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Kinetic Study of Additions of Dialkylmagnesium Compounds to a Cyclopropene

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Reaction of Et$_2$Mg and spiro[2.4]hept-1-ene (1) in tetahydrofuran followed by hydrolysis furnishes mainly 1-ethylspiro[2.4]heptane (3); when hydrolysis is with D$_2$O, $\geq$98% of this is (*Z*)-1-ethylspiro[2.4]heptane-2-*d* (4). Some metalation of 1 and formation of higher molecular weight products incorporating two or three molecules of 1 also take place. Formation of 3 is first order in 1 and in Et$_2$Mg, and at 35.47 °C the rate constant is 1.2×10^{-5} L M^{-1} s^{-1}. Under the same conditions, the rate of addition (1.5×10^{-5} L mol^{-1} s^{-1}) of the Grignard reagent prepared from EtBr is similar. Reactions of 1 with Me$_2$Mg, *i*-Pr$_2$Mg, and *t*-Bu$_2$Mg also furnish the corresponding 1-R-spiro[2.4]heptanes. Relative rates of formation of 1-R-spiro[2.4]heptanes from reactions of 1 with R$_2$Mg are 1, 10.3, 32, and 8 respectively for Me$_2$Mg, Et$_2$Mg, *i*-Pr$_2$Mg, and *t*-Bu$_2$Mg. Added Fe(acac)$_3$ increases the rate of formation of 3 from reactions of 1 with either Et$_2$Mg or the Grignard reagent prepared from EtBr, but additional products also are formed.

Additions of organomagnesium compounds to alkenes are potentially valuable synthetic reactions, producing both a new C–C bond and a new organomagnesium function.[3] Moreover, study of such additions could give significant information about mechanisms of reactions of organomagnesium compounds with multiple bonds and avoid some problems that complicate investigations of the much-studied reactions of organomagnesium compounds with ketones.[4]

One problem is that organomagnesium compounds and ketones form complexes, making it difficult to know precisely the concentrations of free ketone, free organomagnesium compound, and any complex. It is unlikely, however, that intermolecular complexes form between alkenes and Grignard reagents in amounts sufficient to significantly alter the concentrations of free alkene or free organomagnesium compound. Although π complexes have sometimes been proposed as possible transient intermediates in reactions of monoalkenes and organomagnesium compounds,[6] there seems to be no evidence for observable amounts of such complexes, even in intramolecular cases which might be particularly favorable. Postions of ^{1}H NMR and infrared absorptions, as well as observations that such compounds are monomeric rather than dimeric in hydrocarbon solvents, however, have provided evidence for intramolecular metal–alkene interactions in 3-butenyl- and 4-pentenylaluminum compounds.[8,9] In fact, crystalline 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumino-2,5-cyclohexadiene has pairs of molecules arranged so that each Al of one is complexed in a π fashion to an alkene function of the other; this dimeric structure may persist in solution and the gas phase.[10] ^{1}H NMR absorptions of solutions of di-4-pentenylzinc have also been interpreted as indicating an intramolecular metal–alkene interaction.[11] An electron diffraction study[12] has shown that in the gas phase most molecules of this compound and also of di-3-butenylzinc have a conformation which brings the double bond into contact with the metal. In the crystal structure of dimethylallylzinc, the Zn of one molecule is π-complexed to the double bond of another.[13]

A second problem in studying additions of organomagnesium compounds to ketones is that the magnesium alkoxide can react with R$_2$Mg to form higher molecular weight species,[5] further complicating the assignment of reactant concentrations. A new species, R′MgR, also forms as a reaction of R$_2$Mg and an alkene proceeds. Since it is possible to choose conditions under which dialkylmagnesium compounds are monomeric, however, the problem of forming new, *higher molecular weight* species can be avoided.

A potential advantage of alkenes is the possibility of changing the substitution at both atoms of the double bond. Only the two groups attached to the carbonyl carbon of a ketone can be varied, but all four groups attached to the double bond carbons of an alkene are variable, potentially allowing a fuller evaluation of electronic and steric influences on an addition.

While there are obvious incentives to studying such reactions, addition of organomagnesium functions to isolated (nonconjugated) alkene functions unfortunately is not a general reaction. The examples that are known ordinarily involve an unusually reactive organomagnesium compound or alkene, elevated temperature, or some special catalytic feature.[3]

Most studied kinetically have been intramolecular cyclizations of alkenyl organomagnesium compounds.[14]

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[1] Much of this work is taken from ref 2. For a preliminary communication of some of these results, see: Richey, H. G., Jr.; Watkins, E. K. *J. Chem. Soc., Chem. Commun.* **1984**, 772.

[2] Watkins, E. K., Ph.D. Dissertation, The Pennsylvania State University, 1982.

[3] For a brief review of additions of organomagnesium functions to alkene functions, see: Richey, H. G., Jr. In *Inorganic Reactions and Methods*; Hagen, A. P., Ed.; VCH: New York, 1989; Vol. 10, Section 5.4.2.5.1.

[4] Reference 5 provides a brief account and is a general source for literature citations concerning organomagnesium compounds.

[5] Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 4.

[6] For example, see: ref 7.

[7] Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123; *Adv. Organomet. Chem.* **1977**, *16*, 131.

[8] Hata, G. *J. Chem. Soc., Chem. Commun.* **1968**, 7. Dolzine, T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737.

[9] For negative evidence for ^{27}Al NMR spectroscopy for such an interaction, however, see: Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *333*, 155.

[10] Schnöckel, H.; Leimkühler, M.; Lotz, R.; Mattes, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 921. Ahlrichs, R.; Häser, M.; Schnöckel, H.; Tacke, M. *Chem. Phys. Lett.* **1989**, *154*, 104.

[11] St. Denis, J.; Oliver, J. P.; Dolzine, T. W.; Smart, J. B. *J. Organomet. Chem.* **1974**, *71*, 315.

[12] Haaland, A.; Lehmkuhl, H.; Nehl, H. *Acta Chem. Scand., Ser. A* **1984**, *38*, 547.

[13] Benn, R.; Grondey, H.; Lehmkuhl, H.; Nehl, H.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1279.

[14] For critical and thorough reviews of intramolecular cyclizations, see: ref 7. Reference 3 lists some more recent references.

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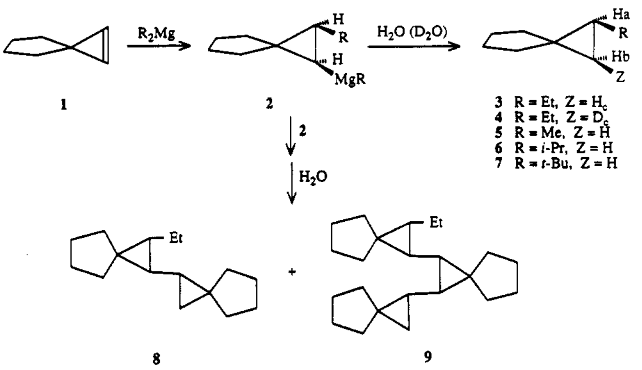
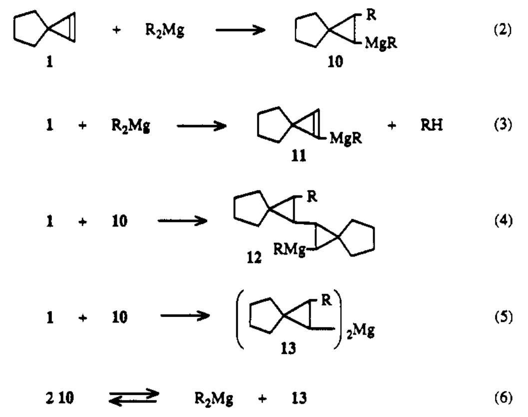
Scheme I



Scheme II



When the organomagnesium and alkene functions are separated by favorable numbers of carbon atoms, these reactions are considerably faster than their intermolecular counterparts. Although these systems do not permit varying relative concentrations of the reacting functions, the effects of altering the organomagnesium and alkene functions show that both influence the cyclization rate (which generally is first order in alkenylmagnesium compound). Efforts to interpret the effects of structure on rate are complicated, however, by considerations of strain and orientation due to the constraints imposed by the intramolecularity of these reactions.

In what is apparently the only kinetic study of intermolecular addition to alkenes, Lehmkuhl and Janssen investigated additions of allylic organomagnesium compounds, which are known to be particularly reactive, to 1-octene, norbornene, and styrene.[15] The reactions were found to be first order in each reagent. These reactions may be atypical, however, since additions of allylic compounds could have mechanistic features that are not general—for example, addition might proceed via a cyclic six-membered transition state.

