids were allowed to settle while the reaction flask was immersed in an ice bath. Samples of the supernatant were removed for analysis while cold and the solution was found to be 1.09 *N* in total base, 0.36 *M* in magnesium, and 0.33 *M* in potassium. The yield of complex was approximately 85% based on *sec*-Bu₂Mg. An nmr spectrum of this solution showed the characteristic multiplet from the methine proton of the *sec*-butyl group at τ 10.75.

D. Reaction of Potassium with the Product from Reaction of Magnesium and *n*-Butyl Chloride.—To a 200-ml three-neck round-bottom flask equipped with a reflux condenser, a rubber septum cap, and a 250-ml pressure-equalizing dropping funnel was added a weight of 3.28 g (0.14 g-atom) of magnesium powder, 60 ml of cyclohexane, and 3.87 g (0.034 mol) of TMEDA. A solution of 9.25 g (0.10 mol) of *n*-butyl chloride in 30 ml of cyclohexane was added to the dropping funnel. After about one third of the butyl chloride was introduced to the magnesium slurry, the mixture was heated to reflux. The remainder of the solution was added dropwise to the reaction mixture, which was refluxed 9 hr after addition was complete. A weight of 7.5 g (0.19 g-atom) of potassium was added to the cooled reaction flask and the mixture was heated to reflux again and vigorously stirred. After a 30-min reflux period, the mixture was cooled and an aliquot was removed for analysis. The supernatant was found to be 0.42 *M* in magnesium, 0.06 *M* in chloride, and to contain no potassium. After a total of 60 min of reflux, the supernatant was still colorless, contained no chloride or potassium, and was 0.41 *M* in magnesium. After a total of 90 min of refluxing, the supernatant had assumed a red-orange color and analysis showed it to be chloride-free, 0.25 *M* in magnesium, and 0.25 *M* in potassium. Nmr spectral analyses showed that the absorption of the α -methylene protons of the *n*-butyl group had shifted from τ 10.60 after 39 min reflux to τ 10.74 after 90 min reflux. The overall yield of total base in the supernatant solution was 50% based on *n*-butyl chloride.

In two additional runs using this same procedure, except that no intermediate analyses were conducted, the product contained magnesium and potassium in a 1:1 ratio and the overall yields were estimated to be 50–60% based on *n*-butyl chloride.

E. Reaction of Rubidium with Di-*sec*-butylmagnesium.—A weight of 1.0 g (0.012 g-atom) of rubidium in a vial was added to a 100-ml three-neck round-bottom flask equipped with a reflux condenser and two septum caps. Enough cyclohexane was added to cover the vial, which was then broken. The rubidium was subsequently dispersed by stirring vigorously and refluxing the cyclohexane. The cyclohexane was removed by syringe from the dispersed metal. The flask was immersed in an ice bath and 25 ml (0.012 mol) of 0.48 *M* di-*sec*-butylmagnesium was added. After stirring vigorously for 1 hr at ice-bath temperature the supernatant was 0.01 *N* in total base and was removed by

(11) Additional details on the preparation of the magnesium alkyls and intermetallic complexes are given in the Doctoral Dissertation of D. B. Malpass, The University of Tennessee, 1970.

syringe. The solids were washed with cold cyclohexane. Benzene (20 ml) was added to the reaction flask and the mixture was stirred for several minutes. An aliquot was removed and centrifuged and analysis of the supernatant showed it to be 0.61 *N* in total base, 0.21 *M* in magnesium, and 0.19 *M* in rubidium.

F. Reaction of Cesium with Di-*sec*-butylmagnesium.—A weight of 1.0 g (0.0075 g-atom) of cesium in a vial was placed in a 100-ml three-neck round-bottom flask equipped with a reflux condenser and two rubber septum caps. The cesium was dispersed under cyclohexane in the usual manner and the dispersing cyclohexane was removed. The reaction flask was immersed in an ice bath, 16 ml (0.0077 mol) of 0.48 *M* di-*sec*-butylmagnesium in cyclohexane was added, and the mixture was stirred vigorously for 3 hr. The supernatant was removed and the solids were washed with two 10-ml portions of cold cyclohexane. To the solids was added 12 ml of dry benzene and the mixture was stirred for several minutes, after which the benzene was removed by syringe and centrifuged. The supernatant separated into an upper, mobile, orange phase and a lower, wine-red, viscous phase. The upper phase was analyzed and found to be 0.30 *N* in total

base, 0.13 *M* in magnesium, and 0.09 *M* in cesium. After all of the upper layer was removed, 8 ml of benzene was added to the remaining lower layer. The tube was shaken vigorously for several minutes and centrifuged once again. Phasing was observed again; however, the volume of the lower layer was decreased. Analysis of the upper layer showed it to be 0.24 *N* in total base, 0.10 *M* in magnesium, and 0.07 *M* in cesium. To the remaining two phases in the centrifuge tube was added 8 ml of diethyl ether and the tube was shaken by hand for a few minutes and centrifuged. No phasing was observed and the solution was found to be 0.61 *N* in total base, 0.23 *M* in magnesium, and 0.15 *M* in cesium.

