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# Ligand exchange reactions of a 1,3-butadiene complex of magnesium

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**Abstract**

The ligand exchange reaction of a diene ligand bound to magnesium was investigated. Reaction of the magnesium-butadiene compound $[Mg(C_4H_6)(thf)_2]_n$ (2) with 1,4-diphenyl-1,3-butadiene afforded Mg(s-*cis*-1,4-diphenyl-1,3-butadiene)$(thf)_3$ (1) together with butadiene. Similarly, treatment of 2 with 1,6-diphenyl-1,3,5-hexatriene, anthracene, and 1,3,5,7-cyclooctatetraene afforded the corresponding magnesium adducts Mg(1,6-diphenyl-1,3,5-hexatriene)$(thf)_3$ (3), Mg(anthracene)$(thf)_3$ (4), and Mg(cot)$(thf)_{2.5}$ (5), respectively, in addition to the liberated butadiene. Reaction of 2 with diphenylacetylene in THF also induced the ligand exchange reaction, resulting in the formation of a diphenylacetylene adduct $[Mg(PhC_2Ph)(thf)]_4$ (6) of magnesium. © 1997 Elsevier Science S.A.

*Keywords:* Magnesium; Ligand exchange; Diene; Triene; Cyclooctatetraene; Anthracene; Diphenylacetylene

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## 1. Introduction

The chemistry of diene dianions has attracted much interest in view of both synthetic and theoretical aspects since they are one of the 6π electron systems [1]. Diene complexes of magnesium have been prepared by reaction of activated magnesium with conjugated 1,3-dienes [2–10]. [1] Rieke et al. [8] and Rieke and Xiong [11,12] reported on the electrophilic nature of the magnesium–diene complexes. We have reported on the synthesis and crystal structure of Mg(s-*cis*-1,4-diphenyl-1,3-butadiene)$(thf)_3$ (1) [13]. Ligand exchange reaction of a diene ligand has never been reported for the diene complexes of magnesium [14], [2] although the magnesium–butadiene compound decomposed in boiling toluene to give metal and free butadiene [15] and the oxidation of a diene–magnesium complex to give the free diene has been reported as well [9,12,15]. Herein, we report ligand exchange reactions of butadiene coordinated to the magnesium atom with (*E,E*)-1,4-diphenyl-1,3-butadiene, (*E,E,E*)-1,6-diphenyl-1,3,5-hexatriene, anthracene, cyclooctatetraene and diphenylacetylene.

## 2. Results and discussion

Treatment of compound 2 $[Mg(butadiene)(thf)_2]_n$ with one equiv. of (*E,E*)-1,4-diphenyl-1,3-butadiene in THF resulted in the quantitative formation of complex 1 together with free butadiene. A solution of (*E,E*)-1,4-diphenyl-1,3-butadiene dissolved in THF was added to 2 suspended in THF at room temperature. The reaction proceeded smoothly and the yellow color of the reaction mixture turned red. Complex 1 was obtained in 98% yield by the addition of hexane and the liberated butadiene was detected by GLC analysis (62% yield). Spectral data and hydrolysis of the product confirmed the formation of 1 [7]. This ligand exchange reaction was accelerated by the addition of HMPA, which increased the

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[1] See also references cited in Ref. [8].

[2] Magnesium anthracene complex 4 has been noted to be in equilibrium with magnesium metal and anthracene, and thus 4 is a source of atomic magnesium.

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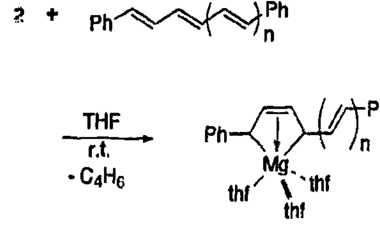
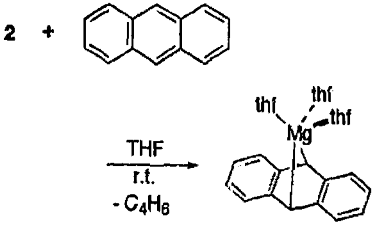
solubility of compound **2** and enhanced the electron transfer process.



