The Bluemel Group Research Interests

The research interests of the Bluemel group span a wide range, from organic and organometallic synthesis, through catalysis and the surface chemistry of amorphous materials, to solid-state NMR spectroscopy. Over the years, our research has expanded especially into the following different areas:

(1) Immobilized Catalysts

The immobilization of catalysts is of growing interest, because the advantages of heterogeneous catalysts can, in principle, be combined with those of homogeneous catalysts. Immobilized or surface-bound homogeneous catalysts are easy to recycle, and they can be highly active and selective. Furthermore, they are amenable to systematic design. Interesting results are obtained with both monometallic and heterobimetallic systems, such as the Sonogashira Pd(0)/Cu(I) catalyst.

(2) The Surface Chemistry of Oxide Materials

Especially in this area the immobilization step requires a thorough understanding of the surface chemistry of the oxide support materials. Therefore, we investigate not only the adsorption and reactivity of metal complexes and linkers with oxide surfaces, but also their mobilities on the surface.

(3) Solid-State NMR Spectroscopy

The most powerful analytical tool for investigating amorphous materials is solid-state NMR spectroscopy. We optimized this method especially for surface-bound species, and in the meantime we can also study reactions on surfaces *in situ*, or analyze the nature of our anchored linkers or catalysts.

1. Immobilized Catalysts

The easiest way to bind homogeneous catalysts to an oxide support is using a bifunctional linker,[1] as in the examples shown here:[2-4]
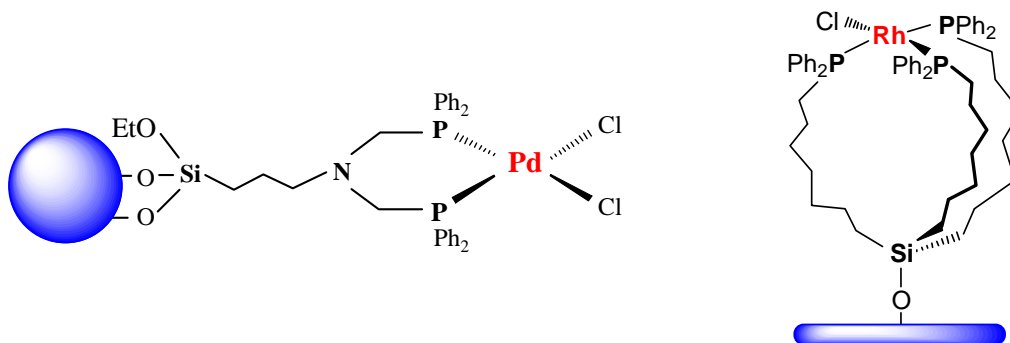

Since most transition metal complexes form stable phosphine adducts, functionalized phosphines such as $Ph_2P(C_6H_4)Si(OEt)_3$ or $Ph_2P(CH_2)_3Si(OEt)_3$ can be used. Chelating phosphines, as shown above, also lead to firmly bound, well-defined catalysts. Since phosphines with anchoring functionalities, such as ethoxysilane groups, are not abundant in the literature, a substantial part of our efforts goes into developing convenient new syntheses of various linkers. One example is shown in Scheme 1.[2,3]
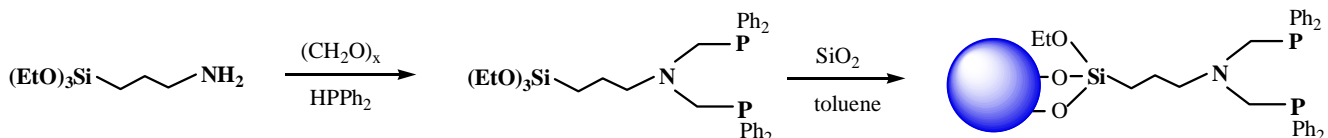

Scheme 1. One-pot synthesis of chelate phosphines with ethoxysilane groups.[2,3]

