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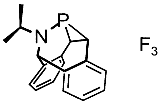
BABAR-Phos Rhodium Complexes: Reversible Metal Insertion into a Three-Membered Ring and Catalytic Hydroborations[**]

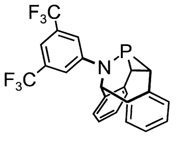
Jürgen Liedtke, Heinz Rüegger, Sandra Loss, and Hansjörg Grützmacher*

Dedicated to Professor Heinrich Vahrenkamp
on the occasion of his 60th birthday

The polycyclic phosphiranes **1a** and **1b** (BABAR-Phos)[1a] are not oxidized by O_2, sulfur, and strongly alkylating agents, and they resist aqueous acids and bases. Furthermore they have electron-withdrawing properties which could make them interesting ligands for hydrosilylation and hydroboration[2] catalysts.[1b] Apart from BABAR-Phos rhodium complexes which were synthesized for this use, we describe here—to our knowledge—the first *reversible* insertion and deinsertion of a metal center into a three-membered heterocycle.[3]

As precursors for the synthesis we used either $[Rh(cod)_2]^+$-$O_3SCF_3^-$ (**2**; cod = 1,5-cyclooctadiene) containing only a weakly coordinating anion or $[Rh_2(\mu_2\text{-}Cl_2)(cod)_2]$ (**4**). Reactions of **2** with **1a** in coordinating solvents, such as acetonitrile, or with the N-aryl-substituted phosphirane **1b** generate brown-red solutions ($\lambda_{max} > 500$ nm), whose ^{31}P NMR spectra display signals in the positive ($\delta = +20$ to $+100$) and negative ($\delta = -60$ to -150) δ range (versus 85% H_3PO_4). The signals are broadened due to chemical exchange between different species. However, when **2** is treated with **1a** in THF, product **3** is obtained almost quantitatively and independently of the initial ratio **2**:**1a** as poorly soluble, orange microcrystals (Scheme 1). The ^{31}P NMR spectrum of complex **3** shows a doublet at $\delta(^{31}P) = -66.9$ ($^1J(Rh,P) = 170$ Hz), and the complex was structurally characterized by X-ray crystal structure analysis (Figure 1).[4] Remarkably, the Rh center, which is located on a fourfold axis of symmetry, deviates by 0.24 Å from the plane of the square planar arrangement of the four phosphorus atoms (sum of angles at P within the ligand framework: 258°). The Rh–P bond lengths in **3** (2.276(1) Å) are slightly shorter than the ones in other known rhodium phosphirane complexes.[5]


1a
^{iPr}BABAR-Phos


1b
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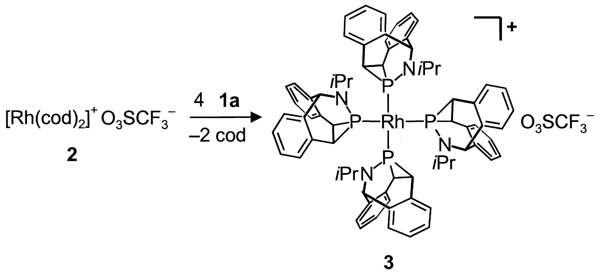

Scheme 1. Synthesis of complex **3**.

Reactions of the chloride-containing rhodium complex **4** with **1a** or **1b** in weakly coordinating solvents again give brown-red solutions containing several components (exchange-broadened ^{31}P signals in the positive or negative δ range). Only the reaction of **4** with **1b** in acetonitrile leads to one pure product **5** (formula $C_{96}H_{62}Cl_4F_{24}N_6P_4Rh_4$), which is obtained as sparingly soluble, deep brown microcrystals (Scheme 2).

