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Bend the Coin Your Way: Ligand Design and Main Group Element Chemistry

Carsten Böhrer, Torsten Büttner, Stephan Deblon, Gionata Frasca, Gilles Frison, Jens Geier, Cécile Laporte, Florian Läng, Sandra Loss, Pascal Maire, Nicola Pè, Hartmut Schönberg, Markus Scherer, Christoph Widauer, and Hansjörg Grützmacher*

Abstract: The dibenzo[a,d]cycloheptatrienyl residue is introduced as platform for the high-yield synthesis of new rigid phosphanes (tropp ligand system) and phosphiranes (BABAR-phos); strained three-membered heterocycles. With tropp as ligands, transition metal complexes with unusual low oxidation states at the metal center could be prepared and isolated. Especially mononuclear paramagnetic rhodium(0) and iridium(0) complexes could be studied in detail. The BABAR-phos compounds show very high thermal and chemical stability, *i.e.* they are remarkably stable against oxygen, sulfur, strong alkylating agents, and aqueous acid and base. Rhodium(I) complexes with BABAR-phos proved to be highly stable active catalyst precursors for hydroborations.

Keywords: Catalysis · Olefin complexes · Paramagnetic organometallics · Phosphanes · Phosphiranes.

Introduction

It is an old and very simple trick to bend a coin in order to predict the side onto which it falls when it is flipped. Used in gambling, a small fortune may be carried away (provided the gambler stopped before his trick was uncovered). Translated into chemistry it means that incorporating directionality into a molecule makes the realization of a desired functionality or property according to a rational plan more likely. There are numerous examples proving this simple rationale. Especially in supramolecular chemistry, ‘pre-organization’ of the building blocks plays an essential role. However even more general, also in molecular transition metal and main group element chemistry this ‘bend-the-coin-principle’ may be successfully applied because, as in supramolecular assemblies, the binding forces in many of these compounds are relatively weak and often a multitude of (not always foreseen) reaction channels are

available. As a simple example, we may cite the reaction between an organic halide, R_3C-X , and an alcohol, $R'-OH$, which affords an ether linkage R_3C-O-R' . In phosphorus chemistry, the analogous reaction between R_2P-X and $R'-OH$ may give the corresponding alkoxide, R_2P-O-R' , and/or the oxide $R_2R'P=O$. Generally, the selectivity of reactions with transition metal or main group element compounds of the higher periods is more difficult to control.

In recent years the Grützmacher group has made use of the dibenzotropyliene (IUPAC: dibenzo[a,d]cycloheptatriene) **1** (Fig. 1) as a platform for the synthesis of some transition metal complexes and phosphorus compounds which show unique properties.

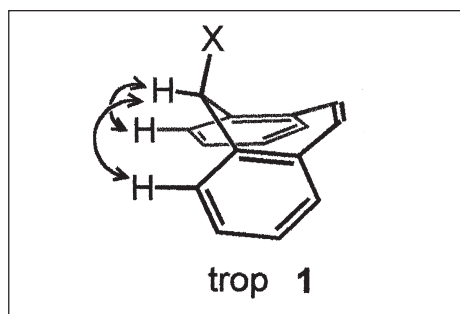


Fig. 1. Schematic representation of the tropp-platform. The double arrows indicate repulsive H–H interactions which force the molecule into a rather rigid boat conformation.

Due to repulsive interactions between the hydrogen atom in the 5-position of the central cycloheptatriene ring and two hydrogen centers on the benzo groups, the seven-membered ring adopts a boat conformation in which the functional group X takes an axial position pointing towards the C=C bond: The coin is bent!

Stable Transition Metal Complexes with Unusual Low Formal Oxidation States

Although the olefin complex $K[PtCl_3(C_2H_4)]$ was detected as early as 1827 by the Danish pharmacist Zeise, ideas about the structures of olefin complexes and the bonding of the C=C unit were not developed until more than 100 years later through the pioneering investigations of Dewar, Chatt, and Duncanson and their co-workers. Nowadays we have a rather precise picture about the binding of an olefin to a metal when compared to an ‘ordinary’ donor ligand, like a phosphane, for example. This is illustrated in Fig. 2.

