Organometallics **2002,** *21,* 3661−3666

Kinetic Study of Reactions of a Ketone with a Dialkylmagnesium Compound and with Organomagnesate Species[1]

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Received April 22, 2002

The initial rate of formation of addition product from reactions of Np_2Mg (Np = neopentyl) and phenyl *tert*-butyl ketone (**1a**) or *o*-methylphenyl *tert*-butyl ketone (**1b**) in benzene is proportional to $[Np_2Mg]^0[\mathbf{1}]^1$ when Np_2Mg is in excess and to $[Np_2Mg]^1[\mathbf{1}]^0$ when ketone is excess. For either ketone, the rate is ca. 15-fold greater when ketone is in excess than when Np_2Mg is in excess; regardless of which reagent is in excess, reactions of **1a** are ca. 600-fold faster than reactions of **1b**. ^1H NMR absorptions of benzene-d_6 solutions prepared with different Np_2Mg/**1b** ratios indicate substantial formation of a 1:1 Np_2Mg−**1b** complex, and when Np_2Mg is in excess, some formation of a 2:1 complex. In THF as solvent, the initial rate of formation of addition product from Np_2Mg and **1a** is proportional to $[Np_2Mg]^1[\mathbf{1a}]^1$, and ^1H NMR observations do not indicate Np_2Mg−**1b** complexation. Formation of addition product from **1b** and an organomagnesate solution prepared from KOMe and Np_2Mg in benzene is 1−2 orders of magnitude faster than from the same concentrations of Np_2Mg and **1b**. Observations are reported for rates of formation of addition product from **1b** and $Np_3Mg^-NpMg(14N4)^+$ (14N4 is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) or $Np_3Mg(THF)^-NpMg(14N4)^+$.

Reactions of organomagnesate species can differ greatly from those of Grignard reagents (RMgX) or diorganomagnesium compounds (R_2Mg).[2] When R has a β-hydrogen, for example, reactions with ketones of RMgX or R_2Mg lead to reduction of as well as addition to the ketone, and reduction can be the major pathway when R is bulky and the ketone is hindered; much less reduction results, however, from reactions of ketones and organomagnesate preparations.[5] We wanted to compare rates of organomagnesate−ketone and R_2Mg−ketone reactions. This paper describes (1) a convenient system for kinetic studies of organomagnesium−ketone reactions, (2) new information about reactions of R_2Mg compounds and ketones including involvement of two R_2Mg−ketone complexes, and (3) comparisons of reactivities of organomagnesates and R_2Mg.

Results and Discussion

Reaction System. The comparisons that we wanted to make require measuring rates of reactions of organomagnesates and of R_2Mg using the same R, ketone, and solvent. Because reactions of most organomagnesium compounds and ketones are very rapid, their rates have often been determined not by observing formation of product or disappearance of reactant but from a less direct parameter: heat of reaction,[6] for example, or disappearance of a UV absorption attributed to a complex[8] of the ketone and an organomagnesium species resulting from addition. We wanted a system with rates slow enough to permit monitoring the amount of addition product and that would not provide products of reduction or metalation of the ketone. Although many of the mechanistic studies of organomagnesium−ketone reactions have used benzophenones, we wanted a ketone other than a benzophenone since effects of the two aryl groups (on the reduction potential, for example) may lead to reaction mechanisms that are not typical for most ketones. We chose to use R_2Mg rather than RMgX to avoid the complication of multiple species due to the Schlenk equilibrium[9] and to study *initial* rates to

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(1) Some of this work is taken from: Chubb, J. E. Ph.D. Dissertation, The Pennsylvania State University, l997.

(2) For reactions of RMgX and R_2Mg see: Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic: London, l995. Refs 3 and 4. Silverman, G. S.; Rakita, P. E. *Handbook of Grignard Reagents*; Marcel Dekker: New York, l996.

(3) Richey, H. G., Jr. *Grignard Reagents: New Developments*, Wiley: Chichester, 2000.

(4) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, l982; Chapter 4. Lindsell, W. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, l995; Vol. 1, Chapter 3.

(5) Richey, H. G., Jr.; DeStephano, J. P. *J. Org. Chem.* **l990**, *55*, 3281.

(6) Studies by Torkil Holm.[7]

(7) Holm, T.; Crossland, I. In ref 4, Chapter 1.

(8) Laemmle, J.; Ashby, E. C.: Neumann, H. M. *J. Am. Chem. Soc.* **l971**, *93*, 5120.