Two of the Cl centers in **5** can be exchanged for poorly coordinating anions $X = O_3SCF_3^-$ or PF_6^- when it reacts with the silver salts **6a** and **6b**, respectively. Deep brown solutions ($\lambda_{max} = 660$ nm) are obtained from which the tetranuclear clusters **7a**, **b** were crystallized. Compound **7b** was also

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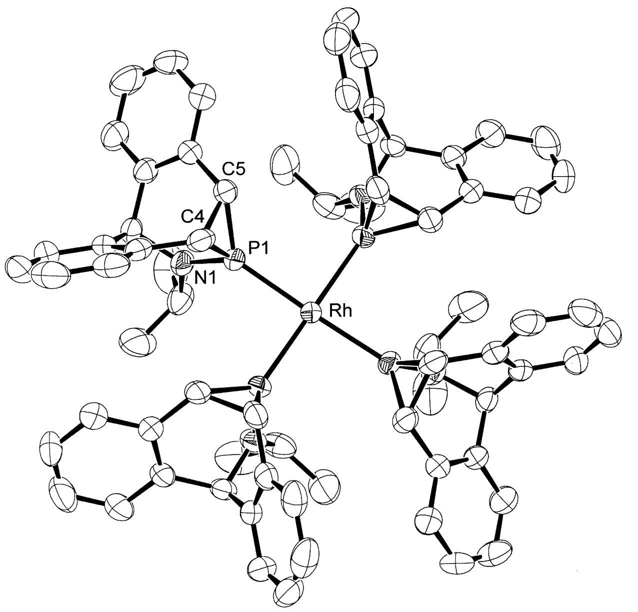


Figure 1. ORTEP plot of the cation of **3**; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh-P1 2.279(1), P1-N1 1.650(4), P1-C5 1.810(5), P1-C4 1.813(6), P1-C4 1.813(6), C4-C5 1.576(8); P1′-Rh-P1 89.367(8), P1″-Rh-P1 167.91(8), N1-P1-C5 102.2(2), N1-P1-C4 103.5(2), C5-P1-C4 51.6(2), N1-P1-Rh 124.4(2), C5-P1-Rh 129.8(2), C4-P1-Rh 122.8(2), C5-C4-P1 64.1(3), C4-C5-P1 64.3(3).

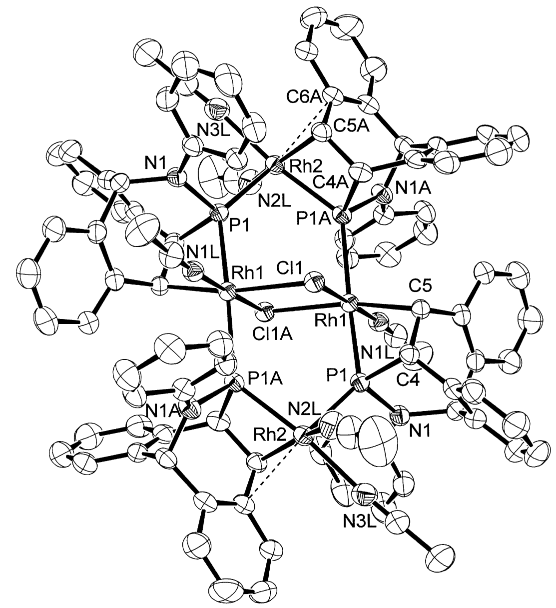
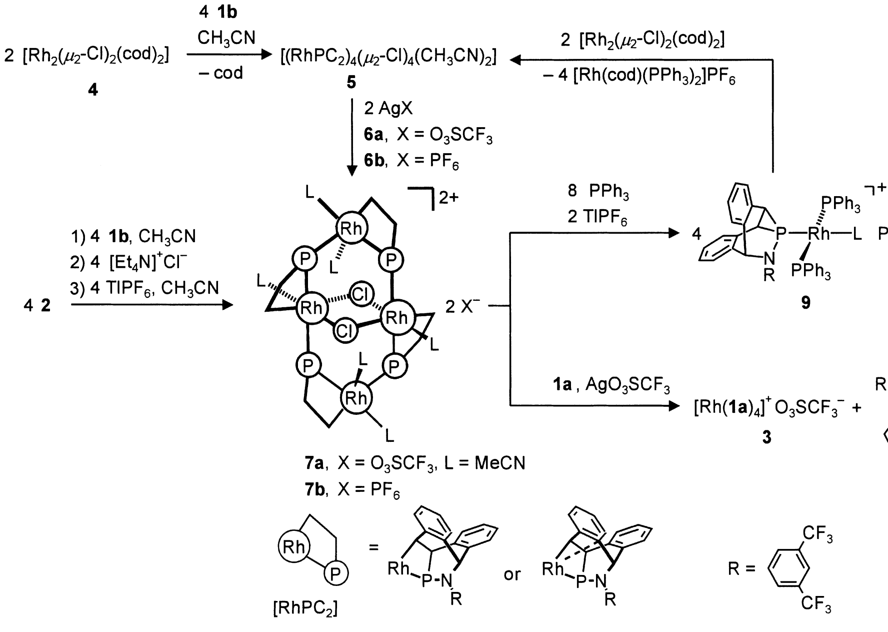