The objective of this study was to investigate additions to an alkene of a group of saturated organomagnesium compounds. We decided to use a cyclopropene as the substrate, since it already was known that a variety of Grignard reagents add to some cyclopropenes under mild conditions.[3,5,16] Moreover, since cyclopropylmagnesium compounds are configurationally stable,[17] the stereochemistry (syn or anti) of an addition can be established. We chose dialkylmagnesium compounds rather than Grignard reagents to avoid having both RMgX and R_2Mg present as reactive species, because of the Schlenk equilibrium[5] (eq 1), a problem when Grignard reagents are used.

$$2R_2Mg \rightleftarrows RMgX + MgX_2 \qquad (1)$$

Results

Products. Spiro[2.4]hept-1-ene (1) was chosen as the substrate. This compound is more readily handled and more easily separated from solvents during GC analysis than are lower molecular weight cyclopropenes. For reasons discussed below, kinetic experiments were done in tetrahydrofuran (THF), most kinetic solutions had $[R_2Mg]_0 \geq 10[1]_0$, and most rates were determined using data obtained before more than 10% of 1 had been consumed. GC analyses of hydrolyzed aliquots of such reactions of Et_2Mg and 1 showed only one significant peak in the region where a simple addition product would be seen. This was identical (retention time and mass spectrum) to the only major peak in that region given by the product of a preparative reaction of EtMgBr and 1. The ^{1}H NMR spectrum of the material responsible for this peak indicated it to have structure 3. When hydrolysis was with D_2O, the absence of an absorption that is assigned to H_c of 3 indicated the product to be 4. Since hydrolysis of organomagnesium compounds proceeds with retention of configuration,[18] the precursor of 3 and 4 was 2 (R = Et) and, therefore, addition of the elements of the organomagnesium compound was syn. As little as 2% of a compound with an H in place of D_c would have been detected, setting this as the upper limit of formation of the stereoisomer of 4 that would result from anti addition. Products obtained from addition of various organomagnesium compounds to other cyclopropenes, followed by carbonation or hydrolysis, also have resulted from syn addition of the organomagnesium compound.[3]

GC analyses also showed peaks due to compounds having higher molecular weights than 3 but present in considerably smaller amounts. The most prominent of these peaks presumably was due to 8. Similar products have been observed before in reactions of cyclopropenes and organomagnesium compounds.[19] The highest molecular weight peaks in the electron ionization (EI) and chemical ionization (CI) mass spectra were consistent with the molecular weight of this structure, and the ^{1}H NMR spectrum of material collected by preparative GC was consistent with a product constructed from one Et and two 1's. Addition of 2 to 1, which would form this product, can proceed with two orientations. Neither the GC analysis nor the ^{1}H NMR spectrum suggested the presence of more than one compound, however. For steric reasons the orientation of addition leading to the structure that is shown is the more probable. Presumably the attachments to the original cyclopropyl ring remain cis (as in 2). The ^{1}H NMR spectra were not of sufficient quality, however, to define the coupling constants that might establish stereochemistry, and so that feature is not indicated for 8. Another GC peak had a retention time and EI and CI

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(15) Lehmkuhl, H.; Janssen, E. *Justus Liebigs Ann. Chem.* **1978**, 1854.

(16) Wakefield, B. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 44.

(17) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288. Walborsky, H. M.; Aronoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 31. Richey, H. G., Jr.; Moses, L. M. *J. Org. Chem.* **1983**, *48*, 4013.

(18) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1965; Chapter 3. Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Kazanskii, B. A. *Dokl. Chem.* (*Engl. Transl.*) **1972**, *207*, 999; *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1972**, *207*, 1362.

(19) Nesmeyanova, O. A.; Rudashevskaya, T. Yu.; Grinberg, V. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, 2399; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2590. Nesmeyanova, O. A.; Rudashevskaya, T. Yu. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1978**, 1364; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 1562. Lehmkuhl, H.; Mehler, K. *Justus Liebigs Ann. Chem.* **1978**, 1841; **1982**, 2244.

mass spectra consistent with being due to **9**.

The GC analyses showed that 20–30% of **1** remained, even after long reaction periods. When hydrolysis was with D_2O, MS analysis showed much of the recovered **1** to be deuterated. Some metalation must have taken place, presumably at a vinyl position to produce **11** (eq 3). Metalation of cyclopropenes by organomagnesium compounds has been noted before.[20]

GC analyses of the solutions obtained following hydrolysis of reactions of **1** with Me_2Mg, i-Pr_2Mg, and t-Bu_2Mg showed only single significant GC peaks with retention times in the ranges expected for **5**, **6**, and **7**. Since some reactions of less polar organometallics (e.g., R_3Al) and cyclopropenes lead to alkenes formed by an addition–rearrangement process,[21] it was important to ascertain if alkene components contributed to these GC peaks. Samples of **5**, **6**, and **7** for NMR spectra had to be isolated by preparative gas chromatography from reactions which had proceeded much further than did typical kinetic reactions; even then the amounts of collected material were small and difficult to obtain completely free of other components. Nevertheless, the ^1H NMR spectra indicated the presence of cyclopropyl H's and the appropriate alkyl group (R) *but the absence of =CH.* EI and CI mass spectra also were consistent with structures **3** and **5–7**. Prominent in the EI spectra were peaks at m/e 95 $(M - R)^+$ and, as expected[22] for these cyclopropanes, 67 $(M - C_2H_4R)^+$. Also significant were peaks corresponding to $(M - C_4H_8)^+$ and $(M - C_4H_9)^+$. In the CI spectra,[23] peaks for $(M + 1)^+$ and $(M - 1)^+$ were significant, and a peak for $(M - R)^+$ increased in prominence with increasing branching of the alkyl group. GC analysis of the reactions of **1** with Me_2Mg, i-Pr_2Mg, and t-Bu_2Mg also showed the presence of higher molecular weight products presumably similar to **8** and **9**.

Kinetic Procedure. Reaction rates were followed by monitoring formation of the addition products (**3** and **5–7**) by GC analysis of quenched reaction aliquots. Preliminary efforts to measure rates of reactions of Et_2Mg and **1** produced data that were not satisfactorily reproducible. Even data obtained in early stages of a reaction, before depletion of **1** was significant, sometimes showed considerable scatter of points in plots of concentration of **3** versus time. Moreover, slopes of such plots for presumably duplicate reactions sometimes varied by as much as a factor of 2.

These problems led to increasing care in the preparation, handling, and mixing of reagents. Since even small amounts of some transition metals significantly affect some organomagnesium reactions,[24] transition metal impurities were an obvious concern. Consistency seemed to improve when metal parts (syringe needles and valve components) which the solutions contacted were new rather than ones already used extensively and likely to have more surface corrosion. Finally, apparatus and procedures were developed that, from the start of the preparation of an organomagnesium solution until an aliquot of a kinetic solution was quenched, allowed solutions to contact only glass and Teflon, never metal, stopcock grease, or the atmosphere. Using this apparatus and the procedures described in the Experimental Section furnished acceptably reproducible kinetic data.[26]

A reaction was initiated by addition of a solution of **1** to a solution of an organomagnesium compound, which also contained an alkane standard. Aliquots of the reaction solution were hydrolyzed and subjected to GC analysis. The concentration of the addition product (**3**, **5**, **6**, or **7**) was determined by comparison of its GC peak to that of the standard. Since other products also form, disappearance of **1** is not an accurate indicator of the addition process in which we are interested. Moreover, because of tailing by the THF peak, which it too closely followed, the GC peak for **1** could not be as accurately determined as could the peaks for the addition products. To determine that a reaction solution initially contained the expected amount of **1**, the stock solution of **1** had a known concentration of a "secondary" alkane standard whose GC peak had a longer retention time than that of **1**. The areas of the peaks due to the two alkane standards were compared to verify that the expected amount of **1** had been introduced.

Observation in the reaction of **1** and Et_2Mg of other products besides **3** influenced the design of the kinetic experiments. Kinetic runs using the usual excess of Et_2Mg and followed to essentially infinite time gave about 65% of **3**. Of the approximately 35% of **1** that did not appear in **3**, 5–10% could be accounted for in **8**, 1–5% in **9**, and 20–30% in recovered **1** (mainly **1** that had been metalated). MS analysis of **1** recovered after quenching with D_2O indicated that metalation of **1** was considerably more significant in reactions with t-Bu_2Mg, being several-fold faster than the addition that led (after hydrolysis) to **7**.

Our goal was to measure the rate of the addition to **1** shown in eq 2. Other pathways (e.g., those in eqs 3 and 4), however, also consume **1**. So that the assumption that $[\text{addition product}]_\infty = [\mathbf{1}]_0$ could be used in the kinetic analysis, depletion of **1** by other pathways was minimized by using data collected before more than 10% or so of the initial **1** had been converted to an addition product. Since metalation (eq 3) was particularly significant when t-Bu_2Mg was used, only data collected before even lower conversions were used in studying its addition. Depletion of R_2Mg was insignificant, of course, since generally $[R_2Mg]_0 \geq 10[\mathbf{1}]_0$.

Plots of their concentrations versus time generally showed more **3**, **8**, and **9** to be present in initial aliquots than was consistent with their later rates of increase. When many early aliquots were taken, in fact, plots showed the burst of formation of **3**, **8**, and **9** to have ended by the time (~60 s) that the first aliquot could be quenched. This rapid product formation may have occurred in locales that during addition of **1** to the organomagnesium solution momentarily had much higher concentrations of **1** than existed after mixing was complete. A small amount of some more reactive component in the large excess of organomagnesium compound might also have played a part. This possibility was eliminated, however, by finding a new, rapid burst of product formation upon addition of a second portion of the stock solution of **1** to a kinetic flask in which about 5% of the **1** had already undergone reaction. Fortunately, this early burst did not involve sufficient material to significantly affect the determination of rate constants.

Kinetic Observations. With the experimental procedures that ultimately were used, plots of ln $([\mathbf{1}]_0 - [\text{addition product}])$ versus time were reasonably linear. The rate observations that will be discussed specifically here are

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[20] Avesov, I. B.; Bolesov, I. G.; Levina, R. Ya. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *10*, 2129; *Zh. Org. Khim.* **1984**, *10*, 2114.

[21] For example, see: Richey, H. G., Jr.; Kubala, B.; Smith, M. A. *Tetrahedron Lett.* **1981**, *22*, 3471.

[22] Dias, J. R.; Djerassi, C. *Org. Mass Spectrom.* **1973**, *7*, 753.

[23] Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983; Chapter 5.

[24] For example, see: ref 25 and references cited therein.

[25] Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

[26] The apparatus and the procedures for its use are described in much greater detail elsewhere [ref 2 and Watkins, E. K. to be submitted for publication in *J. Chem. Educ.*].