(9) For the Schlenk equilibrium and for association and solvation of R_2Mg and RMgX, see particularly ref 4.

10.1021/om020324r CCC: $22.00 © 2002 American Chemical Society
Publication on Web 07/25/2002

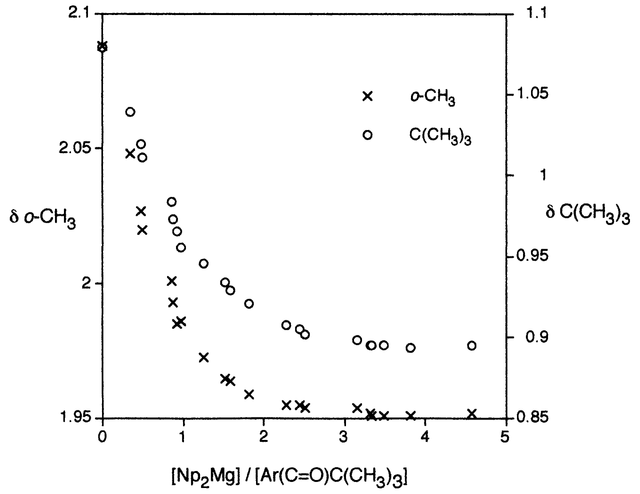
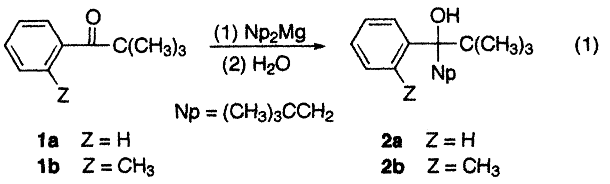


Figure 1. Plot of the chemical shifts of the ^{1}H NMR absorptions of the ortho-methyl and *tert*-butyl hydrogens of **1b** as a function of the ratio of Np_2Mg and **1b** concentrations. The concentration of **1b** is ca. 0.05 M in all solutions.

minimize complications due to further reactions of organomagnesium species formed by addition.

The system that was used is shown in eq 1. Reactions



at 25 °C of **1a** or **1b** with Np_2Mg (Np = neopentyl = $(CH_3)_3CCH_2$) and with some neopentylmagnesate species had rates possible to follow by quenching aliquots followed by GC analysis for **2**. The neopentyl group has several advantages: (1) its lack of β-hydrogens precludes reduction of the ketone; (2) Np_2Mg can be purified by sublimation;[10,11] (3) Np_2Mg is soluble in a range of solvents. Ketones **1a** and **1b** also have advantages: (1) the lack of α-hydrogens precludes metalation, often significant in reactions of ketones with organomagnesium compounds; (2) the carbonyl group is conjugated with only one aryl group, and even that conjugation is reduced by an increased dihedral angle between the planes of the aryl ring and the carbonyl group due to the steric effect of the *tert*-butyl group (and of the *o*-methyl group of **1b**). Reactions of Np_2Mg and di-*tert*-butyl ketone also were investigated but were much slower. Two solvents were used: THF, often used for reactions of RMgX and R_2Mg compounds and known to coordinate extensively to the magnesium atoms, and benzene, a nonpolar, noncoordinating solvent. Initial experiments established that **2a** and **2b** were the only significant products.

NMR Study of Np_2Mg and 1b. The reaction of Np_2Mg and **1b** in benzene-d_6 is sufficiently slow to allow routine ^{1}H NMR observations before product formation is significant. Plots (Figure 1) of the positions of the *o*-methyl and *tert*-butyl absorptions of **1b** versus Np_2Mg/**1b** ratio indicate significant coordination. The small range of absorption positions limits the precision of analysis, however, and the plots are consistent with (1) formation mainly of a 1:1 complex, the equilibrium constant for its formation sufficiently small that excess Np_2Mg is required to convert most of the **1b** to the complex, or (2) formation of both 1:1 and 2:1 Np_2Mg–**1b** complexes. When a solution with a Np_2Mg/**1b** ratio of ca. 2 is diluted (up to 8-fold), however, the absorptions of neither component change significantly (>0.01 ppm). A large change would be expected if the dominant species was a 1:1 complex formed with a relatively small equilibrium constant. Therefore the presence of both 1:1 and 2:1 complexes is probable.[12] Plots versus the **1b**/Np_2Mg ratio of the *o*-methyl and *tert*-butyl absorptions of **1b** (Figure 2) and of the CH_2 and $(CH_3)_3C$ absorptions of Np_2Mg also indicate some formation of a 2:1 complex. The observations suggest therefore that a 1:1 complex is important and that some 2:1 complex forms at Np_2Mg/**1b** ratios >1, but provide no indication of a 1:2 complex. By contrast, ^{1}H NMR observations of THF solutions (90:10 THF–benzene-d_6, v/v) show no significant changes in absorptions of Np_2Mg or **1b** due to the other component.