It can be shown that phosphanes bind strongly *via* $L \rightarrow M$ σ -donation while olefins behave as σ -donors and equally well as π -acceptors but the binding energies are comparatively weak [1]. Indeed, olefins are frequently used as easily substi-

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tutable place-holders for 'vacant' coordination sites when reactive electronically and co-ordinatively unsaturated transition metal fragments are to be generated.

We have mounted a phosphanyl group on the tropp platform and constructed *tropylidene* phosphanes (named tropp) as a new chelating ligand system (Scheme 1) [2]. In a few simple steps starting from the commercially available dibenzosubernone, these chelating ligands can be prepared in large quantities. Due to the fixed arrangement of the PR_2 and olefinic binding site, these ligands form very stable olefin complexes (some complexes melt without decomposition above 250 °C).

Because the C=C unit cannot escape from the coordination sphere, its acceptor properties can now be used to prepare metal complexes in unusual formal low oxidation states. For example, the first stable mononuclear rhodium(0) [3] and iridium(0) [4] complexes were synthesized either by chemical or electrochemical reduction. An example is shown in Fig. 3.

At remarkably low potentials the cationic 16-electron complexes $[\text{M}^+(\text{tropp})_2]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) are reduced to give the 17-electron paramagnetic species $[\text{M}^0(\text{tropp})_2]$ which can be further reduced reversibly to the 18-electron anionic complexes $[\text{M}^-(\text{tropp})_2]^-$. All species were isolated and completely characterized including X-ray analyses, high resolution EPR spectroscopic investigations (in collaboration with Arthur Schweiger and his co-workers at the ETH), and electrochemical measurements (in collaboration with Manfred Rudolph in Jena). Furthermore, we began to study in detail the reactivity of the previously elusive 17-electron complexes [5] which are

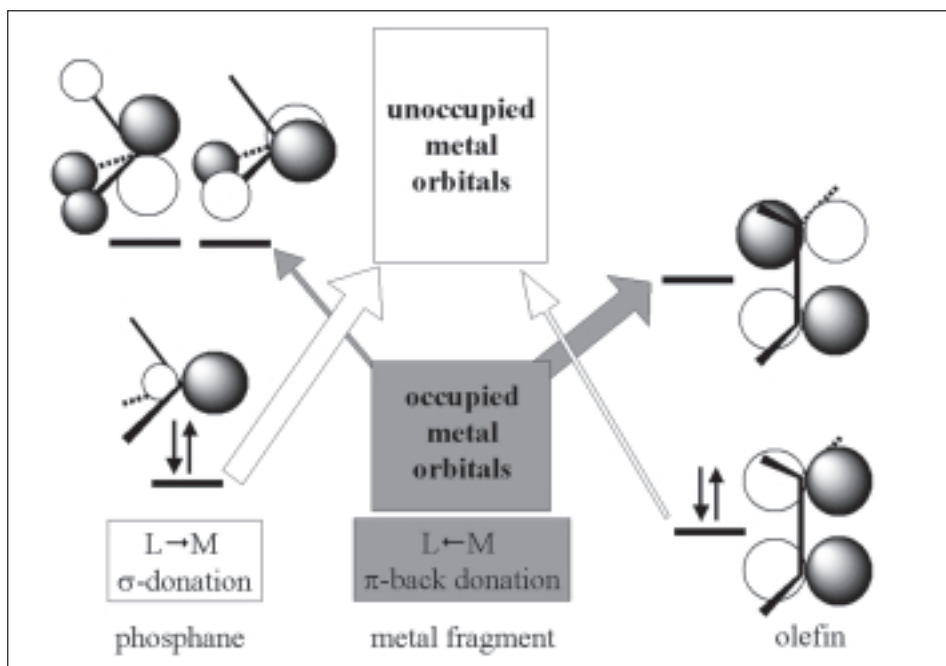
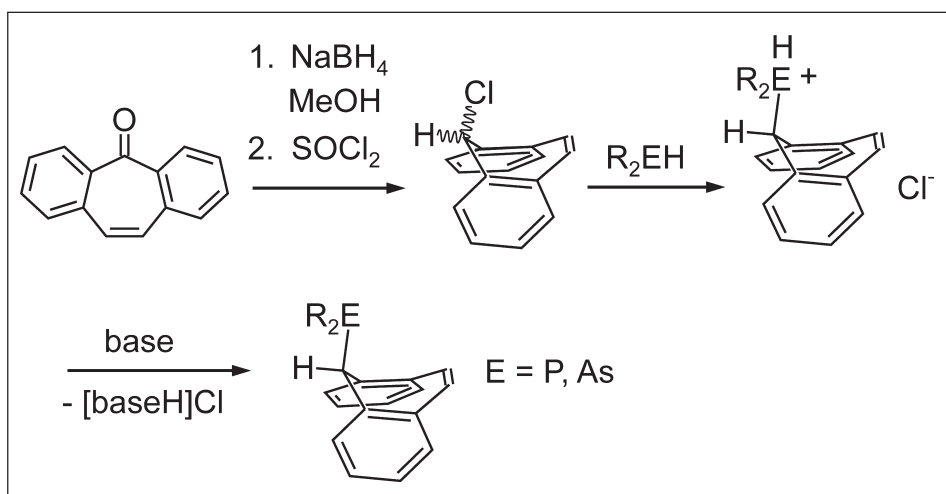


