The sodium in ammonia reduction technique was also utilized for the preparation of 1,1′-dimethylferrocene. The dimethiodide of 1,1′-bis(dimethylaminomethyl)ferrocene[6] was subjected to sodium/ammonia for 15 min. The ammonia was allowed to evaporate; the crude oil after extraction was taken up in petroleum ether and chromatographed on alumina. 1,1′-Dimethylferrocene, identical in all respects with previously reported preparations,[7] was isolated in 66% yield.

In an attempt to prepare 1,3-dimethylferrocene, dimethylaminomethylation of methylferrocene was effected according to Nesmeyanov, *et al.*;[8] the resulting oil was converted into crude methiodide and reduced with sodium/ammonia in 84% yield to what had been tentatively reported as 1,3-dimethylferrocene.[8] Spectral examination revealed, however, that the reduction product, as well as the original amine, was a mixture of all three possible isomers. Others, in the instance of the amine mixture, have reported similar observations.[9]

Experimental Section[10]

Preparation of 1,2-Dimethylferrocene (I).—Dimethylaminomethylferrocene (II, 17.0 g, 0.07 mol) was placed in a 500-ml three-neck flask equipped with a nitrogen inlet and an addition funnel. *n*-Butyllithium (95 ml of a 15 *M* solution in hexane) was added over a 15-min period. The reaction was stirred for a 2.25-hr period after which time 25 g (0.17 mol) of methyl iodide was added. Soon after the addition of the methyl iodide crystallization occurred. The crude crystals were filtered and washed with ether. The solid was dissolved in chloroform, the remainder being removed by filtration. The solution was partially evaporated and petroleum ether was added to precipitate the methiodide. The solid was filtered and dried to give 20.0 g (72% yield) of 2-methyldimethylaminomethylferrocenemethiodide (III). This material was dissolved in methanol and ether was slowly added causing reprecipitation of about half of the material. The product was filtered and dried: mp 178–179° dec. *Anal.* Calcd for $C_{15}H_{22}NIFe$: C, 45.14; H, 5.57; N, 3.51; I, 31.80; Fe, 13.99. Found: C, 44.96; H, 5.46; N, 3.70; I, 32.02; Fe, 13.82.

The methiodide (III, 2.83 g, 7.5 mmol) was placed in a flask equipped with a stirrer and covered with about 200 ml of ammonia. Sodium beads (1.81 g, 79 g-atoms) were added after being cleaned with ethanol. The reaction mixture was stirred for 10 min before quenching with ammonium chloride. The evaporated mixture was partitioned between petroleum ether and water. The organic portion was chromatographed on alumina I with petroleum ether as eluent yielding 1,2-dimethylferrocene (I): mp 33–35°; 1.31 g, 89% yield (99.1% pure by vpc analysis). Anal. Calcd for $C_{12}H_{14}Fe$: C, 67.29; H, 6.54; Fe, 26.17. Found: C, 67.27; H, 6.43; Fe, 25.94. Principal ir absorptions were noted at 3.29, 3.48, 5.6–6.3 (broad), 6.80, 7.10, 7.23, 7.90, 8.30, 9.03, 9.64, 9.97, and 12.40 (broad) μ. An nmr spectrum exhibited singlets at 3.98 ppm (eight protons) and 1.91 ppm (six protons) assigned to the ring and methyl protons, respectively. A mass spectrum was run on a Consolidated Electrodynamics 21–104 (70-eV ionizing voltage, 250° inlet temperature) with the observation of significant peaks at m/e 214 (parent peak), 148, 121, 91, and 56.

Vapor phase chromatography of dimethylferrocene on a 15% Apiezon L on Chromosorb P, 0.25 in. × 6 ft column at 210° with a 60–100-cc He/min flow rate gave the following retention times: 8.5 min, methylferrocene, and 10 min, dimethylferrocene. On a diisodecyl phthalate on 45–60 W A/W DMCS 700 0.25 × 4 ft column at 190° with a 30-cc He/min flow rate the following retention times were recorded: 10.5 min, methylferrocene, and 14 min, 1,2-dimethylferrocene. All chromatograms were run on an F & M Laboratory chromatograph model 700.

