

Immobilization of Carbonylnickel Complexes: A Solid-State NMR Study

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Silica is commonly modified with bifunctional phosphines like $\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ prior to immobilization of catalysts. Here, besides $\text{PPh}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, ligands that are more stable toward oxidation, namely $\text{PPh}_2(\text{C}_6\text{H}_4)\text{Si}(\text{OEt})_3$, $\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2(\text{OEt})$, and $\text{PPh}_2(\text{CH}_2)_4\text{OH}$, are applied. The di- and tricarbonylnickel complexes of these ligands are synthesized, characterized by ^{61}Ni , ^{31}P , ^{13}C , and ^1H NMR and IR spectroscopy, and immobilized on silica. Alternatively, the corresponding phosphine-modified silicas are treated with $\text{Ni}(\text{CO})_4$. The obtained materials are investigated by ^{31}P and ^{13}C solid-state NMR spectroscopy. Di- and tricarbonylnickel species can be distinguished by their different chemical shift anisotropies and also by their IR data. While the first route allows immobilization of both di- and tricarbonylnickel complexes, reaction of surface-bound phosphines with $\text{Ni}(\text{CO})_4$ gives the tricarbonyl species exclusively. Among the different ligands, $\text{PPh}_2(\text{CH}_2)_4\text{OH}$ has optimal qualities: It gives high surface coverages without oxidation or cross-linking, and therefore narrow NMR lines, and it allows ^{13}C CP/MAS NMR spectroscopy.

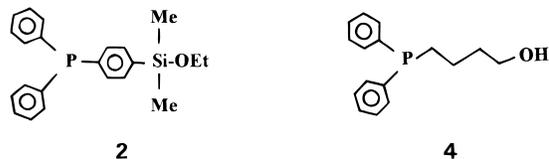
1. Introduction

Immobilized catalysts are of growing interest, because they can, in principle, combine all the advantages of heterogeneous and homogeneous catalysis.^{1–4} They can easily be removed from the reaction mixture, while the reactions themselves are homogeneous, thus providing high selectivity and yield. Hereby, inorganic oxides often serve as support materials, because they are inexpensive and inert against most chemicals and elevated temperatures. The most common support is silica. It is neutral, and its surface properties are already well explored.^{5–8}

Among several analytical tools,⁹ the most powerful method to characterize surface-bound species is multinuclear solid-state NMR spectroscopy.^{1,5,10–12} Since bifunctional phosphines¹¹ are often used as linkers, the spin $1/2$ nucleus of choice is ^{31}P with its great natural abundance (100%) and large chemical shift dispersion. The quality of the spectra can be additionally improved by magic angle spinning (MAS)^{5,12} and cross-polarization (CP)¹³ techniques.

For the immobilization of transition metal catalysts using bifunctional phosphine ligands, several strategies have been

developed. The sol–gel process for instance provides the option of a tailored silica support material with a high loading of catalyst. It has been successfully applied for example by Lindner^{14,15} and Schubert.^{16,17} However, this procedure is only feasible for very stable transition metal complexes, and not all of the catalyst is later easily accessible for the substrate. The steric and chemical environment of the metal nuclei is not very well defined. On the other hand, using commercial silica offers the advantage that even sensitive complexes can be immobilized and all the active catalyst centers on the surface are accessible by reagents. However, care has to be taken to avoid oxidative side reactions of the bifunctional phosphines¹¹ during the immobilization step. Since triarylphosphines are less sensitive toward oxidation, here we use, besides the conventional $\text{PPh}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, phosphines of this kind, namely $\text{PPh}_2(\text{C}_6\text{H}_4)\text{Si}(\text{OEt})_3$ and $\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2(\text{OEt})$. The latter ligand excludes the complicating effect of cross-linking.^{18–22} In order to avoid oxidation, as well as cross-linking, and addition of the ethoxysilyl functions to surface siloxane groups,¹⁸ $\text{PPh}_2(\text{CH}_2)_4\text{OH}$ ¹¹ is included in our study.



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These ligands are successfully applied for the synthesis and immobilization of di- and tricarbonylnickel phosphine complexes. Nickel catalysts are of interest for academic as well as

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Table 1. ^{61}Ni and ^{31}P Chemical Shifts, Line Widths $\nu_{1/2}(^{61}\text{Ni})$, Coupling Constants $^1J(^{61}\text{Ni}-^{31}\text{P})$, and $\nu(\text{CO})$ Values for Di- and Tricarbonylnickel Complexes at Room Temperature (298 K)

compound ^a	no.	$\delta(^{61}\text{Ni})^b$	$\nu_{1/2}(^{61}\text{Ni})$ [Hz] ^c	$^1J(^{61}\text{Ni}-^{31}\text{P})$ [Hz] ^d	$\delta(^{31}\text{P})^f$	$\nu(\text{CO})$ [cm ⁻¹]
(CO) ₃ Ni[PPh ₂ (C ₆ H ₄)SiMe ₂ OEt]	5	24.2	26	234	32.1	2068/1990
(CO) ₃ Ni[PPh ₂ (C ₆ H ₄)Si(OEt) ₃]	6	22.9	50	241	32.1	2066/1993
(CO) ₃ Ni[PPh ₂ (CH ₂) ₃ Si(OEt) ₃]	7	8.0	180	218	23.6	2066/1988
(CO) ₃ Ni[PPh ₂ (CH ₂) ₄ OH]	8	7.0	150	188	24.5	2068/1993
(CO) ₂ Ni[PPh ₂ (C ₆ H ₄)SiMe ₂ OEt] ₂	9	93.0	1050	<i>e</i>	33.7	2001/1940
(CO) ₂ Ni[PPh ₂ (C ₆ H ₄)Si(OEt) ₃] ₂	10	87.3	1150	<i>e</i>	33.8	2001/1942
(CO) ₂ Ni[PPh ₂ (CH ₂) ₃ Si(OEt) ₃]	11	31.6	800	<i>e</i>	24.9	2002/1939

^a Et = ethyl, Me = methyl, Ph = phenyl, (C₆H₄) = para-disubstituted phenyl. ^b The chemical shifts of the complexes, dissolved in THF, are measured with respect to external liquid Ni(CO)₄ as the reference ($\delta = 0$) using the method described earlier.²⁹ ^c Half-widths $\nu_{1/2} \pm 5$ Hz. ^d $^1J(^{61}\text{Ni}-^{31}\text{P}) \pm 1$ Hz. ^e Could not be obtained because of the great line width. ^f Nickel complexes dissolved in acetone-*d*₆; chemical shifts are measured with respect to external 85% H₃PO₄(aq).

commercial reasons.^{23,24} In particular, carbonylnickel phosphine complexes catalyze a variety of reactions,²³⁻²⁵ and therefore early attempts at their immobilization on different supports were undertaken.²⁶⁻²⁸ However, IR spectroscopy was the only analytical tool at that time and all research efforts were obviously halted in their beginnings.

