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^{61}Ni NMR Spectroscopy of Di- and Tricarbonylnickel Complexes

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Di- and tricarbonylnickel phosphine complexes (22) were prepared and their liquid-state ^{61}Ni NMR spectra were recorded with the use of special solenoid glass sample tubes and a solenoid probehead, which are described. The acquired chemical shifts $\delta(^{61}Ni)$, linewidths $\nu_{1/2}(Ni)$, relaxation times T_1 and coupling constants $^1J(^{61}Ni,^{31}P)$ are discussed with reference to the electronegativity of the substituents at the phosphine ligands and the Tolman angle θ of the latter.

KEY WORDS NMR; ^{61}Ni NMR; solenoid probehead; carbonylnickel phosphine complexes

INTRODUCTION

Nickel carbonyl complexes play an important role in preparative and mechanistic chemistry and catalysis.$^{1-3}$ In contrast, only six publications dealing with ^{61}Ni NMR spectroscopy$^{4-9}$ have appeared. The reasons for this are the very unfavourable NMR properties of the ^{61}Ni nucleus: the natural abundance (1.19%) and relative receptivity (0.231 compared with ^{13}C) are low, whereas the quadrupolar moment (0.16×10^{-28} m^2) of this spin-3/2 nucleus is large. The latter leads to extremely broadened ^{61}Ni NMR resonances even for slightly unsymmetric nickel complexes. Therefore owing to the fast relaxation, indirect methods of detection can no longer be applied.^{5} Additionally, the low resonance frequency of 26.8 MHz [with $\nu(^1H) = 300$ MHz] often leads to severe ringing effects and rolling baselines. This renders the detection of broad signals with a chemical shift range of about 2000 ppm very difficult.

In this paper, we describe an easy NMR method to diminish or overcome all the above difficulties. With this method, we routinely acquired new $\delta(^{61}Ni)$, $\nu_{1/2}(^{61}Ni)$ and $^1J(^{61}Ni, ^{31}P)$ values for di- and tricarbonylnickel complexes. In addition to the analytical value [all the $\delta(^{31}P)$ values are similar for di- and tricarbonylnickel complexes], we discuss relationships between the different parameters such as cone angles and electronegativity of the ligands and the NMR data.

RESULTS

Measurements in solenoid probeheads

All the compounds were measured as dilute solutions in solenoid probeheads (for the reason, see below). Since the di- and tricarbonylnickel complexes are more or less air-sensitive, depending on the type of phosphine ligand, special solenoid sample tubes were developed (Fig. 1). The laboratory-made sample tubes with a volume of about 1.5 ml in the horizontal moiety are equipped with a ground-glass joint and stopper, which allows convenient reopening and reuse of the tube. The latter fit well into the commercially available Bruker solenoid probeheads.

The usual application of these solenoid probeheads lies in the field of solid-state NMR (wideline NMR of powders or single crystals with high-power operation). However, measurements of 'difficult' quadrupolar nuclei such as ^{61}Ni in solution are also facilitated by the beneficial characteristics of solenoid probeheads:

(a) They display short ring-down delays with a maximum of 10 μs. This is extremely important for ^{61}Ni NMR spectroscopy, since the T_1 values for most of the compounds are very short (< 10 ms).^{7} This excludes the application of quadrupolar echo techniques, because even with τ delays of 30 μs too much of the initial FID is lost, leading to poor signal intensity and problems with first-order phase correction. Additionally, the short

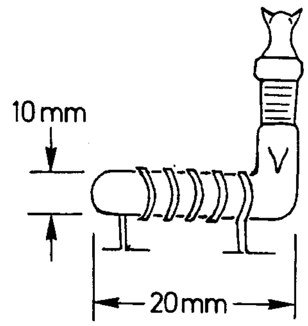

Figure 1. Schematic sideview of an airtight glass sample tube within the solenoidal coil of the probehead: The stopper (5 mm ground-glass joint) is fixed by a rubber band, which is not shown here. Diameter and length of the sample tube: 10 mm and 2 cm, respectively.

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ring-down delays of solenoid probeheads allow pulse repetition times of <100 ms without propagation of ringing.

(b) 90° pulses as short as 6 μs allow the reliable excitation of a large frequency range and thus are a prerequisite for the detection of ^{61}Ni NMR resonances with only one experiment.

