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CERIUM CHLORIDE-PROMOTED UNUSUAL COUPLING REACTIONS OF ALKENYL GRIGNARD REAGENTS AND ALKENYLLITHIUMS

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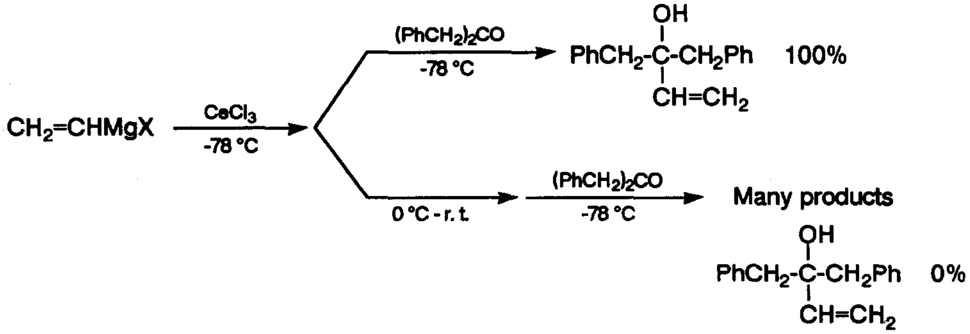
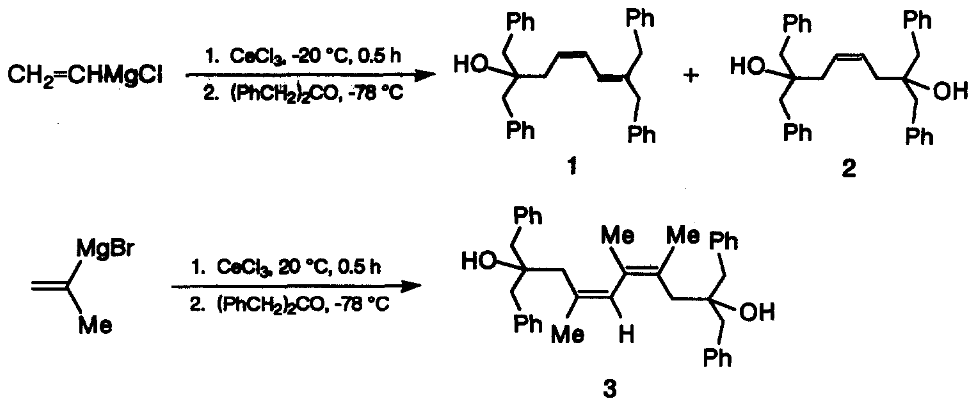
Abstract: Alkenyl Grignard reagents and alkenyllithiums undergo dimerization or trimerization in the presence of anhydrous cerium chloride in THF. The reactions of the resulting dimetallic compounds with 1,3-diphenyl-2-propanone are described.

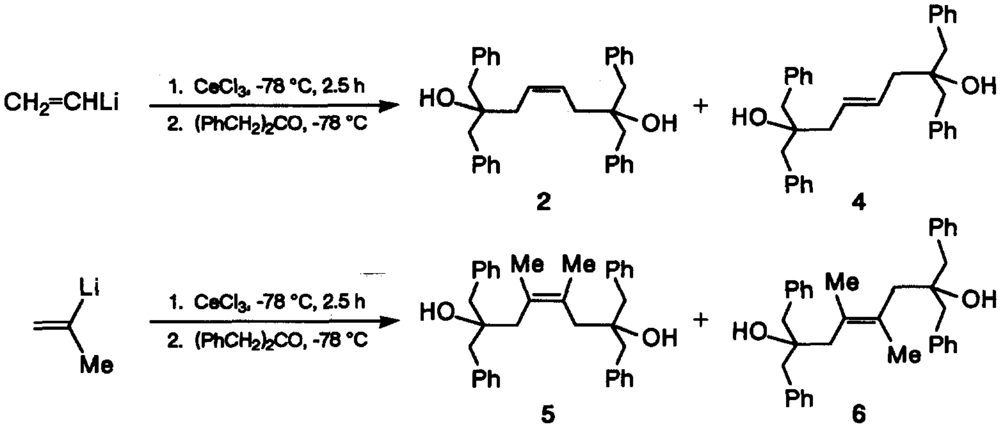
Previously we reported that the addition reactions of Grignard reagents to carbonyl compounds were significantly promoted by cerium chloride.[1] The reactions were usually carried out at 0 °C through to room temperature. However, alkenyl Grignard reagents immediately decomposed under these conditions, and hence the subsequent treatment with carbonyl compounds did not provide the corresponding addition products but other products. A typical example is illustrated in the following scheme.