In this contribution, we show that the concept described earlier,¹¹ together with a proper choice of bifunctional phosphine linkers, can fruitfully be applied to the immobilization of nickel carbonyl complexes. Hereby, solid-state NMR serves as a powerful method for characterizing the surface-attached compounds. For example, early IR results of Basset,²⁸ with a different ligand, could be confirmed. Using a method described elsewhere,²⁹ it is also possible to measure the ^{61}Ni NMR spectra of the catalysts in solution.

2. Results

2.1. Bifunctional Phosphine Ligands. All the applied phosphine linkers, namely PPh₂(C₆H₄)Si(OEt)₃ (**1**), PPh₂(C₆H₄)SiMe₂OEt (**2**), PPh₂(CH₂)₃Si(OEt)₃ (**3**), and PPh₂(CH₂)₄OH (**4**), can be prepared easily in a few steps and in good yields by procedures given in the literature (see Experimental Section). They are grafted with high coverage to the surface of dried silica by a method described earlier (ref 11 and Experimental Section). In the case of **1**, **2**, and **4**, temperatures as high as 90 °C can be applied for the immobilization. After drying, all the materials are reasonably air stable and are only slowly transformed into the phosphine oxides by oxygen in the course of days (**3**, **4**) or weeks (**1**, **2**). ^{31}P CP/MAS NMR spectroscopy shows that the obtained phosphinated silica are free of side products. The signals of surface-immobilized **1** (**1i**) and **2** (**2i**) resemble those of immobilized **3** (**3i**) and **4** (**4i**).¹¹ Their signal shifts correspond to the solution chemical shifts very well (see Experimental Section). The ^{13}C CP/MAS NMR spectra show in the case of **1i**, **2i**, and **3i**, besides the dominant signals of the aryl groups, huge resonances for OEt groups. The latter most often prevent the detection of the signals of the alkyl chain groups. The surface-attached ligand **4i** has optimal qualities for solid-state ^{13}C NMR measurements: The surface coverage of about 0.4

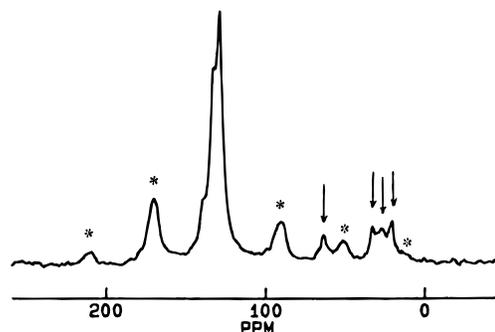


Figure 1. 75.5 MHz ^{13}C CP/MAS NMR spectrum of surface-bound phosphine PPh₂(CH₂)₄-O-{SiO₂} (**4i**). Asterisks denote rotational sidebands of the signal of the phenyl groups; the arrows mark the signals of the butyl chain carbons. For NMR details, see the Experimental Section.

mmol/g of SiO₂ is the highest obtainable, and additionally no OEt signals are present to overlap the desired ^{13}C signals of the immobilized compounds. Therefore, the ^{13}C CP/MAS NMR spectrum of **4i** can easily be recorded even at a low spinning rate, and all ^{13}C signals of the butyl chain are visible (Figure 1): The signals of the phenyl groups at 129 ppm are not resolved. The chemical shift values of 63.3, 34.1, 28.2, and 20.8 ppm for the alkyl chain correspond very well to those of the free phosphine of 61.48, 33.77, 27.52, and 22.07 ppm (for assignment see Experimental Section).

2.2. Carbonylnickel Phosphine Complexes. Di- and tricarbonylnickel complexes can be synthesized in quantitative yield by reaction of Ni(CO)₄ with the corresponding phosphines, using the literature procedure (Scheme 1; Experimental Section). Since the ^{31}P NMR chemical shifts of di- and tricarbonylnickel complexes are very similar (Table 1), ^{61}Ni NMR spectroscopy²⁹ is a useful analytical tool to control the success of the syntheses: As shown earlier,²⁹ tricarbonylnickel phosphine complexes give doublets with small line widths as ^{61}Ni NMR signals, due to coupling of ^{61}Ni with one ^{31}P nucleus. Dicarboxyl complexes, on the other hand, lead to broad ^{61}Ni resonances, whose triplet character (coupling to two ^{31}P nuclei) can generally hardly be predicted (Figure 2).

All the ^{61}Ni NMR and IR data for the molecular complexes **5-11** are given in Table 1. The ^{61}Ni chemical shifts, coupling constants, and line widths of **5**, **6** and **9**, **10** correspond very well to the shifts of (CO)₃Ni(PPh₃) and (CO)₂Ni(PPh₃)₂,²⁹ respectively. The ^{61}Ni NMR data of **7**, **8**, and **11** are in accord with those of the corresponding butyl- and ethyldiphenylphosphine nickel complexes.²⁹ The IR data agree with those of similar di- and tricarbonylnickel complexes very well.^{25,27,28}

2.3. Immobilization of the Carbonylnickel Phosphine Complexes. All the molecular nickel complexes **5-11** can be immobilized on silica under the same mild reaction conditions

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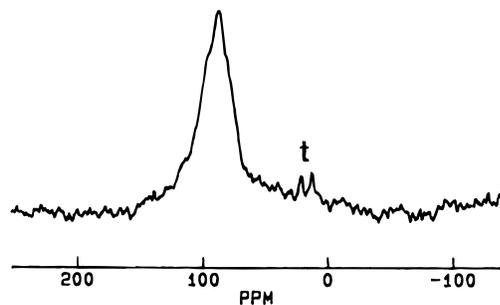


Figure 2. 26.6 MHz ^{61}Ni NMR spectrum of $(\text{CO})_2\text{Ni}[\text{PPH}_2(\text{C}_6\text{H}_4)\text{Si}(\text{OEt})_3]_2$ (**10**) in THF. t denotes the doublet signal of traces of the tricarbonylnickel complex **6**.

