New linker systems for superior immobilized catalysts†

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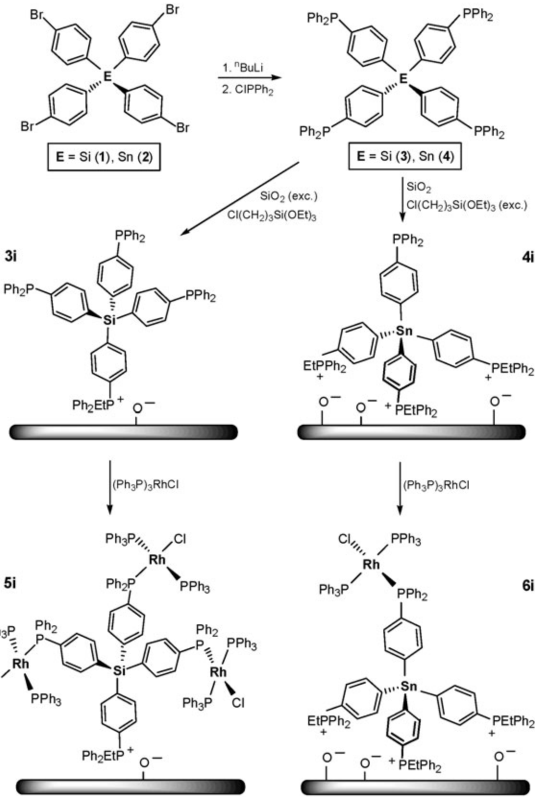
The rigid linkers $E(p\text{-}C_6H_4PPh_2)_4$ (E = Si, Sn) have been synthesized from the corresponding precursors $E(p\text{-}C_6H_4Br)_4$ and immobilized by forming one (E = Si) or three (E = Sn) phosphonium groups that are attached to the silica support by electrostatic interactions. The remaining unquaternized phosphines are coordinated to Wilkinson-type Rh complexes. The catalyst immobilized by the rigid scaffold with three surface-bound phosphonium groups (E = Sn) displays superior catalytic activity and lifetime with respect to the hydrogenation of dodecene. This catalyst can be recycled 30 times in a batchwise manner under standardized conditions.

Immobilized species are important in such diverse areas as combinatorial chemistry,[1] solid-phase synthesis,[2] chromatography,[3] and catalysis.[4,5] Immobilized catalysts[4,5] are of immense academic and industrial interest because they can combine the advantages of homogeneous with those of heterogeneous catalysts. Immobilized catalysts are highly active and selective, while they can easily be separated from the reaction mixture and reused for example in a batchwise manner.[4,5] The most favorable support materials are silica and neutral alumina,[3,6] and bifunctional phosphines, such as the chelate phosphine $Ph_2P(CH_2)_3PPh(CH_2)_3Si(OEt)_3$, are popular linkers.[6,7] The latter have led to very successful immobilized nickel[8] and rhodium[9] catalysts for the cyclotrimerization of acetylenes and olefin hydrogenation, respectively.

However, as demonstrated in previous work, when flexible phosphine linkers with high surface coverages are used catalyst deactivation by dimerization can occur.[9] The catalysts can be "diluted" on the surface to prevent dimerization,[9] but increasing the amount of bulk material in this way is not desirable from an industrial point of view. Additionally, deactivation of the catalysts or linker destruction by reaction with the oxide surface[10] remains possible.

Here, we present a new rigid linker scaffold that allows the clean immobilization of homogeneous catalysts on oxide supports. This linker scaffold prevents catalyst dimerization or contact with the support surface and leads to unprecedented lifetimes and recyclabilities.



