markable resistance to oxgen should stimulate investigations into methods to recycle BABAR-Phos complexes (e.g. by immobilization or making them water soluble).[9]

Experimental Section

3: Compound **1a** (477 mg, 1.7 mmol) was added to a solution of $[Rh(cod)_2]^+O_3SCF_3^-$ (200 mg, 0.42 mmol) in THF (3 mL). The product precipitated as a light yellow microcrystalline powder which was washed with Et_2O (2 × 1 mL) and dried in vacuum (yield 472 mg, 82 %). Crystals suitable for an X-ray analysis were grown from a CH_2Cl_2 solution layered with *n*-hexane. Elemental analysis (%) calcd for $C_{73}H_{72}F_3N_4O_3P_4RhS$: C 64.03, H 5.30, N 4.09; found: C 64.12, H 5.27, N 4.18.

5: Compound **4** (200 mg, 0.41 mmol) and **1b** (365 mg, 0.82 mmol) were combined in MeCN (3 mL). After about 1 h without stirring, the product precipitated in the form of deep brown-red crystals, which were collected by filtration and washed with MeCN (2 × 1 mL). After drying under vacuum **5** was obtained in 91 % yield (458 mg). Elemental analysis (%) calcd for $C_{96}H_{62}Cl_4F_{24}N_6P_4Rh_4$: C 47.39, H 2.57, Cl 5.83, P 5.09, N 3.45; found: C 47.39, H 2.83, Cl 5.95, P 5.10, N 3.60.

7a, b: A suspension of **5** (200 mg, 0.08 mmol) in MeCN (2 mL) was treated with $AgPF_6$ (38 mg, 0.15 mmol) or $AgSO_3CF_3$ (40 mg, 0.15 mmol), respectively. After filtration from precipitated AgCl, the solution was reduced to about about a tenth of its volume. At $-25\,^{\circ}C$, the products crystallized as brown-red rhombs; yields: **7a**: 171 mg (79 %); **7b**: 178 mg (76 %). Elemental analysis (%) calcd for $C_{104}H_{74}Cl_2F_{36}N_{10}P_6Rh_4$ (**7a**): C 44.36, H 2.65, N 4.97; found: C 44.31, H 2.59, N 5.01.

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[1] a) J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H. Grützmacher, *Angew. Chem.* **1999**, *110*, 1724; *Angew. Chem. Int. Ed.* **1999**, *38*, 1623; b) J. Liedtke, S. Loss, H. Grützmacher, *Tetrahedron* **2000**, *56*, 143.

[2] a) C. Widauer, H. Grützmacher, T. Ziegler, *Organometallics* **2000**, *24*, 2097; b) D. G. Musaev, A. M. Mebel, K. Morokuma, *J. Am. Chem. Soc.* **1994**, *116*, 10693; c) A. E. Dorigo, P. von R. Schleyer, *Angew. Chem.* **1995**, *107*, 108; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 115.

[3] a) Irreversible metal insertion reactions into $(R_2C)_2X$ rings ($X = CR_2$; NR, O): D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey, L. Ricard, *J. Chem. Soc. Dalton Trans.* **1993**, 1811; b) formation of epoxide by thermolysis of a 1-nickela-2-oxacyclobutane: A. Miyashita, J. Ishida, H. Nohira, *Tetrahedron Lett.* **1986**, *27*, 2127.