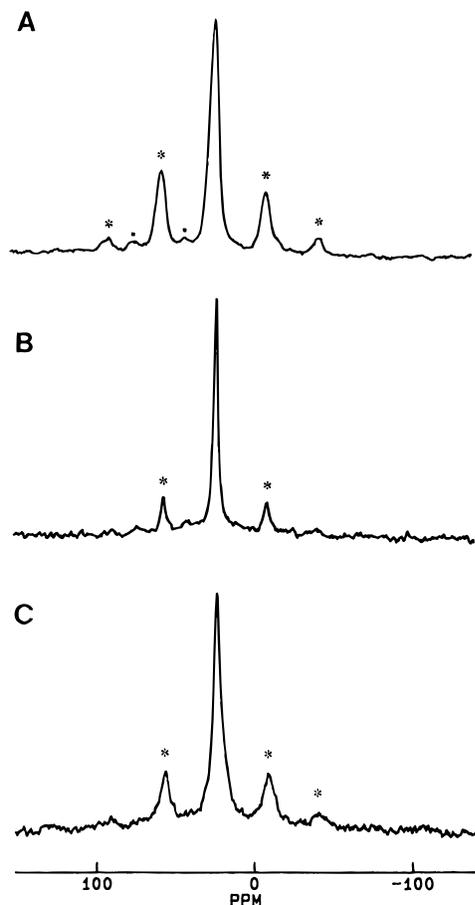


Figure 3. 121.5 MHz ^{31}P CP/MAS NMR spectra of (A) $(\text{CO})_2\text{Ni}[\text{PPH}_2(\text{CH}_2)_3\text{Si}\{\text{O}-\text{SiO}_2\}_3]_2$ (**11i**), (B) $(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{CH}_2)_4\text{O}-\{\text{SiO}_2\}]$ (**8i**), and (C) $(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{CH}_2)_3\text{Si}\{\text{O}-\text{SiO}_2\}_3]$ (**7i**). Spinning sidebands are denoted by asterisks; for NMR details, see the Experimental Section. The dots designate the signal of trace amounts of an oxidic impurity.

that are applied for grafting the ligands on the surface (Experimental Section and ref 11), yielding the surface-attached species **5i–11i**. The success of the procedure is again best controlled by ^{31}P CP/MAS NMR spectroscopy. The $\delta(^{31}\text{P})$ values of **5–11** in solution (Table 1) correspond very well to the chemical shifts of **5i–11i** in the solid state (Table 2). Typical ^{31}P CP/MAS NMR spectra of immobilized di- and tricarbonylnickel complexes are displayed in Figure 3. No signals of uncomplexed phosphines are visible. Spectrum 3A demonstrates that even trace amounts of oxidic impurities show up in the ^{31}P CP/MAS NMR spectra very well. While the $\delta(^{31}\text{P})$ values of di- and tricarbonyl complexes are very similar, the overall shapes of the signals are different: Their chemical shift anisotropy (CSA)^{5,12} and thus their pattern of rotational sidebands, denoted by asterisks in the spectra, change on going

Table 2. MAS NMR and IR Data for Surface-Attached Metal Complexes

compound ^a	no.	$\delta(^{31}\text{P})^b$	$\nu_{1/2}^{(31}\text{P})^c$ [Hz]	$\nu(\text{CO})$ [cm ⁻¹]
$(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{O}-\{\text{SiO}_2\}]$	5i	31.3	330	2069/1999
$(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{C}_6\text{H}_4)\text{Si}\{\text{O}-\text{SiO}_2\}_3]$	6i	31.6	400	2068/1998
$(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{CH}_2)_3\text{Si}\{\text{O}-\text{SiO}_2\}_3]$	7i	22.4	540	2068/1999
$(\text{CO})_3\text{Ni}[\text{PPH}_2(\text{CH}_2)_4\text{O}-\{\text{SiO}_2\}]$	8i	23.5	400	2069/2000
$(\text{CO})_2\text{Ni}[\text{PPH}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{O}-\{\text{SiO}_2\}]_2$	9i	31.3	745	2001/1939
$(\text{CO})_2\text{Ni}[\text{PPH}_2(\text{C}_6\text{H}_4)\text{Si}\{\text{O}-\text{SiO}_2\}_3]_2$	10i	32.3	610	2005/1943
$(\text{CO})_2\text{Ni}[\text{PPH}_2(\text{CH}_2)_3\text{Si}\{\text{O}-\text{SiO}_2\}_3]_2$	11i	22.9	830	2003/1939

^a $\{\text{SiO}_2\}$ denotes the silica support. ^b External reference: 85% $\text{H}_3\text{PO}_4(\text{aq})$. ^c $\nu_{1/2} \pm 5$ Hz.

from the di- to the tricarbonyl species. The ^{31}P CP/MAS spectra of **9i–11i** show an unsymmetric overall appearance (Figure 3A), whereas the spectra of **5i–8i** are nearly totally symmetric (Figure 3B/C) (the use of “symmetric” or “unsymmetric” in this context should not be confused here or below with the symmetry or asymmetry of the ^{31}P shielding tensor¹²). The CSA values have been determined by a nonspinning NMR experiment for two representative cases: σ_{11} , σ_{22} , and σ_{33} for **7i** are 98, 24, and -32 ppm, respectively; the corresponding σ values for **11i** are 85, 34, and -39 ppm, respectively.

The residual line width is greater for immobilized dicarbonyl than for tricarbonyl complexes (Table 2). The narrowest signal can be observed for **8i**.

