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Square-Planar 2-Toluenido(triphenylphosphane)nickel(II) Complexes Containing Bidentate N,O Ligands: An Example of Planar Chirality

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Nickel(II) complexes comprising electronically delocalised *N,O*-chelating ligands are active catalysts in the copolymerisation of carbon monoxide and ethene. Elucidating the mechanism of catalysis presupposes the basic understanding of the intramolecular flexibility of such transition metal complexes. Several nickel(II) complexes with or without planar chirality were synthesised and characterised by NMR spectroscopic techniques and X-ray diffraction.

Introduction

Aliphatic polyketones are a class of new polymers attracting growing interest. They are produced by the catalysed copolymerisation of olefins and carbon monoxide and exhibit outstanding properties, for example, photodegradability through Norrish type I and II mechanisms,[1,2] making them interesting materials in green chemistry. Industrially, aliphatic polyketones are synthesised by the palladium-catalysed copolymerisation of carbon monoxide and olefins.[3] Because of the high cost of the transition metal and because the noble metal remains in the polymer, the search is underway for alternatives. Nickel complexes turned out to be promising candidates for an efficient catalysis,[4–7] as has been shown for the nickel complex[8] depicted in Figure 1, which is currently the most efficient one for the copolymerisation of ethene and CO.

This complex is already structurally characterised[8] and contains a bidentate *N,O*-chelating ligand, which coordinates to the nickel centre in a square-planar manner to form a six-membered chelate ring. We want to obtain more information on the flexibility of the complex, which is an important precondition for understanding the mechanism of the catalytic cycle. In this work we started off from the complex shown in Figure 1 and synthesised and characterised related complexes with special interest in their intramolecular flexibility.

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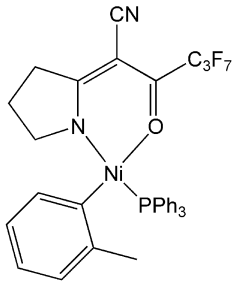
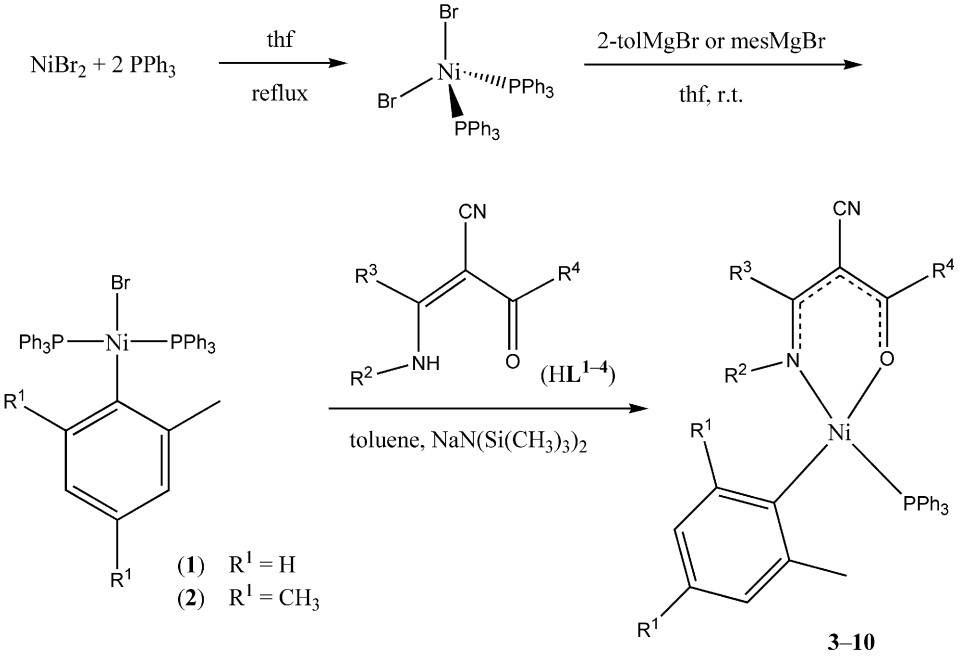


Figure 1. The most efficient nickel complex for the copolymerisation of ethene and CO to date.

Results and Discussion

Complexes of the type **1**–**10** can be prepared in a multistep synthesis according to Scheme 1.

Starting off from anhydrous nickel(II) bromide and triphenylphosphane, the reaction in tetrahydrofuran yields the well-known tetrahedral complex (*T*-4)-[$NiBr_2(PPh_3)_2$], described first by Venanzi et al.[9] We treated this complex at room temperature in situ with the appropriate Grignard compounds 2-toluenidomagnesium bromide (2-tolMgBr) or mesitylenidomagnesium bromide (mesMgBr). This step forms the diamagnetic square-planar nickel complexes (*SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$] (**1**) or (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**), respectively. As is most likely for steric reasons, those complexes are formed exclusively as their (*SP*-4-3) isomer with the two triphenylphosphane groups in *trans* position to each other, as can be inferred from their $^{31}P\{^1H\}$ NMR spectrum, which shows one singlet for the two magnetically equivalent phosphorus atoms. Furthermore, the structure of (*SP*-4-3)-[NiCl(Ph)(PPh_3)$_2$] is known[10] and confirms the square-planar (*SP*-4-3) geometry. Complex **2** has already been structurally characterised,[11] also confirming the square-planar (*SP*-4-3) geometry in accordance with the singlet signal observed for the two phosphorus atoms



Scheme 1. Synthesis of complexes **1**–**10**. See Tables 1 and 2 for substitution patterns of compounds $HL^{1–4}$ and **3**–**10**.

in the $^{31}P\{^1H\}$ NMR spectrum. Reacting either of these complexes with an appropriate bidentate N,O ligand results in catalytically active complexes of the type **3**–**10**. We reported the syntheses of such bidentate N,O ligands containing an electronically delocalised β-enaminonic chelating backbone in a recent paper.[12] The ligands used in this investigation are summarised in Table 1, and the corresponding nickel complexes are shown in Table 2.

Table 1. Prepared ligand molecules $HL^{1–4}$; refer to Scheme 1 for the positions of the substituents.

	R^2	R^3	R^4
HL^1[8,12]	$CH_2CH_2CH_2$		n-C_3F_7
HL^2[12]	$CH_2CH_2CH_2$		n-C_3H_7
HL^3	$CH_2CH_2CH_2$		cyc-C_6F_{11}
HL^4[12]	H	Me	n-C_3F_7

Table 2. Prepared complexes **3**–**10**; refer to Scheme 1 for the positions of the substituents.