As a convenient alternative to ethoxysilane groups for anchoring ligands and metal complexes, one can exploit strong electrostatic interactions: We have recently demonstrated that phosphines can be quaternized by the combined action of the silica surface and ethoxysilane groups, forming ethylphosphonium salts (Scheme 2).[5,6]
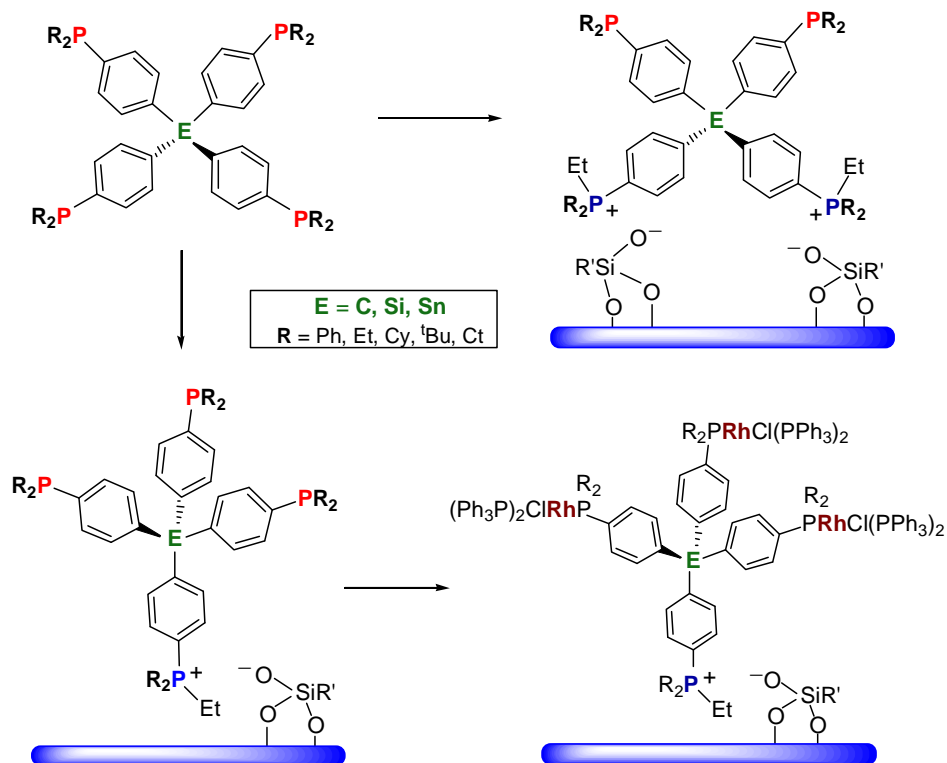
Scheme 2. Immobilized linker system with a tetraphenylelement backbone.[5,6]

This has led us to develop a new generation of linkers, starting from tetraphosphines with rigid backbones[5,6] (Scheme 2), that can prevent interactions of the catalysts with the reactive oxide surface and their dimerization, and thus prolong their lifetimes. The new linkers have the unprecedented feature that one, two, or three phosphine groups can be bound selectively to the surface via electrostatic interactions, while one to three phosphine moieties remain for later metal complexation, as shown in Schemes 2 and 3.[5,6] The Rh complex immobilized by the linker scaffold shown in Scheme 3 catalyzes the hydrogenation of dodecene and can be recycled 30 times in a batchwise manner.[5]
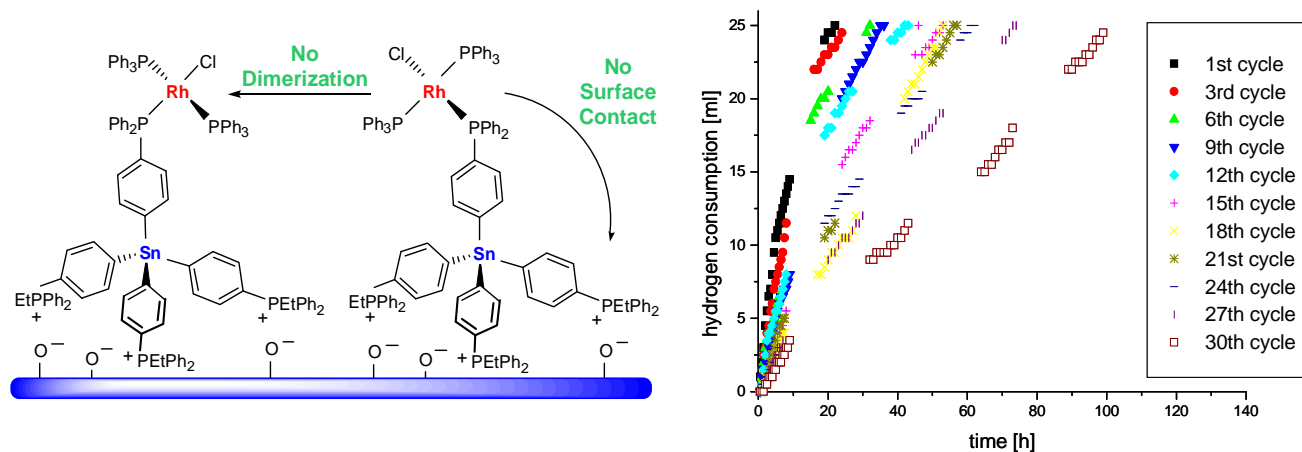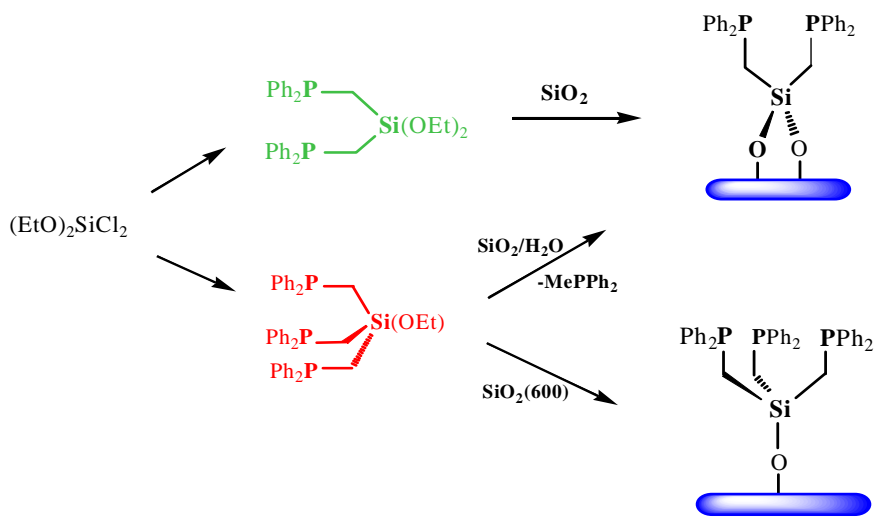