Figure 2. ORTEP plot of the centrosymmetric cation of **7b**; CF_3 groups and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-P1 2.305(1), Rh1-P1A 2.475(1), Rh1-Cl1 2.514(1), Rh1-Cl1A 2.363(1), Rh1-C5 2.131(5), Rh2-P1 2.258(1), Rh2-P1A 2.296(1), Rh2-C5A 2.082(5), P1-N1 1.705(4), P1-C4 1.857(5), C4-C5 1.557(7), P1A-N1A 1.724(4), P1A-C4A 1.865(5), C4A-C5A 1.528(7); P1-Rh1-P1A 170.61(4), P1-Rh2-P1A 95.68(5), Rh2-P1-Rh1 130.71(6), Rh2-P1A-Rh1 132.44(6), N1-P1-Rh1 110.9(2), C4-P1-Rh1 85.6(2), N1-P1-Rh2 110.1(1), C4-P1-Rh2 114.2(2), N1-P1-C4 98.0(2), N1A-P1A-Rh1 116.8(2), C4A-P1A-Rh1 112.0(2), N1A-P1A-Rh2 102.0(2), C4A-P1A-Rh2 86.5(2), N1A-P1A-C4A 98.5(2).

synthesized from **2** and **1b** in the presence of chloride ions and $TlPF_6$ (Scheme 2), and the result of a single-crystal X-ray structure analysis of **7b** is shown in Figure 2.[4]

Each rhodium center has inserted oxidatively into one of the P–C bonds of the PC_2 ring of the BABAR-Phos ligand. The resulting $[(RhPC_2)L_n]^+$ units ($RhPC_2$ denotes a Rh-inserted BABAR-Phos unit; fold angle along the P1–C5 vector 32°; L = MeCN, see Scheme 2) are bridged by the phosphorus centers and form a planar centrosymmetric $Rh_4(\mu_2\text{-}P)_4$ ring. A planar rhombic $Rh_2(\mu_2\text{-}Cl)_2$ ring is arranged perpendicular to this ring. The Rh1 centers lie in distorted octahedral coordination spheres. The Rh2 centers show a distorted square-pyramidal (5+1) coordination with an additional long contact to one of the arene carbon atoms (Rh2–C6A 2.470(5) Å). In view of the similar colors and ^{31}P NMR spectra, we assume that **5** has a comparable structure to those of **7a**, **b** in which the four acetronitrile ligands in the latter are replaced by two chlorine centers in **5**. These probably bridge the clusters in an intermolecular fashion to give a coordination polymer.



Scheme 2. Synthesis and reactions of tetranuclear 2-rhodaphosphetanes **5**, **7a**, **b**, and complex **9**.

A simple experiment allowed the assignment of the ^{103}Rh and ^{31}P NMR chemical shifts and revealed some aspects of the reactivity of **7b**. In a CH_3CN solution containing 10% CD_3CN, one sharp resonance signal integrating for 2.7 H is observed which is assigned to the single MeCN ligand bonded to Rh1. This ligand exchanges slowly with solvent molecules.