(c) In principle, solenoid probeheads provide a signal-to-noise ratio that is about a factor of three better than that obtainable with a saddle-coil design.[10,11] In the case of compound **12** (see Table 2), the signal-to-noise ratio after the same number of scans was about a factor of 1.6 better when a solenoid probehead was used than with measurement of an equal sample concentration and volume in a conventional high-resolution broadband probehead. Unfortunately, reasonable ^{61}Ni NMR spectra of the dicarbonyl compounds could not be obtained with a conventional saddle coil probehead because of major ringing problems. Further, the sensitivity of a solenoid probehead is additionally improved, because every frequency range has its own insert. Therefore, usually 20 mg of the tricarbonylnickel complexes and 50 mg of the dicarbonylnickel complexes were sufficient in order to obtain ^{61}Ni NMR spectra with reasonable signal-to-noise ratios.

(d) The shimming of solenoid probeheads is easy, because the sample is positioned horizontally in the homogeneous zone of the magnet. A linewidth of 7 Hz[12] for the ^{61}Ni resonance of the nickel tetracarbonyl sample can be obtained without an extended shimming procedure. The optimum linewidth for nickel tetracarbonyl was determined to be 3.9 Hz.[7] However, the ^{61}Ni NMR signals of the more unsymmetric compounds are much broader anyway. It is important to note that the sample tube (Fig. 1) does not have to be filled completely. Gas bubbles do not spoil the shim and even a half-filled sample tube will do. Even undissolved solid material on the bottom of the tube does not matter.

Finally, the application of solenoid probeheads is not confined to ^{61}Ni NMR spectroscopy, but can also be used for the measurement of paramagnetic samples[13] or other transition metal nuclei such as ^{195}Pt. Additionally, since the commercially available inserts are made of PTFE, ^{27}Al, ^{11}B or ^{29}Si NMR spectroscopy is not hampered by a probehead background. Special inserts for ^{1}H, ^{13}C and ^{19}F NMR measurements are offered by Bruker.

^{61}Ni NMR data

The ^{61}Ni NMR chemical shift data and signal half-widths $\nu_{1/2}$ of a selection of dicarbonylnickel complexes are given in Table 1. Table 2 shows the $\delta(^{61}\mathrm{Ni})$, $\nu_{1/2}$ and $^{1}J(^{61}\mathrm{Ni},^{31}\mathrm{P})$ data for the related tricarbonylnickel complexes. Since the question of the external chemical shift standard is not yet settled, we used pure $Ni(CO)_4$, in accord with Refs 7–9 and in analogy with the standards for ^{183}W and ^{57}Fe NMR spectroscopy.[17]

Dicarbonylnickel complexes. All the dicarbonylnickel complexes give broad, featureless signals with $\nu_{1/2}$ values of 0.2–2.7 kHz (Table 1). Therefore, the exact determination of a $^{1}J(^{61}\mathrm{Ni},^{31}\mathrm{P})$ coupling is generally not possible. The only exception is the trimethylphosphine complex, the ^{61}Ni NMR spectrum of which shows a triplet structure with a coupling constant of 250 Hz (Fig. 2).

When the extreme narrowing condition is fulfilled, the linewidth of quadrupolar nuclei in solution is given

Table 1. Chemical shifts $\delta(^{61}\mathrm{Ni})$ relative to external $Ni(CO)_4$ ($\delta = 0$) and signal half-widths $\nu_{1/2}$ (kHz) for dicarbonylnickel complexes in THF solution[a]

Compound[b]	No.	$\delta(^{61}\mathrm{Ni})$[c]	$\nu_{1/2}$ (kHz)[d]	θ (°)[e]
$(CO)_2Ni(PMe_3)_2$	**1**	104.0	0.24	118
$(CO)_2Ni(dppe)$	**2**	−160.5	1.20	125
$(CO)_2Ni(PPh_2H)_2$	**3**	−2.9	0.63	128
$(CO)_2Ni[P(OPh)_3]_2$	**4**	−294.0	2.70	128
$(CO)_2Ni[(P^nBu_3)]_2$	**5**	24.0	1.30	132
$(CO)_2Ni(dipe)$	**6**	−240.4	0.81	135
$(CO)_2Ni(PPh_2Cl)_2$	**7**	91.3	3.01	138
$(CO)_2Ni(PPh_2Et)_2$	**8**	18.8	0.72	140
$(CO)_2Ni(PCy_2H)_2$	**9**	−31.2	0.34	142
$(CO)_2Ni(PPh_3)_2$	**10**	90.7	0.75	145
$(CO)_2Ni(PCy_3)_2$	**11**	−10.4	0.63	170

[a] The compounds are arranged in order of increasing Tolman cone angles θ^{14-16} of the phosphine ligands.