Scheme 3. An example of a Rh hydrogenation catalyst that can be recycled a record 30 times.[5]

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Importantly, in contrast to catalysts immobilized via linkers with long alkyl chains that are equally active and recyclable,[4] no Rh nanoparticle formation is observed with rigid linker scaffolds. The formation of metal nanoparticles is investigated in detail using immobilized Ni(0) catalysts[1] at the moment.

We have also had ongoing interests in immobilized heterobimetallic systems. For example, the Sonogashira reaction involves the coupling of aryl acetylenes with aryl halides through the combined action of Pd(0) and Cu(I) complexes,[2,3] (see also NMR section **3**, below). We developed silica-bound catalysts that could be recycled 18 times without major loss of activity.[3]

2. Surface Chemistry of Oxide Materials

The success of an immobilized catalyst is crucially dependent on the choice of the proper support material, and a thorough understanding of its reactivity. Over the years we could demonstrate that silica is the optimal support for complexes attached to the surface by electrostatic interactions (see section **1** above), or via bifunctional phosphines, such as $Ph_2P(CH_2)_3Si(OEt)_3$. Other oxide supports, for example titania or alumina, lead to leaching of the linker. Furthermore, some linkers are vulnerable with respect to moisture on oxide surfaces. For example, the tripod-type linker[1] shown in Scheme 4 loses one Ph_2PCH_2 group on wet silica, while it stays intact on a support rigorously dried in vacuo at 600 °C.

Even without ligand decomposition, a deeper insight into the interactions of phosphines with surfaces is desirable. Therefore, another ongoing project in our group is focused on the adsorption strengths and mobilities of phosphines and phosphine oxides on silica.

Scheme 4. Silicas varying in their degree of dryness lead to different immobilized linkers.