With this information, we assigned the ^{103}Rh resonance signal at $\delta = 3308$ to Rh1 by using ^{103}Rh-^{1}H HMQC spectroscopy; the Rh2 resonance signal is observed at $\delta = 2860$. The ^{31}P resonance signals were assigned by a sequence of ^{31}P-^{1}H COSY and ^{1}H-^{1}H NOESY experiments and are listed in Table 1. The insertion products **5** and **7a**, **b** are characterized by ^{31}P NMR signals in the positive δ range; the $^{1}J(^{103}\mathrm{Rh},^{31}\mathrm{P})$ coupling constant within a $\mathrm{RhPC_2}$ unit is generally smaller than the one between $\mathrm{RhPC_2}$ rings.

Table 1. Selected physical data for **3**, **5**, **7a** and **9**. J in Hz.

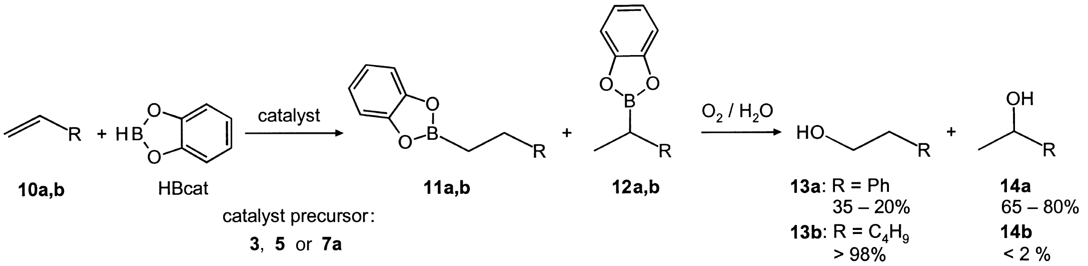
	$\delta(^{103}\mathrm{Rh})$	$\delta(^{31}\mathrm{P})$	$\delta(^{1}\mathrm{H})$ PCHCH	$\delta(^{13}\mathrm{C})$ PCHCH	$\lambda_{\max}$ [nm]	M.p. [°C]
3		-66.9 (d, $^{1}J(\mathrm{Rh,P}) = 170$)	3.05	23.3	382(sh)	> 230 (decomp)
5		44.0 (m, $^{1}J(\mathrm{Rh1,P1}) = 61$, $^{1}J(\mathrm{Rh2,P1}) = 206$, $^{2}J_{trans}(\mathrm{P1A,P1}) = 452$, $\mathrm{P_1}$), 7.7 (m, $^{1}J(\mathrm{Rh2,P1A}) = 55$, $^{1}J(\mathrm{Rh1,P1A}) = 84$, $^{2}J_{trans}(\mathrm{P1,P1A}) = 452$, P1A)				> 185 (decomp)
7a, **b**	3308 (Rh1), 2860 (Rh2)	27.6 (m, $^{1}J(\mathrm{Rh1,P1}) = 53$, $^{1}J(\mathrm{Rh2,P1}) = 153$, $^{2}J_{trans}(\mathrm{P1A,P1}) = 443$, P1), 6.6 (m, $^{1}J(\mathrm{Rh2,P1A}) = 80$, $^{1}J(\mathrm{Rh1,P1A}) = 83$, $^{2}J_{trans}(\mathrm{P1,P1A}) = 443$, P1A)	3.75 (m, $^{2}J(\mathrm{P1,H5}) = 21$, $^{1}J(\mathrm{P1A,H5}) = 5.6$, H5), 5.98 (d, $^{1}J(\mathrm{P1,H4}) = 9$, H4), 3.98 (m, $^{2}J(\mathrm{P1,H5A}) = 12$, H5A), 7.03 (m, H4A)	18.1 (m, C5A), 53.9 (m, C4A), 24.2 (m, C5), 58.9 (d,$^{1}J(\mathrm{P1,C4}) = 83$, C4)	660	> 176 (decomp)
9		-143.3 (sept., $^{1}J(\mathrm{P,F}) = 706$), -60.8 (dt, $^{1}J(\mathrm{Rh,P}) = 235$, $^{2}J_{cis}(\mathrm{P,P}) = 62$), 30.2 (dd, $^{2}J_{cis}(\mathrm{P,P}) = 62$)	2.68 (d, $^{2}J(\mathrm{P,H}) = 4$)	26.3 (d, $^{1}J(\mathrm{P,C}) = 5$)	418	> 133 (decomp)