As noted in the discussion above, 1,2-dimethylferrocene of somewhat lower purity could be obtained by taking the crude methiodide directly to the reduction step.

1,2-Dimethylferrocene was also prepared by reducing the above-produced methiodide (III, 4.0 g, 10.0 mmol) with lithium aluminum hydride (2.5 g, 0.066 mol) in 60 ml of tetrahydrofuran with overnight refluxing. A work-up procedure similar to that recorded above was employed. 1,2-Dimethylferrocene (1.2 g, 56% yield) was again isolated, this material being identical with the previously produced product as shown by the identity of their respective ir spectra.

Preparation of 1,1′-Dimethylferrocene.—The dimethiodide[11] of 1,1′-bis(dimethylaminomethyl)ferrocene (2.9 g, 4.9 mmol) was placed in a flask equipped with a stirrer and covered with ammonia. Excess (about 10:1) sodium was added, and the blue solution was stirred for 5 min before quenching with ammonium chloride. Water was added and the mixture was extracted with ether. Chromatography of the organic portion on alumina (activity I) gave, as the main band, 1,1′-dimethylferrocene (0.7 g, 66% yield), which was identified by its ir spectrum.[12]

Registry No.—I, 12126-15-7; III, 12111-93-2.

Acknowledgment.—We would like to thank Professors P. L. Pauson and W. E. Watts for communicating to us results before they were published. We would also like to thank Professor Gilbert Mains for the mass spectrum of dimethylferrocene. The work performed at Duke University was supported by the National Science Foundation and that at Southern Illinois University by the Petroleum Research Fund.

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(6) (a) G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 4619 (1961); (b) J. M. Osgerby and P. L. Pauson, *ibid.*, 4600 (1961).

(7) (a) E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961); (b) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959); (c) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beinoravichute, and I. L. Malygina, *Dokl. Akad. Nauk SSSR*, **121**, 117 (1958).

(8) A. N. Nesmeyanov, E. G. Perevalova, L. S. Shiloutzeva, and Yu A. Ustynyuk, *ibid.*, **124**, 331 (1959).

(9) (a) A. N. Nesmeyanov, E. G. Perevalova, L. S. Shiloutseva, and A. A. Ponomarenka, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 171 (1967); (b) P. L. Pauson, M. A. Sandhu, W. E. Watts, R. C. Haley, and G. R. Knox, *J. Chem. Soc., C*, 1851 (1967).

(10) Elemental analyses were performed by Alfred Bernhardt, West Germany. Melting points were determined on a Hoover melting point apparatus and were corrected. The nmr spectra were run on a Varian A-56/60 spectrometer using tetramethylsilane as an internal standard. All ir spectra were determined as Nujol mulls or smears on a Perkin-Elmer Model 137 Infracord spectrometer.

(11) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 4604 (1961).

(12) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.* 9, **86** (1959).

Formation of 2-Ferrocenylbenzofuran and Some Acetylenic Derivatives of Ruthenocene[1,2]

M. D. RAUSCH AND A. SIEGEL

Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01002

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Several recent publications have described a variety of excellent routes for the formation of ferrocenylacetylenes.[3-5] During the course of our studies on metallocenylacetylenes, it was of interest to determine if these same methods could be employed for the

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(1) Part XVI of a series "Organometallic π-Complexes." Part XV: M. D. Rausch and A. Siegel, *J. Org. Chem.*, **33**, 4545 (1968).

(2) Taken from the Ph.D. thesis of A. Siegel, University of Massachusetts, 1967.

(3) K. Schlögl and W. Streyer, *Monatsh.*, **96**, 1520 (1965).

(4) M. D. Rausch, A. Siegel, and L. P. Klemann, *J. Org. Chem.*, **31**, 2703 (1966).