Scheme 1 Syntheses of **3** and **4**, the immobilized linkers **3i** and **4i**, and the catalysts **5i** and **6i**.[13]

The silane $Si(p\text{-}C_6H_4Br)_4$ (**1**) (Scheme 1) has been synthesized by the method described by Wuest *et al.*,[11] slightly modified as outlined for the stannane $Sn(p\text{-}C_6H_4Br)_4$ (**2**).[12]

Although $Si(p\text{-}C_6H_4Br)_4$ (**1**) is used extensively as the core building block for constructing networks for various applications,[11] its ^{29}Si NMR data and crystal structure have not yet been reported. The value $\delta(^{29}Si) = -13.76$ ppm for **1** in $CDCl_3$ solution corresponds very well to the value of $SiPh_4$ with −13.98 ppm.[14] In the solid-state NMR[15] spectrum of polycrystalline **1** (Fig. 1) without rotation, a wideline signal with the moderate CSA span $(\delta_{11} - \delta_{33})^{15a}$ of 14 ppm and the CSA values $\delta_{11} = -8$, $\delta_{22} = -15$, and $\delta_{33} = -22$ ppm are obtained. Two isotropic lines at $\delta = -14.3$ and -15.0 ppm are visible at 4 kHz rotational speed. This is corroborated by the single crystal X-ray analysis,[16] where two crystallographically independent molecules generate the asymmetric unit (Fig. 1). Due to the tetragonal symmetry one fragment lies upon a fourfold rotation axis, the other one is placed upon a twofold rotation axis.

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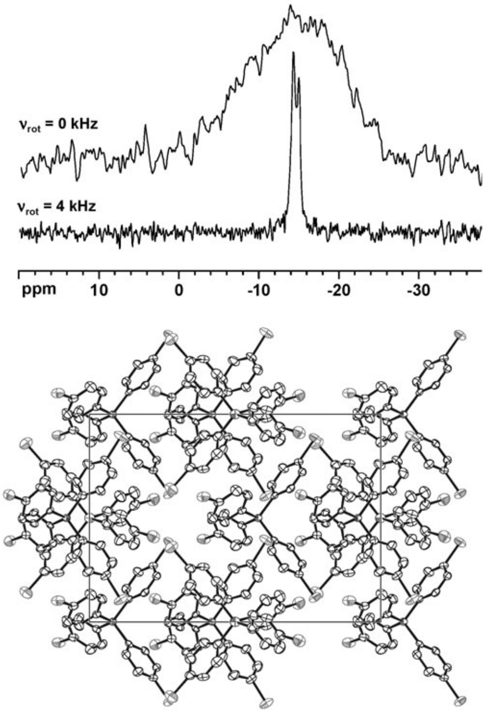

Fig. 1 ^{29}Si wideline (top) and MAS (bottom) NMR spectra of polycrystalline **1**, and unit cell of a single crystal of **1** (view along the crystallographic *a*-axis).[16]

As compared to **1**, polycrystalline Sn(p-C_6H_4Br)$_4$ (**2**)[12] shows a rather large CSA span[15a] of ($\delta_{11} - \delta_{33}$) = 40 ppm in its ^{119}Sn wideline spectrum (Fig. 2), as expected for a heavier nucleus.[15a] The CSA values $\delta_{11} = -92$, $\delta_{22} = -129$, and $\delta_{33} = -133$ ppm are obtained. Only one isotropic line is visible in the ^{119}Sn MAS spectra of **2** (Fig. 2). This is in correspondence with the single crystal X-ray analysis[17] (Fig. 2), which shows that all Sn nuclei are magnetically equivalent.

For both, the tetraphenylsilane and -stannane systems, the intramolecular distance between the bound catalytic centers should be large enough to prevent their dimerization, as the average intramolecular Br$\cdots$Br distances of 10.53 Å for **1** and 11.07 Å for **2** show.

The phosphines **3** and **4** have been synthesized in yields of 55 and 79% by Br/Li exchange, followed by reaction with $ClPPh_2$ (Scheme 1).[13] An alternative synthesis route *via* Br/Li exchange of p-$BrC_6H_4PPh_2$ and reaction with $SiCl_4$ increases the yield of **3** to 70%.[13]

The silane **3** has been immobilized selectively *via* one phosphonium group on silica[18] to give **3i** (Scheme 1) according to the procedure explored in general,[19] and communicated for rigid tetraphosphines previously.[12] In the meantime, we found reaction conditions that also allow us to bind the rigid tetraphosphines to silica *via* three phosphonium groups.

