

Immobilization and chelation of metal complexes with bifunctional phosphine ligands: a solid-state NMR study

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^{29}Si CP MAS NMR shows that a transition-metal complex with two bifunctional phosphine ligands such as $(\text{CO})_2\text{Ni}[\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{OEt}]_2$, when attached to a silica surface according to a commonly used procedure, is mainly anchored by just one ligand.

Immobilized transition-metal complexes are of growing interest,¹ because they can, in principle, combine all the advantages of homo- and hetero-geneous catalysts: they should be easy to recycle and display high activity and selectivity due to a homogeneous reaction. The investigation of immobilized species has been hindered for a long time by the absence of a suitable analytical tool. Nowadays, solid-state NMR spectroscopy² serves as a powerful analytical method. In addition, suspension NMR spectroscopy³ can be applied routinely.

Since most transition metals form stable phosphine complexes, bifunctional phosphines are often used as linkers.^{1,4} Silica is a popular support, since it is resistant against elevated temperatures and most solvents and its surface properties are already well defined.^{2c,5} The greatest drawback of immobilized catalysts is their tendency to detach from the support during catalysis. This problem is known as 'leaching'.¹ Several strategies have been developed in order to avoid leaching: chelating phosphines¹ or a large excess of phosphine on the support¹ have been applied. Very promising in this respect are the materials obtained by the sol-gel process.⁶

We approach the problem from another side and investigate the origins of the leaching phenomenon in order to be able to avoid it in the future. Previous work has already revealed that the formation of P^{V} species is one reason for leaching.⁴ Another reason is insufficient bonding to the support, which is studied in this contribution. For this investigation we used carbonylnickel complexes, because they are reasonably stable⁷ and catalyse a plethora of chemical reactions.⁸

When immobilizing metal complexes with bifunctional phosphines, there are in principle two possibilities: (a) phosphine-modified silica is treated with a suitable precursor of the wanted immobilized complex, and (b) the complex containing the bifunctional phosphine is preformed and then attached to silica. Regarding carbonylnickel complexes, method (a) has the disadvantage that dicarbonylnickel complexes cannot be obtained by reaction of $\text{Ni}(\text{CO})_4$ with phosphinated silica^{7,9} and phosphine exchange reactions are tedious and difficult to be checked.^{1,7} Method (b) on the other hand allows the characterization of the complexes prior to the immobilization for example by ^{61}Ni NMR spectroscopy¹⁰ and to apply a defined P:Ni ratio. When reacting a complex with two bifunctional phosphines with silica according to the procedure given in the literature,^{1,11} it is tacitly assumed that the complex is anchored in a chelate-type fashion *via* both phosphine linkers. This should result in a strong bonding of the complex to the support and later reduced leaching. Phosphines with $\text{Si}(\text{OEt})_3$ groups lead to many different species due to bonding *via* one, two, or three siloxane bridges and there is also the possibility of cross-linking.^{11a,12} Therefore, we used the monoethoxy phosphine $\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{OEt}$ **1** that forms just one siloxane bridge when bonded to the surface, no matter whether a condensation reaction with surface silanol groups or an addition reaction to

surface siloxane groups takes place.¹³ This can be seen in the ^{29}Si CP MAS NMR spectrum of **1**, bound to silica (**1i**) [Fig. 1(b)].

Besides the signals for bulk silicon nuclei at $\delta -110$ and surface silanol signals at $\delta -103$ there is only one signal in the silane region, at $\delta 3.0$. The latter must stem from the surface-bound $\text{RMe}_2\text{Si}-\text{O}-$ group. When $(\text{CO})_2\text{Ni}[\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{OEt}]_2$ **2** is reacted with silica (Scheme 1), the complex can be bound in a chelate-type fashion (**2ii**) or only by one phosphine linker (**2i**).

After applying the immobilization procedure commonly used, *i.e.* adding the complex in excess to silica suspended in

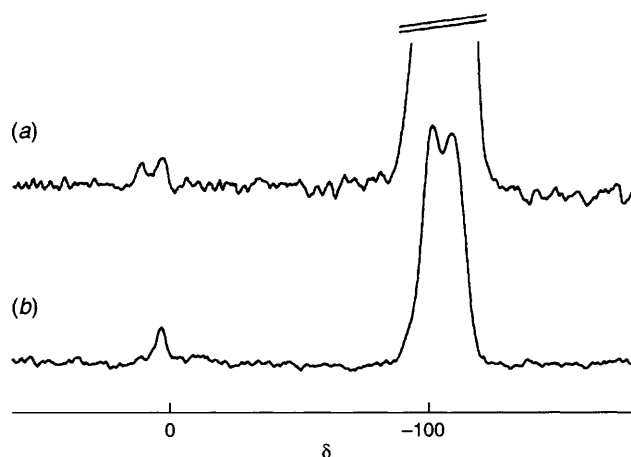
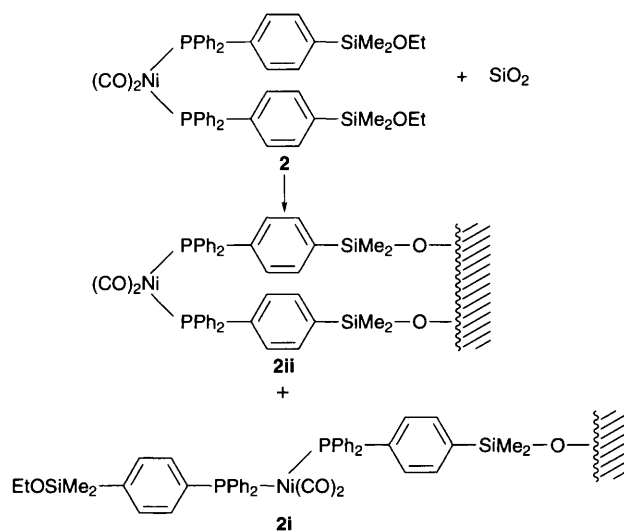