Table I. Rates of Additions of Organomagnesium Compounds to 1 at 35.47 °C in THF

run	Mg source	R_2Mg	$[R_2Mg]_0$, M	$10^2[\mathbf{1}]_0$, M	10^5k,[a] L mol^{-1} s^{-1}
103	Cerac	Et_2Mg	0.330	1.01	1.30
104	Cerac	Et_2Mg	0.330	2.12	1.16
105	Cerac	Et_2Mg	0.330	4.09	1.21
106	Cerac	Et_2Mg	0.300	2.87	1.12
107	Cerac	Et_2Mg	0.300	2.19	0.900
109A	Cerac	Et_2Mg	0.382	1.35	1.01
109B	Cerac	Et_2Mg	0.382	4.05	1.13
112	Dow	Et_2Mg	0.336	2.86	1.06
120	Dow	Et_2Mg	0.489	1.31	1.23
121	Dow	Et_2Mg	0.380	1.27	1.40
122	Dow	Et_2Mg	0.244	1.30	1.16
124	Dow	Et_2Mg	0.649	1.74	1.49
125	Dow	Et_2Mg	0.547	1.59	1.25
126	Dow	Et_2Mg	0.242	1.59	1.16
127	Dow	Et_2Mg	0.103	1.84	1.45
139	Dow	Me_2Mg	0.500	1.59	0.132
140	Dow	Me_2Mg	0.500	1.56	0.107
141	Dow	Me_2Mg	0.500	1.72	0.135
142	Dow	Me_2Mg	0.500	1.44	0.0912
151	Dow	i-Pr_2Mg	0.225	0.505	4.38
152	Dow	i-Pr_2Mg	0.225	0.523	3.48
153	Dow	i-Pr_2Mg	0.225	0.755	3.81
154	Dow	i-Pr_2Mg	0.225	0.537	4.30
155	Dow	i-Pr_2Mg	0.275	0.746	2.94
157	Dow	i-Pr_2Mg	0.275	0.569	3.01
158	Dow	i-Pr_2Mg	0.275	0.719	3.75
169	Dow	t-Bu_2Mg	0.258	1.55	0.818
170	Dow	t-Bu_2Mg	0.258	1.66	1.01
174	Dow	t-Bu_2Mg	0.208	1.90	0.893
144	Dow	EtMgBr	0.438	1.18	1.43
145	Dow	EtMgBr	0.438	1.01	1.78
146	Dow	EtMgBr	0.438	1.22	2.21
148	Dow	EtMgBr	0.487	1.46	1.19
149	Dow	EtMgBr	0.487	1.13	1.56
150	Dow	EtMgBr	0.487	1.17	0.828

[a] The observed pseudo-first-order rate constant for appearance of addition product (**3**, **5**, **6** or **7**) divided by $[R_2Mg]_0$.

included in Table I. Numerous other results were obtained, however. Although many of these were flawed in some way, they are similar to those in Table I, reinforcing our confidence in the reproducibility of the rate determinations.

The reaction of Et_2Mg and **1** was studied to establish the kinetic order in each component. In runs 112, 120–122, and 124–127, $[Et_2Mg]_0$ varied more than 6-fold (and always considerably exceeded $[\mathbf{1}]_0$). A plot of the pseudo-first-order rates for appearance of **3** versus $[R_2Mg]_0$ has a slope of 1.04 (correlation coefficient 0.94). Therefore the order in Et_2Mg is 1. Since Et_2Mg is monomeric in THF,[27] the active organomagnesium component must be *monomeric* Et_2Mg. The order in **1** was established by determining rates of formation of **3** in series of kinetic runs in which $[\mathbf{1}]_0$ was varied while $[Et_2Mg]_0$ was constant and in large excess. Kinetic runs 103–105 are one such series. Values of $[\mathbf{3}]$/time for early aliquots (less than 10% formation of **3**) were averaged; the slope of the plot of these values of ln ($[\mathbf{3}]$/time) versus values of ln $[\mathbf{1}]_0$ is 1.00 (correlation coefficient 1.00). Another series gave a slope of 1.16 (correlation coefficient 1.00). These data indicate that the order in **1** is 1. Second-order rate constants (the pseudo-first-order rates divided by $[R_2Mg]_0$) are included in Table I for each kinetic run.

Effects of oxygen or water in amounts greater than should be present in the solutions we studied are not large. Prior to the introduction of **1** in some reactions, small amounts of water (introduced as a dilute solution in THF) were added to the Et_2Mg solution or this solution was exposed to air. In either type of experiment, formation of **3** was slowed, but only by approximately[28] the amount attributable to the reduction in concentration of the organomagnesium compound.

It is unlikely that the levels of transition metals in the reaction solutions significantly influenced the rates. The average of all rate constants in Table I for Et_2Mg was (1.20 ± 0.12) × 10^{-5} L mol^{-1} s^{-1}. For reactions using Et_2Mg prepared from Dow triply-sublimed Mg, the average was (1.28 ± 0.12) × 10^{-5} L mol^{-1} s^{-1}, and for reactions using Et_2Mg prepared from Cerac Mg, the average was (1.12 ± 0.09) × 10^{-5} L mol^{-1} s^{-1}. Since amounts of crucial transition metals are greater in the Cerac Mg than in the Dow Mg, it is unlikely that the amounts of transition metals in either Mg sample significantly affected the rates. Preliminary experiments using considerably less pure Mg samples, however, gave rates that generally were somewhat faster than those observed when Cerac or Dow magnesium was used. As described in the Experimental Section, amounts of Fe (added as $Fe(acac)_3$) considerably greater than could come from the Mg did significantly increase the rate of formation of **3** in reactions of **1** with either Et_2Mg or the Grignard reagent formed from EtBr. However, significant amounts of other products were formed. Failure to observe these products in the usual kinetic reactions suggests that effects of Fe impurities were not significant. Any residue of the Et_2Hg used to prepare Et_2Mg conceivably might react with **1**.[29] GC analysis of a THF solution of **1** and Et_2Hg showed peaks only for reactants, however, even after 5 days.

An addition product such as **3** can result from reactions of **1** not only with R_2Mg (eq 2) but also with **10** (eq 5). (Similarly, **12** can result from reactions of **1** with either **10** (eq 4) or **13**.) It is possible that the rate of the reaction of **10** and **1** could differ significantly from that of R_2Mg and **1**; equilibration of **10** with R_2Mg and **13** (eq 6) is an added complication. In the kinetic experiments, however, the concentration of R_2Mg always greatly exceeded the maximum concentration of **10** (or **13**) that could have been present. Only if reaction of **1** was very much faster with **10** than with R_2Mg, therefore, would **10** contribute significantly to the formation of addition product. In fact, the absence of systematic changes in rate during the initial portions of reactions that were used to determine rate constants indicates that any involvement of **10** does not significantly alter the observed rates. Before we had decided to use R_2Mg in large excess in the kinetic experiments, however, we briefly studied equilibration in THF solutions prepared from different mole ratios of Et_2Mg and $(cyclopropyl)_2Mg$. Chemical shifts of ^{13}C NMR absorptions of both the Et and cyclopropyl groups changed with composition, and plots of chemical shift versus mole fraction were linear within experimental error. The variation in chemical shifts indicates that significant amounts of Et_2Mg, $(cyclopropyl)_2Mg$, and Et(cyclopropyl)Mg were present.[30] That the single sets of Et and cyclopropyl

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[27] Walker, F. W.; Ashby, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 3845.

[28] Association equilibria [Ashby, E. C.; Nackashi, J.; Parris, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3162, and references cited therein] are a complication when substantial concentrations of ethoxy groups are present.

[29] Formation of some unrearranged product of addition of $Hg(O_2CR)$ and OMe to a cyclopropene was observed in reactions in methanol of more ionic mercury compounds, mercuric acetate [Dombrovskii, V. S.; Yakushina, N. I.; Bolesov, I. G. *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 1184; *Zh. Org. Khim.* **1979**, *15*, 1325] and trifluoroacetate [Kartashov, V. R.; Gal'yanova, N. V.; Skorobogatova, E. V.; Chernov, A. N.; Zefirov, N. S. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 2389; *Zh. Org. Khim.* **1984**, *20*, 2623].

Table II. Average Rates of Additions of Organomagnesium Compounds to 1 at 35.47 °C in THF

R_2Mg	10^5k, L mol^{-1} s^{-1} (average deviation)	relative rate
Me_2Mg	0.116 (±0.017)	1
Et_2Mg	1.20 (±0.12)	10.3
i-Pr_2Mg	3.67 (±0.45)	32
t-Bu_2Mg	0.91 (±0.07)	~8

absorptions were sharp, even at −90 °C, indicated that equilibration involving the unsubstituted cyclopropyl group was rapid on the NMR time scale, as is equilibration[5] of other alkyl groups.

Complexation of the metal to the π electrons of the alkene has often been considered to be a likely step on the pathway of addition of a polar main-group organometallic compound to an alkene.[7,31] As described above, in favorable Al and Zn cases such complexation may occur to a significant degree. To be certain that complexation of R_2Mg was not considerably more favorable with a cyclopropene than with more routine alkenes, ^1H and ^{13}C NMR spectra of THF solutions containing 1 and Et_2Mg were examined. The absence of significant NMR shifts of either component suggests that not much complex can be present.

Some kinetic observations of reactions of 1 with Me_2Mg, i-Pr_2Mg, and t-Bu_2Mg to form addition products of structures 5–7, respectively, are included in Table I. The average of all rates in Table I for each R_2Mg is listed in Table II. Also included in Table I are some rates (average $(1.50 \pm 0.35) \times 10^{-5}$ L M^{-1} s^{-1}) observed for formation of 3 from reactions of 1 and an ethyl Grignard reagent ("EtMgBr"). This reagent also is monomeric in THF.[27] Since both Et_2Mg and EtMgBr are present in the Grignard solution (eq 1, R = Et), the observed rate, k["EtMgBr"][1], where ["EtMgBr"] is the concentration of "Grignard reagent" (e.g., the concentration of Mg), equals k_a[Et_2Mg][1] + k_b[EtMgBr][1] (assuming the reaction of 1 and EtMgBr to be first order in each component, as is the reaction of 1 and Et_2Mg). With use of the value (4.82) that can be calculated from literature data[32] for the equilibrium constant for $Et_2Mg + MgBr_2 \rightleftarrows 2EtMgBr$ in THF at 35.47 °C and the value of k_a from Table II, k_b is calculated to be 2.3×10^{-5} L M^{-1} s^{-1}.[33] Although the uncertainty in k_b is large because of the uncertainties in the values used for its calculation, it is evident that the rates of addition to 1 of Et_2Mg and EtMgBr are similar.