	R^1	R^2	R^3	R^4
3[8]	H	$CH_2CH_2CH_2$		n-C_3F_7
4	Me	$CH_2CH_2CH_2$		n-C_3F_7
5	H	$CH_2CH_2CH_2$		n-C_3H_7
6	Me	$CH_2CH_2CH_2$		n-C_3H_7
7	H	$CH_2CH_2CH_2$		cyc-C_6F_{11}
8	Me	$CH_2CH_2CH_2$		cyc-C_6F_{11}
9	H	H	Me	n-C_3F_7
10	Me	H	Me	n-C_3F_7

Complex **3** is already known and structurally characterised.[8] We found an improved yield and shorter reaction times by using sodium bis(trimethylsilyl)amide instead of triethylamine for ligand deprotonation during the synthesis. The unit cell of the reported[8] crystal structure of **3** contains both the R_P and S_P isomers, which are enantiomers of one another (see Figure 2).

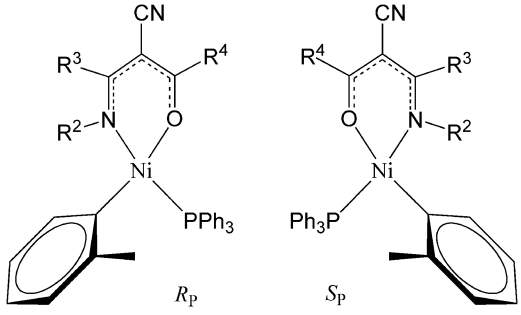


Figure 2. R_P and S_P enantiomers formed for complexes **3**, **5**, **7** and **9** comprising R^1 = H.

We were interested in finding out whether those two enantiomers were two stable conformers that did not convert into each other or the complex racemised easily in solution. To elucidate this problem, we recorded a ^{19}F NMR spectrum of complex **3**. The signal of the α-CF_2 group is shown in Figure 3.

Obviously, the two fluorine atoms in the α-CF_2 group of **3** are diastereotopic and therefore magnetically nonequivalent. One of the reasons for this might be that the rotation of the 2-toluenido substituent around the Ni–C bond is hindered under the given circumstances, that is, in dichloromethane solution at room temperature. Consequently, the complex comprises planar chirality, and the square-planar plane is split into two hemispheres: the methyl group of the 2-toluenido substituent is pointing into one hemisphere, in the corresponding position the 6-H atom of the 2-toluenido

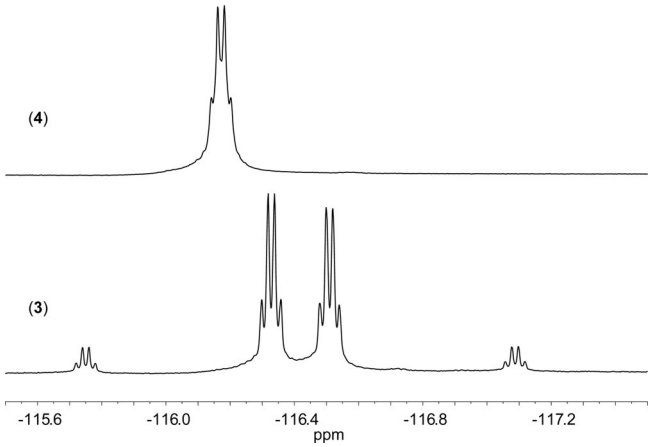


Figure 3. 470 MHz ^{19}F NMR spectrum of complexes **3** and **4** in CD_2Cl_2 at room temperature between –115.5 and –117.5 ppm, α-CF_2 groups $C(O)CF_2$. AB part of $ABMNX_3$ for **3**. A_2 part of $A_2M_2X_3$ for **4**.

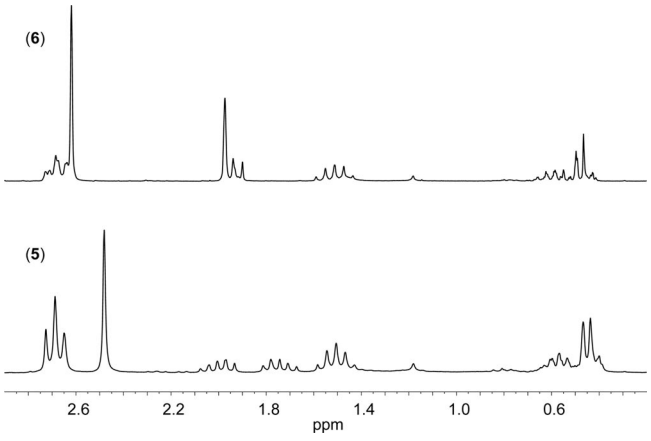


Figure 4. 200 MHz ^1H NMR spectrum of complexes **5** and **6** in CD_2Cl_2 between 0.2 and 2.9 ppm. The AB part of $ABCDE_3$ in **5** appears between 1.65–1.85 ppm and 1.90–2.10 ppm. The AB part of ABC_2D_3 in **6** appears between 1.85–2.00 ppm, overlapped by the singlet signal of the 4-methyl group.

substituent points into the other hemisphere. This induces diastereotopicity to the fluorine atoms of both the α- and the β-CF_2 groups, and thus the mentioned fluorine pairs appear anisochronous and magnetically nonequivalent. We have prepared the corresponding complex comprising a mesitylenido substituent in **4** instead of the 2-toluenido in **3**. In this case the geminal fluorine atoms are enantiotopic and magnetically equivalent. Therefore the ^{19}F NMR signal of the α-CF_2 group shows only the expected quadruplet due to the $^4J_{FF}$ coupling with the terminal CF_3 group, while the internal coupling, $^2J_{FF}$, remains inaccessible and the vicinal coupling, $^3J_{FF}$, unresolved. The $^3J_{FF}$ couplings[13–15] are very small in perfluorinated alkyl chains and are in practice very often not resolved.[16] Abraham and Cavalli[17] found more precise relations for the $^3J_{FF}$ couplings in $F–CR^aR^b–CR^cR^d–F$ systems. The $^3J_{FF}$ herein depends on the sum of electronegativities of the four neighbouring substituents, $R^a–R^d$, attached to the ethane skeleton.