[b] dppe = $(Ph_2PCH_2CH_2PPh_2)$; dipe = $^iPr_2PCH_2CH_2P^iPr_2$; Ph = C_6H_5; Cy = C_6H_{11}.

[c] δ ± 0.5 ppm [high-frequency shifts are positive with respect to external $Ni(CO)_4$].

[d] $\nu_{1/2}$ ± 20 Hz.

[e] Tolman cone angle taken from Refs 14–16 or calculated with the procedure given there.

Table 2. Chemical shifts $\delta(^{61}\mathrm{Ni})$ relative to external $Ni(CO)_4$ ($\delta = 0$), signal half-widths $\nu_{1/2}$ (Hz) and $^{1}J(^{61}\mathrm{Ni},^{31}\mathrm{P})$ (Hz) of tricarbonylnickel complexes in THF solution[a]

Compound[b]	No.	$\delta(^{61}\mathrm{Ni})$[c]	$\nu_{1/2}$(Hz)[d]	$^{1}J(^{16}\mathrm{Ni},^{31}\mathrm{P})$ (Hz)[e]	θ (°)[f]
$(CO)_3Ni(PMe_3)$	**12**	25.8	140	230	118
$[(CO)_3Ni]_2(dppe)$	**13**	−2.1	—[g]	210	125
$[(CO)_3Ni]_2(dppb)$	**14**	6.7	131	236	127
$(CO)_3Ni(PPh_2H)$	**15**	5.0	90	234	128
$(CO)_3Ni[P(OPh)_3]$	**16**	−129.5	—[g]	351	128
$(CO)_3Ni(P^nBu_3)$	**17**	−16.2	—[g]	196	132
$(CO)_3Ni(PPh_2Cl)$	**18**	48.5	—[g]	236	138
$(CO)_3Ni(PPh_2Et)$	**19**	−0.1	131	236	140
$(CO)_3Ni(PCy_2H)$	**20**	−23.5	55	230	142
$(CO)_3Ni(PPh_3)$	**21**	24.2	16	236	145
$(CO)_3Ni(PCy_3)$	**22**	−11.2	55	211	170

[a] The compounds are arranged in order of increasing Tolman cone angle θ^{14-16} of the phosphine ligand.

[b] Ph = C_6H_5; dppe = $Ph_2PCH_2CH_2PPh_2$; dppb = $Ph_2P(CH_2)_4PPh_2$; Cy = C_6H_{11}.

[c] δ ± 0.1 ppm [high-frequency shifts are positive with respect to external $Ni(CO)_4$].

[d] Half-width $\nu_{1/2}$ ± 5 Hz.

[e] $^{1}J(^{61}\mathrm{Ni},^{31}\mathrm{P})$ ± 1 Hz.

[f] Tolman cone angle taken from Refs 14–16 or calculated with the procedure given there.

[g] $\nu_{1/2}$ could not be determined because the two lines of the doublet overlapped.

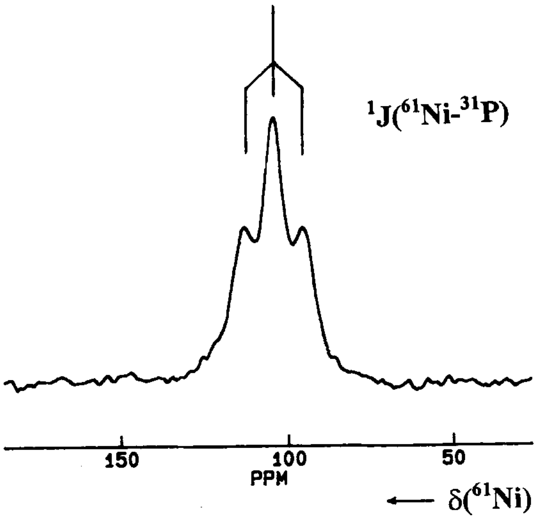

Figure 2. 26.8 MHz ^{61}Ni NMR spectrum of $(CO)_2Ni(PMe_3)_2$, dissolved in THF. $^1J(^{61}Ni, ^{31}P) = 250 \pm 2$ Hz. Time required for the measurement: 3 h.