Fig. 2. Schematic picture of the bonding in transition metal phosphane and olefin complexes. White arrows indicate L \rightarrow M σ -donation, gray arrows L \leftarrow M π -back donation. The thickness of the arrow gives a qualitative indication of the contribution to the binding energy.



Scheme 1. Synthesis of the tropp ligand system.

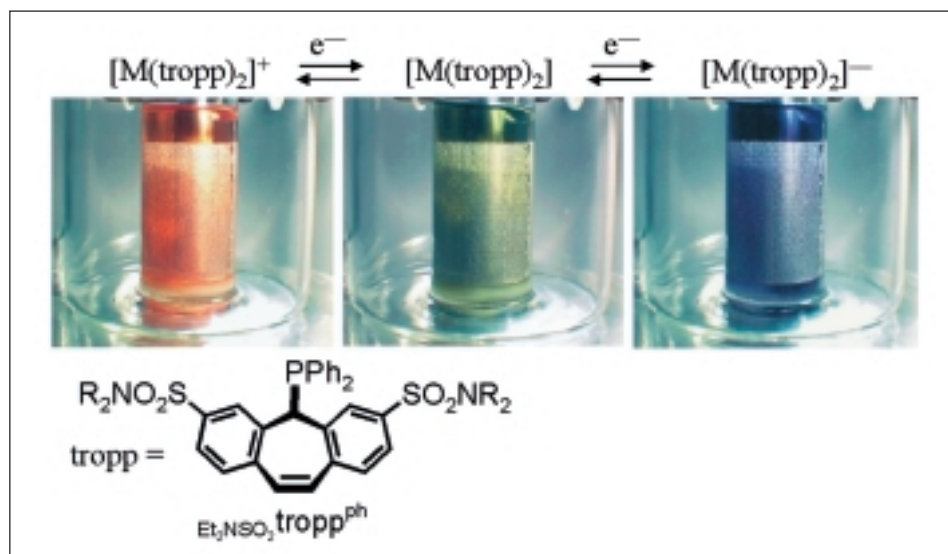


Fig. 3. 'Chemistry is beautiful': Electrochemical reduction of an orange $[\text{M}(\text{tropp})_2]^+$ complex cation to a green $[\text{M}(\text{tropp})_2]$ organometallic radical and further to a deep-blue anionic $[\text{M}(\text{tropp})_2]^-$ complex on a platinum net. In the presented example, rhodium was chosen as metal and a sulfonamide substituted tropp ligand (see formula below). This combination gives rise to especially low reduction potentials ($E^{1/2} = -0.679 \text{ V}$; $E^{2/2} = -0.932 \text{ V}$ vs. Ag/AgCl , $T = 298 \text{ K}$). In tropp compounds the superscript indicates substituents bonded to phosphorus, the subscript substituents bonded to the hydrocarbon unit.