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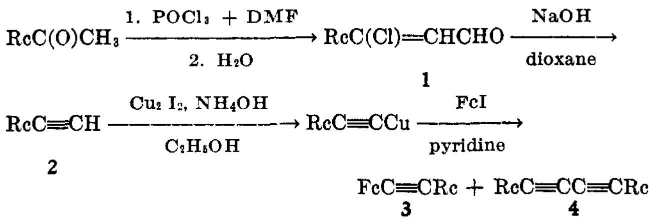
synthesis of analogous acetylenic ruthenocenes. After completion of our program in this area,[2] Hofer and Schlögl independently reported certain similar results.[6]

Treatment of acetylruthenocene with a solution of phosphorus oxychloride and dimethylformamide according to the method of Arnold and Žemlička[7] afforded β-formyl-α-chlorovinylruthenocene (**1**) in 89% yield. When a dioxane solution of **1** at reflux was caused to react with aqueous sodium hydroxide according to the general procedure of Bodendorf and Kloss,[8] ethynylruthenocene (**2**) was obtained in 83% yield. A subsequent reaction between the copper(I) salt of **2** and iodoferrocene in refluxing pyridine solution afforded the mixed metallocenylacetylene, ferrocenylruthenocenylacetylene (**3**), together with a small amount of the oxidative coupling product, diruthenocenylbutadiyne (**4**).[9] These reactions are illustrated in Scheme I.

SCHEME I



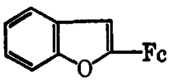
$$\mathrm{RcC(O)CH_3} \xrightarrow[\text{2. } \mathrm{H_2O}]{\text{1. } \mathrm{POCl_3 + DMF}} \underset{\mathbf{1}}{\mathrm{RcC(Cl){=}CHCHO}} \xrightarrow[\text{dioxane}]{\mathrm{NaOH}}$$

$$\underset{\mathbf{2}}{\mathrm{RcC{\equiv}CH}} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{Cu_2I_2,\ NH_4OH}} \mathrm{RcC{\equiv}CCu} \xrightarrow[\text{pyridine}]{\mathrm{FcI}}$$

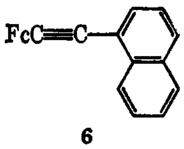
$$\underset{\mathbf{3}}{\mathrm{FcC{\equiv}CRc}} + \underset{\mathbf{4}}{\mathrm{RcC{\equiv}CC{\equiv}CRc}}$$

The two reaction products **3** and **4** exhibit very similar solubility properties and virtually identical R_f values on thin layer chromatography (tlc). All attempts to obtain an analytically pure sample of **3** by means of preparative tlc or fractional sublimation were unsuccessful. The nmr spectrum of **3** exhibits resonances characteristic of both monosubstituted ferrocenyl and ruthenocenyl substituents, and is in accordance with the assigned structure. The mass spectrum of the reaction product between ruthenocenylethynylcopper(I) and iodoferrocene is especially informative, since it exhibits a principal parent molecular ion peak at *m/e* 440, assignable to **3**, and a minor molecular ion peak at *m/e* 510, assignable to the coupling product **4**. Additional peaks in the mass spectrum are likewise assignable to fragmentation products derived from **3** and **4**.

Stephens and Castro[9a,10] observed that, in reactions between cuprous acetylides and aryl iodides in which the latter bears an *ortho* nucleophilic substituent, such as NH_2, COOH, OH, etc., arylacetylenes are not obtained, but rather cyclization occurs to produce the corresponding heterocycle. In our studies, we have found that a reaction between *o*-iodophenol and ferrocenylethynylcopper(I) produces 2-ferrocenylbenzofuran (**5**) in 85% yield. The absence of any acetylenic or hydroxylic absorption bands in the ir spectrum of **5**, and the marked downfield shifts of the 2,5 and the 3,4 protons in the nmr spectrum of **5** compared with corresponding proton resonances for ferrocenyl acetylenes clearly exclude any uncyclized structure.