When **7b** reacts with eight equivalents of $\mathrm{PPh_3}$ in presence of $\mathrm{TlPF_6}$, the mononuclear BABAR-Phos complex **9** is obtained quantitatively (Scheme 2). Probably, in the first reaction step each $[\mathrm{RhPC_2}]$ unit in **7b** is transformed into a $[(\mathrm{Rh^{III}PC_2})(\mathrm{PPh_3})_2]^+$ complex.[6b] By subsequent reductive P–C bond coupling the intact BABAR-Phos ligand is reconstituted ($\delta(^{31}\mathrm{P})$ of **1b** in **9**: -60.8, $^{1}J(\mathrm{Rh,P}) = 235$ Hz). On the other hand, when **4** is added to a solution of **9** in acetonitrile (Scheme 2), the tetranuclear cluster **5** is reformed and precipitates. Also when **7b** is treated with an eightfold excess of N-isopropyl-substituted BABAR-Phos **1a** in presence of $\mathrm{AgO_3SCF_3}$, ring closure regenerates **1b**, which is replaced by **1a** under formation of **3** (Scheme 2). Note that when **7b** is treated with **1b** under comparable conditions, the analogous $[\mathrm{Rh}(\mathbf{1b})_4]^+$ complex does not form. In their pioneering work, Marinetti, Mathey, Nixon, and co-workers have shown that metal centers insert irreversibly into three-membered $\mathrm{PC_2}$ heterocycles.[6] However, a reversible reaction as described here has not been observed yet to our knowledge. Comparison of the data of the isolated complexes **3**, **7a**, **b**, and **9** with the ^{31}P NMR and UV/Vis data obtained for the more complex red-brown reaction solutions mentioned above show that here also equilibria exist between compounds containing ring-opened and intact BABAR-Phos ligands. To this end we find that rhodium centers may reversibly insert into BABAR-Phos ligands **1a** and **1b**, the latter giving the more stable insertion products. The presence of "hard" donor ligands also leads to insertion products since these ligands stabilize the rhodium center in the formally +3 oxidation state.

Complexes **3**, **5**, and **7a** were tested as catalyst precursors in hydroborations.[7] A solution of catechol borane (HBcat) in THF was added to a mixture of an olefin (1-hexene or styrene) and 1 – 0.01 mol% catalyst in THF as solvent (Scheme 3).

All catalysts show activity comparable to other rhodium complexes (turnover frequency (TOF) with 0.1 mol% **3**: > 30000 h^{-1}). In reactions with styrene, the ratio of 2-phenylethanol (**13a**) (35 – 20%) to 1-phenylethanol (**14a**) (65 – 80%) is comparable to results obtained with $[\mathrm{RhCl(PPh_3)_3}]$ as catalyst. However, when a second catalytic run is started using $[\mathrm{RhCl(PPh_3)_3}]$ by re-addition of **10a** and HBcat to the reaction mixture (which turned dark), almost no catalytic activity is observed. On the other hand, the BABAR-Phos complexes **3**, **5**, and **7a** showed no drop of catalytic activity even after five catalytic cycles. The reaction mixtures did not change color and the intact BABAR complexes were identified by ^{31}P NMR spectroscopy.[8]

Like the uncomplexed ligands, BABAR-Phos complexes are stable under an atmosphere of pure $\mathrm{O_2}$, and even at 50 °C no destruction of **3** was observed. In contrast, $[\mathrm{RhCl(PPh_3)_3}]$ rapidly decomposes under formation of $\mathrm{Ph_3P{=}O}$. This re-



Scheme 3. Hydroborations with **3**, **5**, or **7b** as catalyst precursors.

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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 °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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[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 *P*4*nc*; $a = 16.5970(5)$, $c = 11.7946(3)$ Å; $V = 3248.9(2)$ Å^3; $Z = 2$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 52.72°$; 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, $\beta = 104.093(1)°$; $V = 6139.7(3)$ Å^3; $Z = 2$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 52.74°$; 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).

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[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**

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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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