We were interested in finding out whether those nonequivalence effects could also be observed in the corresponding nonfluorinated compound, as perfluorinated alkyl chains are known to be more rigid than their nonfluorinated equivalents. In analogy to **3**, we prepared complex **5**, in which the $CF_3–CF_2–CF_2$ group used in **3** is substituted by a $CH_3–CH_2–CH_2$ unit. Synthesis was carried out by a heterogeneous reaction with Ag_2O as base, which was used for deprotonation of the ligand molecule. The ^1H NMR spectrum of complex **5** at room temperature shows the corresponding nonequivalence effects for the protons in the alkyl chain, which give rise to an $ABCDE_3$ spin system. The geminal protons in $C(O)CH_2$ of **6**, the corresponding achiral mesitylenido complex, which we have also prepared in order to provide evidence, are deceptively simple, imitating the case of magnetic equivalence, as can be seen from the AB part of an ABC_2D_3 system shown in Figure 4.

To unambiguously elucidate this stereochemical effect, we created a ligand with higher steric demand, which overhangs in both hemispheres and therefore acts as a more sensitive sensor group. We synthesised the novel ligand $(\mathbf{L^3})^-$ comprising a perfluorocyclohexyl moiety bound to the carbonyl group. Ligand synthesis was performed by reacting pyrrolidin-(2*E*/2*Z*)-ylideneacetonitrile with 1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexanecarbonyl chloride in the presence of triethylamine acting as a base. Remarkably, when using the nonfluorinated cyclohexanecarbonyl chloride (for comparative studies) in this reaction, we found that only *N*-acylation took place to yield the unwanted [1-cyclohexanecarbonylpyrrolidin-(2*E*)-ylidene]acetonitrile.[12] Hence, the nonfluorinated analogue of $H\mathbf{L^3}$ remains inaccessible by this method. The complexation of $(\mathbf{L^3})^-$ to yield the desired nickel complexes **7** or **8** is accomplished by reacting stoichiometric amounts of $H\mathbf{L^3}$ with (*SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$] (**1**) or (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**), respectively, in the presence of sodium bis(trimethylsilyl)-amide as base. The ^{19}F NMR spectra of complexes **7**, the 2-toluenido derivative, and **8**, the mesitylenido derivative, are shown in Figure 5. The range from –110 to –145 ppm corresponds to signals generated by the five CF_2 groups of the cyclohexane ring system. The signals of the tertiary CF units, not shown in Figure 5, appear at –173.6 ppm (for **7**) and –173.3 ppm (for **8**), respectively.

The spectrum shows an ABCDEFGHIJX spin system for **7**, which unambiguously supports the interpretation of a planar chiral complex resulting from the hindrance of the rotation of the 2-toluenido substituent around the Ni–C bond. The spectrum simplifies to an $[ABCD]_2EFX$ spin system in the achiral case of complex **8**, as anticipated.

The effect is also obvious in the proton NMR spectra of **7** and **8**. The protons on the pyrrolidine ring form an ABCDEF spin system in the chiral complex **7** and an $[ABC]_2$ spin system in the achiral complex **8**. The ABCD part of **7** is shown in Figure 6; it appears in the range 2.53–2.77 ppm and is overlapped by the singlet signal of the 2-methyl group. In **8** this system simplifies to an $[AB]_2$ system, which is also shown in Figure 6.

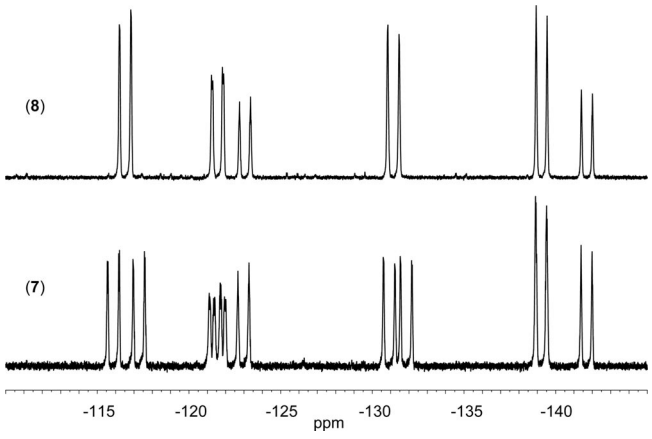


Figure 5. 470 MHz ^{19}F NMR spectra of complexes **7** and **8** in C_6D_6. Signals for CF_2 groups between –110 and –145 ppm, the ABCDEFGHIJX system for **7** and the $[ABCD]_2EFX$ system for **8** are shown.

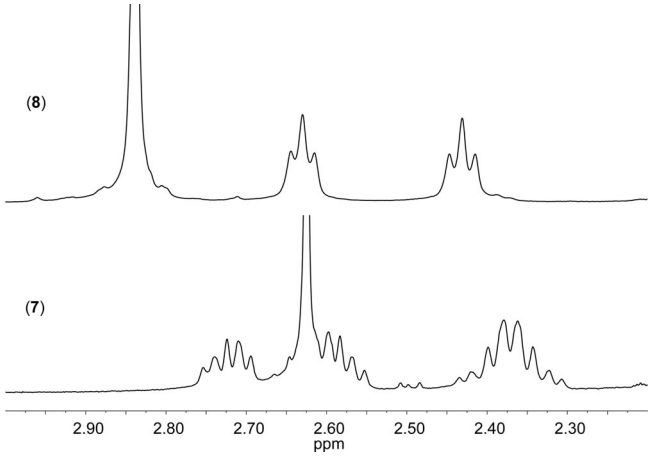


Figure 6. 500 MHz ^1H NMR spectra of complexes **7** and **8** in C_6D_6 between 2.2 and 3.0 ppm. The truncated signals correspond to the singlets of the 2-methyl groups in **8** and **7**. The ABCD part of ABCDEF for **7** and $[AB]_2$ part of $[ABC]_2$ for **8** are shown.

Thorough analyses of the spin systems found in complexes **7** and **8** as well as those in the other complexes discussed in this work are the subject of a forthcoming paper.[18]

To investigate whether the rotation around the Ni–C bond becomes fast on the NMR spectroscopic timescale at higher temperatures, we recorded a series of variable-temperature (VT) ^{19}F NMR spectra of complex **7**. If the rotational barrier is overcome at higher temperatures, we would expect the ^{19}F NMR spectrum of **7** to approach that of **8**, that is, a reduced set of signals due to higher symmetry. We used $[D_8]$toluene as solvent up to 100 °C and did not find significant changes in the VT-NMR spectra. At 100 °C, an irreversible line broadening occurs, probably due to paramagnetic decomposition of the complex.