suspected to play a crucial role in some important catalytic reactions, such as photolytic water splitting, hydroformylations, and even C–H activation chemistry (the ‘holy grail’ of homogeneous transition metal catalysis). To this end we learned:

- Independent of the formal oxidation state, the $[M(\text{tropp})_2]^n$ ($n = +1, 0, -1$; $M = \text{Co}, \text{Rh}, \text{Ir}$) complexes have very similar structures showing a severe distortion from a square plane towards a tetrahedron.
- While the 16-electron and 18-electron complexes $[M^{+1}(\text{tropp})_2]^+$ and $[M^{-1}(\text{tropp})_2]^-$, respectively, are stereochemical rigid, the 17-electron complexes $[M^0(\text{tropp})_2]$ are highly dynamic (intramolecular rotation of the tropp ligands).
- The paramagnetic complexes $[M^0(\text{tropp})_2]$ are surprisingly *unreactive*. It turns out that because the rate of the disproportionation reaction $2 [M^0(\text{tropp})_2] \rightleftharpoons [M^{+1}(\text{tropp})_2]^+ + [M^{-1}(\text{tropp})_2]^-$ is sufficiently fast ($k \approx 10^4$), the observed reactivity is evoked by the diamagnetic complexes rather than by the paramagnetic one.

This latter observation has led us to develop, by a simple modification of the tropp system, new paramagnetic cobalt(0), rhodium(0), and iridium(0) complexes which are even stable under aqueous conditions. Such complexes may find interesting applications as marker-molecules and in the development of redox-devices, topics which are now under current investigation.

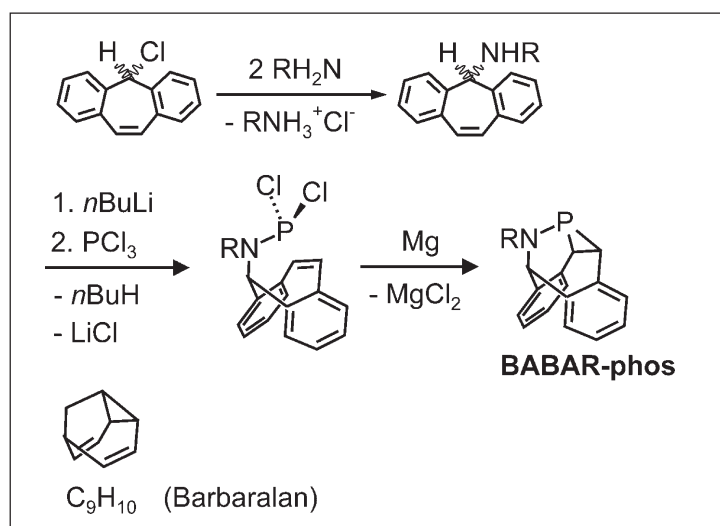
The Synthesis of Highly Robust Phosphiranes

At least since the discovery of the homogeneously catalyzed hydrogenation with the complex $[\text{RhCl}(\text{PPh}_3)_3]$ – the famous Wilkinson catalyst – in the mid-sixties of the past century, phosphanes have played an important role as ligands in transition metal chemistry. Indeed, there are many catalytic reactions in which phosphane complexes proved to be by far the most effective catalysts. However, a severe problem arises when working with phosphanes and their complexes: These compounds are intrinsically oxygen sensitive which leads to catalyst deactivation.

A simple qualitative MO diagram shows that with a decreasing sum of bond angles around the phosphorus atom, $\Sigma^\circ(\text{P})$, the energy of the highest occupied orbital (HOMO) corresponding to the

lone pair at the phosphorus atom decreases which should make a phosphane more stable against oxidation. The smallest $\Sigma^\circ(\text{P})$ one can think of should be obtained when the phosphorus atom is incorporated into three-membered rings (*i.e.* in P_4 , $\Sigma^\circ(\text{P})$ equals 180°). Realistic ligands may be PC_2 -heterocycles – phosphiranes ($\Sigma^\circ(\text{P}) \approx 250^\circ$) – which are known since 1963. But their synthesis is often laborious and they remained laboratory curiosities with limited use in co-ordination chemistry [6]. The particular structural features of the tropp platform allowed the simple synthesis of a new type of phosphiranes in which the PC_2 -heterocycle is embedded in a polycyclic framework (Scheme 2).