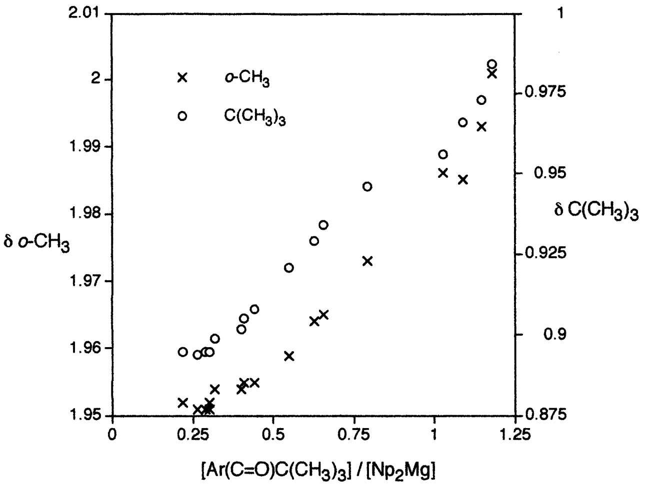


Figure 2. Plot of the chemical shifts of the ^{1}H NMR absorptions of the ortho-methyl and *tert*-butyl hydrogens of **1b** as a function of the ratio of **1b** and Np_2Mg concentrations. The concentration of **1b** is ca. 0.05 M in all solutions.

Kinetic Experiments with Np_2Mg. The experimental procedure—preparing small volumes of solutions, extracting aliquots, and GC analysis—is simple but has limitations: (1) rates were reproducible only to ca. ±5% for a reaction series using the same solutions and to ca. ±10% for independent reactions; (2) the portion of a reaction to be studied cannot be shorter than a few minutes. The procedure has the advantage, however, of measuring the product, not an indirect parameter, and, unlike some earlier studies, permits using *either* the organomagnesium compound or ketone in excess.

For reactions in benzene, the rate behavior depended on which reagent was in excess. Four concentration regimes were studied: (1) Np_2Mg in excess and varied,

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[10] Andersen, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809.

[11] Akkerman, O. S.; Schat, G.; Evers, E. A. I. M.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 109.

[12] To the extent that the equilibrium constant for formation of a 2:1 complex is small, dilution would reduce its amount, causing the NMR absorptions to move closer to those of the reactants. Within the limits of the precision of the spectra, however, the absorptions were not altered significantly.

Table 1. Rates of Formation of Addition Product from Reactions of Np_2Mg and 1a or 1b in Benzene or THF at 25.0 °C

solvent	ketone	reagent in excess	rate
THF	**1a**	either	6.5×10^{-5} L mol^{-1} s^{-1}
benzene	**1b**	Np_2Mg	4.8×10^{-6} s^{-1}
benzene	**1b**	ketone	6.3×10^{-5} s^{-1}
benzene	**1a**	Np_2Mg	2.6×10^{-3} s^{-1}
benzene	**1a**	ketone	4.1×10^{-2} s^{-1}

(2) Np_2Mg in excess and ketone varied, (3) ketone in excess and varied, and (4) ketone in excess and Np_2Mg varied. The initial concentration of the reagent in excess was 2.5 times that of the other reagent.[13] Only data collected before reaction of 10% of the limiting reactant were used in determining rate constants.