[4] Crystal structure analyses: **3**: tetragonal, space group $P4nc$; $a = 16.5970(5)$, $c = 11.7946(3)$ Å; $V = 3248.9(2)$ Å^3; $Z = 2$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 52.72^{\circ}$; 21747 reflections, 3324 independent ($R_{int} = 0.0728$); $R_1 = 0.05$, $wR_2 = 0.1232$ (based on F^2) for 199 parameters and 2746 reflections with $I > 2\sigma(I)$. **7b**: monoclinic, space group $P2_1/n$; $a = 17.98168(5)$, $b = 18.9535(5)$, $c = 18.5737(4)$ Å, $\beta = 104.093(1)^{\circ}$; $V = 6139.7(3)$ Å^3; $Z = 2$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 52.74^{\circ}$; 45154 reflections, 12557 independent ($R_{int.} = 0.0791$); $R_1 = 0.0494$, $wR_2 = 0.0931$ (based on F^2) for 772 parameters and 8201 reflections with $I > 2\sigma(I)$. Both structures were solved by using direct methods and were refined against full matrix (versus F^2) with SHELXTL (Version 5.0). Non-hydrogen atoms were treated anisotropically, hydrogen atoms were refined on calculated positions using the riding model. The triflate anion in **3** was refined as a rigid group disordered over four equivalent positions with isotropic temperature factors. Noncoordinating acetonitrile molecules in **7b** were refined with isotropic temperature factors, one of the molecules was disordered over two equivalent positions with an occupancy factor of 0.4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137943 (**3**) and CCDC-137942 (**7b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] A. Marinetti, F. Mathey, L. Ricard, *Organometallics* **1993**, *12*, 1207.

[6] a) F. A. Ajulu, P. B. Hitchcock, F. Mathey, R. A. Michelin, J. F. Nixon, A. J. L. Pombeiro, *J. Chem. Soc. Chem. Commun.* **1993**, 142; b) F. A. Ajulu, D. Carmichael, P. B. Hitchcock, F. Mathey, M. F. Meidine, J. F. Nixon, L. Ricard, M. L. Riley, *J. Chem. Soc. Chem. Commun.* **1992**, 750; c) S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey, J. F. Nixon, *J. Chem. Soc. Dalton Trans.* **1991**, 905.

[7] a) D. Männig, H. Nöth, *Angew. Chem.* **1985**, *97*, 854; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 878; b) Review: K. Burgess, M. J. Ohlmeyer, *Chem. Rev.* **1991**, *91*, 1179; c) J. M. Brown, G. C. Lloyd-Jones, *J. Am. Chem. Soc.* **1994**, *116*, 866, and references therein.

[8] In the presence of the olefin alone, no reaction is observed, while addition of borane alone caused a slight color change and ^{31}P NMR signals appeared in the region of the intact BABAR-Phos ligand. However, we have been unable to isolate any pure product yet.

[9] The alcohols **13a**, **b** and **14a**, **b** can be obtained by passing a stream of oxygen (or air) through the reaction mixtures. Unfortunately, although the complexes were stable under O_2 they decomposed in the presence of the organoboranes **11a**, **b**, **12a**, **b**. However, the ligands **1a**, **b** could be recovered. Workup with alkaline H_2O_2 destroys the phosphiranes as well. Probably these decomposition reactions are caused by radicals being formed from organoboranes and O_2 (see: H. J. Brown, M. M. Midland, *Tetrahedron* **1987**, *43*, 4059) or by the high oxidizing power of alkaline H_2O_2. However, one could circumvent catalyst destruction by separation before workup.

Halogen–Magnesium Exchange via Trialkylmagnesates for the Preparation of Aryl- and Alkenylmagnesium Reagents[**]

Kazuya Kitagawa, Atsushi Inoue, Hiroshi Shinokubo, and Koichiro Oshima*

The utility of organometallic ate complexes such as R_2CuLi, R_3ZnLi, and R_4AlLi in organic synthesis is well known, and numerous studies have been devoted to the development of new methods which make use of these reagents. Several synthetic methods which utilize R_3MnLi have also been reported recently.[1] These organometallic ate complexes are known to induce halogen–metal exchange reactions in some cases.[2]

Recently, Knochel et al. have shown that polyfunctional arylmagnesium and alkenylmagnesium reagents can be prepared by an iodine–magnesium exchange reaction using RMgX.[3, 4] It then occurred to us that a magnesium-ate complex (R_3MgLi)[5] would be more effective than an alkylmagnesium halide (RMgX) for the halogen–magnesium exchange reaction. Indeed, we have found that treatment