5



6

A reaction between ferrocenylethynylcopper(I) and 1-iodonaphthalene proceeded normally to produce the expected acetylene, ferrocenyl-1-naphthylacetylene (**6**), in 83% yield.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer, and nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Mr. Charles Meade of the University of Massachusetts Microanalytical Laboratory.

β-Formyl-α-chlorovinylruthenocene (1).—Acetylruthenocene[11] (600 mg, 2.20 mmol) was added in small portions to a preformed solution of the Vilsmeier complex (from 3.0 ml of phosphorus oxychloride and 30 ml of dimethylformamide) at 0°. The orange-red solution was stirred for 15 min at 0° and 2 hr at 25° and then poured into 75 ml of cold, saturated sodium acetate solution. After stirring for 1 hr, the yellow precipitate which had formed was filtered, washed repeatedly with water, and was dried, resulting in 675 mg of yellow crystals, mp 109.5–110.5°. The product was recrystallized from heptane to produce 620 mg (89% yield) of **1** as bright yellow crystals, mp 114–115°.

Anal. Calcd for $C_{13}H_{11}ClORu$: C, 48.83; H, 3.47. Found: C, 48.68; H, 3.43.

The nmr spectrum ($CDCl_3$) showed τ 0.00 (d, 1, $J = 7$ Hz, CHO), 3.62 (d, 1, $J = 7$ Hz, =CH), 4.90 (t, 2, 2,5 protons), 5.20 (t, 2, 3,4 protons), and 5.35 ppm (s, 5, π-C_5H_5). The ir spectrum (CCl_4) showed 1668 (C=O) and 1601 cm^{-1} (C=C).

Ethynylruthenocene (2).—β-Formyl-α-chlorovinylruthenocene (150 mg, 0.47 mmol) was dissolved in 25 ml of dioxane and heated to reflux under nitrogen. With stirring, 15 ml of hot 5 *N* sodium hydroxide solution was added in one portion. The reaction mixture was stirred *vigorously* at reflux for an additional 30 min and then allowed to cool to room temperature. The resulting mixture was concentrated *in vacuo* overnight and extracted repeatedly with ethyl ether until the extracts were colorless, and the combined extracts were washed with water and dried over magnesium sulfate. After evaporation of the solvent, a tlc experiment on the resulting residue (pentane as eluent) indicated a band of relatively high R_f as well as several bands of appreciably lower R_f. The residue was subsequently chromatographed on alumina using pentane as the eluent to give 100 mg (83% yield) of **2** as pale yellow crystals. After one recrystallization from pentane, **2** had mp 73–74°.

Anal. Calcd for $C_{12}H_{10}Ru$: C, 56.45; H, 3.95. Found: C, 56.19; H, 3.75.

The nmr spectrum ($CDCl_3$) showed τ 5.13 (t, 2, 2,5 protons), 5.38 (s, 5, π-C_5H_5), 5.43 (t, 2, 3,4 protons), and 7.33 ppm (s, 1, acetylenic proton). The ir spectrum (CCl_4) showed 2110 cm^{-1} (C≡C).

Ferrocenylruthenocenylacetylene (3).—Iodoferrocene (47 mg, 0.15 mmol) and ruthenocenylethynylcopper (I) (48 mg, 0.15 mmol, prepared by the method of Stephens and Castro[10]) were heated at reflux in 25 ml of pyridine (dried over potassium hydroxide and refluxed over barium oxide before use) for 8 hr under nitrogen. The reaction mixture was allowed to cool to room temperature, diluted with *ca.* 25 ml of water, and filtered. The residue was dissolved in a minimum volume of chloroform and chromatographed on an alumina column. Elution with 1:1 hexane–benzene produced 40 mg (60% crude yield) of **3**, contaminated with diruthenocenylbutadiyne (**4**), as an orange powder, mp 259.5–261° (N_2). The product was subsequently vacuum sublimed at 180° (1 mm); the melting point did not change.

Anal. Calcd for $C_{22}H_{18}FeRu$: C, 60.15; H, 4.13. Found: C, 59.31; H, 3.97.