We have been interested in these reactions and have investigated them using vinylmagnesium chloride, isopropenylmagnesium bromide, and 1,3-diphenyl-2-propanone as the probe compounds. A solution of vinylmagnesium chloride (3 mmol) in THF was added to a suspension of anhydrous cerium chloride (3 mmol) at -78 °C. The temperature of the mixture was elevated to -20 °C, whereupon the color of the mixture turned to dark brown. After 30 min, the mixture was cooled to -78 °C, and 1,3-diphenyl-2-propanone (1 mmol) was added. The usual workup of the mixture afforded unexpected addition products 1[2] and 2[3] in 9% and 19% yield, respectively.[4-6] In a similar manner, isopropenylmagnesium bromide was successively treated with cerium chloride and 1,3-diphenyl-2-propanone, and compound 3[7] was isolated in 22% yield from the reaction mixture.



Next, the reactions of alkenyllithiums with anhydrous cerium chloride were examined. First, vinyllithium was treated with cerium chloride. In this case, the color of the mixture turned to dark brown even at -78 °C, and the subsequent reaction with 1,3-diphenyl-2-propanone provided diols 2 and 4[8] in 11% and 21% yield, respectively. Under similar conditions, isopropenyllithium was converted to compounds 5[9] and 6[10] in 7% and 14% yield, respectively.[12]



These results indicate that the parent alkenyl derivatives of Mg or Li are subjected to dimerization or trimerization in the presence of cerium chloride to generate dimetallic compounds.[13] To our knowledge, this type of reaction is unprecedented, while there have been reported many coupling reactions of organometallic compounds such as oxidative dimerizations.[14,15] Mechanistic study on this new coupling reaction is now in progress in our laboratory.

Acknowledgement: We thank Mr. N. Shimizu and Mr. Y. Saito, Idemitsu Kosan Co., Ltd., for the measurements of field desorption mass spectra.

References and Notes

1. T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya, *J. Am. Chem. Soc.*, 111, 4392 (1989).
2. Compound **1**: Oil; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.54 (s, 1 H), 2.28 (d, J = 7.4 Hz, 2 H), 2.85 (s, 4 H), 3.24 (s, 2 H), 3.42 (s, 2 H), 5.64 (dt, J = 7.4, 11.0 Hz, 1 H), 6.11 (d, J = 11.6 Hz, 1 H), 6.56 (dd, J = 11.0, 11.6 Hz, 1 H), 7.18 - 7.31 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 35.4, 36.3, 43.4, 45.7, 74.6, 123.2, 126.1, 126.2, 126.4, 126.5, 127.1, 128.2, 128.3, 128.4, 128.7, 129.1, 130.8, 137.2, 139.5, 141.3; IR (neat) 3400, 3020, 2900, 1600, 1500, 1455 cm^{-1}. Anal. Calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 89.03; H, 7.62. The structure of **1** was demonstrated by the NOE experiments.
3. Compound **2**: Mp 115-115.5 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.59 (br s, 2 H), 1.98 (d, J = 5.0 Hz, 4 H), 2.75 (d, J = 13.7 Hz, 4 H), 2.76 (d, J = 13.7 Hz, 4 H), 5.76 (t, J = 4.6, 2 H), 7.17 - 7.33 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 36.4, 45.7, 74.4, 126.5, 127.8, 128.2, 130.8, 137.2; IR (KBr) 3400, 3000, 2880, 1580, 1480, 1440 cm^{-1}. Anal. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61. Found: C, 85.71; H, 7.70. The structure of this compound was determined by single-crystal X-ray analysis (Fig. 1).

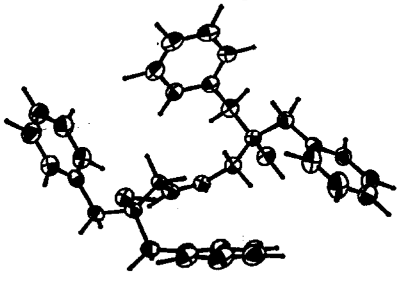


Fig. 1. ORTEP drawing of **2**.

4. Use of vinylmagnesium bromide instead of vinylmagnesium chloride provided almost the same results.
5. CeF_3, CeI_3, $Ce(OSO_2CF_3)_3$, $NdCl_3$, $LaCl_3$, $YbCl_3$, and cerium metal were also tested for the reaction under similar conditions. The use of $Ce(OSO_2CF_3)_3$, CeI_3, and $NdCl_3$ instead of $CeCl_3$ afforded almost the same result, while the others did not react with vinylmagnesium chloride at room temperature.
6. In order to confirm the existence of C_4-species as the reactive intermediates, the reaction mixture of vinylmagnesium chloride and cerium chloride was treated with water. Analysis of the reaction mixture by GC and GC-MS indicated the formation of (*Z*)-2-butene, (*E*)-2-butene, 1-butene, and butane.
7. Compound **3**: Mp 138 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.54 (s, 2 H), 1.57 (s, 3 H), 1.70 (d, J = 1.1 Hz, 3 H), 1.73 (s, 3 H), 1.96 (s, 2 H), 2.10 (s, 2 H), 2.58 (d, J = 13.5 Hz, 2 H), 2.62 (d, J = 13.5 Hz, 2 H), 2.73 (d, J = 13.5 Hz, 2 H), 2.75 (d, J = 13.5 Hz, 2 H), 5.68 (s, 1 H), 7.16-7.30 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 19.4, 20.7, 25.6, 42.3, 44.7, 46.4, 74.6, 75.5, 126.2, 126.3, 128.0, 128.3, 130.8, 131.2, 131.6, 132.9, 137.6, 137.7; IR (KBr) 3500, 3000, 2900, 1600, 1500 cm^{-1}; FDMS *m/z* 544 (M^+). Anal. Calcd for $C_{39}H_{44}O_2$: C, 85.99; H, 8.14. Found: C, 86.04; H, 8.23. The structure of this compound was determined by single-crystal X-ray analysis (Fig. 2).