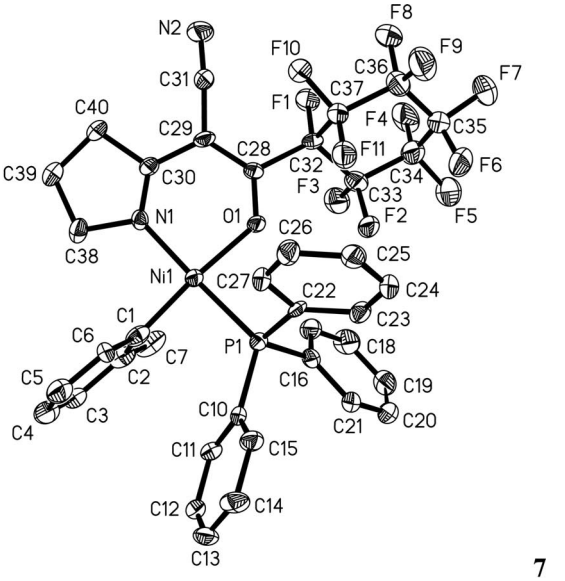
The rotation around the Ni–C bond is most likely hindered because of steric effects of the neighbouring triphenylphosphane group, which prevents a twist of the 2-toluenido ligand around the Ni–C bond, the methyl group interfering with the phenyl rings of the PPh_3 unit. We were interested to see if the second neighbouring group, the pyrrolidine ring, provides an additional steric demand and thus also hinders a twist around the Ni–C bond. To gain access to the answer, we synthesised complex **9**, bearing the triphenylphosphane ligand next to the 2-toluenido ligand just as in complex **3**, but cleaved the pyrrolidine ring to leave a proton (R^2) on the coordinating nitrogen atom and a methyl group (R^3) on the other end, thus forming an open-chain ligand (see Scheme 1). In **9** we reduced the steric demand on the nitrogen donor site to a minimum, that is, to that of a single proton, and at the same time retained the steric demand of the triphenylphosphane on the other side. The ^{19}F NMR spectral pattern of complex **9** is similar to that of complex **3**, exhibiting $ABMNX_3$ character as mentioned in Figure 3. We conclude from these observations that rotation around the Ni–C bond, which would move the methyl group past the NH into the other complex hemisphere, and thus would be a mechanism of racemisation, is even hindered in this sterically nondemanding case. So, planar chirality is maintained even with no steric demand on the coordinating nitrogen atom. As expected, this effect is absent in the achiral mesitylenido complex **10**, whose ^{19}F NMR spectral pattern appears to be identical to that of complex **4** (see Figure 3). VT-^{19}F NMR spectroscopic measurements of complex **9** in $[D_8]$toluene ranging from room temperature up to 100 °C show that the AB character for the α-CF_2 group is uniformly retained with insignificant small shifts in resonance frequencies. Hence we conclude that no racemisation takes place, and a twist around the Ni–C bond, which moves the methyl group past the NH, is hindered under these conditions.

Table 3 compares the ^1H NMR chemical shifts of the methyl protons of the 2-toluenido substituent in complexes **1**, **3**, **5**, **7** and **9** with the three signals of the mesitylenido substituent in complexes **2**, **4**, **6**, **8** and **10**. The chemical shift of the 2-CH_3 protons is shifted by about 0.1 ppm downfield in the case of the mesitylenido complexes relative to the corresponding 2-toluenido analogues. Upon coordination of a bidentate N,O ligand to complexes **1** and **2**, the chemical shift moves downfield by about 0.5 ppm for the 2-CH_3 signal in the 2-toluenido complexes and between 0.1 and 0.4 ppm for the signals of the mesitylenido substituent, respectively.

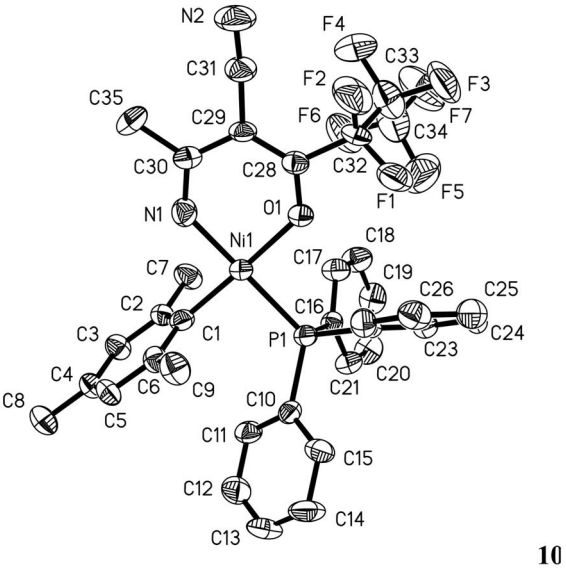
Table 3. Comparison of the ^1H chemical shifts in CD_2Cl_2 (500 MHz, room temperature) of the methyl protons of the 2-toluenido substituent and the three signals of the mesitylenido substituent.

Complex	2-CH_3	Complex	2-CH_3	4-CH_3	3-H
1	2.07	**2**	2.37	1.90	5.81
3	2.59	**4**	2.72	2.06	6.18
5	2.57	**6**	2.70	2.06	6.17
7	2.58	**8**	2.76	2.01	6.11
9	2.58	**10**	2.67	2.07	6.24

We were able to grow single crystals of complex **7** as well as those of **10** and determined their molecular structures, which are shown in Figure 7. Selected bond lengths and angles for both compounds are given in Table 4.



7



10

Figure 7. Perspective diagrams of the molecular structures of complexes **7** and **10** in the crystals of **7**·C_7H_8 and **10**·0.5C_5H_{12}, respectively. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

The nickel centre is coordinated in a square-planar manner such that the nickel is raised by only 0.02 Å above the N–O–P–C mean plane. The mean plane of the mesitylenido ligand is nearly rectangularly distorted by 85.2° against the N–O–P–C mean plane. These values are almost identical to those of the already known structure of **3**, where the nickel centre is raised above the N–O–P–C mean plane by 0.03 Å and the 2-toluenido ligand is distorted by 88.5° against this plane. In the structure of (*SP*-4-3)-[NiCl(Ph)(PPh_3)$_2$], which is also known[10], the phenyl ring is distorted by 82.3° against the P–Cl–P–C mean plane (coincidentally the same value as in **7**). The coordination of the primary amine in **10** shortens the Ni–N bond length significantly to 1.87 Å, relative to the coordination of the secondary amines in **3** and **7** (see Table 5). The angle N–Ni–O, often referred to as the "bite angle", that is, the angle under which the metal "sees" the ligand, of all bidentate N,O ligands, is nearly rectangular. The electronically delocalised N,O ligand framework N–C–C(CN)–C–O, which forms a six-membered chelate with the coordinating nickel atom, is in all cases nearly coplanar to the square-planar coordination sphere. Only ligand $(\mathbf{L^3})^-$ in complex **7** is distorted to the square-planar plane by 8.7°. The X-ray structures do not indicate agostic[19,20] interactions between the nickel centre and the 2-toluenido methyl hydrogen atoms in **3** and **7** or the 2,6-mesitylenido methyl hydrogen atoms in **10**. The ^{1}H

Table 4. Selected bond lengths [Å] and angles [°] of complexes **7** and **10**.