1: n = 0
3: n = 1

(1)

This type of ligand exchange reaction can be applied to higher conjugated linear polyene compounds such as 1,6-diphenyl-1,3,5-hexatriene as well as cyclic hydrocarbons such as anthracene and cyclooctatetraene. Reaction of **2** with 1,6-diphenyl-1,3,5-hexatriene afforded Mg(PhCH=CHCH=CHCH=CHPh(thf)$_3$ (**3**) [13], whose formulation was confirmed by the structure of products (1,6-diphenylhexadienes) obtained by hydrolysis along with magnesium metal determined by the chelate titration. Treatment of **2** with an equimolar amount of anthracene in THF at room temperature resulted in the formation of Mg(anthracene)(thf)$_3$ (**4**) (91% yield) (Eq. (2)) [15–21]. Similarly, addition of one equiv. of cyclooctatetraene (cot) to **2** in THF induced a smooth change of the color of the solution from yellow to off-white due to the formation of Mg(cot)(thf)$_{2.5}$ (**5**) [20–22].[3] In these reactions, butadiene was also detected by GLC. Products **4** and **5** were characterized by comparing their spectral data with those of literature [20,21], as well as by the structure of products obtained by hydrolysis, i.e., 9,10-dihydroanthracene and a mixture of 1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene [22], respectively.



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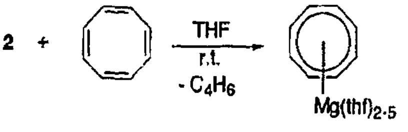
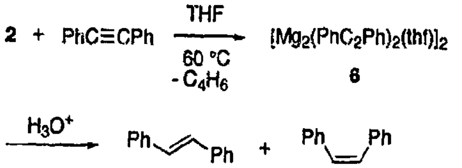
(2)



5

(3)

It is noteworthy that **2** reacts with diphenylacetylene. Treatment of **2** with one equiv. of diphenylacetylene in THF at 60°C afforded [Mg(PhC$_2$Ph)(thf)]$_4$ (**6**), which gave a 1:2 mixture of *cis*- and *trans*-stilbene in 75% yield upon hydrolysis by aq. HCl. The compound **6** was recently characterized by X-ray analysis by Tinga et al. [23], who reported that **6** was prepared only by the sublimation of magnesium metal into a solution of diphenylacetylene in THF at −100°C. Our synthetic method has an advantage due to the convenience although it resulted in contamination with the polymers of the liberated butadiene.



(4)

Ligand exchange reaction with neutral unsaturated organic compounds described above also resulted in the oxidation of **2** with O$_2$ and I$_2$ giving free butadiene.

In summary, we demonstrated the first ligand exchange reaction of the magnesium–diene compound **2** with unsaturated organic compounds such as 1,4-diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, anthracene, cyclooctatetraene and diphenylacetylene accompanied by the liberation of the diene ligand.

## 3. Experimental section

### 3.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. THF and hexane were dried over sodium benzophenone ketyl and then distilled before use.

Nuclear magnetic resonance [$^1$H (400 MHz and 270 MHz)] spectra were measured on a JEOL JNM-GX400, JEOL JNM-GSX-270 and JEOL EX-270 spectrometers. All $^1$H NMR chemical shifts were reported in ppm relative to the resonance of the impurity in deuterated solvents as follows: chloroform-*d*, singlet at 7.26 ppm; benzene-$d_6$, singlet at 7.20 ppm. Other spectra were recorded by the use of the following instruments: IR, Hitachi 295; UV/vis spectra, Jasco Ubest-30 and Shimadzu UV-265FS; gas chromatographic (GLC) analyses, Shimadzu GC-14A equipped with a flame ionization detector; HPLC analyses, Jasco PU-980 using UV detector.

### 3.2. Reaction of 2 with 1,4-diphenyl-1,3-butadiene

To a rigorously stirred suspension of compound (**2**) [Mg(butadiene)(thf)$_2$]$_n$ (58 mg, 0.26 mmol) in THF (1.0 ml) was added a solution of (*E*,*E*)-1,4-diphenyl-1,3-butadiene (54 mg, 0.26 mmol) in THF (2.6 ml) at room

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[3] It has already been reported that complex **4** reacted with cyclooctatetraene to give **5** [20].

temperature. At the early stage of this reaction, the color of the reaction mixture turned to yellow and then a deep red solution containing orange solid of Mg(s-*cis*-1,4-diphenyl-1,3-butadiene)(thf)$_3$ (**1**) was obtained after stirring for 10 h. The liberated butadiene was detected by GLC to be 62% yield. The solution was evaporated to dryness to give **1** as orange solid (98% yield). Complex **1** was hydrolyzed in THF by aq. HCl to give 1,4-diphenyl-1-butene and 1,4-diphenyl-2-butene (total 87% yield by $^1$H NMR spectroscopy). UV spectrum of **1** was superimposable with that of the literature [7].

