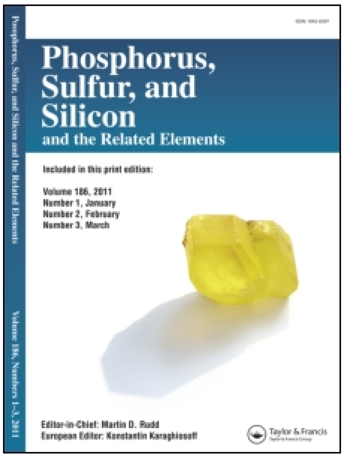

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Syntheses and Chemistry of Very Robust Phosphiranes

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SYNTHESES AND CHEMISTRY OF VERY ROBUST PHOSPHIRANES

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BABAR-Phos is a very stable polycyclic phosphirane that readily forms complexes with rhodium and platinum. Depending on the oxidation state and further co-ligands, either phosphirane complexes or metallaphosphetanes (as products of a metal insertion) prevail. However, these insertion reactions are reversible. These rhodium BABAR-Phos complexes are active catalysts for the selective hydroboration of olefins.

Keywords: Catalysis; hydroboration; phosphiranes; rhodium complexes

INTRODUCTION

In many homogeneously catalyzed reactions, phosphane transition metal complexes are used as catalyst precursors. A severe problem is the sensitivity of the non-complexed phosphanes and their complexes towards oxygen. The Wilkinson catalyst, $[RhCl(PPh_3)_3]$ (**1**) becomes rapidly oxidized upon exposure to oxygen, and $Ph_3P{=}O$ is formed. Apart from catalyst destruction, this may also significantly alter the selectivity of the catalyzed reaction. In the hydroboration reaction of styrene with catechol borane, HBcat, the ratio of 1-phenylethanol (1-PhEtOH) to 2-phenylethanol (2-PhEtOH) is highly dependent on the quality of **1** (1-PhEtOH prevails with non-oxidised **1**).[1] A simple molecular orbital (MO) diagram for an eight valence electron configurated: AB_3 species shows that with increasing pyramidalisation at A, the energy of the highest occupied orbital (HOMO) decreases, thus rendering AB_3 more difficult to oxidize. On the other hand, AB_3 becomes a poorer donor

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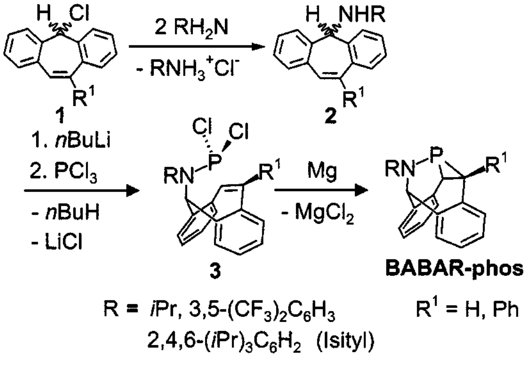
towards a metal center, and therefore may be only a weakly binding ligand. In phosphiranes, compounds containing a three-membered PC_2 heterocycle, a very small $\Sigma^{\circ}(P)$ can be realized, and we decided to explore their coordination chemistry to transition metals relevant to catalysis.[2–3]

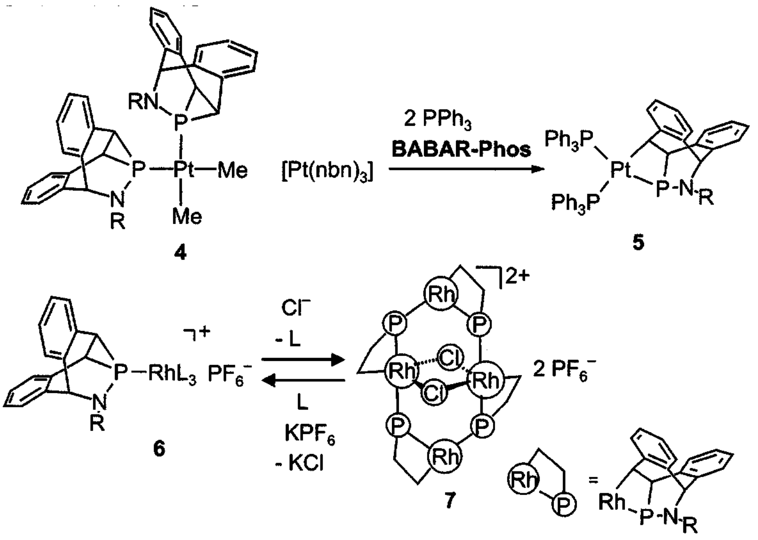
RESULTS AND DISCUSSION

The synthesis of BABAR-Phos is shown in Scheme 1. Starting from chlorocycloheptatrienes (dibenzotropylidenylchlorides) **1**, the amines **2** and after lithiation and reaction with PCl_3, the (tropylidenylamino)dichlorophosphanes **3** are obtained in excellent yields. Usually the dehalogenation reaction, $RPCl_2 + Mg \rightarrow (RP)_{\infty} + MgCl_2$, leads to mixture of polyphosphanes; however, due to the proximity of the PCl_2 group to the C=C unit, the intermediate [tropNR-P=Mg] is intercepted in a [2 + 1] cycloaddition reaction, giving BABAR-Phos in very high yields (>90%).[4] BABAR-Phos is robust and does not react with O_2, S_8, alkylating reagents, aqueous base, or acid.