4i (Scheme 1) can be generated by adding a 100-fold excess of $Cl(CH_2)_3Si(OEt)_3$ to **4** and SiO_2 and stirring at 90 °C for 5 days. The quantitative ^{31}P MAS spectrum[12,15d] (Fig. 3), recorded with a long relaxation delay of 10 s, proves the number of binding sites per linker molecule by the intensity ratio of *ca.* 3 : 1 for the phosphonium and the phosphine signals at 23.8 and −5.2 ppm.

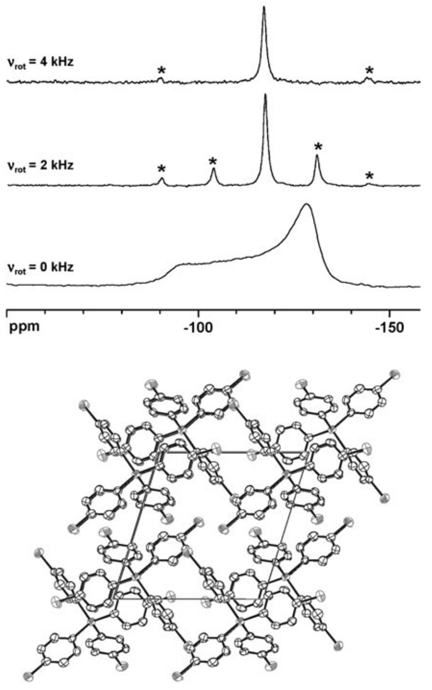

Fig. 2 ^{119}Sn wideline (bottom spectrum) and MAS (top two) NMR spectra of polycrystalline **2** (asterisks denote rotational sidebands), and unit cell of a single crystal of **2** (view along the crystallographic *a*-axis).[17]

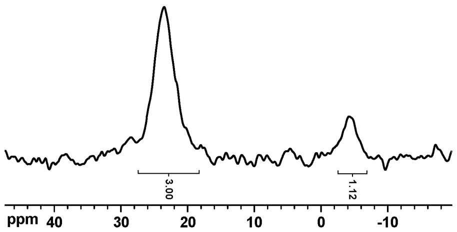

Fig. 3 ^{31}P MAS NMR spectrum of **4i**. $\nu_{rot} = 4$ kHz.

The Rh catalysts **5i** and **6i** (Scheme 1) have been obtained *via* ligand exchange by stirring **3i** and **4i** with a slight excess of Wilkinson's catalyst, and removing the surplus $ClRh(PPh_3)_3$ and PPh_3 by washing with toluene. Both catalysts **5i** and **6i** have been tested with respect to the hydrogenation of 1-dodecene, a catalytic reaction that allows the comparison with ample previous data[9] under the applied standard conditions described earlier.[9c]

Since the support material settles down quickly after each catalytic run, **5i** and **6i** could be recycled by decanting the supernatant and washing the solid thoroughly with toluene.

Catalyst **5i** could be recycled 13 times before the consumption of H_2 was no longer 100% within 100 h. This activity and lifetime scenario is comparable to cases where complexes are immobilized *via* flexible chelate linkers such as $Ph_2P(CH_2)_3PPh(CH_2)_3Si(OEt)_3$.[9] Therefore, if the scaffold is only bound *via* one phosphonium group, the active catalytic centers might still get deactivated by contact with the reactive silica surface.