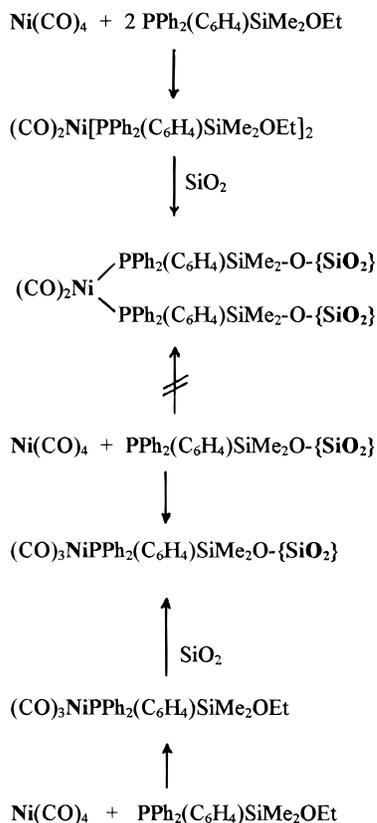
The $\nu(\text{CO})$ values do not change significantly when the free nickel complexes (Table 1) are bound to silica (Table 2).

2.4. Reaction of $\text{Ni}(\text{CO})_4$ with Phosphinated Silica. After the surface-bound phosphines **1i–4i** are treated with $\text{Ni}(\text{CO})_4$ (Scheme 1), the obtained ^{31}P CP/MAS NMR spectra of the materials are identical with those of **5i–8i** (Figure 3B/C). This result is independent of the applied Ni:P ratio, provided a stoichiometric amount of $\text{Ni}(\text{CO})_4$ is added. No resonances indicative of oxidized species, free phosphines, or dicarbonylnickel complexes can be detected. Therefore, reaction of surface-bound phosphines with $\text{Ni}(\text{CO})_4$ gives the corresponding immobilized tricarbonylnickel complexes exclusively. This result is additionally supported by the IR data (Tables 1, 2) of the materials.

2.5. Reaction of $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$ with Phosphinated Silica. When the immobilized phosphines **1i–4i** are treated repeatedly with fresh phosphine-free $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$, the resulting ^{31}P CP/MAS NMR spectra are identical with those of **9i–11i** (Figure 3A). Again, no resonances indicative of other than the immobilized dicarbonylnickel phosphine complexes are visible. Identical spectra are obtained, however, when an excess of $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$ is applied to phosphinated silica only once.

3. Discussion

3.1. Bifunctional Phosphine Ligands. The above results show, that on the basis of ref 11, a variety of bifunctional triaryl- and diarylalkylphosphines can be grafted onto a silica surface without side reactions of any kind. While ^{31}P CP/MAS NMR spectroscopy is successfully applied to all the immobilized phosphines, ^{13}C CP/MAS NMR is somewhat hampered by the signals of ethoxy groups in the case of **1i**, **2i**, and **3i**. These signals could stem from residual ethoxy groups that have not undergone a condensation with surface silanol groups. The presence of OEt groups in the case of **2i**, however, suggests that an addition of ethoxysilyl groups to surface siloxane groups also takes place. This type of surface reaction has been demonstrated to be even dominant in an earlier study of the reactions of ethoxysilanes with silica.¹⁸ With respect to solid-state ^{13}C NMR spectroscopy, ligand **4** is superior to the others,

Scheme 1. Generally Valid Immobilization Reactions for Di- and Tricarbonylnickel Complexes^a

^a Ligand **2** is depicted as an example. Details of the reaction conditions are given in the Experimental Section. {SiO₂} denotes the silica support.

since there are no overlapping signals of OEt groups after immobilization. Additionally, the high surface coverage is advantageous for the sensitivity-limited ¹³C CP/MAS NMR method. We interpret the higher coverage of **4i** as compared to **1i–3i** as the result of denser packing of the ligands on the surface due to the minor steric demand of the long unbranched alkyl chain. In comparison, studies of the esterification of silica surfaces with alcohols^{8,30} have shown that the surface coverages are densest for primary, unbranched alcohols like 1-butanol.³⁰ Therefore, although in the meantime a plethora of methods have been developed for modifying silica,³¹ the esterification via the hydroxyl group of an alcohol still presents a very easy alternative. The water liberated by the condensation reaction of **4** with surface silanol groups can easily be removed in vacuo, while there is at present no way to selectively remove residual or surface-bound ethoxy groups in the case of **1–3**. Additionally, oxidative side reactions due to the combined action of ethoxy groups and silica surface do not take place.¹¹ The rotational sidebands of the ¹³C phenyl signal (Figure 1) could be removed entirely by faster spinning rates (>10 kHz), if necessary.

3.2. Carbonylnickel Phosphine Complexes. The results described under section 2.2 have shown that ⁶¹Ni NMR spectroscopy can routinely be used in order to check the purity of the obtained compounds. As in the case of other nickel complexes with monofunctional phosphine ligands,²⁹ the line

width increases dramatically on going from the tri- to the dicarbonylnickel species (Table 1). We interpret this as the result of a less symmetric electronic environment around the quadrupolar ⁶¹Ni nucleus, and hence a greater electric field gradient *q_{zz}*.²⁹ A comparison of the *ν*_{1/2}(⁶¹Ni) values of compounds **5**, **6** and **9**, **10** with the corresponding values of (CO)₃NiPPh₃ (16 Hz)²⁹ and (CO)₂Ni(PPh₃)₂ (750 Hz)²⁹ shows that the greater electric field gradient *q_{zz}*²⁹ might also play a role here. The line widths increase with the number of ethoxy groups present. The *ν*_{1/2} values are greater for compounds with Si(OEt)₃ groups than for those with SiMe₂(OEt) groups. One might suggest that the former is a more effective anchor than the latter, leading to a longer correlation time due to the greater steric demand. Comparison of the *δ*(⁶¹Ni) values of **5**, **6** and **9**, **10** with those of (CO)₃NiPPh₃ and (CO)₂Ni(PPh₃)₂, respectively, shows, that the ethoxysilane function has only little influence on the chemical shift.