	7	**10**
Ni1–P1	2.2063(11)	2.1841(14)
Ni1–O1	1.935(2)	1.912(3)
Ni1–N1	1.921(3)	1.865(4)
Ni1–C1	1.889(5)	1.891(5)
P1–C10	1.825(4)	1.815(5)
P1–C16	1.801(4)	1.802(5)
P1–C22	1.815(4)	1.817(5)
O1–C28	1.267(4)	1.251(6)
N1–C30	1.283(4)	1.296(7)
N1–C38	1.497(4)	–
N2–C31	1.147(4)	1.143(7)
C28–C29	1.388(5)	1.372(7)
C28–C32	1.575(5)	1.539(8)
C29–C30	1.457(5)	1.420(7)
C29–C31	1.439(5)	1.422(8)
C30–C35	–	1.500(7)
C30–C40	1.518(4)	–
C38–C39	1.541(5)	–
C39–C40	1.520(5)	–
P1–Ni1–O1	86.45(8)	91.38(10)
P1–Ni1–N1	172.97(11)	177.35(17)
P1–Ni1–C1	89.37(11)	90.49(15)
O1–Ni1–N1	91.52(12)	89.67(18)
O1–Ni1–C1	175.06(15)	178.08(19)
N1–Ni1–C1	92.93(15)	88.4(2)

Table 5. Comparison of bond lengths [Å] and angles [°] of complexes **3**,[8] **7** and **10**.

	3[8]	**7**	**10**
Ni–N	1.93	1.92	1.87
Ni–O	1.92	1.94	1.91
Ni–P	2.19	2.21	2.18
Ni–C	1.89	1.89	1.89
Ni raised out of the N–O–P–C mean plane	0.03	0.04	0.02
Intersection angle of the C–Ni–P plane with the N–Ni–O plane	2.5	7.0	1.7
Intersection angle of the arenido mean plane with the N–O–P–C mean plane	88.5	82.3	85.2
"Bite angle" N–Ni–O	91.1	91.5	89.6
Intersection angle of the N–O–P–C mean plane with the ligand N–C–C(CN)–C–O mean plane	0.9	8.7	1.7

NMR signals of the methyl groups are sharp singlets showing no effects of magnetic nonequivalence inside the CH_3 units.

Conclusions

We have prepared a series of novel diamagnetic square-planar arenidobis(triphenylphosphane)nickel(II) complexes comprising a bidentate N,O ligand containing an electronically delocalised β-enaminonic chelating backbone. We have shown for arenido = 2-toluenido, that is, complexes **3**, **5**, **7** and **9**, that the rotation around the Ni–C bond is hindered and thus planar chirality is introduced. Therefore, the corresponding atoms that are enantiotopic in the mesitylenido compounds turn into diastereotopic atoms in the toluenido-substituted complexes. We have shown by VT-NMR spectroscopic techniques that twisting around the Ni–C bond is hindered even at 100 °C in complexes **7** and **9**, the latter comprising a sterically nondemanding environment at the coordinating nitrogen atom. The type of Ni complexes described here are active catalysts in the copolymerisation of ethene and CO, yielding aliphatic polyketones. By the use of chiral catalysts, it might be possible to gain access to stereoregular aliphatic polyketones when using, for example, propene instead of ethene.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques unless stated otherwise. All solvents were purified and degassed by standard procedures. Chemicals were bought from commercial sources like Acros, Sigma–Aldrich, Merck, Fluorochem, etc. 1D NMR spectra were recorded at room temperature with a Bruker Avance DRX 200 spectrometer for ^1H and ^{31}P NMR spectroscopy. Additional 1D and 2D spectra were obtained for nuclei ^1H, ^{31}P, ^{13}C and ^{19}F (the latter also with the VT-NMR spectroscopic technique) by using a Bruker Avance DRX 500 spectrometer. The proton and carbon chemical shifts are given in ppm and referenced to the signal of internal TMS or the residual solvent signals[21] ($CDCl_3$: ^1H 7.26 ppm, ^{13}C 77.16 ppm; CD_2Cl_2: ^1H 5.30 ppm, ^{13}C 53.52 ppm; C_6D_6: ^1H 7.16 ppm, ^{13}C 128.1 ppm). Fluorine chemical shifts are referenced to internal C_6F_6 (^{19}F –162.9 ppm),[22] while external 85% H_3PO_4 was used for ^{31}P NMR spectroscopy. Coupling constants are reported as absolute values and given in Hz. Spectra were evaluated with programs WinNMR, WinDaisy, TopSpin (available from Bruker SpectroSpin) and MestReNova (from MestreLab Research). Details of NMR spectroscopic theory and evaluation are beyond the scope of this paper and will be published separately.[18] Infrared spectra were recorded with a FTIR Bruker IFS 66 spectrometer. EI-MS data were obtained with a Varian MAT 311 A instrument. Elemental analyses were performed by using a Perkin–Elmer CHN-2400/II elemental analyser.

Compounds **1** and **2** were prepared according to modified literature procedures.[23–25] The preparation of pyrrolidin-(2*E*/2*Z*)-ylideneacetonitrile and the ligands 4,4,5,5,6,6,6-heptafluoro-3-oxo-2-pyrrolidin-(2*Z*)-ylidenehexanenitrile (H**L**^{1}), 3-oxo-2-pyrrolidin-(2*Z*)-ylidenehexanenitrile (H**L**^{2}) and 2-[1-amino-eth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxo-hexanenitrile (H**L**^{4}) was reported previously.[12]

Crystal Structure Determinations: Crystals of compounds **7**·C_7H_8 and **10**·0.5C_5H_{12} suitable for X-ray study were investigated with a STOE Imaging Plate Diffraction System using graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements on the positions of 4225 and 5997 reflections in the range 2.00° < θ < 25.20 and 2.05° < θ < 24.0°, respectively. The anorthic lattices are consistent with space group types $P1$ and $P\bar{1}$, but the latter proved to be the correct one for both compounds in the course of structure refinements. Lorentz polarisation corrections were applied to all the intensity data. The structures were solved by direct methods,[26] and the positions of all but the hydrogen atoms of the solvent molecules were found via ΔF syntheses. Refinements by full-matrix least-squares calculations[27] on F^2 converged (max. shift/esd: 0.000 and 0.001, respectively) to the indicators given in Table 6. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Appropriate distance and displacement parameter restraints were applied for the disordered pentane molecule of **10**·0.5C_5H_{12} that resides on a crystallographic inversion centre. Idealised bond lengths and angles were used for the CH_3, CH_2 and CH groups; the riding model was applied for their H atoms. In addition, the H atoms of the CH_3 groups were allowed to rotate around the neighbouring C–C bonds. Isotropic displacement parameters of the H atoms were kept equal to 150, 130 and 120% of the equivalent isotropic displacement parameters of the parent primary, secondary and "aromatic" carbon atoms, respectively.