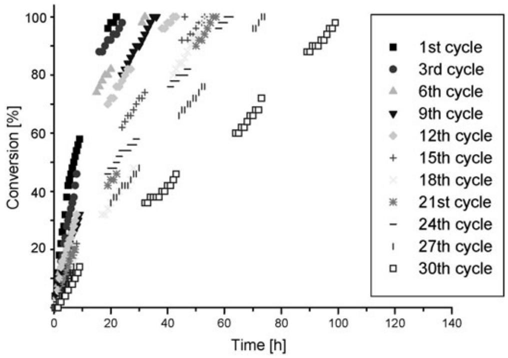

Fig. 4 Batchwise recycling of **6i** after the hydrogenation of 1-dodecene.[9] Ratio dodecene/Rh: 100/1; concentration of dodecene in toluene: 0.1 mol l^{-1}; pressure 1.1 bar; reaction temperature 25 °C.

In the case of catalyst **6i**, which is bound by a ligand platform with three phosphonium groups, no flexibility should be left. Therefore, no catalyst deactivation by dimerization or contact with the support surface should occur. Accordingly, **6i** showed unprecedented activity and lifetime, and could be recycled for the record number of 30 times under the standard conditions[9c] (Fig. 4). The ^{31}P CP/MAS spectra before and after catalysis show the same signals (see ESI†), in analogy to previously studied successful catalysts with different linker systems.[9b]

In summary, it has been demonstrated that catalysts with rigid linker scaffolds are easy to synthesize and analyze. These linkers prevent the dimerization of the catalytically active metal centers and their deactivation by contact with the reactive support surface. Especially catalysts surface-bound by tetrahedral systems with three phosphonium binding sites per linker show unprecedented activities and lifetimes.

Acknowledgements

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13 Analytical data see ESI†.

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16 X-Ray data and parameters of **1**: colourless crystal (irregular), dimensions 0.20 × 0.14 × 0.10 mm^3, crystal system tetragonal, space group $I\bar{4}$, $Z = 6$, $a = b = 13.6296(1)$ Å, $c = 18.9768(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3525.24(5)$ Å^3, $\rho = 1.843$ g cm^{-3}, $T = 200(2)$ K, $\theta_{\max} = 24.11°$, radiation MoK$_\alpha$, $\lambda = 0.71073$ Å, 0.3°ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 13 920 reflections measured, 2791 unique ($R_{\text{int}} = 0.0490$), 2482 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, $\mu = 6.91$ mm^{-1}, $T_{\min} = 0.34$, $T_{\max} = 0.55$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (6.12) software package, 197 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 0.037(16), goodness of fit 1.02 for observed reflections, final residual values $R_1(F) = 0.036$, $wR(F^2) = 0.090$ for observed reflections, residual electron density −0.66 to 0.49 eÅ^{-3}. CCDC 742605 contains the supplementary crystallographic data for this structure†.

17 X-Ray data and parameters of **2**: colourless crystal (irregular), dimensions 0.24 × 0.08 × 0.04 mm^3, crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.7752(6)$ Å, $b = 11.2894(6)$ Å, $c = 11.8628(7)$ Å, $\alpha = 70.695(1)°$, $\beta = 74.850(1)°$, $\gamma = 79.261(2)°$, $V = 1185.4(1)$ Å^3, $\rho = 2.081$ g cm^{-3}, $T = 200(2)$ K, $\theta_{\max} = 22.46°$, radiation MoK$_\alpha$, $\lambda = 0.71073$ Å, 0.3° ω-scans with CCD area detector, 8197 reflections measured, 3093 unique ($R_{\text{int}} = 0.0493$), 2361 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, $\mu = 7.83$ mm^{-1}, $T_{\min} = 0.26$, $T_{\max} = 0.74$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (6.12) software package, 262 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values $R_1(F) = 0.043$, $wR(F^2) = 0.101$ for observed reflections, residual electron density −0.77 to 1.46 eÅ^{-3}. CCDC 742606 contains the supplementary crystallographic data for this structure†.

18 The silica (Merck, 40 Å average pore diameter, 0.063 to 0.2 mm average particle size, specific surface area 750 m^2 g^{-1}) has been rigorously dried *in vacuo* at 500 °C for 4 days to remove adsorbed water and condense surface silanol groups.

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