One set of experiments in regime 1 exemplifies the procedure. The initial concentration of **1b** was 0.050 M, and that of Np_2Mg was varied from 0.24 to 0.67 M. The concentration of **2b** in each aliquot was determined by comparing its GC peak with that of an internal standard. Data for the first 120 min were used, corresponding to ≤4% formation of **2b**. The concentration of **2b** was plotted against time; slopes (S) of the resultant least-squares lines are reasonably linear (R^2 averages 0.99), indicating that over that range of reaction the rate is not affected significantly by possible complicating processes such as reaction or complexation of **1b** with an addition product. Since **1b** concentration was essentially constant, a plot of log S against $\log[Np_2Mg]_o$ provides the order in Np_2Mg. The slope of this plot is 0.00 (average variation of rates = ±6%). Under these circumstances, therefore, the kinetic order in Np_2Mg is zero. Similar experiments with solutions having Np_2Mg in excess but varying **1b** concentrations (regime 2) found an order in **1b** of 0.94. With excess Np_2Mg, therefore, rate $= k_{Me}[Np_2Mg]^{0.00}[\mathbf{1b}]^{0.94}$. Experiments with solutions having excess **1b** found rate $= k'_{Me}[Np_2Mg]^{1.02}[\mathbf{1b}]^{0.03}$. Reactions with **1a** were much faster than with **1b**, and the results more prone to error, but similar rate laws were derived: rate $= k_H[Np_2Mg]^{0.05}[\mathbf{1a}]^{1.10}$ with excess Np_2Mg and rate $= k'_H[Np_2Mg]^{0.97}[\mathbf{1a}]^{0.03}$ with excess **1a**.

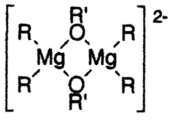
With THF as the solvent, **1a** was used since reactions of **1b** were very slow. Data were collected in the four concentration regimes, but essentially the same rate law was obtained regardless of relative concentrations: rate $= k[Np_2Mg]^{1.06}[\mathbf{1a}]^{0.97}$ for Np_2Mg in excess (average $k = 6.4 \times 10^{-5}$ L mol^{-1} s^{-1}) and rate $= k'[Np_2Mg]^{1.13}[\mathbf{1a}]^{0.96}$ for **1a** in excess (average $k' = 6.6 \times 10^{-5}$ L mol^{-1} s^{-1}).

For purposes of discussion, we assume kinetic orders to be precisely 0 or 1: in THF, rate $= k[Np_2Mg]^1[\mathbf{1}]^1$; in benzene, rate $= k[Np_2Mg]^0[\mathbf{1}]^1$ when Np_2Mg is in excess and rate $= k'[Np_2Mg]^1[\text{ketone}]^0$ when ketone is in excess. We then can assign the rate constants in Table 1 and draw several conclusions. (1) For reactions in benzene, regardless of which reagent is in excess, an ortho-methyl group in the ketone has essentially the same rate-decreasing effect: $k_H/k_{Me} = 540$ and $k'_H/k'_{Me} = 650$. (2) For reactions in benzene of either ketone, the rate is somewhat greater when ketone rather than Np_2Mg is in excess: $k'_H/k_H = 16$ and $k'_{Me}/k_{Me} = 13$. (3) Rates in benzene and THF are not strictly comparable since the kinetic behavior is different. At concentrations useful for preparative reactions, however, product formation is significantly faster in benzene (e.g., 200-fold faster if **1a** is 0.1 M and Np_2Mg is 0.2 M).

Kinetic Experiments with Organomagnesates. Some R_2Mg compounds and macrocycles in benzene form $R_3Mg^-RMg(\text{macrocycle})^+$.[14] 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), a particularly effective RMg^+ coordinator,[15] converts[16,17] a variety of R_2Mg compounds quantitatively to $R_3Mg^-RMg(14N4)^+$. Except at low concentrations, however, Np_2Mg and 14N4 in benzene formed two liquid phases, the ions mainly in the denser and smaller phase. This behavior, observed with some R_2Mg−macrocycle reactions in benzene, limits the concentration of Np_3Mg^- available in a homogeneous solution and precludes studying solutions having Np_3Mg^- in large excess. A study of solutions having **1b** in excess and different (but low) concentrations of $Np_3Mg^-NpMg(14N4)^+$ found the rate to be proportional to $[Np_3Mg^-]^{0.92}$. The rate constant is 1.6×10^{-4} L mol^{-1} s^{-1} *if* the reaction also is first-order in **1b** or 7.4×10^{-6} s^{-1} if it is zero-order in **1b**.

Phase separation of Np_2Mg−14N4 preparations did not occur if 1 equiv of THF was present. The enhanced solubility must result from bonding of THF to the anion to form $Np_3Mg(THF)^-$.[18] With the THF-containing solutions, kinetic studies were feasible with either reagent in excess. Addition was approximately first-order in each reagent regardless of which was in excess. Using solutions in which one reactant was 0.05 M and the other varied over the range 0.02−0.12 M, the rate was proportional to $[\mathbf{1b}]^{1.04}[Np_3Mg(THF)^-]^{0.88}$ and $k = 4.2 \times 10^{-4}$ L mol^{-1} s^{-1} (k determined by varying initial concentrations of **1b** and of $Np_3Mg(THF)^-$, respectively, was 4.4×10^{-4} and 4.0×10^{-4} L mol^{-1} s^{-1}). With comparable reactant concentrations, addition was a few-fold faster in the reactions having 1 equiv of THF.