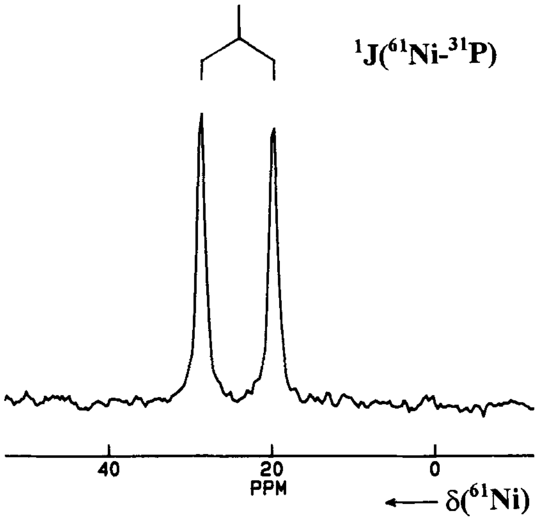

Figure 3. 26.8 MHz ^{61}Ni NMR spectrum of $(CO)_3Ni(PPh_3)$, dissolved in THF. Time required for the measurement: 0.5 h.

by the equation[18]

$$\nu_{1/2} = 3/10\pi(2I + 3)/I^2(2I - 1)\chi^2\tau_c \qquad (1)$$

where I represents the nuclear spin quantum number, χ the nuclear quadrupole coupling constant and τ_c the correlation time.[18] On the basis of Eqn (1) an attempt was made to minimize the correlation time and thus the linewidth. However, the linewidth showed only minimal changes when the solvent was varied (toluene, benzene, diethyl ether, ethanol, acetone, DME), being optimum for THF. The same observation was made when the temperature was increased. For example, measurement of the triphenylphosphine nickel complex in toluene at 298 K gavea $\nu_{1/2}$ value of 0.75 kHz and at 360 K $\nu_{1/2}$ was still 0.74 kHz. This linewidth far exceeds the expected coupling constant of about 250 Hz (see above). The ^{61}Ni chemical shifts of the dicarbonyl complexes show a strong temperature dependence. For example, $\delta(^{61}Ni)$ of **5** changes from 24.0 to 41.5 when the measurement temperature is increased from 298 to 320 K.

Attempts to obtain the $^1J(^{61}Ni,^{31}P)$ values from the ^{31}P NMR spectra were unsuccessful, probably owing to the large expected linewidth of the nickel satellites (see the next section).

Tricarbonylnickel complexes. All the signals for the tricarbonylnickel complexes show narrow lines (for half-widths $\nu_{1/2}$, see Table 2) and therefore all coupling constants $^1J(^{61}Ni,^{31}P)$ can be determined. A typical doublet signal is shown in Fig. 3 for the triphenylphosphine nickel complex. In this case, the $^1J(^{61}Ni,^{31}P)$ value can be obtained alternatively by measuring the ^{31}P NMR spectrum of a saturated THF solution of the complex. As Fig. 4 shows, the central signal is flanked by four nickel satellites with equal intensity, as is expected for a ^{31}P NMR signal, coupled to a spin-3/2 ^{61}Ni nucleus. However, the time required for the measurement of the spectrum was about 12 h and careful shimming was necessary in order to obtain a sufficiently narrow signal base. Additionally, since the satellites have extremely small signal intensities of about 0.3% compared with the central signal, minute amounts of impurities can have a disastrous effect on the spectrum quality. For example, traces of the dicarbonyl complex show up in the spectrum in Fig. 4. Further, the nickel satellites have a half-width of about 18 Hz, and hence, owing to the neighborhood of quadrupolar ^{61}Ni to the phosphorus nucleus, are much broader than the central signal (0.3 Hz). This reduces the intensities of the nickel satellites even more, and unfortunately prevents the exact determination of the ^{61}Ni secondary isotope effect on the ^{31}P NMR chemical shift. On the other hand, the direct ^{61}Ni NMR measurement takes just 0.5 h and no shimming is required.