Two additional observations are related to other studies. Addition of 15-crown-5 to solutions of R_2Mg increases the rates of addition to pyridines and metalation of fluorene, presumably because magnesiate ions (e.g., R_3Mg^-) are formed.[34] When 15-crown-5 (1 equiv/Et_2Mg) was added to a solution of Et_2Mg and 1, the rate of formation of 3 increased about 5-fold. This preliminary finding suggests that further study of such reactions is warranted. In other kinetic runs, 1 equiv of $HN(CH_2CH_2OMe)_2$ was added to Et_2Mg prior to addition of 1. This amine and Et_2Mg form $EtMgN(CH_2CH_2OMe)_2$, a species which (in diethyl ether, at least) in dimeric and presumably has a structure in which each Mg is bonded to one Et group, to both N atoms, and probably to one O atom.[35] No addition product was noted, even after 2 weeks, although some of the 1 was metalated. Metalation of the substrate also was the major path in reactions (in diethyl ether) of this organomagnesium compound and diisopropyl ketone.[35]

Discussion. That addition of R_2Mg to 1 is first order in each component is not surprising. Similar rate behavior has been observed for additions in diethyl ether of allylic organomagnesium compounds to alkenes[15] and of dimethylmagnesium to ketones[36] and to nitriles.[37] That the rates of addition of Me_2Mg, Et_2Mg, i-Pr_2Mg, and t-Bu_2Mg are so similar is remarkable, however. In few reactions involving bond cleavage and formation at carbons do the rates of reaction of the members of a methyl to *tert*-butyl series span such a small range. Cyclizations of alkenylorganomagnesium compounds exhibit similar behavior, however. Alkenes having primary, secondary, and tertiary organomagnesium functions have similar cyclization rates, and the secondary systems also are the most rapid.[7] Effects of methyl substitution on the additions of allylic organomagnesium compounds also are relatively small and vary in a manner suggesting that more than one factor is important.[15] The observation that rates of addition of a dialkylmagnesium compound and a Grignard reagent to 1 are about the same is similar to what is found for addition of allylmagnesium compounds to norbornene.[15] R_2Mg reacts somewhat more rapidly than a Grignard reagent, however, in additions of methylmagnesium compounds to ketones[36] and nitriles,[37] and generally also in cyclizations of alkenylmagnesium compounds.[7]

Increasing bulk of the organic group in the series from Me to t-Bu will tend to significantly decrease the rate of any reaction whose rate-determining step requires close approach of the organomagnesium compound to the alkene. Of the reaction processes that have been considered for additions of organomagnesium compounds, single electron transfer[38] from the organomagnesium function to the unsaturated function is the most likely to have a transition state with a considerable separation between these functions. Electron transfer to isolated alkene functions is unlikely, however, because of their high reduction potentials.[39]

The order of rates most likely results because the steric effect of an alkyl group is approximately canceled by another effect, probably electronic, that becomes more favorable for addition in the series Me to t-Bu. It is probable that the transition state for addition is four-centered,[31,40]

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[30] A linear plot indicates that $K \simeq 4$ for the equilibrium $Et_2Mg + (cyclopropyl)_2Mg \rightleftarrows Et(cyclopropyl)Mg$ [Spiro, T. G.; Hume, D. N. *J. Am. Chem. Soc.* **1961**, *83*, 4305. Beck, M. T.; Gazier, F. *Acta Chim. Hung.* **1964**, *41*, 423. House, H. O.; Latham, R. A.; Whitesides, G. M. *J. Org. Chem.* **1967**, *32*, 2481]. Given, however, the small chemical chemical shift ranges (~0.5 ppm), the scatter in the points, and the possible errors in assigning solution concentrations, K can only be assigned an approximate value in the range 2–8. A similar equilibrium involving Et_2Hg and $(cyclopropyl)_2Hg$ favors Et(cyclopropyl)Hg (K = 130 for the neat liquids at 90 °C) [Reynolds, G. F.; Daniel, S. R. *Inorg. Chem.* **1967**, *6*, 480].

[31] O'Neill, M. E.; Wade, K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 1. Eisch, J. J. in *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon, Oxford, U.K., 1982; Chapter 6.

[32] Smith, M. B.; Becker, W. E. *Tetrahedron* **1967**, *23*, 4215.

[33] Since [Et_2Mg] = [$MgBr_2$], then [EtMgBr]/[Et_2Mg] = $(4.82)^{0.5}$ = 2.20. It follows that [Et_2Mg] = ["EtMgBr"]/4.20 and [EtMgBr] = 2.20-["EtMgBr"]/4.20. Using the average values of 1.20×10^{-5} L mol^{-1} s^{-1} for k for Et_2Mg and of 1.50×10^{-5} L mol^{-1} s^{-1} for k for "EtMgBr", $k_b = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}.

[34] Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

[35] Squiller, E. P. Ph.D. Dissertation, The Pennsylvania State University, 1984.

[36] Reference 25. Ashby, E. C.; Laemmle, J.; Neumann, H. M. *Acc. Chem. Res.* **1974**, *7*, 272.

[37] Ashby, E. C.; Chao, L.-C.; Neumann, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 4896, 5186.

[38] For a review of single-electron transfer involving organomagnesium compounds, see: Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987; Chapter 8. Also see: Holm, T. *Acta Chem. Scand., Ser. B* **1983**, *37*, 567.

[39] Fry, A. J.; Reed, R. G. In *The Chemistry of Double-Bonded Functional Groups*, Supplement A; Patai, S., Ed.; Wiley: London, 1977; Chapter 5. Kariv-Miller, E.; Pacut, R. I.; Lehman, G. K. *Top. Current Chem.* **1988**, *97*, 148.

and the degree of formation of the new C—C and C—Mg bonds and cleavage of the old C=C and C—Mg bonds is sensitive to the substitution at these C atoms. Complexes having bonding primarily between the π electrons of the alkene and the magnesium[41] may well precede the transition state, but there is no evidence that the concentrations of such complexes ever are significant.

Experimental Section

Materials. Diethyl ether and tetrahydrofuran (THF) were refluxed over Na under a nitrogen atmosphere (the blue color of benzophenone ketyl was used as an indication of dryness) and distilled immediately before use. The concentration of water in the THF was determined by titratration using a Karl Fisher reagent with 2-methoxyethanol as a solvent.[42] The concentrations found ($<10^{-5}$ M) following transfer using gas-tight syringes were negligible by comparison to those (generally >0.2 M) of organomagnesium compounds in the kinetic experiments.

Several grades of Mg were used: Puratonic (Alfa Products), Cerac (Cerac, Inc., Stock No. M-1000), and Dow triply-sublimed (a gift of Dow Chemical Co.). The following (ppm) amounts of transition elements are reported for these samples: Puratonic, Cd <1, Cr <1, Co 2, Cu <1, Fe 20, Mn 10, Mo 2, Ni 1, Ag <1, Ti 5, V 2, Zn 1; Cerac, Cu 5, Fe 5, Mn 6, Ni 5, Zn 15; Dow, Cu <1, Fe <4, Zn <100.[43] The chunks of triply-sublimed Mg were broken up with a mortar and pestle prior to use.

Equipment. Analytical GC was performed with gas chromatgraphs equipped with flame ionization detectors, using He as the carrier gas and the following glass columns: A, SE-30 (20%) on Gas Chrom Q (100–120 mesh), 2-mm i.d. × 6 ft; B, SP-2100 (3%) on Supelcoport (100–120 mesh), 2-mm i.d. × 6 ft. Peak areas were measured using an electronic integrator (Varian Instruments Model CDS-111L). "Preparative" GC was performed with a gas chromatograph equipped with a thermal conductivity detector, using He as the carrier gas and the following aluminum column: C, SE-30 (20%) on Gas Chrom Q (60–80 mesh), 0.25 in. × 10 ft. Small samples were collected by using glass U-shaped tubes cooled in liquid nitrogen and inserted into the exit port of the chromatograph.

^{1}H NMR chemical shifts are reported in parts per million (δ) to higher frequency from internal Me_4Si and with the use of the following notations: s, singlet; d, doublet; t, triplet; q, quartet; c, complex overlapping absorptions. ^{13}C NMR spectra are proton decoupled; chemical shifts of hydrocarbons are reported in parts per million (δ) to higher frequency from internal Me_4Si, and chemical shifts of organomagnesium solutions are relative to internal cyclohexane taken as δ 27.50. Mass spectra were obtained using GC/MS instruments and GC columns similar to those described above. An ionizing voltage of 70 eV was used for EI mass spectra. The gas for CI mass spectra was methane.

The spinning band columns (Perkin-Elmer Model-131T and Model 151) were vacuum jacketed and had Teflon bands. The glovebox (Vacuum Atmospheres Co., Model DL-001-S-P) had a nitrogen atmosphere that was recirculated through a purification train. Gas-tight syringes (Hamilton Co., Inc., and Glenco Scientific, Inc.) were used to transfer anhydrous solvents and organometallic solutions.