### *3.3. Reaction of* **2** *with 1,6-diphenyl-1,3,5-hexatriene*

To a solution of ($E,E,E$)-1,6-diphenyl-1,3,5-hexatriene (0.116 g, 0.50 mmol) in THF (40 ml) was added 1 equiv. of **2** (THF solution, 2 ml, 0.52 mmol) at −78°C. The color of the solution changed from pale yellow to deep red as the temperature increased to room temperature during 12 h. After removal of the undissolved impurities by centrifugation, the solvent was removed in vacuo to give Mg(1,6-diphenylhexatriene)(thf)$_3$ (**3**) as deep red powder. The yield of liberated butadiene was determined to be 62% by GLC. M.p. 100–110°C (dec.). Metal contents; 6.1% by 8-quinolinol method; 6.12%, calc. for $C_{26}H_{32}O_2Mg$. UV (THF) $\lambda_{max} = 471$ nm ($\varepsilon$ $3.0 \times 10^3$). The $^1$H NMR was measured in THF-$D_8$, but only broad signals were observed. Hydrolysis of **3** using aq. HCl afforded a mixture of 1,6-diphenylhexadienes in 79% yield (GLC and HPLC analysis). Oxidation of **3** in THF by the addition of iodine afforded a quantitative yield of 1,6-diphenyl-1,3,5-hexatriene (HPLC analysis).

### *3.4. Reaction of* **2** *with anthracene*

Addition of anthracene (46 mg, 0.26 mmol) in THF (2.6 ml) to **2** (58 mg, 0.26 mmol) suspended in THF (1.0 ml) at room temperature gave a yellow solution. After being stirred for 10 h at room temperature, a yellow solution containing orange solids of Mg(anthracene)(thf)$_3$ (**4**) [20,21] was obtained. The yield of liberated butadiene was determined to be 75% by GLC. The solution was evaporated to dryness to give **4** as orange solid (91% yield). Complex **4** was hydrolyzed by aq. HCl to give 9,10-dihydroanthracene (90% yield by $^1$H NMR spectroscopy).

### *3.5. Reaction of* **2** *with 1,3,5,7-cyclooctatetraene*

A solution of 1,3,5,7-cyclooctatetraene (0.11 ml, 1.0 mmol) in THF (5.0 ml) was added to a rigorously stirred suspension of **2** (223 mg, 1.0 mmol) in THF (1.4 ml) at room temperature to give a yellow solution. After being stirred for 10 h at room temperature, a yellow-green solution containing off-white solid of Mg(cot)(thf)$_{2.5}$ (**5**) was obtained. The yield of liberated butadiene was determined to be 98% by GLC. The solution was evaporated to dryness to give **5** as white-green solids. Complex **5** was hydrolyzed by aq. HCl to give a mixture of 1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene (total 77% yield by GLC).

### *3.6. Reaction of* **2** *with diphenylacetylene*

A solution of diphenylacethylene (93 mg, 0.52 mmol) in THF (2.6 ml) was added at 60°C to a rigorously stirred suspension of **2** (116 mg, 0.52 mmol) in THF (2.0 ml). The color of the solution turned gradually to orange. The reaction mixture was stirred for 24 h at 60°C to give a deep red solution containing yellow solids of **6**. The liberated butadiene was detected to be 28% yield by GLC; the low yield was due to the polymerization of the liberated butadiene during prolonged heating. The solution was evaporated to dryness to give **6** with contamination of polybutadiene. Hydrolysis of **6** by aq. HCl gave a 2:1 mixture of *trans*- and *cis*-stilbene in 75% combined yield determined by the $^1$H NMR spectrum.

### *3.7. Reaction of* **2** *with* $O_2$

To **2** (116 mg, 0.52 mmol) suspended in THF (2.0 ml) was added an excess of $O_2$ at room temperature. The rapid reaction proceeded, and the white-green color of the solution faded out. After 1 h at room temperature, a solution containing white solids was obtained. The yield of liberated butadiene was determined to be 57% by GLC.

### *3.8. Reaction of* **2** *with* $I_2$

To a suspension of **2** (58 mg, 0.26 mmol) in THF (1.0 ml) was added a solution of $I_2$ (66 mg, 0.26 mmol) in THF (2.6 ml) at room temperature. The rapid reaction proceeded, and the white-green color of the solution changed to an off-white solution. After 10 h at room temperature, a solution containing white solids of $MgI_2$ was obtained. The liberated butadiene amounted to 68% yield by GLC.

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