Table 6. Summary of crystal data, details of intensity measurements and structure refinements of **7**·C_7H_8 and **10**·0.5C_5H_{12}.

	7·C_7H_8	**10**·0.5C_5H_{12}
Empirical formula	$C_{45}H_{36}F_{11}N_2NiOP$	$C_{75}H_{72}F_{14}N_4Ni_2O_2P_2$
Molecular mass	919.42	1506.69
Crystal system	triclinic	triclinic
Space group; no.	$P\bar{1}$; 2	$P\bar{1}$; 2
a [Å]	11.0654(10)	11.7024(11)
b [Å]	13.3802(12)	12.7618(11)
c [Å]	15.5168(13)	14.5080(14)
α [°]	81.209(10)	114.657(10)
β [°]	77.744(10)	90.273(11)
γ [°]	69.039(10)	111.196(10)
V [Å^3]	2089.0(4)	1804.7(4)
Z	2	1
F(000)	940	778
$D_{calcd.}$ [Mg·m^{-3}]	1.462	1.386
μ (Mo-K_α) [mm^{-1}]	0.590	0.650
Crystal size [mm]	0.18 × 0.18 × 0.17	0.31 × 0.30 × 0.28
T [K]	173(2)	291(2)
θ range [°]	2.00 < θ < 25.00	2.09 < θ < 25.00
hkl ranges	–13 ≤ h ≤ 13; –15 ≤ k ≤ 15; –18 ≤ l ≤ 16	–13 ≤ h ≤ 13; –15 ≤ k ≤ 15; –17 ≤ l ≤ 17
No. of reflns. measd.	14481	23714
No. of unique reflns.	6984	5986
No. of reflns. obsd. $I > 2\sigma(I)$	2949	2497
No. of param./restraints	552/0	475/61
R_1 [$I > 2\sigma(I)$][a]	0.0433	0.0637
Weight[a]	σ^{-2}	σ^{-2}
wR_2 (all data)[a]	0.0618	0.1129
Max./min. $\Delta\rho$ [e Å^{-3}]	0.48/–0.27	0.59/–0.40

[a] As defined in *SHELXL 97–2*.

CCDC-749818 (**10**·0.5C_5H_{12}), -749819 (**7**·C_7H_8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3-Oxo-2-pyrrolidin-(2*Z*)-ylidene-3-undecafluorocyclohexylpropionitrile (HL^3): Pyrrolidin-(2*E*/2*Z*)-ylideneacetonitrile[12] (540 mg, 5 mmol) was dissolved in toluene (50 mL), and triethylamine (505 mg, 5 mmol) was added. The mixture was cooled in an ice bath and 1,2,2,3,3,4,4,5,5,6,6-undecafluorocyclohexanecarbonyl chloride (1.72 g, 5 mmol) was added dropwise with stirring. The mixture was stirred overnight at room temp., and the solvent was removed in vacuo. Dichloromethane (50 mL) was added, and the solution was extracted with water (3 × 50 mL). The dichloromethane solution was dried with Na_2SO_4, and the solvent was removed in vacuo to yield 1.6 g (78%) of HL^3 as a white solid. ^{1}H NMR (200 MHz, C_6D_6, room temp.): δ = 0.63 (qt, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2-C*H*$_2$-CH_2), 1.96 (td, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 0.8 Hz, 2 H, CH_2-C=C), 2.12 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.0 Hz, 2 H, CH_2-N-C), 9.68 (s (br), 1 H, NH) ppm. ^{1}H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.12 (qt, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2-C*H*$_2$-CH_2), 3.09 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-C=C), 3.85 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.0 Hz, 2 H, CH_2-N-C), 10.77 (s (br), 1 H, NH) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, room temp., only protonated carbons): δ = 20.0 (*C*H$_2$-C=C), 35.1 (CH_2-*C*H$_2$-CH_2), 50.9 (*C*H$_2$-N-C) ppm. ^{19}F NMR (470.52 MHz, C_6D_6, room temp.): δ = –118.6 (d, $^2J_{FF}$ = 293.1 Hz, 2 F, 2,6-CF_{ax}), –122.4 (d, $^2J_{FF}$ = 282.5 Hz, 2 F, 3,5-CF_{ax}), –123.6 (d, $^2J_{FF}$ = 285.5 Hz, 1 F, 4-CF_{ax}), –131.2 (d, $^2J_{FF}$ = 295.1 Hz, 2 F, 2,6-CF_{eq}), –138.6 (d, $^2J_{FF}$ = 280.5 Hz, 2 F, 3,5-CF_{eq}), –141.0 (d, $^2J_{FF}$ = 285.5 Hz, 1 F, 4-CF_{eq}), –178.1 (tt, $^3J_{FF}$ = 17.6 (gauche), $^3J_{FF}$ = 34.2 Hz (fork), 1F, C(O)CF) ppm. ^{19}F NMR (470.54 MHz, $CDCl_3$, room temp.): δ = –119.2 (d, $^2J_{FF}$ = 304 Hz, 2 F, 2,6-CF_{ax}), –122.6 (d, $^2J_{FF}$ = 282 Hz, 2 F, 3,5-CF_{ax}), –123.7 (d, $^2J_{FF}$ = 282 Hz, 1 F, 4-CF_{ax}), –131.4 (d, $^2J_{FF}$ = 283 Hz, 2 F, 2,6-CF_{eq}), –138.9 (d, $^2J_{FF}$ = 280 Hz, 2 F, 3,5-CF_{eq}), –141.3 (d, $^2J_{FF}$ = 281 Hz, 1 F, 4-CF_{eq}), –178.8 (hept, $^{4,5}J_{FF}$ = 17 Hz, 1F, C(O)CF) ppm. IR (KBr disk): $\tilde{\nu}$ = 3274 (s, N–H) 2997 (m, C–$H_{aliphat.}$) 2213 (vs, C≡N) 1634 (vs, C=O) 1583 (s, C=C) 1236 (m, C–F) cm^{-1}. MS (EI): *m*/*z* = 416 [M$^+$], 135 [M$^+$ – C_6F_{11}]. $C_{13}H_7F_{11}N_2O$ (416.19): calcd. C 37.52, H 1.70, N 6.73; found C 37.66, H 1.59, N 6.49.