R_2Mg compounds in benzene are converted completely to ions of structure **3** by reaction with ≥1 equiv of a potassium alkoxide.[19] Decomposition of solutions prepared from KOMe and Np_2Mg unfortunately was suf-



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[13] Kinetic behavior was more complex at lower ratios.

[14] Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510. Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660. Richey, H. G., Jr. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D. Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 1 (Gokel, G. W., Ed.), Chapter 21.

[15] Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **2000**, *19*, 4810.

[16] Pajerski, A. D. Ph.D. Dissertation, The Pennsylvania State University, 1990.

[17] Also see: Pajerski, A. D.; Chubb, J. E.; Fabicon, R. M.; Richey, H. G., Jr. *J. Org. Chem.* **2000**, *65*, 2231. Tang, H.; Richey, H. G., Jr. *Organometallics* **2001**, *20*, 1569.

[18] Enhanced solubility of $RMg(\text{macrocycle})^+R_3Mg^-$ (R = alkyl or aryl) by 1 equiv of an O or N donor has been noted before.[16] X-ray structures of solids having $RMg(14N4)^+$ ions show magnesium to be so enveloped by 14N4 that specific interactions with donor molecules must be minimal [ref 16 and Tang, H.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1996**, *15*, 5281].

[19] Hanawalt, E. M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4983.

ficiently rapid to preclude accurate determination of kinetic orders.[20] For given concentrations of **1b** and organomagnesate, however, product formation was 1−2 orders of magnitude faster than with the same concentrations of **1b** and Np_2Mg.

Discussion.[21] The first-order kinetics of reactions of Np_2Mg and **1** in benzene are consistent with schemes in which these reactants form a complex, the equilibrium constant for its formation sufficiently large that it incorporates most of the deficit reactant. Such schemes accord with the complex formation indicated by NMR observations. The transition state of the rate-determining step must have the composition of the complex; possibilities for this step include a unimolecular reaction of a complex (the one observed in NMR spectra or a structurally different but isomeric complex) or a bimolecular reaction between components of the complex (e.g., uncoordinated Np_2Mg and ketone from a 1:1 complex).

The observation that rate is an order of magnitude greater when ketone rather than Np_2Mg is in excess indicates a difference in a reactant in accord with the indications from NMR data that a 1:1 Np_2Mg−ketone complex is a major species when the ketone is in excess and a 2:1 complex is a significant component when Np_2Mg is in excess. Differing aggregation of Np_2Mg, however, also could be the cause of the greater rate when ketone is in excess. The average molecular weight of Np_2Mg in benzene (ca. 0.06−0.10 M) corresponds to aggregation to approximately $(Np_2Mg)_3$.[10] When Np_2Mg is in excess, therefore, the major Np_2Mg species in solution are aggregates. When the ketone is in excess (and the amount of Np_2Mg not coordinated to ketone hence is small), however, a larger fraction of the Np_2Mg may be monomeric and hence perhaps more reactive.

Formation of ketone−RMgX complexes (assumed to be 1:1) has been inferred from UV and IR observations and kinetic analyses.[22,24] Laemmle, Ashby, and Neumann found formation of addition product from Me_2Mg and *o*-methylbenzophenone in diethyl ether to be first-order in each reactant.[8] Me_2Mg−ketone complexation was not significant enough to have to be considered, although for the reaction of MeMgBr with the same ketone, a 1:1 complex ($K = 1.35$ L mol^{-1}) had to be included in the kinetic analysis (which found a first-order dependence on each reactant). Complexation of a ketone by R_2Mg generally is somewhat less than by a corresponding RMgX compound.[22] Complexation of *p*-methylthioacetophenone is more significant than of *o*-methylbenzophenone; Smith and Billet[25] found from UV data that $K = 6.2$ L mol^{-1} for formation of a 1:1 complex[26] with Me_2Mg and found the rate of formation of addition product to be proportional to the concentration of complex (i.e., first-order in each reactant). The second-order rate dependence and lack of spectral evidence for complexation that we found for THF solutions of Np_2Mg and **1** were noted previously for RMgX compounds and ketones in that solvent.[27]

Complexes of ketones and organomagnesium compounds are absent in THF, a strongly coordinating solvent, but often present, although with small values of *K*, in diethyl ether, a more weakly coordinating solvent. We find complexation to be essentially complete in the noncoordinating solvent benzene. R_2Mg−THF complexation must be sufficiently strong to preclude formation of kinetically significant amounts of Np_2Mg−**1b** complexes. The slower rate in THF than in benzene also is in accord with observations that additions of organomagnesium compounds to ketones generally are slower in coordinating solvents than in hydrocarbon solvents.