Preparation of Methylenecyclopentane. The procedure was based on a brief literature description.[44] To each of three ampules were added 1,5-hexadiene (15.2 g, 0.185 mol), a toluene solution of diisobutylaluminum hydride (5 mL, 1.5 M, 75 mmol), and toluene (8 mL, stored over Na). The ampules were sealed and placed for 42 h in an oil bath maintained at 110–120 °C. Each ampule was cooled in an ice bath and opened; a magnetic stirring bar was added and the solution hydrolyzed by addition of ice followed by stirring for at least 2 h. The combined contents of the ampules then were filtered through a sintered-glass funnel. During the filtration, volatile material was collected in a trap cooled in liquid nitrogen. The materials in the trap and in the filter flask were combined, the aqueous and organic layers were separated, the aqueous layer was washed with several portions of toluene, and the combined organic layers were dried (K_2CO_3). Distillation (spinning band column) gave 21.6 g (0.263 mol, 48%) of methylenecyclopentane: bp 75–77 °C [lit.[45] 75–76 °C]. By GC analysis (column A, 60 °C), this compound was 95% pure.

Preparation of 1-Bromospiro[2.4]heptane. This procedure was a variation of the preparations of similar compounds.[46] To a stirred sample of hexamethyldisilazane (100 g, 0.62 mol) maintained under nitrogen was added a hexane solution of butyllithium (400 mL, 1.4 M, 0.56 mol, concentration determined[47] by titration) at a rate that led to steady gas evolution. After addition was completed, solvent was removed at reduced pressure (essential, since any remaining hexane subsequently reacted significantly with bromocarbene to produce bromoheptanes, which were difficult to remove from the desired product). Methylenecyclopentane (25 g, 0.30 mol) was added and the system heated to 80 °C and stirred until the lithium salt dissolved. Then dibromomethane (90 g, 0.52 mol) was added over about 3 h, while the solution was maintained between 80 and 100 °C. The reaction mixture was cooled in an ice bath, water (100 mL) was added, the layers were separated, and the organic layer was dried (K_2CO_3). The aqueous layer was washed with pentane (four 25-mL portions), and these were combined and dried (K_2CO_3). The first organic layer was distilled through a short Vigreux column to a head temperature of 100 °C (this distillate was saved as it contained significant methylenecyclopentane). To the pot residue was added the pentane extract, and most of the pentane was removed by distillation. Then the distillation flask was cooled in an ice bath, and methanol (50 mL) was added, very slowly at first. After addition was complete, the solution was heated at reflux until gas evolution stopped. All material boiling up to a head temperature of 65 °C then was removed. The pot residue was distilled through a short Vigreux column, and the fraction that boiled between 69 and 77 °C at 24 Torr was collected. This fraction, which contained 1-bromospiro[2.4]heptane and unsaturated isomers of that compound, was cooled in an ice bath and washed successively with portions of 20, 50, and 80% sulfuric acid. If reaction became too vigorous, as evidenced by rapid darkening of the organic layer, water was added quickly to dilute the acid. The organic layer was washed with 10% aqueous NaOH and with water and then dried (K_2CO_3). The yield of the resulting 1-bromospiro[2.4]heptane typically was about 40%: ^{1}H NMR (60 MHz, CCl_4) δ 0.82 (d of d, 1, H_a (cyclopropane H trans to Br), J_{ab} = 6 Hz, J_{ac} = 4 Hz), 1.20 (d of d, 1, H_b (cyclopropane H cis to Br), J_{bc} = 7.5 Hz), 1.12–2.17 (c, 8, $(CH_2)_4$), 2.97 (d of d, 1, H_c (CHBr)); EIHRMS *m/z* 176.0030 (M^+ calculated for $C_7H_{11}Br$ 176.0024).

Preparation of Spiro[2.4]hept-1-ene (1). This procedure was based on one described elsewhere.[48] Dimethyl sulfoxide (125 mL, distilled[49] from CaH_2) and potassium *tert*-butoxide (34 g, 0.31 mol, sublimed[50]) were added to a round-bottomed flask equipped with a magnetic stirring bar, thermometer, addition funnel, and a Vigreux column in series with a trap maintained at −60 °C, a second trap cooled in liquid nitrogen, and a water aspirator. The 1-bromospiro[2.4]heptane (23.2 g, 0.133 mol) was added over 2 h to the reaction flask maintained at a temperature between 40 and 50 °C and at a pressure between 20 and 30 Torr.

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(40) Model systems for such additions on which MO calculations have been done include ethylene plus AlH_3 [Gropen, O.; Haaland, A. *Acta Chem. Scand., Ser. A* **1982**, *36*, 435] and plus LiH or MeLi [Houk, K. N.; Rondan, N. G.; Schleyer, P. v. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821].

(41) MO calculations have been done on a π complex between MgH_2 and ethylene [Gropen, O.; Haaland, A.; Defrees, D. *Acta Chem. Scand., Ser. A* **1985**, *39*, 367].

(42) *Technical Data on So-K-3 Karl Fisher Reagent*; Fisher Scientific Co.: October, 1963.

(43) The analyses of the Puratronic and Cerac samples were provided for the specific lots by the manufacturer. The analysis of Dow triply-sublimed magnesium is from: Salinger, R. M.; Mosher, H. S. *J. Am. Chem. Soc.* **1964**, *86*, 1782.

(44) Chum, P. W.; Wilson, S. E. *Tetrahedron Lett.* **1976**, 1257.

(45) Conia, J.-M.; Limasset, J.-C. *Bull. Soc. Chim. Fr.* **1967**, 1936.

(46) Martel, B.; Hiriart, J. M. *Synthesis* **1972**, 201.

(47) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(48) Binger, P.; Schuchardt, U. *Chem. Ber.* **1981**, *114*, 1649. Binger, P. *Synthesis* **1974**, 190.

(49) Traynelis, V. J.; Hergenrother, W. L.; Livingston, J. R.; Valicenti, J. A. *J. Org. Chem.* **1962**, *27*, 2377.

(50) Pearson, D. E.; Buehler, C. A. *Chem. Rev.* **1974**, *74*, 45.

After 2 additional hours, the material from the traps was collected, washed with 10–15 portions of water, and dried (K_2CO_3) to give 1 (6.24 g, 0.0663 mol, 50% yield): ^1H NMR (60 MHz, CCl_4) δ 0.52–2.88 (c, 4, $(CH_2)_4$), 6.99 (s, 1, $=CH$); ^{13}C NMR (20 MHz, $CDCl_3$) δ 26.58 ($CH_2(CH_2)_2CH_2$), 37.58 ($CH_2(CH_2)_2CH_2$), 118.47 ($=C$) [no absorption observed for the spiro C]. By GC analysis (column A, 60 °C), this sample was 99% pure.

Preparation of 1-Ethylspiro[2.4]heptane (3). Glassware used in this preparation was cleaned in a fresh sulfuric acid–potassium chromate bath and then rinsed repeatedly with water, rinsed with an aqueous ammonia solution, rinsed repeatedly with water, rinsed twice with acetone, rinsed with methylene chloride, and dried in an oven. Magnesium (Puratonic, 0.30 g, 0.012 mol) was added to a flask equipped with a magnetic stirring bar, a septum, an addition funnel with a septum, and a condenser with an argon inlet. The system was heated with a heat gun while nitrogen flowed through it. After the apparatus had cooled, THF (10 mL) was added to the flask, which then was cooled in an ice bath, and over 45 min a solution of ethyl bromide (1.64 g, 15 mmol, freshly distilled) in THF (13 mL) was added through the addition funnel, following which the flask was allowed to warm to room temperature. After about 3 h all of the metal had dissolved. To this solution, 1 (0.95 g, 10.1 mmol) was added via a syringe, and the resulting solution was stirred for 17 h. The flask then was placed in an ice bath and a saturated aqueous ammonium chloride solution (20 mL) was added slowly, followed by water (20 mL). The layers were separated, the aqueous layer was washed with hexane (three 10-mL portions), and the combined organic layers were dried (K_2CO_3). Most of the solvent was removed by distillation using a spinning band column, and 3 was isolated from the residue by preparative gas chromatography (column C, 50 °C): ^1H NMR ($CDCl_3$, 200 MHz) δ 0.01 (appearance of t but must be d of d, 1, H_c, $J_{ab} \cong J_{ac} \cong 3.5$ Hz), 0.50–0.80 (c, 2, H_a and H_b), 0.96 (t, 3, CH_3, $J = 7.2$ Hz), 1.05–1.80 (c, 10, all CH_2's); EIMS m/z (rel intensity) 124 (7), 109 (1), 96 (11), 95 (70), 94 (5), 93 (5), 91 (3), 83 (6), 82 (24), 81 (16), 80 (3), 79 (11), 78 (1), 77 (5), 70 (1), 69 (7), 68 (28), 67 (100), 66 (10), 65 (5), 56 (4), 55 (24), 54 (11), 53 (15), 52 (22), 51 (4), 43 (3), 42 (3), 41 (3), 40 (8), 39 (25); EIHRMS m/z 124.1247 (M^+ calcd for C_9H_{16} 124.1252); CIMS m/z (rel intensity) 126 (2), 125 (31), 124 (32), 123 (100), 122 (2), 111 (12), 109 (22), 97 (18), 96 (2), 95 (18), 85 (7), 84 (8), 83 (86), 82 (20), 81 (77), 71 (12), 70 (11), 69 (83), 68 (7), 67 (38), 66 (2), 61 (3).

Preparation of (*Z*)-1-Ethylspiro[2.4]heptane-2-*d* (4). Except for the use of a 6-fold larger scale and for an alteration of the hydrolysis procedure, the preparation was essentially the same as that of 3. The reaction solution, cooled in an ice bath, was quenched with D_2O (50 mL), and the resulting viscous slurry was stirred for 1 h. A saturated aqueous ammonium chloride solution (100 mL) was added, the layers were separated, and the aqueous layer was washed with water (50 mL). The combined aqueous layers were washed with diethyl ether (three 50-mL portions), and the combined organic layers were dried (K_2CO_3). Distillation and preparative GC then gave 4: ^1H NMR ($CDCl_3$, 360 MHz) δ 0.51 (d, 1, H_b, $J_{ab} = 8.2$ Hz), 0.60 (appearance of q but must be d of t, 1, H_a, $J_{ab} \cong J_{cd} \cong 7.5$ Hz (H_d's, are CH_2CH_3)), 0.96 (t, 3, CH_3, $J = 7.3$ Hz), 1.10–1.75 (c, 10, all CH_2's). An absorption for H_c representing more than 0.02 H would have been noted.