Regarding the greater line widths *ν*_{1/2}(⁶¹Ni) of compound **8** as compared to **5**, one might suppose an intramolecular Ni–O bond and therewith increased distortion. This is for example observed in the case of ether phosphine complexes of ruthenium.^{14,32} However, then the *δ*(⁶¹Ni) and *ν*_{1/2}(⁶¹Ni) values should be very different from the ones of the oxygen-free model compound PPh₂Et (−0.1 ppm, 131 Hz),²⁹ which is obviously not the case. Additionally, the *ν*(CO) values of **5** and **8** are very similar (Table 1).

Unfortunately, due to the NMR properties of the ⁶¹Ni nucleus, measurements in the solid state are at present not possible.²⁹

3.3. Immobilization of the Carbonylnickel Phosphine Complexes. The results described under section 2.3 have demonstrated that all the di- and tricarbonylnickel complexes with different types of bifunctional ligands can be immobilized without side reactions. Since there are no resonances of free phosphines visible in the ³¹P CP/MAS NMR spectra (Figure 3), we conclude that no ligand dissociation reactions occur during the immobilization procedure. The spectra can also be recorded with smaller rotors and higher spinning speeds, in order to remove all rotational sidebands. However, much information would be lost, since the CSA can be estimated from the intensities of the spinning sidebands.¹² Here, for example, it is possible to judge from the overall appearance of the spectra, recorded with a moderate spinning speed (4 kHz), whether a di- or tricarbonyl species is present. All di- and tricarbonylnickel species display similar ³¹P signal shapes, respectively. The residual line widths of the immobilized dicarbonylnickel complexes are always greater than those of the corresponding tricarbonylnickel complexes. This might reflect the reduced mobility¹² and diminished ordering in the surroundings of ³¹P of the chelate-type bound dicarbonyl- in contrast to the tricarbonylnickel complexes.

The smallest line width is obtained for **8i**, and we tentatively suggest that the local environment is most ordered here due to a “brush” type configuration³¹ of the unbranched ligands on the surface.

While the *ν*(CO) values are different for di- and tricarbonylnickel complexes, the IR data do not change significantly when the molecular nickel complexes (Table 1) are bound to the silica surface (Table 2). Therefore, we conclude that the electronic environment of the complexes is not changed by the immobilization.

3.4. Reaction of Ni(CO)₄ with Phosphinated Silica. Reaction of Ni(CO)₄ with surface-immobilized phosphines gives selectively the silica-bound tricarbonylnickel complexes (Scheme 1). This has already been anticipated by Basset, using IR spectroscopy.²⁸ Our solid-state NMR study shows that this

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reaction behavior is general and independent of the type of phosphine and the reaction conditions. Additionally, no signals of uncomplexed phosphines are detectable in the ^{31}P CP/MAS NMR spectra. This means, that all the surface-bound phosphines—and therewith later the nickel complexes—are easily accessible to reagents, a great advantage of the surface-immobilization of catalysts described here in contrast to the sol-gel process.

3.5. Reaction of $(\text{CO})_2\text{Ni}(\text{PPh}_3)_2$ with Phosphinated Silica.

Phosphine ligand exchange reactions are a very common method for immobilizing catalysts.¹ However, there is, in principle, the possibility of 1- and 2-fold exchange.¹ The latter should be more favorable with respect to the disadvantageous effect of "bleeding" during catalysis. The exchange rate can be determined by the ratio of excess complexed to free PPh_3 in the solution after the exchange process. However, the ^{31}P CP/MAS NMR spectra of the obtained modified silica did not change with the phosphine exchange rate. Therefore, we conclude that, for example, the surface species $(\text{CO})_2\text{Ni}(\text{PPh}_3)[\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{O}-\{\text{SiO}_2\}]$ cannot be distinguished from **9i** by solid-state ^{31}P NMR spectroscopy. This can also be anticipated from the similarity of the ^{31}P NMR signal shapes of all immobilized dicarbonylnickel complexes, irrespective of the type of phosphine applied. The IR data are also not sensitive to the degree of ligand exchange. Since ligand exchange is a tedious and costly procedure because of catalyst wasting, we prefer the immobilization strategy displayed in Scheme 1 for studies of catalyst activity. Then the interpretation of data is not hampered by ignorance of the nature of the surface-bound catalyst.

4. Conclusion

In summary, we have shown that, on the basis of earlier studies,^{11,18} various bifunctional phosphines and their di- and tricarbonylnickel complexes can selectively be immobilized on silica without side reactions. While the free nickel complexes can be investigated in solution by ^{61}Ni NMR spectroscopy,²⁹ the surface-bound species are best studied by ^{13}C and ^{31}P solid-state NMR spectroscopy. The nickel complexes are easily accessible to reagents and strongly bound to the support, as can be demonstrated by the absence of ^{31}P resonances of free phosphines in the ^{31}P CP/MAS NMR spectra. Immobilized di- and tricarbonylnickel complexes can be clearly distinguished by their ^{31}P CP/MAS NMR spectra, and also by IR spectroscopy. An early IR study by Basset,²⁸ using a different ligand, could be confirmed. With regard to studying catalytic processes with the immobilized nickel complexes, ligand **4** is superior to the others, because its surface-attached nickel derivatives give narrow ^{31}P NMR lines and above all ^{13}C CP/MAS NMR spectroscopy is possible without overlapping ethoxy signals.

Studies to compare the catalytic activities of the different components in solution and on silica are presently underway.

5. Experimental Section

All the experiments were performed under inert gas by Schlenk techniques. Solvents were dried by standard methods, and oxygen was removed. The identity of molecular compounds was checked by elemental analysis (all values were satisfactory within a range of $\pm 0.5\%$ for carbon and hydrogen), mass spectrometry, and their solution-state NMR spectra. All the applied compounds are commercially available, if not described below. All the experiments were carried out with Merck silica 40 (specific surface area $750\text{ m}^2/\text{g}$; average pore size 40 \AA ; particle size $0.063\text{--}0.2\text{ mm}$) that was dried at $600\text{ }^\circ\text{C}$ in vacuo (10^{-2} Pa for 12 h) in order to condense surface silanol groups.⁸ The IR data were obtained after mixing an appropriate amount of free nickel complex or supported complex with KBr and pressing the mixture into a disk. Usually, less than 100 scans gave a satisfactory S/N ratio.