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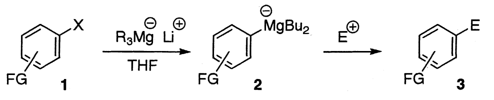
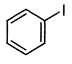
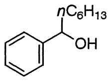
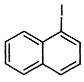
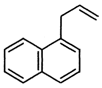
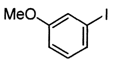
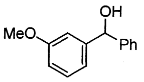
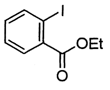
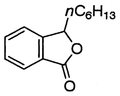
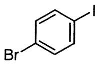
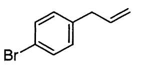
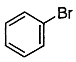
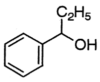
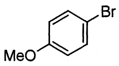
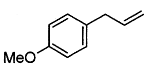
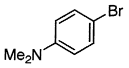
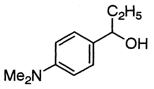
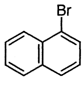
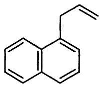
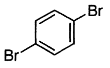
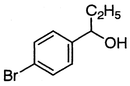
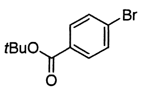
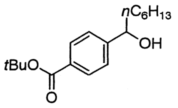
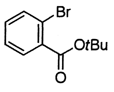
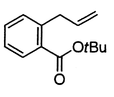
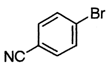
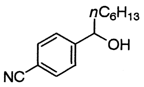
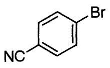
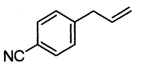
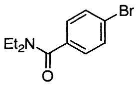
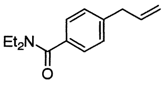
Table 1. Preparation of arylmagnesates and their reaction with electrophiles.[a]



Entry	ArX	Conditions[a] Reagent	T [°C]	t [h]	Electrophile	Product	Yield [%]
1		A	0	0.5	n-$C_6H_{13}CHO$		80
2		A	0	0.5	CH_2=$CHCH_2Br$		87
3		A	−78	0.5	PhCHO		93
4		A	−78	1	n-$C_6H_{13}CHO$		60
5		A	0	0.5	CH_2=$CHCH_2Br$		73
6		A	0	0.5	C_2H_5CHO		87
7		A	0	0.5	CH_2=$CHCH_2Br$		84
8		A	0	0.5	C_2H_5CHO		94
9		A	0	0.5	CH_2=$CHCH_2Br$		97
10		B	0	0.5	C_2H_5CHO		78
11		A	−78	1	n-$C_6H_{13}CHO$		50
12		B	−78	1	n-$C_6H_{13}CHO$		71
13		B	−78	1	CH_2=$CHCH_2Br$[b]		99
14		B	−78	1	n-$C_6H_{13}CHO$		60
15		B	−78	1	CH_2=$CHCH_2Br$[b]		87
16		B	−78	1	CH_2=$CHCH_2Br$[b]		79

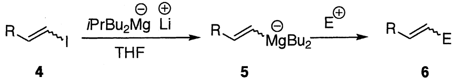
[a] Reagent A: nBu$_3$MgLi, reagent B: iPrBu$_2$MgLi. [b] In the presence of CuCN · 2 LiCl.