Equipment for Kinetic Runs.[26] Several items of specialized glassware were constructed in such a manner that the solutions came in contact only with glass and Teflon, never with metal. Stopcocks had Teflon plugs so that stopcock grease did not have to be used. Gas-tight syringes (Glenco Scientific, Inc.) were incorporated into the apparatus to effect transfers of liquids. The accuracy of transfers using syringes was checked by weighing samples of expelled 2,2,4-trimethylpentane; the average deviation was <0.01 mL for 1-mL syringes and a somewhat smaller fraction of their capacities for the larger syringes. All operations were conducted under argon which was passed first through a tube filled with Drierite and molecular sieves (4A) and then through a tube filled with catalyst R 3-11[51] (Badische Anilin- and Soda-Fabrik, AG). Transfers that required opening a flask were done in the glovebox. Glassware and Teflon-coated stirring bars were cleaned between uses by soaking in a sulfuric acid solution of Nochromix (Godax Laboratories, Inc.) for at least 1 h, rinsing with water, soaking in 10% aqueous ammonia, rinsing five times with water, rinsing with acetone, rinsing with methylene chloride, and drying in an oven. Other plastic items were rinsed with water, rinsed with acetone, and allowed to dry for an extended period. Plastic valves and Teflon tubes were placed in an ultrasonic cleaner with a liquid cleanser (Supelco, Inc., 2-2662) for several hours prior to the rinsing procedure. Gas-tight syringes were rinsed with distilled water and acetone. The barrels were dried in an oven and then allowed to cool in a desiccator before use.

Preparation of Solutions of Organomagnesium Compounds for Kinetic Experiments. Magnesium (the source indicated in Table I) and a Teflon stirring bar were added to the preparation flask. This flask had a water-cooled condenser with a stopcock at the top which could be connected to a manifold which provided vacuum or purified argon. The flask also had a side arm with a stopcock following which was a septum. A Teflon tube could be inserted through the septum and, when the stopcock was open, pushed through the stopcock so that its end reached the bottom of the flask. The Teflon tube was connected to one arm of a three-way valve, whose other connections were to a Teflon tubing assembly connected to a syringe and to a Teflon tube through which waste liquid could be expelled. When vacuum was to be applied, the Teflon tube could be withdrawn above the level of the stopcock and the stopcock closed. Before a preparation, the flask was evacuated and heated with a heat gun, and then argon was admitted. The cycle of evacuating, heating, and admitting argon was repeated twice. When solvents were needed, large amounts were introduced directly from a solvent still and small amounts using syringes. During a preparation, the system was maintained under a slight positive pressure of Ar.

For the preparation of dimethylmagnesium and diethylmagnesium, the appropriate dialkylmercury compound (ca. 10 g, freshly distilled) and a drop of Hg were added to the flask, which already contained Mg (ca. 1 g, 0.04 mol). The contents were stirred, and the flask was heated at 80–90 °C for at least 18 h. The flask was then evacuated (<0.005 Torr) with occasional heating with a heat gun to remove any residual dialkylmercury compound.

Diisopropylmagnesium was prepared by adding diethyl ether (100 mL) to the reaction flask already containing Mg (2.42 g, 0.100 mol) followed by cooling in an ice bath and addition of 2-bromopropane (12.6 g, 0.102 mol, freshly distilled). The solution was allowed to warm slowly to room temperature and was stirred for several hours. The flask was again cooled in an ice bath, and dioxane (9.41 g, 0.107 mol, distilled from CaH_2) was added. The mixture was allowed to warm slowly to room temperature and then stirred vigorously for 12 h. The contents of the flask were transferred (in a glovebox) into a centrifuge tube. The tube was centrifuged, and then (again in a glovebox) the clear liquid was transferred with a syringe to a clean preparation flask. The flask was evacuated until most of the diethyl ether had been removed, and then THF (10 mL) was added. The process of evacuation and then adding THF was repeated twice. After most of the last portion of solvent had been removed, the flask was evacuated at low pressure (<0.005 Torr) at ambient temperature. The same procedure was used for the preparation of di-*tert*-butylmagnesium from *tert*-butyl chloride.

To prepare ethylmagnesium bromide for kinetic studies, THF (40 mL) was added to the preparation flask that contained Mg (0.92 g, 38 mmol), following which the flask was cooled in an ice bath and ethyl bromide (4.59 g, 42 mmol, freshly distilled) was added. The flask was allowed to warm slowly to room temperature and the contents then were stirred overnight. The flask was evacuated until most of the THF had been removed, and then THF (10 mL) was added. The process of evacuation and then adding THF was repeated twice. After most of the last portion of solvent had been removed, the flask was evacuated at low pressure (<0.005 Torr) at ambient temperature.

Solutions were prepared from the solid organomagnesium compounds with the aid of a volumetric flask (250 mL) which had a standard taper joint permitting attachment to a THF purification still. The flask also had a side arm with a septum through which was inserted a Teflon tube; this tube was connected to one

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[51] *Technical Leaflet for BASF Catalyst R 3-11*; Badische Anilin- and Soda-Fabrik, AG: April 1971.

arm of a three-way valve, whose other connections were to a Teflon tubing assembly connected to a syringe and to a Teflon tube used for waste disposal. THF was distilled into the volumetric flask to above the mark. Then some THF was removed through the valve and into the syringe and then expelled from the syringe through the waste tube. This process of removing liquid was repeated at least three times until the THF filled the volumetric flask to the mark. This syringe and its tubing assembly were removed from the valve. Another syringe was fitted to a tubing assembly, and this combination was weighed. An alkane (ca. 1 g) to be used as an internal GC standard was drawn into the syringe, and the syringe–tubing assembly combination was reweighed. Nonane was used with Me_2Mg and octane with all other organomagnesium compounds. The tubing assembly then was reconnected to the valve, and the contents of the syringe were added to the volumetric flask; liquid was passed back and forth several times between the syringe and volumetric flask to be certain that essentially all of the alkane had been added.

Some of the THF solution of alkane was taken into a syringe, which then was connected via its tubing assembly to the three-way valve of the organomagnesium preparation flask. The excess of the THF–alkane solution was forced through the valve and out the waste disposal tube; the amount needed then was transferred into the organomagnesium preparation flask. The concentrations of the resulting organomagnesium solutions were determined by a double titration procedure,[52] using 0.5-mL aliquots removed through the tubing system. After the addition of carbon tetrachloride, samples were allowed to stir overnight (rather than just 15 min) prior to quenching with water. Since the resulting solutions were colorless, titration could be done using an indicator (bromothymol blue) instead of potentiometrically.

Procedure for Kinetic Reactions. The reactions were carried out in pear-shaped flasks having a side arm with a stopcock followed by a septum. When the stopcock was open, a Teflon tube inserted into the septum could be pushed through the stopcock so that its end reached the bottom of the flask. The Teflon tube was connected to a three-way valve, whose other connections were to a Teflon tubing assembly connected to a gas-tight syringe and to a Teflon tube which could be used for expelling liquid waste or could be inserted through the septum of one of the small vials used for quenching. Between the stopcock and the septum was a side arm, with another stopcock, which was attached to a vacuum manifold.

The reaction flask was evacuated and heated, and then argon was admitted. The cycle of evacuating, heating, and filling with argon was repeated twice. Then the stopcock to the vacuum manifold was closed. A small amount of the organomagnesium solution was removed from the preparation flask through its valve into the syringe, and then argon was drawn into the syringe until it was opened to its full capacity. Then the syringe was emptied through the waste tube. This process was repeated twice. Then a portion of the organomagnesium solution was taken into the syringe. The syringe and its tubing assembly were removed from the valve of the preparation flask and connected to the valve of the reaction flask. A portion of the organomagnesium solution (0.5–1 mL) was passed through the valve of the reaction flask and expelled. A measured portion then was introduced into the kinetic flask. The Teflon tube inserted into the kinetic flask then was withdrawn sufficiently to permit the stopcock through which it had passed to be closed. The valve and tube used for connection to the quenching vials then were rinsed with THF.

When 15-crown-5 or bis(2-methoxyethyl)amine was to be added, a kinetic flask containing the diethylmagnesium solution was taken into the glovebox, where a weighed amount of the additive (freshly distilled with KOH) was introduced. These flasks were then supplied with fresh septa, tubing, and valves.

Kinetic flasks were immersed in a constant temperature bath which was regulated to ±0.03 °C. The bath temperature, 35.47 °C, was determined using a National Bureau of Standards certified thermometer. A flask was left in the bath overnight before adding **1**. A stopcock on the flask was opened and the Teflon tube reintroduced into the bottom of the flask. A solution was prepared in a weighed, 10-mL volumetric flask from **1** (ca. 1 g, accurately weighed), the "secondary" alkane standard (ca. 1 g, accurately weighed), and THF (sufficient to fill the flask to the mark); the flask then was reweighed to determine the density of the solution. Nonane was used for reactions with $i\text{-}Pr_2Mg$, and 4-methylnonane for all other reactions. A syringe and its tubing assembly were weighed, a portion of this solution was drawn into the syringe, and the syringe–tubing assembly combination was reweighed. The tubing assembly then was attached to the valve of the reaction flask. The contents of the syringe were added to the flask, and the time of addition was recorded. Small amounts of liquid were passed between the syringe and the kinetic flask several times to assure thorough mixing of the organomagnesium and cyclopropene solutions. A portion of the solution (1 mL) then was drawn into the syringe and expelled into a quenching vial (dead volume of the tubing was ~0.2 mL so ~0.8 mL was transferred) that had been cooled in a refrigerator and contained 1.0 mL of a saturated aqueous solution of ammonium chloride. The time of quenching was recorded. For subsequent quenches, an amount of the kinetic solution exceeding the dead volume of tubing was introduced into the syringe and then passed through the quenching tube as waste. A portion of the kinetic solution (0.8 mL) then was introduced into the syringe and expelled into a quenching vial. The time for each quench was recorded. Quenching vials then were capped with solid screw caps and stored in a refrigerator.