5.1. Liquid-State NMR Spectroscopy. All the spectra were recorded on a Bruker MSL 300 NMR spectrometer, equipped with a multinuclear 10 mm broad-band probehead. The spectra were recorded with acetone- d_6 as the solvent, if not stated otherwise. The measured nuclei were ^1H (300.1 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz), ^{31}P (121.5 MHz), and ^{61}Ni (26.6 MHz). ^{31}P and ^{61}Ni NMR data for all nickel complexes are given in Tables 1 and 2. Hexamethyldisiloxane ($\delta(^{29}\text{Si}) = 6.87^{33}$), 85% $\text{H}_3\text{PO}_4(\text{aq})$ ($\delta(^{31}\text{P}) = 0$), and $\text{Ni}(\text{CO})_4$ ($\delta(^{61}\text{Ni}) = 0^{29}$) served as external chemical shift standards. For ^1H and ^{13}C measurements, the solvents were used as internal standards and the shifts were recalculated with respect to TMS. The ^{61}Ni NMR spectra were recorded using a solenoid probehead and special sample tubes described earlier.²⁹

5.2. Solid-State NMR Spectroscopy. All the spectra were recorded on a Bruker MSL 300 NMR spectrometer, equipped with a 7 mm broad-band double-bearing MAS probehead and ZrO_2 rotors. The modified silica was loosely filled into the rotors under nitrogen. Cross polarization (CP)¹³ and magic angle spinning (MAS)^{5,12} with a rotational speed of 4 kHz were applied for all the spectra shown. The isotropic lines were determined by variation of the spinning speed, if not obvious. The contact times were 5 ms (^{13}C) and 1 ms (^{31}P), and the relaxation delays were 4 s for all surface-immobilized compounds. In the case of ^{31}P CP/MAS NMR spectra, 500–1000 transients gave satisfactory signal to noise ratios. Simple high power decoupling with long relaxation delays gave identical spectra but required much more time for measurement. The applied ^{31}P CP/MAS NMR parameters give optimal S/N ratios also for uncomplexed surface-bound phosphines and P(V) side products.¹¹ The ^{13}C CP/MAS NMR spectrum (Figure 1) required 10 000 scans. All spectra were recorded at room temperature (298 K). The ^{31}P CP/MAS NMR spectra were referenced with respect to 85% $\text{H}_3\text{PO}_4(\text{aq})$ by setting the ^{31}P NMR peak of solid $\text{NH}_4\text{H}_2\text{PO}_4$ to $+0.81\text{ ppm}$. The ^{13}C CP/MAS NMR spectra were referenced with respect to external adamantane.³⁴ The Hartmann–Hahn match was also set by using solid $\text{NH}_4\text{H}_2\text{PO}_4$ and adamantane. For the exponential multiplication, a line-broadening factor of 100 Hz was applied.

5.3. Preparation of Bifunctional Phosphines. 5.3.1. $\text{PPh}_2(\text{C}_6\text{H}_4)\text{Si}(\text{OEt})_3$ (1**).** Compound **1** was synthesized in 90% yield via (*p*-bromophenyl)diphenylphosphine³⁵ by the procedure given in ref 36. Only $\text{Si}(\text{OEt})_4$ was used instead of $\text{Me}_2\text{Si}(\text{OEt})_2$. Spectral data: mass spectrum (70 eV) *m/e* (relative intensity) 297 (11.4), 262 (20.7), 255 (3.3), 240 (11.1), 255 (4.4), 200 (27.2), 195 (38.6), 183 (38.0), 162 (33.1), 149 (100.0), 139 (28.1), 119 (18.8), 77 (5.8), 51 (6.0); ^1H NMR δ 7.72–7.12 (m, 14H, aryl H), 3.87 (q, $J = 7.0\text{ Hz}$, 6H, OCH_2), 1.20 (t, $J = 7.0\text{ Hz}$, 9H, CH_3); ^{13}C NMR δ 138.25–129.4 (signals overlapping, aryl C), 59.26 (OCH_2), 18.55 (CH_3); ^{31}P NMR δ -4.53 ; ^{29}Si NMR δ -54.93 .

5.3.2. $\text{PPh}_2(\text{C}_6\text{H}_4)\text{SiMe}_2(\text{OEt})$ (2**).** Compound **2** was synthesized via (*p*-bromophenyl)diphenylphosphine³⁵ by the procedure given in ref 36. The ^1H NMR data are in agreement with the literature data.³⁶ Data not given in ref 36: mass spectrum (70 eV) *m/e* (relative intensity) 364 (67.3, M^+), 349 (4.4), 305 (12.3), 262 (100.0), 183 (82.3), 152 (8.9), 108 (34.9), 75 (7.2), 57 (6.1); ^{13}C NMR δ 138.16 ($^1J(^{31}\text{P}-^{13}\text{C}) = 12.0\text{ Hz}$, C_{ipso}), 137.94 ($^1J(^{31}\text{P}-^{13}\text{C}) = 12.0\text{ Hz}$, C_{ipso}), 134.49–129.46 (overlapping, aryl C), 59.04 (OCH_2), 18.79 (CH_2CH_3), -1.60 (SiCH_3); ^{31}P NMR δ -4.50 ; ^{29}Si NMR δ 4.77.

5.3.3. $\text{PPh}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ (3**).** Compound **3** was prepared from $\text{Ph}_2\text{PLi}^{37}$ and (3-chloropropyl)triethoxysilane according to the procedure given by Capka.³⁸ Since the NMR data do not seem to be literature known yet, they are given here. The signal assignments were made on the basis of the data of PPh_3 and $(^n\text{Bu})_3\text{P}$, given in ref 39: ^1H NMR (CDCl_3) δ 6.90–6.77 (m, 10H, aryl H), 3.27 (q, 6H, $J = 6.6\text{ Hz}$, OCH_2) 1.62 (t, $J = 7.3\text{ Hz}$, 2H, PCH_2), 1.09 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.67 (t, J

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= 6.6 Hz, 9H, CH₃), 0.32 (t, *J* = 8.0 Hz, 2H, SiCH₂); ¹³C NMR (CDCl₃) δ {¹J(¹³C–¹H)} 138.79 {–} (¹J(³¹P–¹³C) = 12.1 Hz, C_{ipso}), 132.53 {161.6} (²J(³¹P–¹³C) = 19.3 Hz, C_{ortho}), 128.18 {164.1} (C_{para}), 128.15 {159.2} (³J(³¹P–¹³C) = 7.2 Hz, C_{meta}), 58.12 {142.3} (OCH₂), 31.35 {127.9} (¹J(³¹P–¹³C) = 12.1 Hz, PCH₂), 19.40 {127.9} (²J(³¹P–¹³C) = 19.3 Hz, CH₂CH₂CH₂), 18.09 {125.5} (CH₃), 12.08 {120.6} (³J(³¹P–¹³C) = 12.1 Hz, SiCH₂); ³¹P NMR (CDCl₃) δ –16.3.