The critical step in this synthesis is the dehalogenation reaction with elemental magnesium. Usually such reactions lead to a messy mixture of polyphosphanes, $\text{RPCl}_2 + \text{Mg} \rightarrow (\text{RP})_\infty + \text{MgCl}_2$. However, because in the dichloro(tropamino)phosphane the PCl_2 group is placed in proximity of the C=C unit (closest P–C contact $\approx 3.2 \text{ \AA}$) the intermediate magnesium phosphinidene complex, $[\text{tropp}=\text{P}=\text{Mg}]$, is trapped by the C=C unit in an intramolecular [2+1] cycloaddition reaction in excellent yields ($> 90\%$). In analogy to the hydrocarbon C_9H_{10} , *barbaralane*, we name the new phosphiranes BABAR-phos. We wish to emphasize, that despite the odd look of BABAR-phos, these compounds can be made in few



Scheme 2. Synthesis of BABAR-Phos.

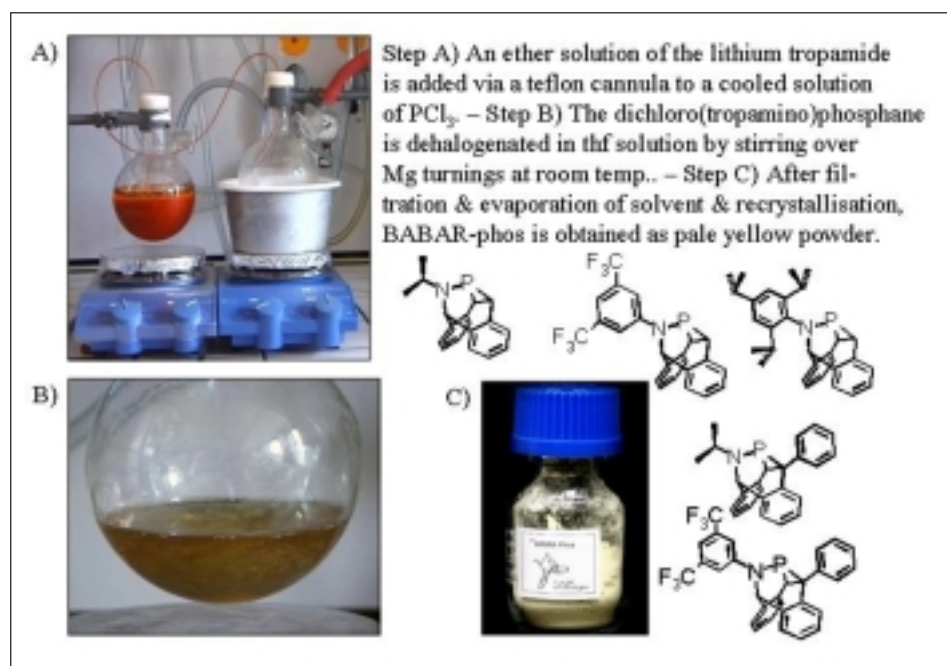
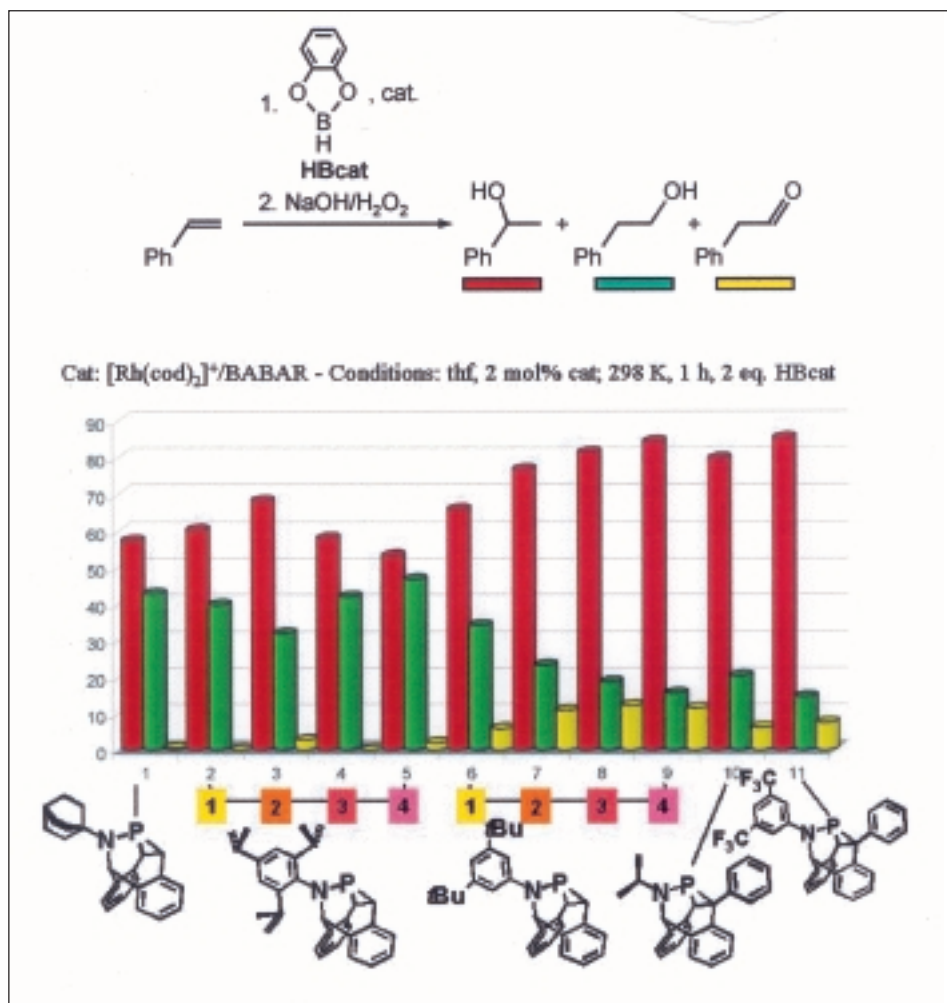