Analysis of Kinetic Solutions. The organic layer of each vial was analyzed by GC using column A (column 60 °C, injector 160 °C, detector 160 °C). When aliquots were analyzed for high molecular weight products, column B was used (injector 200 °C, detector 190 °C, column 50 °C initially but following injection increased at a rate of 50 °C/min until 175 °C was reached, which temperature then was maintained). Weights of the compounds were generally assumed to be proportional to peak areas, a reasonable assumption for hydrocarbons.[53] Correction factors relative to octane were determined (peak areas must be multiplied by these factors) and used, however, for **3** (1.05) and 4-methylnonane (1.05). Typical elution times (column, min) of reactants, reference alkanes, and products are as follows: THF (A 0.62, B 0.69), **1** (A 1.06, B 0.92), **5** (A 1.96), **4** (A 3.49, B 1.85), **6** (A 4.87), **7** (A 7.79), **8** (B 3.10), **9** (B 4.62), octane (A 1.84, B 1.26), nonane (A 3.62), 4-methylnonane (A 5.33, B 1.95).

To determine if tailing of THF might introduce errors into the measurement of those components most closely following it, standard THF solutions of nonane and octane (combined octane plus nonane concentration $\sim 10^{-2}$ M) were analyzed. Nonane was a component with which THF tailing was not evident, and octane eluted before any of the products. To check the reproducibility of such peak area measurements following quenching, portions of the octane–nonane solutions also were shaken with equal volumes of a saturated aqueous ammonium chloride solution, and then the organic layers were analyzed. In either experiment, agreement of the average observed values with the expected values was within considerably less than 2%.

Identification of Products of Kinetic Reactions of 1 and Organomagnesium Compounds. Each reaction showed only one significant GC peak with a retention time that would be reasonable for a 1:1 addition product (**3**, **5**, **6**, or **7**) or an isomer of it. EI and CI mass spectra constituted one part of the identification of the compound responsible for this peak. In the case of **3**, these spectra were identical to those of the sample prepared on a significant scale. The compound responsible for each peak also was collected by preparative GC of the combined organic layers of several hydrolyzed aliquots.

1-Methylspiro[2.4]heptane (**5**): ^1H NMR (60 MHz, CCl_4) δ 0.05–0.65 (c, cyclopropyl H's), 0.95 (s, CH_3) 1.05–1.80 (CH_2's of cyclopentane ring); EIMS m/z (rel intensity) 111 (1), 110 (5), 109 (1), 96 (1), 95 (22), 94 (1), 93 (2), 91 (2), 83 (1), 82 (8), 81 (27), 80 (3), 79 (12), 78 (2), 77 (4), 70 (1), 69 (12), 68 (38), 67 (100), 66 (14), 65 (7), 64 (1), 63 (2), 56 (2), 55 (11), 54 (7), 53 (14), 52 (3), 51 (4), 50 (1), 43 (1), 42 (3), 40 (8), 39 (27), 38 (1); EIHRMS m/z 110.1091 (M^+ calcd for C_8H_{14} 110.1095); CIMS m/z (rel intensity) 112 (4), 111 (62), 110 (23), 109 (100), 108 (1), 97 (12), 95 (8), 74

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(1), 73 (28), 72 (3), 71 (9), 61 (4), 60 (19), 59 (98), 58 (10), 57 (38), 56 (4).

1-Isopropylspiro[2.4]heptane (**6**): ^{1}H NMR (60 MHz, CCl_4) δ 0.15–0.65 (c, cyclopropyl H's), 0.90 (m, CH_3), 1.10–1.80 (CH_2's of cyclopentane ring and CH of isopropyl group); EIMS *m/z* (rel intensity) 138 (1), 125 (1), 121 (1), 110 (1), 97 (2), 96 (5), 95 (70), 94 (4), 93 (5), 91 (3), 89 (1), 83 (4), 82 (28), 81 (18), 80 (4), 79 (17), 78 (1), 77 (6), 71 (1), 70 (13), 69 (21), 68 (19), 67 (100), 66 (4), 65 (5), 57 (4), 56 (8), 55 (32), 54 (8), 53 (13), 52 (2), 51 (2), 44 (2), 43 (2), 42 (5), 41 (54), 40 (11), 39 (20); EIHRMS *m/z* 138.1405 (M^+ calcd for $C_{10}H_{18}$ 138.1408); CIMS *m/z* (rel intensity) 139 (2), 138 (5), 137 (42), 124 (4), 123 (34), 111 (5), 98 (2), 97 (26), 96 (3), 95 (38), 85 (3), 84 (8), 83 (100), 82 (12), 81 (63), 79 (2), 73 (2), 71 (7), 70 (3), 69 (40), 68 (1), 67 (9).

1-*tert*-Butylspiro[2.4]heptane (**7**): ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.30, 0.34, and 0.70 (each a d of d; each 1; probably H_c, H_b, and H_a, respectively, although assignments to H_a and H_b perhaps should be reversed; J_{ab} = 9.2 Hz, J_{ac} = 6.7 Hz, and J_{bc} = 4.1 Hz); 0.92 (s, 9, CH_3), 1.20–1.90 (c, 8, CH_2's of cyclopentane ring); EIMS *m/z* (rel intensity) 109 (7), 96 (32), 95 (27), 84 (3), 83 (13), 82 (7), 81 (12), 79 (12), 71 (1), 70 (100), 69 (40), 68 (6), 67 (63), 66 (3), 65 (3), 57 (64), 55 (56), 53 (16), 43 (1), 42 (12), 41 (82), 40 (28), 39 (20); EIHRMS *m/z* 152.1562 (M^+, calcd for $C_{11}H_{20}$ 152.1565); CIMS *m/s* (rel intensity) 153 (2), 152 (1), 151 (27), 143 (2), 138 (2), 137 (58), 127 (2), 117 (2), 115 (3), 114 (1), 113 (3), 111 (4), 110 (1), 109 (5), 98 (5), 97 (73), 96 (22), 95 (100), 88 (2), 87 (3), 86 (3), 85 (4), 84 (4), 83 (86), 82 (4), 81 (29), 71 (8), 70 (7), 69 (22), 67 (7), 66 (1), 61 (3).

1-(1-Spiro[2.4]heptyl)-2-ethylspiro[2.4]heptane (**8**): EIMS *m/z* (rel intensity) 148 (4), 141 (6), 131 (3), 129 (3), 128 (3), 120 (5), 119 (5), 117 (5), 116 (2), 115 (5), 107 (3), 106 (3), 105 (12), 102 (3), 98 (18), 97 (45), 95 (9), 94 (3), 93 (15), 92 (8), 91 (38), 85 (5), 84 (27), 83 (3), 82 (14), 81 (14), 80 (26), 79 (47), 78 (8), 77 (21), 72 (3), 71 (100), 70 (6), 69 (6), 68 (6), 67 (43), 66 (12), 65 (9), 63 (3), 56 (4), 55 (18), 54 (4), 53 (3), 44 (4), 41 (3), 40 (5); CIMS *m/s* (rel intensity) 219 (12), 218 (38), 217 (57), 152 (3), 151 (7), 149 (32), 148 (2), 137 (47), 136 (1), 135 (45), 125 (3), 124 (5), 123 (72), 122 (8), 121 (33), 115 (10), 114 (2), 113 (2), 111 (3), 110 (4), 109 (79), 108 (5), 107 (32), 102 (4), 98 (6), 97 (6), 96 (10), 95 (100, 94 (4), 93 (4), 89 (11), 88 (1), 87 (1), 85 (4), 82 (3), 81 (23), 79 (3), 71 (1). Mass spectra could be obtained of the 3.10-min peak using a routine kinetic solution, but sufficient material for NMR spectroscopy required using a solution that was more concentrated than the kinetic solutions and was permitted to react for a longer time. To a THF solution of diethylmagnesium (1.0 mL, ~0.3 M, 0.3 mmol) was added **1** (~30 mg, 0.3 mmol), and this preparation was left in the glovebox for 15 days before hydrolysis. Analytical GC (column B) showed, besides the peak at 3.10 min, at least 20 other, smaller peaks in that region that were not observed in GC analysis of the kinetic solutions; the peak at 3.10 min, however, corresponded to about 70% of the combined areas of the peaks in that region. A sample of the material responsible for the 3.10-min peak that was obtained by preparative GC was slightly contaminated by other components. The ^{1}H NMR spectrum (360 MHz, $CDCl_3$) showed, in approximately the area ratios expected for **8**, absorptions for cyclopropyl H's (δ 0.15–0.25 and δ 0.55–065), CH_3 (δ 0.85–0.99, c), and CH_2 and perhaps CH (1.25–1.95, c). No absorptions were observed in the =CH region, though there were some relatively small absorptions (~δ 3.73 c; ~δ 3.93 c) that may have been due to small amounts of H's α to an O.

A CIMS of the 4.62-min component (column B) gave 311 as the highest significant *m/e* value. This corresponds to $(M - 1)^+$ for **9**.

In some reactions, aliquots were quenched by addition to D_2O. The deuterium content of **1** was estimated from the relative intensities of the *m/e* 94 and 95 peaks.