(*SP*-4-3)-[NiBr(2-tol)(PPh$_3$)$_2$] (1): Anhydrous $NiBr_2$ (4.4 g, 20 mmol) was dissolved in tetrahydrofuran (100 mL) and PPh_3 (10.5 g, 40 mmol). The mixture was refluxed until the dark-green (*T*-4)-[$NiBr_2(PPh_3)_2$] complex formed. Upon cooling to room temperature, 2-toluenido magnesium bromide, prepared from Mg (0.6 g, 25 mmol) and 2-bromotoluene (4.3 g, 25 mmol) in tetrahydrofuran (50 mL), was added by means of a syringe. After the mixture was stirred for 2 h at room temperature, the solvent was removed in vacuo, and methanol (100 mL) was added, whereupon a yellow precipitate formed. It was washed twice with methanol and then twice by pentane to yield 9.2 g (61%) *(SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$]. The orange-yellow product was dried in vacuo and stored under a nitrogen atmosphere. ^{1}H NMR (200 MHz, CD_2Cl_2, room temp.): δ = 2.07 (s, 3 H, CH_3), 5.88 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, *2-tol*), 6.24 (m, 2 H, *2-tol*), 7.05 (d, $^3J_{HH}$ = 6.0 Hz, 1 H, *2-tol*), 7.23 (m, 18 H, PPh_3), 7.49 (m, 12 H, PPh_3) ppm. ^{31}P{^{1}H} NMR (81 MHz, CD_2Cl_2, room temp.): δ = 23.2 ppm. MS (MALDI, $CHCl_3$): *m*/*z* = 755 [M + H]$^+$, 739 [M – CH_3]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3050 (m, C–$H_{aromat.}$) 2979 (m, C–$H_{aliphat.}$) 1434 (m, P–C) cm^{-1}.

(*SP*-4-3)-[NiBr(mes)(PPh$_3$)$_2$] (2): The reaction was carried out as for **1**, except that 2-bromomesitylene (5.0 g, 25 mmol) was used. Yield: 15.4 g (79%) of (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$]. ^{1}H NMR (200 MHz, $CDCl_3$, room temp.): δ = 1.90 (s, 3 H, *p*-CH_3), 2.37 (s, 6 H, *o*-CH_3), 5.81 (s, 2 H, mes), 7.23 (m, 18 H, PPh_3), 7.50 (m, 12 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, room temp., only protonated carbons): δ = 20.0, 26.0, 68.4, 127.6, 129.1, 132.5 ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, room temp.): δ = 19.3 ppm. MS (FAB): *m*/*z* = 782 [M]$^+$, 582 [Ni(PPh_3)$_2$]$^+$, 381 [PPh_3 + mes]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3054 (m, C–$H_{aromat.}$) 2959 (m, C–$H_{aliphat.}$) 1432 (m, P–C) cm^{-1}.

(*R*$_P$)/(*S*$_P$)-(*SP*-4-3)-[Ni(L^1)(2-tol)(PPh$_3$)] (3): 4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-pyrrolidin-(2*Z*)-ylidenehexanenitrile (HL^1) (365 mg, 1.2 mmol) was dissolved in toluene (50 mL). Sodium bis(trimethylsilyl)amide (2.0 mL, 1.2 mmol, 0.6 M in toluene) was added, and the mixture was stirred for 2 h. A solution of (*SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$] (**1**) (905 mg, 1.2 mmol) in toluene (50 mL) was added dropwise with stirring. After complete addition, stirring was continued overnight, and the reaction mixture was filtered through Celite. The solvent was removed in vacuo, and pentane (20 mL) was added to the residue. After stirring overnight, the yellow precipitate was filtered, washed with pentane and dried in vacuo to yield 695 mg (81%) of **3**. ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 1.65 (qt, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-C*H*$_2$-CH_2), 2.59 (s, 3 H, CH_3), 2.88 (m, 4 H, CH_2-C=C + CH_2-N-C), 6.39 (dd, $^3J_{HH}$ = 6.8, $^4J_{HH}$ = 1.6 Hz, 1 H, *2-tol* 3-H), 6.43, 6.51 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, *2-tol* 4,5-H), 7.21 (dd, $^3J_{HH}$ = 2.4, $^4J_{HH}$ = 1.2 Hz, 1 H, *2-tol* 6-H), 7.25 (m, 6 H, PPh_3), 7.31 (m, 9 H, PPh_3) ppm. ^{1}H NMR (500.13 MHz, C_6D_6, room temp.): δ = 0.81 (m, 2 H, CH_2-C*H*$_2$-CH_2), 2.36 (m, 2 H, CH_2-C=C), 2.59 (s, 3 H, CH_3), 2.59 (m, 2 H, CH_2-N-C), 6.49 (d, $^3J_{HH}$ = 6.5 Hz, 1 H, *2-tol* 3-H), 6.58, 6.72 (t, $^3J_{HH}$ = 6.5 Hz, 2 H, *2-tol* 4,5-H), 6.98 (m, 10 H, PPh_3 + *2-tol* 6-H), 7.45 (m, 6 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, room temp., not all carbons observed): δ = 19.4, 24.4, 37.9, 62.3, 121.9, 122.4, 126.8, 127.1, 128.7, 129.0, 134.9, 142.1, 147.0, 147.4, 170.6 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 27.5 ppm. ^{19}F NMR (470.55 MHz, CD_2Cl_2, room temp.): δ = –81.6 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –116.3, –116.8 (dq, $^2J_{FF}$ = 272, $^4J_{FF}$ = 9 Hz, 2 F, C(O)CF_2), –126.5, –126.6 (d, $^2J_{FF}$ = 292 Hz, 2 F, C*F*$_2$-CF_3) ppm. ^{19}F NMR (470.55 MHz, C_6D_6, room temp.): δ = –81.0 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –115.4 (m, 2 F, C(O)CF_2), –125.8 (s, 2 F, C*F*$_2$-CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3050 (m, C–$H_{aromat.}$) 2919 (m, C–$H_{aliphat.}$) 2216 (vs, C≡N) 1632 (vs, C=O) 1584 (vs, C=C) 1434 (m, P–C) 1231 (s, C–F) cm^{-1}. MS (ESI, MeOH): *m*/*z* = 715 [M + H]$^+$, 1451 [2M + Na]$^+$, 353 [PPh_3 + 2-tol]$^+$. $C_{35}H_{28}F_7N_2NiOP$ (715.27): calcd. C 58.77, H 3.95, N 3.92; found C 58.60, H 3.90, N 3.78.