The kinetic observations do not distinguish between two alternatives often considered for the rate-determining step of organomagnesium−ketone reactions: transfer of the organic group to the carbonyl carbon or transfer of an electron from the organomagnesium compound to the ketone.[7,28] The observation that addition to **1b** is considerably slower than to **1a** is consistent with the close approach of the organomagnesium compound and ketone that would be necessary for group transfer. By increasing the dihedral angle between the carbonyl group and the aryl ring, however, the ortho-methyl group of **1b** must diminish conjugation between them and make the reduction potential of the ketone less favorable for electron transfer.

Efforts to compare rates of additions of organomagnesate preparations with those of Np_2Mg encountered problems of limited solubility and of decomposition. The rates of reaction in benzene of **1b** with $Np_3Mg(THF)^-$ and with Np_2Mg have a different kinetic dependence and hence are not strictly comparable. With concentrations typical of preparative reactions (e.g., [**1b**] = 0.1−0.5 M, $[R_2Mg]$ or $[R_3Mg(THF)^-] = 0.2-1.0$ M), however, product formation is 1−2 orders of magnitude faster with $Np_3Mg(THF)^-$ than with Np_2Mg.[29] That $Np_3Mg(THF)^-$ is not less reactive than Np_3Mg^- suggests that dissociation of THF from $Np_3Mg(THF)^-$ is not crucial

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[20] Decomposition of R_2Mg−KOMe preparations with some other R groups had been considerably less rapid.[19]

[21] An extensive amount of literature concerns kinetics of reactions (mainly in diethyl ether) of ketones with RMgX, and to a lesser extent with R_2Mg [for summaries see refs 22 and 23]. It is likely, however, that the results of many of the pioneering studies were affected by complications due to the Schlenk equilibrium, reactions of intermediates (e.g., RC(OMgR)R′R″) resulting from initial addition of R_2Mg or RMgX to the ketone (R′R″C=O), and transition metal impurities.

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

[23] Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 5421.

[24] Other evidence for RMgX−ketone complexation: Holm, T. *Acta Chem. Scand.* **1967**, *21*, 2753.

[25] Smith, S. G.; Billet, J. *J. Am. Chem. Soc.* **1967**, *89*, 6948.

[26] A value of $K = 1.3$ L mol^{-1} for formation of a complex from Me_2Mg and 2,4,6-triisopropyl-4′-methoxybenzophenone was obtained from UV observations [Smith, S. G. *Tetrahedron Lett.* **1963**, 409], and a value of $K \approx 8$ L mol^{-1} for a complex of $(cyclopentyl)_2Mg$ and *p*-methylthioacetophenone was extracted from kinetic observations [Rudolph, S. E.; Charbonneau, L. F.; Smith, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 7083].

[27] Bikales, N. M.; Becker, E. I. *Can. J. Chem.* **1963**, *41*, 1329. Holm, T. *Acta Chem. Scand.* **1966**, *20*, 1139. Also see: Holm, T. *Acta Chem. Scand.* **1966**, *20*, 2821.

[28] Recent references: Gajewski, J. J.; Bocian, W.; Harris, N. J.; Olson, L. P.; Gajewski, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 326. Lund, T.; Ohlrich, D.; Borling, P. *Acta Chem. Scand.* **1999**, *53*, 932. Hoffmann, R. W.; Hölzer, B. *Chem. Commun.* **2001**, 491.

[29] In a THF solution, $Np_3Mg(THF)^-$ probably also would react much faster than Np_2Mg since $Np_3Mg(THF)^-$ will not undergo additional coordination by THF, but this could not be tested since conversion of R_2Mg compounds to $RMg(14N4)^+$ and organomagnesate anions is not general in THF. Reactions of $Np_3Mg(THF)^-$ and **1b** in benzene and of Np_2Mg and **1a** in THF have the same kinetic dependence. *If* the ca. 600-fold greater reactivity of **1a** than of **1b** found for reactions with Np_2Mg in benzene also prevails in reactions in THF, then $Np_3Mg(THF)^-$ in benzene reacts with **1a** about 4000 times faster than does Np_2Mg in THF.

for the rate-determining step and favors mechanisms in which bonding to magnesium is not significant in the rate-determining step.