Analysis of Kinetic Data. The amounts in a reaction solution of organomagnesium compound, **1**, alkane standard, and "secondary" alkane standard were available from the volumes or weights determined in the preparation of this solution. Their concentrations were calculated with the assumption that the total volume of a kinetic solution equaled the volume of the stock organomagnesium compound that was used plus the (relatively small) volume of the stock solution of **1**, calculated from the density of this solution and the weight that was used. The concentration of addition product was calculated from the area of its GC peak relative to that of the standard and the known concentration of the standard. The concentration of the "secondary" standard could also be calculated from the area of its GC peak relative to that of the standard, and usually agreed within a few percent with that based on the preparation of the reaction solution. In the few cases where the concentration determined by GC analysis was significantly less, however, the kinetic run was discarded. Such discrepancies probably were due to leakage in a joint between a Teflon tube and a valve during the injection of the solution of **1**.

The slope of the line ln ($[\mathbf{1}]_0$ – [addition product]) versus time was calculated by a linear least-squares regression analysis. All data points were used since, in spite of the more rapid disappearance of **1** often noted at the very beginning of a reaction, slopes obtained in this way did not differ significantly from those obtained using only later data points.

Reactions of 1, Organomagnesium Compounds, and Fe(acac)$_3$. $Fe(acac)_3$ (33 mg, 0.093 mmol) was added to a THF solution of Et_2Mg (4.5 mL, 0.49 M, 2.2 mmol) that had been prepared from Puratonic Mg. The clear, colorless organomagnesium solution bubbled and turned an opaque black. To this mixture at room temperature was added **1** (94 mg, 1.0 mmol), and the reaction was monitored by GC analysis of quenched aliquots. No **1** remained after 8 min.

In another experiment, an ethylmagnesium bromide solution (8.6 mL, 0.56 M, 4.8 mmol) was placed in the constant temperature bath. Then **1** (38.2 mg, 0.41 mmol) and 3-methylheptane (19.3 mg), used as the alkane GC standard [column A, 1.62 min, using conditions described above for analysis of kinetic solutions], were added. The reaction was followed by the usual GC analysis of quenched aliquots. Another reaction was essentially identical except that $Fe(acac)_3$ (55 mg, 0.16 mmol) was added before the flask containing ethylmagnesium bromide was placed in the constant temperature bath. The rate constants for the initial appearance of **3**, calculated with the usual assumption that $[\mathbf{3}]_\infty = [\mathbf{1}]_0$, was 10–20 times greater for the reaction containing Fe. The rate may have been even somewhat faster than calculated on this assumption, however, because the ultimate yield of **3** was low. GC analysis of a late aliquot from the reaction containing Fe showed two additional peaks not observed in prior reactions. The EIMS of the first (GC peak area about the same as that for **3**) showed a peak at 96 as the peak at highest *m/e* and a peak at 67 as the base peak; this compound may be spiro[2.4]heptane. The EIMS of the second (GC peak area about one-fourth that of **3**) had a peak at 122 as the peak at highest *m/e* and significant peaks at 92, 91, and 71; the compound could be 1-ethylspiro[2.4]hept-1-ene.

Preparation of Dicyclopropylmercury. A procedure already described[54] was followed until the overnight reflux was finished. Then the reaction flask was cooled in an ice bath, and a saturated aqueous solution of ammonium chloride (50 mL) was added. The contents were suction filtered through a sintered-glass funnel. The precipitate was washed with diethyl ether (50- and 25-mL portions) and the organic layer with a saturated aqueous ammonium chloride solution (six 25-mL portions). The combined aqueous layers were washed with pentane (two 50-mL portions) and dried ($MgSO_4$). Most of the solvent was removed by rapid distillation through a long Vigreux column. Two distillations through a short Vigreux column gave dicyclopropylmercury (13.4 g, 0.0474 mol, 62%): bp 115–118 °C (22 Torr) [lit.[54] 110–112 °C (18 Torr)]. By GC analysis (column A, 60 °C), this sample was 98% pure.

Preparation of Dicyclopropylmagnesium.[55] Magnesium (Cerac, 2.21 g, 0.091 mol) was added to a flask equipped with a magnetic stirring bar, a stoppered addition funnel, and a condenser with a nitrogen inlet. The system was heated with a heat gun while nitrogen flowed through it. After the apparatus had cooled,

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[54] Reynolds, G. F.; Dessy, R. E.; Jaffé, H. H. *J. Org. Chem.* **1958**, *23*, 1217.

[55] Attempts to prepare dicyclopropylmagnesium from dicyclopropylmercury and magnesium using temperatures between 60 and 120 °C were unsuccessful. Decomposition to give a dark brown residue accompanied the formation of small amounts of dicyclopropylmagnesium, even when mercury or diethylmercury was added in an attempt to catalyze the reaction.

a solution of bromocyclopropane (freshly distilled, 13.0 g, 0.107 mol) in THF (50 mL) was added to the addition funnel. A few drops of this solution were added to the flask. Once reaction seemed to have begun, the remainder of the solution was added dropwise to the reaction flask, which periodically was cooled with an ice bath to maintain approximately ambient temperature. After addition was complete, more magnesium (0.50 g, 0.021 mol) was added. The mixture was stirred at ambient temperature until most of the magnesium had disappeared, following which it was refluxed for 30 min. The flask was cooled with an ice bath, dioxane (9.52 g, 0.108 mol) was added dropwise, and the mixture was stirred overnight. The reaction contents were transferred to a centrifuge tube under a blanket of nitrogen. After centrifugation, the clear supernatant liquid was removed from the precipitate with a syringe and the concentration determined.[52]

NMR Observations of Solutions of Diethylmagnesium and Dicyclopropylmagnesium. ^{13}C NMR spectra (20 MHz) were taken of two series of solutions prepared using stock THF solutions of diethylmagnesium and of dicyclopropylmagnesium; the combined concentration of the two components was ~0.3 M in one series and ~0.4 M in the other. Only single sets of absorptions were seen for ethyl and cyclopropyl groups. These absorptions were sharp between +30 and −90 °C, although particularly below 0 °C a downfield shift (~0.5 ppm) of absorptions for carbons bound to Mg was noted as the temperature was lowered. As the mole fraction of dicyclopropylmagnesium increased, the absorptions at 25 °C of CMg of both the ethyl and cyclopropyl groups moved linearly to lower frequency.

NMR Observations of Solutions of Me_2Mg and 1. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were taken in THF solutions having 1.0 M concentrations of Me_2Mg, of 1, or of both. The ^1H (^{13}C) absorption of $=CH$ of 1 was δ 7.168 (118.60) when alone and δ 7.170 (118.60) when Me_2Mg was present; the absorption of Me_2Mg was δ −1.855 (−17.04) when alone and δ −1.868 (−16.87) when 1 was present. A shift of similar magnitude to higher frequency of the ^{13}C NMR absorption of Me_2Mg was seen when dilution was with an alkane rather than with 1.

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Nucleophilic Ring Opening of Bridging Thietane Ligands in Trirhenium Carbonyl Cluster Complexes

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The reactions of 3,3-dimethylthietane, $\overline{SCH_2CMe_2C}H_2$ (3,3-DMT), and thietane, $\overline{SCH_2CH_2C}H_2$, with $Re_3(CO)_{10}(NCMe)_2(\mu\text{-}H)_3$, **1**, have yielded the new complexes $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2C}H_2](\mu\text{-}H)_3$, **2a**, and $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2C}H_2](\mu\text{-}H)_3$, **2b**. Compound **2a** was characterized crystallographically and was found to consist of a trirhenium cluster with three bridging hydride ligands and a bridging thietane ligand coordinated through its sulfur atom. **2a** and **2b** react with halide ions by ring-opening additions to the 3,3-DMT ligand to yield the complex anions $[Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2X)(\mu\text{-}H)_3]^-$, **3a–6a**, X = F (71%), Cl (71%), Br (84%), I (87%), and $[Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)_3]^-$, **4b** (67%). Similarly, addition of NMe_3 to **2a** and **2b** yielded the ring-opened zwitterions $Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2NMe_3)(\mu\text{-}H)_3$, **7a** (43%), and $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, **7b** (44%). Compounds **4a** and **7b** were characterized crystallographically. They are zwitterions positively charged at the nitrogen atoms and negatively charged on the trirhenium clusters. Complex **7b** was also obtained in a 48% yield from the reaction of $Re_3(CO)_{12}(\mu\text{-}H)_3$ with Me_3NO in the presence of thietane, but the corresponding reaction using 3,3-DMT yielded only **2a** and $Re_3(CO)_{11}(\overline{SCH_2CMe_2C}H_2)(\mu\text{-}H)_3$, **8**. Attempts to obtain a ring-opening addition to **2a** by reaction with PMe_2Ph yielded only $Re_3(CO)_{10}(PMe_2Ph)_2(\mu\text{-}H)_3$ by ligand substitution. Attempts to obtain ring-opening addition to **8** by reaction with I^- yielded only $[Re_3(CO)_{11}I(\mu\text{-}H)_3]^-$ by ligand substitution. Crystal Data: for **2a**, space group = $C2/c$, a = 15.749 (2) Å, b = 9.082 (2) Å, c = 31.799 (5) Å, β = 99.17 (1)°, Z = 8, 2325 reflections, R = 0.037; for **4a**, space group = $P\bar{1}$, a = 13.140 (2) Å, b = 17.966 (4) Å, c = 12.252 (3) Å, α = 93.27 (2)°, β = 101.31 (2)°, γ = 74.90 (2)°, Z = 2, 4495 reflections, R = 0.034; for **7b**·$0.5Me_2C{=}O$, space group = $P2_1/c$, a = 8.475 (1) Å, b = 11.740 (5) Å, c = 26.085 (3) Å, β = 93.74 (1)°, Z = 4, 2234 reflections, R = 0.032.

Introduction

In recent studies we have shown that the bridging thietane ligands in the osmium carbonyl cluster complexes $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$,[1,2] $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CMe_2C}\text{-}H_2](\mu_3\text{-}S)$,[3] and $Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$[4] are activated toward ring-opening addition of nucleophiles through the cleavage of one of the carbon–sulfur bonds (e.g. eqs 1 and 2). An important step

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