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Registry No.—Di-*sec*-butylmagnesium, 17589-14-9; di-*tert*-butylmagnesium, 14627-81-7; di-*n*-butylmagnesium, 1191-47-5; *n*-butyl chloride, 109-69-3; magnesium, 7439-95-4.

Acid-Catalyzed Reaction of Acetylferrocene with Triethyl Orthoformate

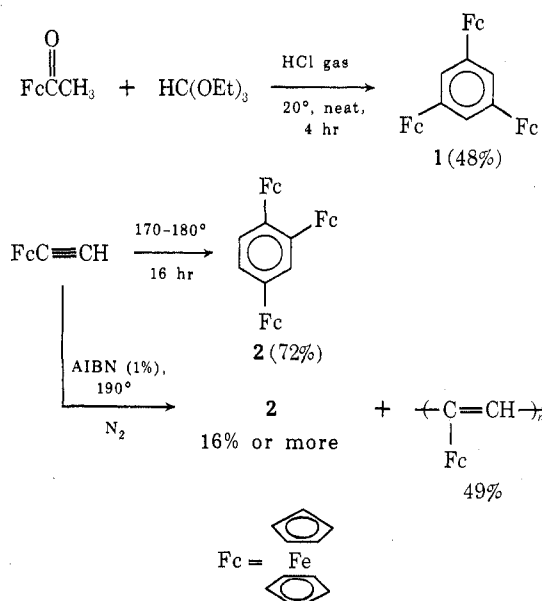
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The major product obtained when acetylferrocene was allowed to react with triethyl orthoformate and dry hydrochloric acid was 1,3-diferrocenylbut-2-en-1-one, and only a small amount of the cyclic trimer, 1,3,5-triferrocenylbenzene, was obtained. This result was found using either benzene or methylene chloride as the solvent or upon running the reaction without solvent. The reaction of acetylferrocene with triethyl orthoformate in ethanol, upon catalysis by *p*-toluenesulfonic acid, gave 2-ferrocenylpropene, ethyl ferrocenoate, polyvinylferrocene, a more complex polymer, and small amounts of 1,3,5-triferrocenylbenzene, 1,2,4-triferrocenylbenzene, and 1,3-diferrocenylbut-2-en-1-one. These results are compared with previous studies, and mechanisms are discussed.

Schlögl¹ reported that the reaction of acetylferrocene with a slight excess of triethyl orthoformate (1.2 equiv) in the presence of anhydrous hydrochloric acid at 20° for 4 hr gave a 48% isolated yield of 1,3,5-triferrocenylbenzene (1). The unsymmetrical 1,2,4 isomer, 2, was not formed and other products were



not discussed. The 1,2,4 isomer has been prepared by the thermal cyclotrimerization of ethynylferrocene,¹ and it is also a by-product in the free-radical polym-

erization of ethynylferrocene.^{2,3} Since ketones readily give ketals in the presence of triethyl orthoformate and catalytic amounts of acids,⁴ the formation of 1 reported by Schlögl was presumed to proceed *via* an elimination product of the diethyl ketal of acetylferrocene. To our surprise, attempts to generate 1 by Schlögl's method resulted in the isolation of large quantities of 1,3-diferrocenylbut-2-en-1-one (3), and only small amounts of the cyclotrimer 1. Thus, we studied this reaction under several different conditions and found that the use of *p*-toluenesulfonic acid led to a complex mixture of products, including 2-ferrocenylpropene (one carbon addition) and ethylferrocenoate (one carbon removed). Increased yields of cyclotrimer 1 can be obtained at very high gaseous HCl rates of bubbling into the reaction.

Results and Discussion

Acetylferrocene was allowed to react at 20° with triethyl orthoformate and dry HCl gas (1) in dry benzene, (2) in dry methylene chloride, and (3) without solvent (Schlögl's conditions). In each case the major product was dimer 3, and only small yields of symmetrical cyclotrimer 1 were observed. None of the unsymmetrical trimer 2 was detected. The yields of

(2) C. Simionescu, T. Lixandru, J. Mazilu, and L. Tataru, *Makromol. Chem.*, **147**, 69 (1971).

(3) C. U. Pittman, Jr., and Y. Sasaki, unpublished results using AIBN as the initiator.

(4) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1206.

(1) K. Schlögl and H. Soukup, *Monatsh. Chem.*, **99**, 927 (1968).