Experimental Section

Procedures involving organometallic compounds were performed under nitrogen (purified by passing through columns of manganese oxide oxygen scavenger and molecular sieves (4 Å)) using Schlenk techniques, a glovebox, and a vacuum line. Solutions for NMR analysis were prepared in the glovebox and transferred into NMR tubes to which an extension of routine glass tubing had been added to facilitate sealing with a flame. An NMR tube was capped temporarily with a rubber septum, removed from the glovebox, immersed in liquid nitrogen, and sealed at the extension. ^{1}H NMR spectra were taken at 200 MHz and, except where noted, in benzene-d_6; absorptions are reported relative to internal C_6D_5H (δ 7.15) for benzene-d_6 solutions and to internal TMS (δ 0.00) for $CDCl_3$ solutions; the following notations are used: s, singlet; d, doublet; m, complex multiplet; c, complex overlapping absorptions; b, broad. ^{13}C NMR spectra were taken at 90 MHz in benzene-d_6, and absorptions are reported relative to internal C_6D_6 (δ 128.0). Immediately prior to use, diethyl ether and THF were distilled under nitrogen from sodium benzophenone ketyl and benzene and dioxane from CaH_2. The magnesium generally used was 99.95% purity (Aldrich Chemical Co.). α-*tert*-Butyl-α-neopentylbenzyl alcohol (**2a**) has been reported previously.[30]

Np_2Mg. 1,2-Dibromoethane (ca. 100 mg) was added to a stirred mixture of Mg (2.41 g, 0.099 mol) in refluxing THF or diethyl ether (10 mL) followed, after reaction appeared to begin, by dropwise addition of a solution of neopentyl bromide (10 g, 0.066 mol) in the same solvent (40 mL). After addition was complete, the reaction mixture was maintained at reflux for >2 h. It then was cooled, and samples were hydrolyzed and titrated for total base (addition of sufficient standard HNO_3 solution to dissolve all solids and then back-titration with a standard NaOH solution to a phenolphthalein endpoint). Dioxane (1 equiv per equiv of base determined by titration) was added dropwise, and the slurry was stirred for ≥6 h. The slurry was centrifuged, and the solvent was removed (to ca. 85 °C and 0.01 Torr) from the supernatant liquid, leaving a solid, which was sublimed (85−95 °C and 0.01 Torr) to furnish a white solid. ^{1}H NMR spectra indicated THF/Np_2Mg and dioxane/Np_2Mg ratios typically of 1−2 and 0.05, respectively, for preparations in THF. A second sublimation generally yielded solvent-free Np_2Mg from preparations in diethyl ether. ^{1}H NMR: δ 0.25 (s, 2H), 1.21 (s, 9H).

$Np_3Mg^-NpMg(14N4)^+$ Solutions. A 0.040 M solution was prepared from Np_2Mg (132.6 mg, 0.80 mmol), 14N4 (102.2 mg, 0.40 mmol), and benzene (10.0 mL). ^{1}H NMR: δ (Np_3Mg^-) 0.27 (s, 6H), 1.66 (s, 27H); ($NpMg(14N4)^+$) −0.55 (s, 2H), 1.11 (s, 9H), 1.66 (s, 12H), 2.5 (bc, 4H), 1.2−2.2 (c, ca. 16H). More concentrated preparations separated into two liquid layers on standing. A preparation (0.2 M) also containing THF (0.2 M) remained homogeneous. ^{1}H NMR: δ (Np_3Mg^-) 0.22 (s, 6H), 1.62 (s, 27H); ($NpMg(14N4)^+$) −0.60 (s, 2H), 1.13 (s, 9H), 1.62 (s, 12H), 2.54 (c, 4H), 1.2−2.2 (c, ca. 16H); (THF) 1.36 (m, 4H), 3.54 (m, 4H).

Np_2Mg−KOMe Solutions. Solutions were prepared by stirring a benzene solution of Np_2Mg (ca. 0.1 M) with an excess of solid KOMe for 30−45 min.[19] ^{1}H NMR spectra showed an absorption at δ 0.89 (due to $(CH_3)_4C$) which increased with time.