Fig. 4. The synthesis of BABAR-phos can be easily performed in standard glassware (*i.e.* 250 ml balloons) giving about 10 g ($> 90\%$) of product in a short time (1 d).



Scheme 3. Hydroboration of styrene with catechol borane, **HBcat**, using various rhodium BABAR-phos complexes as catalyst precursors. The ratio of 1-phenylethanol (red) : 2-phenylethanol (green) : 2-phenylacetaldehyde (yellow) depends on the BABAR-phos ligand and the rhodium/ligand ratio (the numbers below entries 2–5 and 6–9 indicate the equivalents of BABAR-phos).

steps in large quantities using standard laboratory equipment as shown in Fig. 4.

BABAR-phos truly has some unique properties: It does not react, as phosphanes usually do, with oxygen or sulfur even under harsh conditions. It does not react with strongly alkylating agents such as Me-SO₃CF₃ (magic methyl) and is stable against aqueous base or acid. Various substituents can be introduced at the nitrogen center and it should be noted that BABAR-phos compounds bearing a C-bonded phenyl substituent are chiral whereby principally applications in enantioselective catalysis can be envisioned.

BABAR-phos readily forms complexes with relevant transition metals such as Rh(I), Ir(I), Pt(II), Pt(0), etc. [7][8]. These complexes proved to be active catalysts for hydrosilylations and hydroborations. A representative example for a catalyzed hydroboration reaction is shown in Scheme 3 [9]. The best results were obtained with the BABAR-phos ligand (entry 11). The activity of the catalysts was comparable to the ones described previously in the literature. However, the stability of BABAR-phos complexes is by far superior. Up to seven

subsequent catalytic runs could be performed without significant loss of activity or selectivity. Future work will be directed towards the use of BABAR-phos ligands in enantioselective catalysis, their use in new catalytic reactions, and immobilization on inorganic supports or organic polymers.

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