5.3.4. PPh₂(CH₂)₄OH (4). Compound **4** was synthesized from PPh₂Li³⁷ and THF using the procedure given by Garner.⁴⁰ Since the NMR data do not seem to be literature known yet, they are reported here. Signal assignments are made as above (section 5.3.3). Additionally, selective ¹H decoupling was used: ¹H NMR (CDCl₃) δ 7.05–6.88 (m, 8H, H_{ortho}, H_{meta}), 6.80 (t, *J* = 8.0 Hz, 2H, H_{para}), 3.25 (s, broad, 1H, OH), 3.17 (t, *J* = 6.6 Hz, 2H, CH₂OH), 1.69 (t, *J* = 8.0 Hz, 2H, PCH₂), 1.30 (quint, *J* = 7.8 Hz, 2H, CH₂CH₂OH), 1.16 (quint, *J* = 7.8 Hz, 2H, PCH₂CH₂); ¹³C NMR (CDCl₃) δ {¹J(¹³C–¹H)} 138.54 {–} (¹J(³¹P–¹³C) = 13.2 Hz, C_{ipso}), 132.30 {160.6} (²J(³¹P–¹³C) = 18.3 Hz, C_{ortho}), 128.06 {160.6} (³J(³¹P–¹³C) = 7.1 Hz, C_{meta}), 127.85 {160.6} (C_{para}), 61.48 {140.0} (CH₂OH), 33.77 {123.9} (¹J(³¹P–¹³C) = 13.2 Hz, PCH₂), 27.52 {128.5} (²J(³¹P–¹³C) = 11.2 Hz, PCH₂CH₂), 22.07 {121.6} (³J(³¹P–¹³C) = 16.2 Hz, CH₂CH₂OH); ³¹P NMR (THF) δ –16.1.

5.4. Synthesis of Nickel Complexes. All the di- and tricarbonylnickel complexes were prepared by reaction of Ni(CO)₄ with the appropriate amount of the corresponding phosphines at room temperature according to the literature.²⁵ All the ⁶¹Ni and ³¹P NMR data are given in Table 1. The compounds are colorless or slightly cream colored. The mass spectra generally do not give the M⁺ peak, due to facile ligand dissociation.

5.4.1. (CO)₃Ni[PPh₂(C₆H₄)SiMe₂OEt] (5). Mass spectrum (70 eV) *m/e* (relative intensity) 364 (20.2), 262 (100.0), 183 (20.0), 154 (6.8), 108 (4.0); ¹H NMR δ 7.79–7.19 (m, 14H, aryl H), 3.70 (q, *J* = 7.1 Hz, 2H, CH₂CH₃), 1.13 (t, *J* = 7.1 Hz, 3H, CH₂CH₃), 0.36 (s, 6H, SiCH₃); ¹³C NMR δ {¹J(¹³C–¹H)} 196.84 (CO), 138.22–129.75 (overlapping, aryl C), 59.11 {139.1} (OCH₂), 18.77 {125.7} (CH₂CH₃), –1.63 {118.9} (SiCH₃).

5.4.2. (CO)₃Ni[PPh₂(C₆H₄)Si(OEt)₃] (6). Mass spectrum (70 eV) *m/e* (relative intensity) 424 (53.1), 262 (97.2), 183 (100.0), 154 (31.5), 108 (28.6); ¹H NMR δ 7.80–7.21 (m, 14H, aryl H), 3.90 (q, *J* = 6.8 Hz, 6H, OCH₂), 1.22 (t, *J* = 6.8 Hz, 9H, CH₃); ¹³C NMR δ {¹J(¹³C–¹H)} 196.72 {–} (CO), 138.71–129.55 (m, aryl C), 59.31 {142.9} (CH₂), 18.54 {125.7} (CH₃).

5.4.3. (CO)₃Ni[PPh₂(CH₂)₃Si(OEt)₃] (7). ¹H NMR δ 7.21–7.08 (m, 10H, aryl H), 3.38 (q, *J* = 6.7 Hz, 6H, OCH₂), 2.05 (t, *J* = 7.5 Hz, 2H, PCH₂), 1.24 (quint, *J* = 7.5 Hz, 2H, CH₂CH₂CH₂), 0.39 (t, *J* = 7.5 Hz, 2H, SiCH₂); ¹³C NMR δ {¹J(¹³C–¹H)} 197.16 {–} (CO), 137.05 {–} (d, ¹J(³¹P–¹³C) = 31.8 Hz, C_{ipso}), 132.57 {160.2} (d, ²J(³¹P–¹³C) = 12.4 Hz, C_{ortho}), 130.43 {161.6} (C_{para}), 129.30 {161.6} (d, ³J(³¹P–¹³C) = 8.3 Hz, C_{meta}), 58.65 {142.2} (OCH₂), 33.87 {129.8} (d, ¹J(³¹P–¹³C) = 20.7 Hz, PCH₂), 19.41 {125.7} (d, ²J(³¹P–¹³C) = 5.5 Hz, CH₂CH₂CH₂), 18.58 {125.7} (CH₃), 12.74 {117.4} (d, ³J(³¹P–¹³C) = 15.2 Hz, SiCH₂).