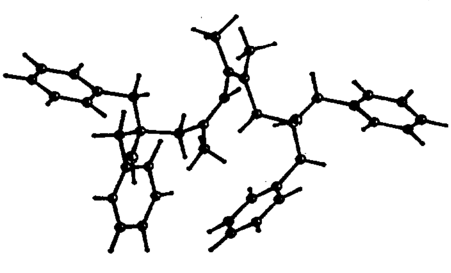
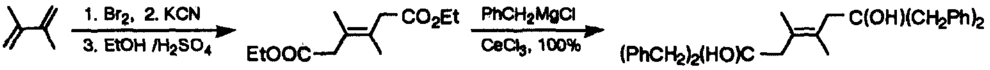
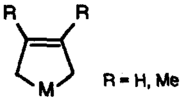


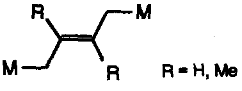
Fig. 2. ORTEP drawing of **3**.

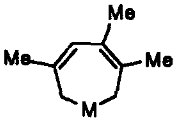
8. **Compound 4**: Mp 160.5-161.0 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.53 (s, 2 H), 2.13-2.20 (m, 4 H), 2.80 (s, 8 H), 5.54-5.61 (m, 2 H), 7.23-7.32 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 42.1, 45.7, 74.0, 126.5, 128.2, 129.8, 130.8, 137.3; IR (KBr) 3500, 3000, 2900, 1500, 1440 cm^{-1}. Anal. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61. Found: C, 85.51; H, 7.60.
9. **Compound 5**: Mp 170.0-170.5 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.51 (s, 2 H), 1.79 (s, 6 H), 2.11 (s, 4 H), 2.51 (d, J= 13.5 Hz, 4 H), 2.61 (d, J= 13.5 Hz, 4 H), 7.16-7.32 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 21.8, 43.8, 46.3, 74,6, 126.3, 128.0, 130.1, 130.9, 137.8; IR (KBr) 3500, 3000, 2900, 1600, 1490, 1440 cm^{-1}. Anal. Calcd for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99. Found: C, 85.83; H, 8.00.
10. **Compound 6**: Mp 171-172 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.54 (s, 2 H), 1.63 (s, 6 H), 2.30 (s, 4 H), 2.72 (d, J= 13.7 Hz, 4 H), 2.86 (d, J= 13.5 Hz, 4 H), 7.21-7.34 (m, 20 H); ^{13}C NMR (100 MHz) ($CDCl_3$) δ 22.0, 44.0, 46.6, 75.2, 126.4, 128.1, 129.9, 130.9, 137.6; IR (KBr) 3550, 3000, 2900, 1600, 1500, 1450 cm^{-1}. Anal. Calcd for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99. Found: C, 85.83; H, 8.19. This compound was identical with the compound prepared according to the following scheme.[1,11]



11. G. Lohaus, *Chem. Ber.*, **87**, 1708 (1954).
12. When vinyllithium and isopropenyllithium were treated with $CeCl_3$ at -30 °C, only (Z)-isomers, **2** and **5**, were isolated in 16% and 12% yield, respectively; (E)-isomers, **4** and **6**, were not produced under these conditions, even in trace amounts.
13. We tentatively propose the following structures for the dimetallic compounds which react with 1,3-diphenyl-2-propanone to afford compounds **1**-**6**. These organometallic compounds may be produced via carbometallation.







14. A. McKillop. L. F. Elsom, and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 2423 (1968); C. A. Maryanoff, B. E. Maryanoff, R. Tang, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 5839 (1973); S. K. Taylor, S. G. Bennett, K. J. Heinz, and L. K. Lashley, *J. Org. Chem.*, **46**, 2194 (1981).
15. Formation of *gem*-dimetallic compounds from alkenyl organometallic derivatives and allylic zinc bromides was reported. M. Gaudemar, *Compt. Rend. Acad. Sc. Paris, Serie C*, **273**, 1669 (1971); Y. Frangin and M. Gaudemar, *ibid.*, **278**, 885 (1974); M. Bellassoued, Y. Frangin and M. Gaudemar, *Synthesis*, **1977**, 205; P. Knochel and J. F. Normant, *Tetrahedron Lett.*, **27**, 1039 (1986); P. Knochel and J. F. Norman, *ibid.*, **27**, 1043 (1986); P. Knochel and J. F. Normant, *ibid.*, **27**, 4427 (1986); P. Knochel and J. F. Normant, *ibid.*, **27**, 4431 (1986); P. Knochel and J. F. Normant, *ibid.*, **27**, 5727 (1986).

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