As with dicarbonylnickel complexes, the ^{61}Ni chemical shifts of the tricarbonyl complexes are strongly temperature dependent. For example, $\delta(^{61}Ni)$ of **22** changes from −11.2 to 3.7, when the measurement temperature is raised from 298 to 330 K.

The small linewidth of the tricarbonylnickel complexes in solution led to their NMR investigation in

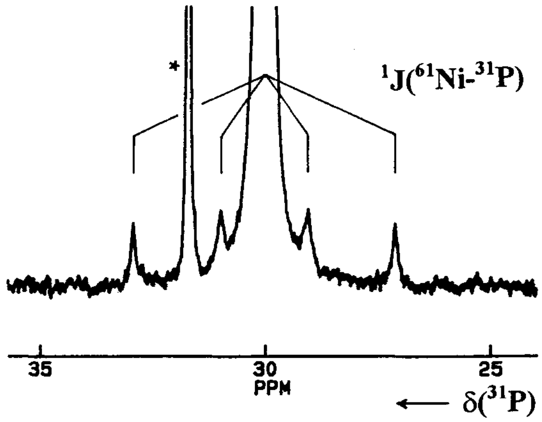

Figure 4. 121.5 MHz ^{31}P NMR spectrum of a saturated THF solution of $(CO)_3Ni(PPh_3)$. The asterisk denotes the ^{31}P NMR signal of traces of $(CO)_2Ni(PPh_3)_2$.

the solid state. Unfortunately, all attempts to obtain solid-state ^{61}Ni NMR spectra were unsuccessful. Even the symmetric compound $(COD)_2Ni$ (COD = cyclooctadiene) and fast sample rotation (4 kHz) in a 7 mm magic angle spinning probehead did not give the solid-state NMR signal.

DISCUSSION

The above results show that ^{61}Ni NMR spectra of di- and tricarbonylnickel complexes can be acquired routinely and used for analytical purposes. On the basis of the above ^{61}Ni NMR data, two effects can be studied, namely the role of the stereochemistry and electronic effects, depending on the phosphine ligands. Of course, it is not possible to separate exactly electronic and stereochemical effects, but for the sake of clarity we shall do this on a formal basis.

Chemical shifts $\delta(^{61}Ni)$

With the exception of **16** and **18**, all chemical shifts for the tricarbonylnickel complexes lie within the narrow range from -23.5 to 25.8 ppm (Table 2). This observation is in accord with earlier work,[5,8] when different chemical shift standards and measurement temperatures are taken into account. It shows that obviously the influence of the phosphorus ligand[19–22] is electronically buffered to some extent by the three carbonyl moieties. Only phosphine ligands with strongly electronegative substituents such as $P(OPh)_3$ or PPh_2Cl lead to a greater shielding or deshielding, respectively, of the ^{61}Ni nucleus. The dicarbonylnickel complexes show a larger ^{61}Ni NMR chemical shift range (Table 1). Usually, for carbonyl complexes stepwise substitution of CO by PR_3 ligands leads to successive deshielding of the metal nucleus.[5,23,24] This observation is in accord with most of our complexes (Tables 1 and 2) with tertiary phosphine ligands such as **1**/**12**, **10**/**21** and **7**/**18**. However, there are also several examples that show successive shielding of the ^{61}Ni nucleus with substitution of CO by PR_3 ligands, e.g. and **4**/**16** and **9**/**20**.

In analogy with iron and molybdenum chelate complexes,[5,25] the ^{61}Ni nucleus of nickel chelate complexes is strongly shielded, as can be seen in the negative chemical shift values of **2** and **6** as compared with the non-chelate analogue **8**. For example, chelate complex **2** has a ^{61}Ni chemical shift value of -160.5 ppm, whereas its non-chelate analogue **8** gives a value of 18.8 ppm. However, a detailed discussion of the chemical shielding, depending on the ring size, would need more data.

The geometry of the dicarbonylnickel complexes, which might be approximately reflected by the steric demand of the phosphine ligand, does not seem to have a strong influence on the $\delta(^{61}Ni)$ values, since there is no correlation between the chemical shift and the Tolman cone angle θ[14–16] of the phosphine ligands (Table 1). In order to establish a chemical shift tendency with θ, the database of phosphine complexes of similar electronegativity but varying steric demand would have to be enlarged.

