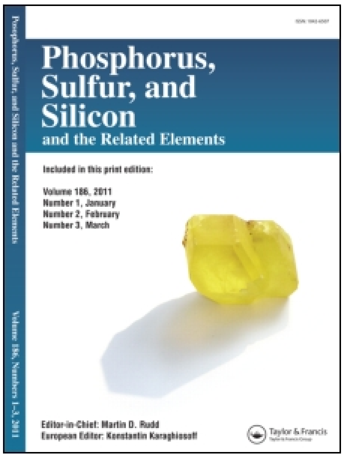

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Ligands Make the Catalyst: Synthesis of Novel Functionalized Phosphines

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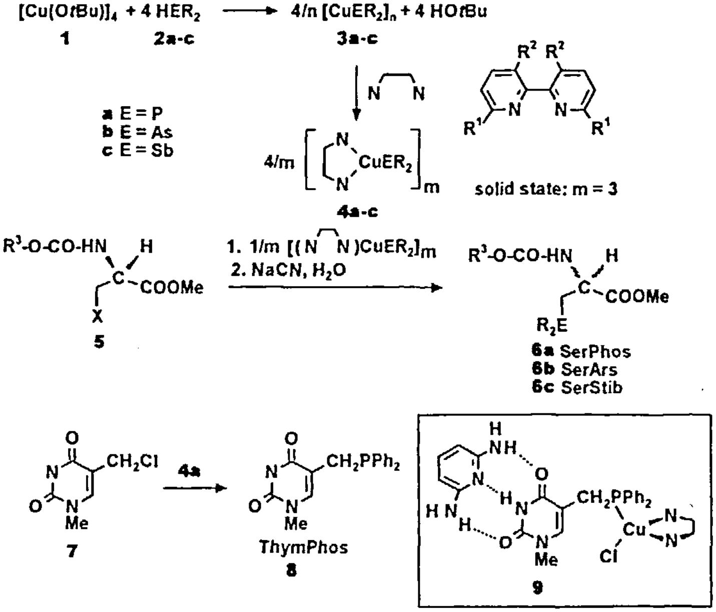
Many catalytic active transition metal complexes contain phosphines as ligands which control decisively the activity and selectivity of the catalyst. Therefore synthetic methods which allow the *preparation of highly functionalized phosphines are needed to match the increasing demands for* higher activity and selectivity in catalytic processes. In this report we introduce a simple general new method for the synthesis of phosphines, arsines, and stibines. This allowed for example the preparations of phosphines based on serine and thymine derivatives (*Ser*Phos and *Thym*Phos, respectively).

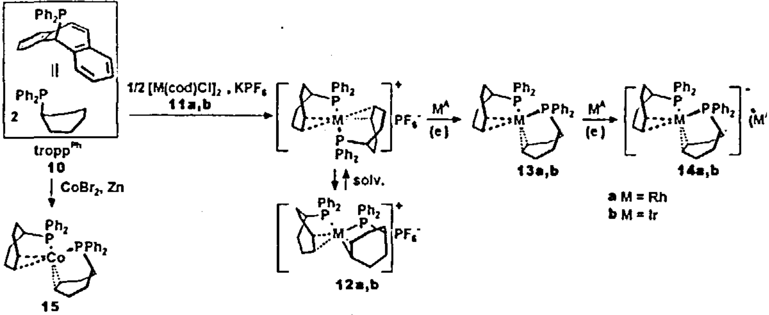
Scheme 1



Organocopper compounds are long known as selective reagents in C-C bond forming reactions. We found that copper pnictogenide bipyridine (bipy) complexes **4a-c** may be used in selective P-C bond forming reactions (Scheme 1)[1]. In this reaction carbon halide bonds are selectively replaced by ER_2 units (E = P, As, Sb) which allowed the synthesis of amino acid derivatives **6a-c** or the preparation of the nucleo base derivative **8**. The previously unknown phosphine **8** (ThymPhos) allowed the planned synthesis of a complex containing a supra molecular phosphine (*SUMO*-phos, **9**) which was characterized by an X-ray analysis.

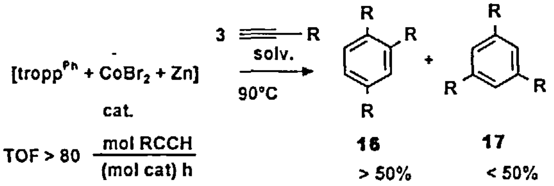
In the following, we will show examples how properly designed functional phosphines help to synthesize new transition metal complexes which in turn may enhance the efficiency of catalytic reactions. It may be assumed, that the reactions shown above are electron transfer reactions in which the d^{10}-Cu(I)/ d^9-Cu(II) redox couple is involved. We thus became interested in the synthesis of organometallic compounds containing tetracoordinated d^9/d^{10}-transition metal centers. In particular, it was tempting to use rhodium or iridium as metals because of their high catalytic potential which eventually may lead also to novel approaches in phoshine synthesis. The search for a suitable functionalized phosphine which would stabilize the d^9- and d^{10}-oxidation states on these metals led us to the synthesis of *trop*ylidene *p*hosphines **10** (tropp) shown in Scheme 2[2].