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[7] Z. Arnold and J. Žemlička, *Proc. Chem. Soc.*, 227 (1958).

[8] K. Bodendorf and P. Kloss, *Angew. Chem. Intern. Ed. Engl.*, **2**, 98 (1963).

[9] The formation of oxidative coupling products in this type of reaction has been noted earlier: (a) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966); (b) M. D. Rausch, A. Siegel, and L. P. Klemann, *ibid.*, **34**, 468 (1969).

[10] C. E. Castro and R. D. Stephens, *ibid.*, **28**, 3313 (1963).

[11] M. D. Rausch, E. O. Fischer, and H. Grubert, *J. Amer. Chem. Soc.*, **82**, 76 (1960).

The nmr spectrum ($CDCl_3$) showed τ 5.13 (t, 2, 2,5 protons of ruthenocenyl group), 5.40 (s, 5, π-C_5H_5 of ruthenocenyl group), 5.43 (t, 2, 3,4 protons of ruthenocenyl group), 5.52 (t, 2, 2,5 protons of ferrocenyl group), 5.80 (s, 5, π-C_5H_5 of ferrocenyl group), and 5.82 ppm (t, 2, 3,4 protons of ferrocenyl group).

2-Ferrocenylbenzofuran (5).—*o*-Iodophenol (3.3 g, 15 mmol) and ferrocenylethynylcopper (I)[4] (4.1 g, 15 mmol) were heated to reflux in 100 ml of dried pyridine for 8 hr under nitrogen. After work-up in the usual manner, followed by chromatography of the product on alumina using hexane as the eluent, 3.6 g (80% yield) of a pale orange solid, mp 128–130°, was isolated. After recrystallization from hexane, pink needles of **5**, mp 130–131°, were obtained.

Anal. Calcd for $C_{18}H_{14}FeO$: C, 71.55; H, 4.67. Found: C, 71.21; H, 4.64.

The nmr spectrum ($CDCl_3$) showed τ 2.57 (m, 4, aryl protons), 3.25 (s, 1, H-3 on furan ring), 5.16 (t, 2, 2,5 protons on ferrocenyl group), 5.57 (t, 2, 3,4 protons on ferrocenyl group), and 5.80 ppm (s, 5, π-C_5H_5).

Ferrocenyl-1-naphthylacetylene (6).—1-Iodonaphthylene (Eastman, 3.80 g, 15 mmol) and ferrocenylethynylcopper (I)[4] (4.1 g, 15 mmol) were heated to reflux in 100 ml of dried pyridine under nitrogen for 8 hr. The reaction mixture was allowed to cool to room temperature, diluted with water, and extracted with methylene chloride. The latter was washed with water, 5% hydrochloric acid, 5% sodium hydroxide solution, and water and dried over magnesium sulfate. Evaporation of the solvent *in vacuo* followed by recrystallization of the residue from hexane afforded 2.8 g (83% yield) of **6**, mp 162–162.5°. An analytical sample was prepared by sublimation at 180° (1 mm).

Anal. Calcd for $C_{22}H_{16}Fe$: C, 78.59; H, 4.80. Found: C, 78.41; H, 4.75.

The nmr spectrum ($CDCl_3$) showed τ 2.35 (m, 7, naphthyl protons), 5.50 (t, 2, 2,5 protons), 5.78 (s, 5, π-C_5H_5), and 5.80 ppm (t, 2, 3,4 protons). The ir spectrum (KBr) showed 2200 cm^{-1} ($C{\equiv}C$).

Registry No.—**1**, 12337-23-4; **2**, 12337-22-3; **3**, 12337-26-7; **5**, 12337-24-5; **6**, 12337-25-6.