Not only linkers show surprising reactivity with oxide supports, but also metal complexes on their own. In lucky cases the reaction of a metal complex with an oxide surface leads to an active catalyst. This is the case with the Union Carbide (UC) ethylene polymerization catalyst,[7] which is the reaction product of chromocene and silica (Scheme 5). We could demonstrate that the UC catalyst is composed of several mono- and dinuclear surface-bound Cr(II) and Cr(III) surface species. Depending on the immobilization conditions the one or other product is favored. The most active species for polymerization is the mononuclear surface-bound Cr(III) halfsandwich compound shown in Scheme 5.[7]
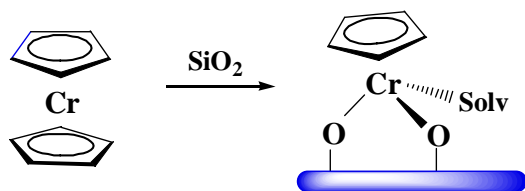

Scheme 5. The active component of the Union Carbide catalyst.[5]

Another important result is that the UC catalyst ages with time by dimerization of the Cr(III) halfsandwich complex, even prior to catalysis, corroborating earlier findings on its polymerization activity. All these results are supported by the synthesis of suitable mono- and dinuclear model compounds.[7] Paramagnetic solid-state NMR spectroscopy is the method of choice for studying the structures and mobilities these catalysts.[7]

3. Solid-State NMR Spectroscopy

Since many years one of our main research interests is solid-state NMR spectroscopy, especially with respect to surface-bound linkers and catalysts. Besides the "classical" solid-state NMR (CP/MAS) with fast rotation of a dry sample, we have pioneered the art of measuring slurries of materials in solvents (HRMAS).[1-4,8] The latter has the advantage that the linewidths become very small, and therefore HRMAS allows even two-dimensional NMR. This is for example demonstrated in Scheme 6. The ^{31}P HRMAS spectrum of the surface-bound Cu complex gives very narrow lines even at the low spinning rate of 2 kHz, in contrast to the ^{31}P CP/MAS of the dry material. This allows the application of the two-dimensional NOESY experiment, analogous to that commonly conducted with liquid samples. In this case, the NOESY cross-peak proves the close proximity of the different ^{31}P nuclei, establishing the structure of the catalyst.[3]
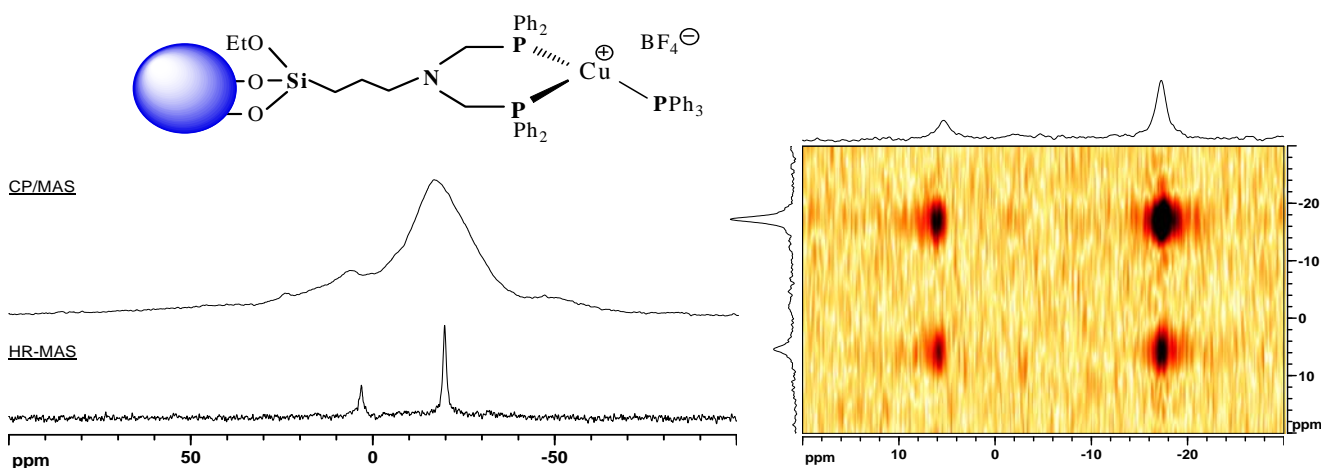
Scheme 6. ^{31}P NMR spectra of the depicted Cu complex. Top left: ^{31}P CP/MAS (4 kHz rotational speed), bottom left: ^{31}P HRMAS (2 kHz). Right: Two-dimensional $^{31}P,^{31}P$ NOESY spectrum of the Cu complex.[3]

Another advantage of the HRMAS method is that dynamic processes on the surface can be studied in the presence of solvents. This allows, for example, the *in situ* investigation of metal complex migration from one surface-bound linker to another.[2] Furthermore, HRMAS quickly identifies solvents that are not "innocent" during, or even prior to catalysis and, e.g., replace ligands from the metal centers.[2]

Selected References

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