α-*tert*-Butyl-α-neopentyl-*o*-methylbenzyl Alcohol (2b). A solution of **1b** (0.50 g, 2.8 mmol), prepared following a literature procedure,[31] was added to a benzene solution of Np_2Mg (5.0 mL, 0.75 M, 3.8 mmol). After 14 h, the preparation was hydrolyzed with a saturated aqueous sodium chloride solution and extracted with diethyl ether. The diethyl ether solution was dried ($MgSO_4$), the mixture was filtered, and the solvent was evaporated from the solution. The resulting solid was melted (30−40 °C), placed under a stream of N_2 to remove residual solvent, and then sublimed (60 °C, 0.1 Torr) to yield colorless crystals (0.23 g): 33% yield; mp 46.5−47.5 °C. ^{1}H NMR ($CDCl_3$): δ 0.79 (s, 9H), 0.90 (s, 9H), 1.62 (s, 1H), 1.80 (d, J = 15 Hz, 1H), 2.25 (d, J = 15 Hz, 1H), 2.64 (s, 3H), 7.04 (bc, 3H), 7.09 (bd, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 25.3, 25.8, 31.3, 32.3, 41.6, 47.4, 85.3, 123.5, 126.0, 130.0, 133.2, 137.7, 141.0. Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.24; H, 11.25.

NMR Spectra of Np_2Mg−1b Solutions. Aliquots of a stock benzene-d_6 solution of Np_2Mg were placed in NMR tubes, which were sealed with septums before being removed from the glovebox. A portion of a stock solution of **1b** was added to each NMR tube using a gastight syringe (injection volumes were accurate to ca. 2−3%), and NMR data were recorded within less than 10 min. Single sets of neopentyl and **1b** absorptions were the only significant absorptions.

Reactions of Organomagnesium Species with 1a and 1b. A solution of organomagnesium reagent was injected into a 5-mL round-bottomed flask using a gastight syringe (the injected amount determined by weighing the syringe before and after addition) followed by additional solvent. The flask was sealed with a septum and removed from the glovebox. A needle attached to a purified nitrogen source was inserted into the septum (to maintain a positive pressure of nitrogen in the flask), and the flask was immersed in a constant-temperature bath. The bath temperature, 25.00 °C (Bureau of Standards certified thermometer), was regulated to ±0.1 °C. After 20 min, a solution of **1** (volume much less than solution already in the flask), also containing a known concentration of tetradecane (internal standard for GC analysis), was injected in a similar fashion, and the clock was started. The total volume was ca. 2.0 mL. In assigning concentrations, it was assumed that the density of a solution was the same as that of the solvent. Aliquots (0.1 mL) were removed with a syringe and quenched by addition to a mixture of a saturated aqueous NaCl solution (1 mL) and diethyl ether (1 mL). The layers were separated, and the organic layer was dried ($MgSO_4$).

Analysis of Kinetic Solutions. GC analysis used a capillary column with an immobilized poly(dimethylsiloxane) coating (Alltech EC-1 “SE-30”, 0.53 mm id × 15 m), a splitter, helium as the carrier gas, and a flame ionization detector. Injections used the “hot needle” technique.[32] Benzene (0.5 μL), then the sample (0.5−1 μL, less if concentrated), and finally benzene (0.2 μL) were drawn into the barrel of the syringe (10 μL), leaving the needle empty; after insertion into the injection port, the needle was allowed to heat for ca. 5 s before injection. The temperature program for reactions with **1a** was 2 min at 120 °C, then an increase of 40 °C/min to 210 °C. Typical retention times and the response factors[33] used: **1a** (1.9 min, 1.146), tetradecane (3.2 min, 1.000), and **2a** (3.8 min, 1.050). The temperature program for reactions with **1b** was 2 min at 130 °C, then an increase of 40 °C/min to 250 °C. Typical retention times and the response factors used: **1b** (2.03 min, 1.130), tetradecane (2.94 min, 1.000), **2b** (3.92 min, 1.046).

Analysis of Kinetic Data. The amounts of organomagnesium compound, **1**, and tetradecane in a reaction solution were known from its preparation. The concentration of **2** was calculated from the area of its GC peak relative to that of the

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standard and the known concentration of the standard. The slope of the line through the points of a plot of concentration of **2** versus time was calculated by a linear least-squares regression analysis. R^2 for these plots ordinarily was ≥ 0.99 and always >0.96.

Acknowledgment. We thank the National Science Foundation for supporting this research.

OM020324R