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Nuclear Magnetic Resonance Spectroscopy. Low-Temperature Studies of Diallylmagnesium[1]

HERMAN E. ZIEGER[2] AND JOHN D. ROBERTS

Contribution No. 3706 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

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Allylic organoalkali metal compounds have been observed to exhibit reversible changes in nmr spectra (*e.g.*, $AA'BB'C \rightarrow AB_4$ for allyllithium) over the temperature range from −100 to +110°.[3] In contrast, allymagnesium bromide is reported to display a simple AB_4 spectrum at −80°[4] and diallylmagnesium to behave similarly from −60 to +37° in tetrahydrofuran.[3a]

It has now been found that magnesium halide free diallylmagnesium (from diallylmercury) in tetrahydrofuran shows the same AB_4 type of nmr spectrum as was reported for allylmagnesium bromide[4] over the temperature range from +37 to −120 ± 5°.[5]

Observation of reversible changes in pmr spectra with temperature for allyllithium[3a] and pentadienyllithium[3c] has led to suggestions that these substances are ionic and that exchange of the magnetic environments of the hydrogens on the terminal carbons is rapid at high temperatures, either as the result of rotation about the $C\overset{\cdots}{-}C$ bonds of the allylic anion or through transient covalent bond formation with the metal cation to give the simple organometallic compounds with a C—C single bond available for rapid rotation. However, the picture of simple discrete ions, or even ion pairs that are solvent separated, is clouded by evidence that allyllithium is rather highly aggregated ($n_{app} > 1.4$ at 0.8 *M*)[3a] even in tetrahydrofuran solution.[6]

The general pattern of the chemical shifts in allyl- and γ-methylallyl Grignard reagents,[4,7] and the corresponding R_2Mg compounds, is in best agreement with the suggestion[4,7] that in these substances there is a rapid intramolecular (or intermolecular)[8] allylic exchange of magnesium between the terminal atoms ($XMgCH_2CH{=}CH_2 \rightleftharpoons CH_2{=}CHCH_2MgX$; X = Br or alkenyl). However, the chemical-shift argument loses some of its force because the proton chemical shifts of allyllithium where ionic character seems quite important[3] are rather similar to those for diallylmagnesium (see Table I) and allylmagnesium bromide. Nonetheless, it is difficult to conceive of diallylmagnesium as an ion pair of two allyl anions and a dipositive magnesium cation. Furthermore, it seems unlikely that a γ-methylallyl anion–magnesium bromide ion pair would have just the chemical shifts for the α and γ protons which correspond to expectations for the covalent structure. That there may be substantial differences in structure between the allyllithium and allylmagnesium compounds is corroborated to some degree by the infrared double-bond stretching absorption of diallylmagnesium which is intermediate between

TABLE I

AVERAGE PROTON CHEMICAL SHIFTS OF ALLYL-X COMPOUNDS

X	H (β), ppm	H (α and γ), ppm
Li	6.38[a]	2.17[a]
-MgBr	6.38[b]	2.50[b]
C_3H_5Mg-	6.30[c]	2.45

[a] Reference 3. [b] Reference 4. [c] In tetrahydrofuran, not sufficiently soluble in ether to give satisfactory spectra.

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[1] Supported in part by the National Science Foundation.

[2] On sabbatical leave from Brooklyn College of the City University of New York, 1967–1968.

[3] (a) P. West, J. I. Purmort and S. V. McKinley, *J. Amer. Chem. Soc.*, **90**, 797 (1968); (b) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *ibid.*, **90**, 495 (1968); (c) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

[4] G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962); *J. Amer. Chem. Soc.*, **84**, 2010 (1962).

[5] Addition of N,N,N′,N′-tetramethylethylenediamine to a dimethyl ether solution of diallylmagnesium permitted going to −135 ± 5°, but there was no change in the nmr pattern. Viscosity broadening of the N-methyl group signals led to overlap with the B_4 doublet (terminal carbon protons) below −130°. Perdeuteriotetrahydrofuran solutions of diallylmagnesium exhibited similar behavior. Crystallization of diallylmagnesium occurred at temperatures from −75 to −105° for solutions ranging from 2.65 to 1.33 *M*.

[6] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

[7] J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961).

[8] Recent evidence for intermolecular exchange of alkyl groups in dialkylmagnesium compounds suggests that intermolecular exchange may be quite important; see H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).