5.4.4. (CO)₃Ni[PPh₂(CH₂)₄OH] (8). ¹H NMR δ 7.80–7.19 (m, 10H, aryl H), 3.60 (t, *J* = 7.0 Hz, 2H, CH₂OH), 3.41 (s, broad, 1H, OH), 2.42 (t, *J* = 6.9 Hz, 2H, PCH₂), 1.63 (m, 2H, CH₂CH₂OH), 0.94 (m, 2H, PCH₂CH₂); ¹³C NMR δ 197.32 (CO), 132.9–128.5 (overlapping, aryl C), 61.73 (CH₂OH), 34.80 (d, ¹J(³¹P–¹³C) = 14.0 Hz, PCH₂), 30.96 (d, ²J(³¹P–¹³C) = 21.1 Hz, PCH₂CH₂), 22.29 (d, ³J(³¹P–¹³C) = 7.0 Hz, CH₂CH₂OH).

5.4.5. (CO)₂Ni[PPh₂(C₆H₄)SiMe₂OEt]₂ (9). Mass spectrum (70 eV) *m/e* (relative intensity) 754 (2.1), 713 (2.9), 651 (7.8), 568 (13.6), 467 (66.8), 365 (100.0), 262 (19.0); ¹H NMR δ 7.68–7.15 (m, 28H,

aryl H), 3.68 (q, *J* = 7.0 Hz, 4H, OCH₂), 1.14 (t, *J* = 7.0 Hz, 6H, CH₂CH₃), 0.34 (s, 12H, SiCH₃); ¹³C NMR δ {¹J(¹³C–¹H)} 200.35 {–} (CO), 140 {–} (aryl C), 139.20 {–} (d, ¹J(³¹P–¹³C) = 37.0 Hz, C_{ipso}), 137.72 (d, ¹J(³¹P–¹³C) = 30.1 Hz, C_{ipso}), 138.10–129.02 (overlapping, aryl C), 59.07 {141.0} (OCH₂), 18.83 {124.5} (CH₂CH₃), –1.55 {119.1} (SiCH₃).

5.4.6. (CO)₂Ni[PPh₂(C₆H₄)Si(OEt)₃]₂ (10). Mass spectrum (70 eV) *m/e* (relative intensity) 882 (7.9), 772 (11.8), 610 (17.0), 587 (49.3), 424 (100.0), 262 (12.1); ¹H NMR δ 7.59–7.10 (m, 28H, aryl H), 3.86 (q, *J* = 6.9 Hz, 12H, OCH₂), 1.22 (t, *J* = 6.9 Hz, 18H, CH₃); ¹³C NMR δ {¹J(¹³C–¹H)} 200.35 {–} (CO), 140.57–128.97 (overlapping, aryl C), 59.29 {142.9} (CH₂), 18.58 {125.7} (CH₃).

5.4.7. (CO)₂Ni[PPh₂(CH₂)₃Si(OEt)₃]₂ (11). ¹H NMR δ 7.49–7.21 (m, 20H, aryl H), 3.63 (q, *J* = 7.0 Hz, 12H, OCH₂), 1.70 (m, 4H, PCH₂), 1.35 (m, 4H, CH₂CH₂CH₂), 1.12 (t, *J* = 7.0 Hz, 18H, CH₃), 0.40 (t, *J* = 7.5 Hz, 4H, SiCH₂); ¹³C NMR δ 201.47 (CO), 133–129 (m, aryl C), 58.56 (OCH₂), 33.83 (d, ¹J(³¹P–¹³C) = 21.1 Hz, PCH₂), 19.44 (d, ²J(³¹P–¹³C) = 7.0 Hz, CH₂CH₂CH₂), 18.55 (CH₃), 12.73 (d, ³J(³¹P–¹³C) = 15.2 Hz, SiCH₂).

5.5. Immobilization of Phosphines and Nickel Complexes. All the phosphines and their di- and tricarbonylnickel complexes are immobilized using the procedure given in ref 11: SiO₂ (1 g) is suspended in ca. 10 mL of toluene. A solution of 0.4 g of phosphine or nickel complex in ca. 10 mL of toluene is added under rigorous stirring. Then the mixture is stirred at room temperature for 12 h. Higher temperatures should be avoided, because they do not increase the surface coverage substantially but lead to side products¹¹ and decomposition of the nickel complexes with formation of Ni⁰. Finally, the supernatant solution is decanted, and the silica is washed three times with 50 mL portions of toluene and dried in vacuo (10^{–2} Pa) for about 5 h. Their resulting ³¹P CP/MAS NMR data are given in Table 2 and ref 11. The δ(³¹P) values of immobilized **1i** and **2i** are –4.3 and –5.7 ppm, respectively.

The surface coverages were not determined by carbon elemental analysis, because there is always a variable amount of residual and surface-bound ethoxy groups or adsorbed solvent present (ref 18 and section 3.1). A more reliable and reproducible method is treating a known amount of silica with an excess of phosphine or nickel complex and weighing the residual phosphine or nickel complex after removal of the solvents of the supernatant solution. Typical values (in parentheses) for the surface coverages (mmol/g of SiO₂): **1i** (0.2), **2i** (0.3), **3i** (0.3), **4i** (0.4), **5i** (0.3), **6i** (0.2), **7i** (0.3), **8i** (0.4), **9i** (0.1), **10i** (0.1), **11i** (0.2).

5.6. Reaction of Phosphinated Silica with Ni(CO)₄. Ni(CO)₄ was condensed into a Schlenk flask, weighed, and diluted with toluene. The appropriate amount of solution was transferred into a dropping funnel and added slowly to a suspension of the respective phosphinated silica in toluene under rigorous stirring. Irrespective of the amount of Ni(CO)₄ or the dropping rate or dilution, the tricarbonylnickel complexes were always the result exclusively.

5.7. Reaction of (CO)₂Ni(PPh₃)₂ with Phosphinated Silica. A suspension of phosphinated silica in toluene was stirred with a solution of (CO)₂Ni(PPh₃)₂ in toluene. The ligand exchange was followed by ³¹P NMR of the solution. The liquid phase was removed several times and replaced by PPh₃-free solutions of (CO)₂Ni(PPh₃)₂. The ³¹P CP/MAS NMR spectra of the obtained material did not change with the degree of ligand exchange.

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