Scheme 2. (For clarity the benzo groups are omitted).



Tropp ligands **10** have a concave rigid binding site in which transition metals are tightly bonded by a phosphorus center and the olefinic unit of the central seven-membered carbocycle. Indeed, the cationic d^8-rhodium and iridium complexes **12a,b** can be easily reduced by alkali metals M^A = Li, Na, K, Cs to give remarkably stable neutral d^9- and anionic d^{10}-metal complexes **13a,b** or **14a,b** in almost quantitative yield[3]. As in copper redox enzymes, only minor structural changes are observed between the paramagnetic d^9- and anionic d^{10}-complexes, respectively, and in both oxidation states the metal center adopts a coordination sphere intermediate between square planar and tetrahedral. This explains the very low reduction potentials (E < -1.3 V) when compared to previously reported values[4] and we currently explore the use of tropp complexes as catalysts in electrocatalytic cross-coupling reactions like $R_2P\text{-}X + R^1\text{-}X \rightarrow R_2P\text{-}R^1$. The unique properties of tropp ligands in stabilizing formally low oxidation states of organometallic complexes is seen as well in the simple preparation of the neutral paramagnetic d^9-cobalt(0) complex **15** from $CoBr_2$ and zinc powder in excellent yield. Again, the tetrahedral complex **15** is very stable (it can be even handled shortly on air. The potential of the tropp ligand in catalysis was demonstrated by preliminary experiments as for instance the cyclotrimerization of alcynes to arenes which proceeds with higher efficiency than the corresponding reactions employing Cp*Co-complexes as catalysts (Scheme 3).

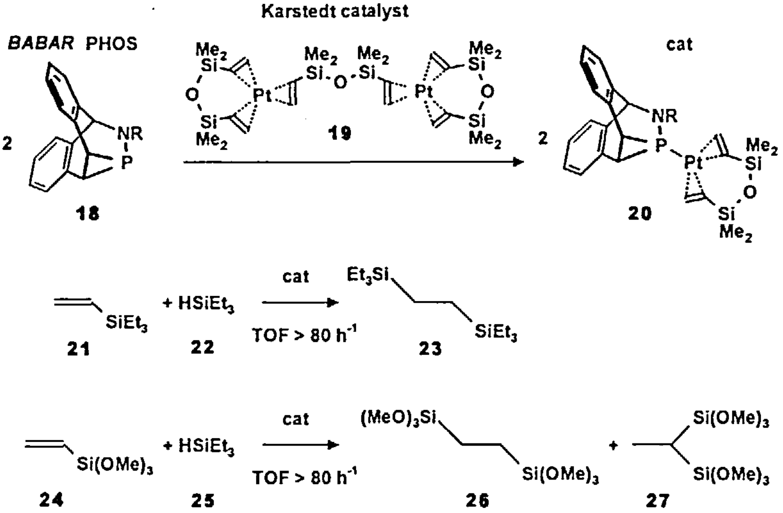
Scheme 3



Interestingly, the sterically more crowded isomer **16** is formed in excess over the symmetric isomer **17** when R = Ph.

We have finally used the tropylidene "platform" for the preparation of a further functionalized phosphine with particular electronic properties. The novel tricyclic phosphirane dibenzo-phospha-aza-barbaralane **18** (*BABAR*-Phos) is obtained in high yields and in contrast to other phosphiranes[5] is indefinitely stable at room temperature and can be handled on air [R = iPr, 3,5-$(CF_3)_2C_6H_3$][6].

Scheme 4



Because of their electronic properties[6] (low nucleophilicity, high inversion barriers, insensitivity against oxidation) phosphiranes shall serve as interesting ligands for transition metal catalysts. In particular, those catalytic processes were the reductive elimination as the final step within a catalytic cycle determines the overall efficiency may profit from strong trans influence of phosphiranes. Indeed, we found that BABAR-Phos shows an excellent performance in hydrosilylations. Not only is the complex **20** the first stable Pt(0) phosphirane complex, it also has the same activity as the industrial used Karstedt catalyst **19** but a better selectivity (**26** > 70%, **27**

< 30%) and a much higher stability. Several catalytic cycles were run to completion without loss of activity of the platinum-BABAR-Phos catalyst.

We are confident, that novel phosphines like *SerPhos*, *ThymPhos*, *SUMO*-phosphines, *tropp*, and *BABAR-Phos* will open up new horizons in the application of phosphines as ligands and even may lead to the development of new catalytic reactions.

Acknowledgments

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