SCHEME 1 Synthesis of BABAR-Phos.

The co-ordination chemistry of BABAR-Phos platinum and rhodium complexes was investigated (Scheme 2). While the reaction with $PtMe_2$(cod) leads quantitatively to the stable platinum(II) complex **4**, reaction with platinum(O) complexes like $Pt(nbn)_3$ (nbn = norbornene) furnishes the platinaphosphetane **5**.[5] However, the metal insertion can be reversed, and when **5** is reacted with malenic anhydride (malan), the uncomplexed BABAR-Phos is formed beside $Pt(PPh_3)_2$ (malan).



SCHEME 2 Synthesis of BABAR-Phos metal complexes.

These unusual insertion/de-insertion reactions are dependent on the reaction conditions, as is illustrated by the reversible transformation **6** $\leftrightarrows$ **7**.[6] When L is a labile ligand (i.e., acetonitrile), addition of Cl^- to **6** leads to the quantitative formation of **7**. When a strongly binding ligand $L = PPh_3$ is added to **7** and Cl^- is exchanged for the weakly coordinating PF_6^- anion, the complex **6** ($3\ L = 2\ PPh_3$, MeCN) is reconstituted quantitatively.

The influence of the BABAR-Phos substituents R and R^1 on the selectivity in the catalyzed hydroboration of styrene was investigated (Figure 1). The selectivity and activity depends strongly on steric factors and the BABAR-Phos/Rh ratios. The highest selectivity for 1-PhEtOH was obtained with the electron withdrawing aryl substituent $R = 3,5\text{-}(CF_3)_2C_6H_3$ resting in conjugation via the nitrogen center with the PC_2 ring and $R^1 = Ph$ at the ring carbon atom. Both the activity and selectivity augment with increasing BABAR-Phos/Rh ratios. When R stands for a bulky alkyl or 2,6-substituted aryl group and no substituent is bonded to the PC_2 ring, the selectivity is rather low. In any case, the catalyst remained active and could be used for several catalytic runs.

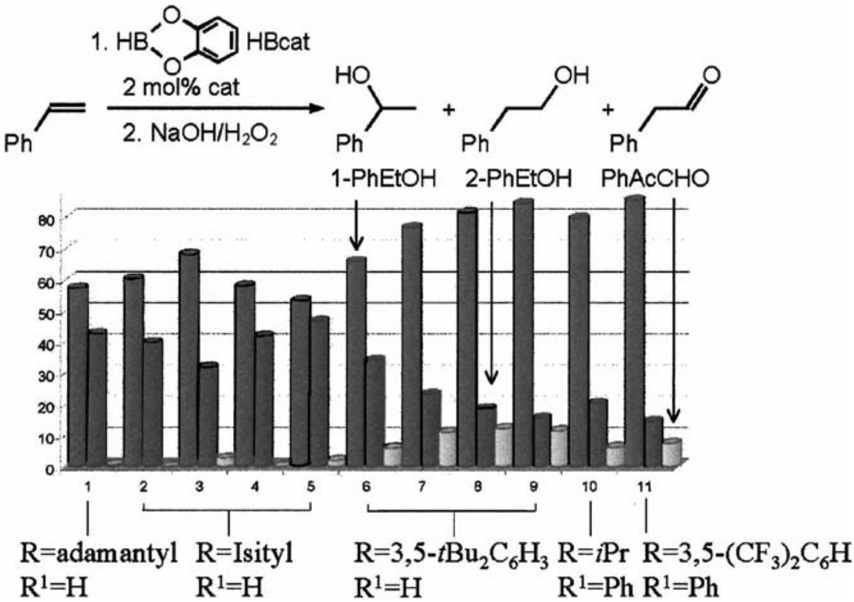


FIGURE 1 Hydroboration of styrene with catechol borane, HBcat, using 2 mol% $[Rh(cod)_2]O_3SCF_3$/BABAR-Phos catalyst precursors in thf at $T = 298$ K for 1 h. The substituents R, R^1, and/or BABAR-Phos/Rh ratio were varied: Entry 1: ratio 1/1; Entries 2–5: ratios 1/1, 2/1, 3/1, 4/1; Entries 6–9: ratios 1/1, 2/1, 3/1, 4/1; Entry 10: preparation with $[Rh(\mu_2\text{-}Cl)(cod)]_2$, ratio 3/1; Entry 11: ratio 3/1.

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