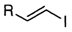
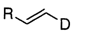
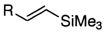
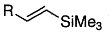
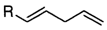
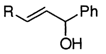
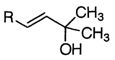
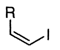
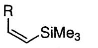
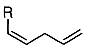
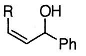
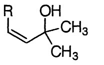
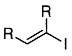
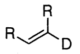
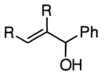
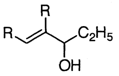
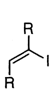
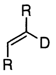
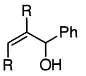
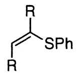
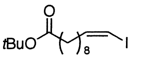
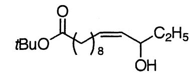
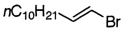
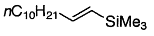
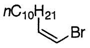
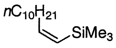
of aryl halides or alkenyl iodides with trialkylmagnesate, derived from RMgX and two equivalents of alkyllithium, provided the corresponding organomagnesium reagents in good to excellent yields. The representative results are shown in Table 1.[6] Several features of the reaction are noteworthy. Not only aryl iodides but also aryl bromides[7] can be converted into the corresponding magnesium reagents efficiently. Functional groups (FG) such as ester, amide, or cyano groups are tolerated during the exchange procedure and lead to functionalized arylmagnesates of type **2**. For the preparation of the latter, the mixed magnesate iPrBu$_2$MgLi was required, which was generated from iPrMgBr and nBuLi, and was found to be more reactive than nBu$_3$MgLi for the exchange reaction. Whereas nBu$_3$MgLi could convert aryl iodides into the corresponding magnesate at −78 °C, the reagent could not complete the magnesiation reaction of aryl bromide at that temperature. In contrast, bromine–magnesium exchange of aryl bromides could be easily performed with iPrBu$_2$MgLi at −78 °C.[8] Although the reaction of **2** with allyl bromide at 0 °C provided the allylated products in good yields, the reaction did not proceed at −78 °C. However, the addition of a catalytic amount of CuCN · 2 LiCl to the reaction mixture facilitated the allylation at −78 °C, and the desired products were obtained in excellent yields (entries 13, 15, and 16; Table 1).

This new procedure was utilized for the preparation of alkenylmagnesates from alkenyl halides. The results are shown in Table 2. The iodine–magnesium exchange of alkenyl iodides proceeded with complete retention of configuration of the double bond. The reaction of (Z)-1-iodo-1-dodecene afforded the corresponding (Z)-alkenylmagnesate, and (E)-iodoalkene provided the E isomer. The resulting alkenylmagnesate could be easily trapped by various electrophiles such as chlorotrimethylsilane, allyl bromide, benzaldehyde, or acetone. The presence of an ester functionality is compatible with the formation of alkenylmagnesate at −78 °C (entry 17; Table 2).

In contrast, the bromine–magnesium exchange of alkenyl bromide is not as effective. The treatment of (E)-1-bromo-1-dodecene with iPrBu$_2$MgLi followed by an addition of chlorotrimethylsilane provided (E)-1-trimethylsilyl-1-dodecene in 71 % yield along with 1-trimethylsilyl-1-dodecyne (29 %). The alkynylsilane results from silylation of the dehydrobromination product (1-dodecyne). Meanwhile, the reaction of the Z isomer gave (Z)-1-trimethylsilyl-1-dodecene in only 27 % yield in addition to 59 % of the silyldodecyne (entries 18 and 19; Table 2).

Table 2. Preparation of alkenylmagnesates and their reaction with electrophiles.



Entry	Substrate	Conditions		Electrophile	Product	Yield
		T [°C]	t [h]			[%]
1	 R = $n\mathrm{C}_{10}\mathrm{H}_{21}$	0	1	D_2O		93
2		0	1	Me_3SiCl		93
3		– 78	1	Me_3SiCl		95
4		0	1	CH_2=$CHCH_2Br$[a]		70
5		0	1	PhCHO		69
6		0	1	CH_3COCH_3		75
7	 R = $n\mathrm{C}_{10}\mathrm{H}_{21}$	– 78	1	Me_3SiCl		83
8		0	1	CH_2=$CHCH_2Br$[a]		78
9		0	1	PhCHO		78
10		0	1	CH_3COCH_3		66
11	 R = $n\mathrm{C}_5\mathrm{H}_{11}$	0	1	D_2O		87
12		0	1	PhCHO		87
13		0	1	C_2H_5CHO		65
14	 R = $n\mathrm{C}_5\mathrm{H}_{11}$	0	1	D_2O		88
15		0	1	PhCHO		70
16		0	1	PhSSPh		77
17		– 78	0.5	C_2H_5CHO		80
18		0	1	Me_3SiCl		71 (29)[b]
19		0	1	Me_3SiCl		27 (59)[b]

[a] In the presence of CuCN · 2LiCl. [b] Yields of 1-trimethylsilyl-1-dodecyne in parentheses.