Linewidths $\nu_{1/2}$

According to Eqn (1),[18] the NMR linewidth of a quadrupolar nucleus depends on the correlation time τ_c and the nuclear quadrupole coupling constant χ. The temperature- and solvent-dependent measurements showed that τ_c can be reduced, but the theoretically possible gain in decreasing the signal half-width was not obtained. Therefore, we assume that, in analogy with ^{95}Mo NMR spectroscopy,[24] the signal broadening is mainly quadrupolar for these unsymmetric compounds. Therefore, χ must be the crucial factor determining the linewidth, which can also be written as[18]

$$\chi = e^2Qq_{zz}/h \qquad (2)$$

where q_{zz} represents the electric field gradient and Q the electric quadrupole moment. Therefore, the linewidth $\nu_{1/2}$ is directly proportional to q_{zz}. This electric field gradient q_{zz} is due to unsymmetrical charge distribution at the quadrupolar nucleus. Hence, in contrast to our initial 'common sense of symmetry,' the charge distribution at the ^{61}Ni nucleus is more symmetric for tricarbonyl than for dicarbonylnickel compounds. From the $\nu_{1/2}$ values of quadrupolar nuclei in the extreme narrowing condition, the relaxation times T_1 (and T_2, since $T_1 \approx T_2$ in this case) can be estimated using the equation[26]

$$\nu_{1/2} = 1/(\pi T_1) \qquad (3)$$

The T_1 relaxation times for the triphenylphosphine complexes **10** and **21** are, for example, about 0.4 ms (disregarding additional broadening due to the coupling to ^{31}P) and 19.9 ms, respectively. We could not find a proportionality between the linewidths of di- and tricarbonylnickel complexes and the steric demand of the phosphine ligands, namely θ.

Coupling constants $^1J(^{61}Ni, ^{31}P)$

Unfortunately, we have just one example at hand which shows that the one-bond coupling constants $^1J(^{61}Ni, ^{31}P)$ do not change with the degree of substitution of the carbonyl complexes, an observation in accord with Ref. 20. The coupling constant of **1** is 250 Hz (Fig. 2) and that of the tricarbonyl analogue **12** is 230 Hz.

Most of the determined $^1J(^{61}Ni,^{31}P)$ coupling constants lie within a very narrow range (Table 2). For example, compounds **12**, **14**, **15** and **18**–**21** all have coupling constants of 230–236 Hz. Obviously, the CO groups again compensate for the electronic effects of the phosphine ligands. Even the Cl substituent in **18** does not lead to a greater J value, as should be the case for more electronegative ligands.[5,8] However, the phosphite ligand in **16** produces the largest $^1J(^{61}Ni,^{31}P)$ value of our series (351 Hz). It is again tempting to search for a correlation between $^1J(^{61}Ni,^{31}P)$ and θ, but on the basis of the acquired data (Table 2) no tendency can be detected.

In conclusion, we have developed an NMR method for routinely acquiring liquid-state NMR data for 'difficult' nuclei. This has been demonstrated with the ^{61}Ni NMR spectroscopy of di- and tricarbonylnickel complexes. A wealth of new $\delta(^{61}\mathrm{Ni})$, $\nu_{1/2}(^{61}\mathrm{Ni})$ and $^{1}J(^{61}\mathrm{Ni}, {}^{31}\mathrm{P})$ data has been obtained and tendencies in their relationship to the electronegativity and Tolman cone angle of the phosphine ligands have been discussed.

EXPERIMENTAL

NMR spectroscopy

All the ^{61}Ni NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer equipped with a multinuclear solenoid probehead as described above. For the measurements of the tricarbonyl and dicarbonylnickel complexes, 20 and 50 mg, respectively, were dissolved in about 1.5 ml of purified and oxygen-free THF and filled into the solenoid sample tubes under nitrogen.

A 90° pulse length of 6 μs, a dead time delay of 10 μs and a pulse repetition time of 100 ms were applied, together with a simple single pulse sequence. The temperature was held constant at 298 K in all measurements, if not stated otherwise.

Preparation of the nickel complexes

All the nickel complexes were prepared by reaction of nickel tetracarbonyl with the appropriate amount of phosphine according to Ref. 1, using the Schlenk technique and purified solvents, free of oxygen. Compound **13** and **14** were obtained as dinuclear species only, as determined by ^{31}P NMR spectroscopy, and in analogy with Ref. 27.

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