Fig. 1 59.6 MHz ^{29}Si CP MAS NMR spectra of (a) $[\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{OEt}]_2\text{Ni}(\text{CO})_2$ **2** and (b) $\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{OEt}$ **1** immobilized on SiO_2 (for details see text). Rotational frequency: 4 kHz; pulse delay: 10 s; contact time: 6 ms; number of scans: 6400 (a) and 2000 (b).



Scheme 1 Two possible products of the immobilization of **2** on silica, **2i** and **2ii**. For details see text.

toluene and refluxing the mixture for several hours, the ^{29}Si CP MAS NMR spectrum of the material [Fig. 1(a)] shows two signals in the silane region at δ 3.0 and 9.1 with an intensity ratio of approximately 1 : 1.5. The S/N is not as good as that in Fig. 1(b), most probably because here the CP magnetization transfer is less efficient due to traces of paramagnetic impurities that are formed on the silica surface by some slight decomposition of transition-metal complexes.^{2c} While $\delta(^{29}\text{Si})$ of 3.0 is in excellent agreement with the chemical shift of a surface-bound $\text{RSiMe}_2\text{-O-}$ group [Fig. 1(b)], we attribute the signal at δ 9.2 to a free $\text{EtOSiMe}_2\text{-}$ moiety. This shift corresponds well to the $\delta(^{29}\text{Si})$ of **1** in solution.⁷ Therefore, we conclude that **2i** is the main product on the surface and the desired species **2ii** constitutes only a minor fraction.† This result is also supported by carbon elemental analysis. Although the surface coverage cannot be derived exactly from the carbon value due to surface-bound ethoxy groups,^{7,13} a value for immobilized **2** of 11% as compared to **1i** with 6% under the same reaction conditions and with the same silica, is indicative of the formation of a double layer of linker as is the case for **2i**. Additionally, the presence of **2i** can be proved by phosphine exchange reactions and ^{31}P NMR spectroscopy of the supernatant solutions: When an excess of PMe_3 is stirred with immobilized **2** in toluene suspension at room temperature for 12 h, a considerable amount of free **1** and $(\text{CO})_2\text{Ni}(\text{PMe}_3)_2$ is found in the supernatant solution, besides traces of $(\text{CO})\text{Ni}(\text{PMe}_3)_3$. Since PMe_3 does not detach **1i** from the support, free **1** can only result from the replacement of the non-surface-bound phosphine ligand of **2i** to yield $(\text{PMe}_3)\text{-Ni}(\text{CO})_2\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{-O-}\{\text{SiO}_2\}$. The latter can undergo further phosphine exchange, giving finally $(\text{CO})_2\text{Ni}(\text{PMe}_3)_2$, $(\text{CO})\text{Ni}(\text{PMe}_3)_3$, and **1i**. On the other hand, reaction of **2ii** with PMe_3 only leads to $(\text{CO})_2\text{Ni}(\text{PMe}_3)_2$ and $(\text{CO})\text{Ni}(\text{PMe}_3)_3$ in the supernatant solution, but no **1** can be found.

The desired chelate-type complex **2ii** can only be obtained exclusively when **2**, dissolved in a large amount of toluene, is added to the silica suspension dropwise, over several hours, and at room temperature. Then the surface coverage with regard to the nickel complex is much lower and matches the surface coverage obtainable with free phosphine ligand. This result means that the reaction of ethoxysilane reagent with silica surfaces must be much faster than assumed previously, which preliminary experiments confirm. For example, when triethoxysilanes are reacted with silica, maximal surface coverage is already obtained after stirring for 15 min at room temperature. Prolonged reaction times or elevated temperatures do not enhance the surface coverage, but just increase the number of formed siloxane bonds per silane group, a result that is in accord with earlier studies.^{11a} A quantitative investigation of the immobilization step of ethoxysilanes and bifunctional phos-

phines is important for the selective generation of surface-bound chelate-type species and for avoiding later leaching. Therefore, it is part of our ongoing research interests.

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Footnote

† Note that suspension NMR spectroscopy³ did not give a silane ^{29}Si NMR signal, most probably due to reduced mobility and long relaxation times of the ^{29}Si nuclei.

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