Experimental Section

Butyllithium (1.6 M solution in hexane, 1.5 mL, 2.4 mmol) was added to a solution of isopropylmagnesium bromide (1.0 M solution in THF, 1.2 mL, 1.2 mmol) in THF (5 mL) at 0 °C. After being stirred for 30 min, the resulting mixture was cooled to – 78 °C and a solution of *tert*-butyl *p*-bromobenzoate (0.26 g, 1.0 mmol) in THF (2 mL) was added. The mixture was stirred for 1 h at – 78 °C and then heptanal (3.0 mmol) was added. The reaction mixture was stirred for additional 1 h at – 78 °C, and then the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. Purification by column chromatography (silica gel) gave *tert*-butyl 4-(1-hydroxyheptyl)benzoate as a colorless liquid (0.21 g, 71 %).

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[4] For further examples of halogen – magnesium exchange reactions, see: a) N. Furukawa, T. Shibutani, H. Fujihara, *Tetrahedron Lett.* **1987**, *28*, 5845 – 5848; b) H. Nishikawa, K. Isaka, K. Itoh, K. Ohno, H. Nagase, K. Matsumoto, H. Yoshiwara, *J. Org. Chem.* **1992**, *57*, 407 – 410; c) H. Shinokubo, H. Miki, T. Yokoo, K. Oshima, K. Utimoto, *Tetrahedron* **1995**, *51*, 11681 – 11692; d) F. Trécourt, G. Breton, V. Bonnet, F. Mongin, F. Marsais, G. Quéguiner, *Tetrahedron Lett.* **1999**, *40*, 4339 – 4342.

[5] The crystal structures of $[Li(TMEDA)]_2Me_4Mg$ and $[Li(TMEDA)]_2[Ph_2MgPh_2MgPh_2]$ (TMEDA = *N,N,N',N'*-tetrametylethylenediamine) have been reported. a) T. Greiser, J. Kopf, D. Thoennes, E. Weiss, *Chem. Ber.* **1981**, *114*, 209 – 213; b) D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3726 – 3731. An NMR study on CH_3Li-$(CH_3)_2Mg$ has been reported: L. M. Seitz, T. L. Brown, *J. Am. Chem. Soc.* **1966**, *88*, 4140 – 4147.

[6] The amount of the magnesate reagent can be reduced in some cases. The reaction of *p*-bromoanisole with 0.6 equivalents of $n\mathrm{Bu}_3\mathrm{MgLi}$ provided the corresponding product in 85 % yield upon treatment with propanal.

[7] Knochel et al. have reported that Br – Mg exchange of aryl bromides with *i*PrMgBr or $i\mathrm{Pr}_2\mathrm{Mg}$ is efficient when the substrate bears an electron-withdrawing group.[3f] In contrast, Br – Mg exchange with trialkylmagnesate proceeded effectively without such an activating group. For example, the corresponding phenylmagnesate species was formed quantitatively in the reaction of bromobenzen with $i\mathrm{PrBu}_2\mathrm{MgLi}$, whereas bromobenzene did not react *i*PrMgBr at – 78 °C.

[8] The reaction of excess benzaldehyde with arylmagnesium reagent, which was derived from aryl bromide and $i\mathrm{PrBu}_2\mathrm{MgLi}$, provided no isopropyl-substituted alcohol. The isopropyl group was consumed for the exchange reaction. This result indicates that the isopropyl residue in the mixed ate complex is active.