(*SP*-4-3)-[Ni(L^1)(mes)(PPh$_3$)] (4): The synthesis was carried out as for **3**, except that (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**) (939 mg, 1.2 mmol) was used. Yield: 785 mg (88%). ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 1.66 (qt, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2-C*H*$_2$-CH_2), 2.06 (s, 3 H, *p*-CH_3), 2.72 (s, 6 H, *o*-CH_3), 2.85 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2-C=C), 2.89 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-N-C), 6.18 (s, 2 H, mes-H), 7.29 (m, 15 H, PPh_3) ppm. ^{1}H NMR (500.13 MHz, C_6D_6, room temp.): δ = 0.84 (qt, $^3J_{HH}$ = 7.9 Hz, 2 H, CH_2-C*H*$_2$-CH_2), 2.14 (s, 3 H, *p*-CH_3), 2.40 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-C=C), 2.64 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, CH_2-N-C), 2.85 (s, 6 H, *o*-CH_3), 6.28 (s, 2 H, mes-H), 6.97 (m, 9 H, PPh_3), 7.39 (m, 6 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, room temp., not all carbons observed): δ = 20.6, 20.9, 25.8, 39.3, 63.5, 126.8, 128.1, 130.4, 133.6, 134.5, 139.3, 142.1 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 24.9 ppm. ^{19}F NMR (470.55 MHz, C_6D_6, room temp.): δ = –81.0 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –115.1 (q, $^4J_{FF}$ = 9 Hz, 2 F, C(O)CF_2), –125.5 (s, 2 F, C*F*$_2$-CF_3) ppm. ^{19}F NMR (470.55 MHz, CD_2Cl_2, room temp.): δ = –81.6 (t, $^4J_{FF}$ = 10 Hz, 3 F, CF_3), –116.2 (q, $^4J_{FF}$ = 9 Hz, 2 F, C(O)CF_2), –126.3 (s, 2 F, C*F*$_2$-CF_3) ppm. MS (MALDI, CH_3OH): *m*/*z* = 381 [PPh_3 + mes]$^+$, 765 [M + Na]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3059 (w, C–$H_{aromat.}$) 2915 (m, C–$H_{aliphat.}$) 2217 (vs, C≡N) 1587 (vs, C=O) 1513 (vs, C=C) 1435 (m, P–C) 1230 (s, C–F) cm^{-1}. $C_{37}H_{32}F_7N_2NiOP$ (743.33): calcd. C 59.79, H 4.34, N 3.77; found C 60.00, H 4.33, N 3.51.

(R_P)/(S_P)-(*SP*-4-3)-[Ni(L^2)(2-tol)(PPh_3)] (5): (*SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$] (**1**) (754 mg, 1 mmol) was dissolved in tetrahydrofuran (50 mL). 3-Oxo-2-pyrrolidin-(2*Z*)-ylidenehexanenitrile (HL^2) (178 mg, 1 mmol) and subsequently Ag_2O (116 mg) were added. The resulting black suspension was stirred overnight, filtered, and the solvent was removed in vacuo. After addition of pentane (20 mL) and stirring overnight, a yellow precipitate formed, which was collected and washed with pentane to yield 448 mg (76%) of **5**. ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 0.53 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH_2-CH_3), 0.67 (m, 2 H, CH_2-CH_3), 1.60 (qt, $^3J_{HH}$ = 7.0 Hz, 2 H, CH_2-CH_2-CH_2), 2.57 (s, 3 H, *2-tol* CH_3), 1.81 + 2.07 (m, 1+ 1 H, CHH'-CH_2-CH_3), 2.78 (m, 4 H, CH_2-C=C + CH_2-N-C), 6.39 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, *2-tol* 3-H), 6.49, 6.57 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, *2-tol* 4,5-H), 7.25 (m, 10 H, *2-tol* 6-H + PPh_3), 7.39 (m, 6 H, PPh_3) ppm. ^{1}H NMR (200.13 MHz, C_6D_6, room temp.): δ = 0.58 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_2-CH_3), 0.83 (m, 2 H, CH_2-CH_3), 0.98 (hex, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2-CH_2-CH_2), 2.06 + 2.32 (m, 1+ 1 H, CHH'-CH_2-CH_3), 2.54 (m, 2 H, CH_2-C=C), 2.75 (m, 2 H, CH_2-N-C), 2.75 (s, 3 H, *2-tol* CH_3), 6.65 (m, 3 H, *2-tol* 3,4,5-H), 6.96 (m, 10 H, *2-tol* 6-H + PPh_3), 7.48 (m, 6 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, room temp., not all carbons observed): δ = 13.5, 18.6, 21.0, 25.3, 38.2, 39.9, 62.1 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 28.8 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6, room temp.): δ = 29.4 ppm. IR (KBr disk): $\tilde{\nu}$ = 3050 (m, C–$H_{aromat.}$) 2958 (m, C–$H_{aliphat.}$) 2196 (vs, C≡N) 1574 (vs, C=O) 1478 (vs, C=C) 1435 (m, P–C) cm^{-1}. $C_{35}H_{35}N_2NiOP$ (589.34): calcd. C 71.33, H 5.99, N 4.75; found C 71.50, H 5.95, N 4.66.

(*SP*-4-3)-[Ni(L^2)(mes)(PPh_3)] (6): The synthesis was carried out as for **5**, except that (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**) (782 mg, 1 mmol) was used. Yield: 494 mg (80%). ^{1}H NMR (200.13 MHz, C_6D_6, room temp.): δ = 0.57 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH_2-CH_3), 0.84 (sext, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2-CH_3), 1.00 (qt, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2-CH_2-CH_2), 2.18 (s, 3 H, *p*-CH_3), 2.29 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, CH_2-CH_2-CH_3), 2.56 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-C=C), 2.74 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, CH_2-N-C), 2.93 (s, 6 H, *o*-CH_3), 6.34 (s, 2 H, mes-H), 6.96 (m, 9 H, PPh_3), 7.43 (m, 6 H, PPh_3) ppm. ^{1}H NMR (200.13 MHz, CD_2Cl_2, room temp.): δ = 0.55 (t, $^3J_{HH}$ = 6.4 Hz, 3 H, CH_2-CH_3), 0.65 (sext, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2-CH_3), 1.60 (qt, $^3J_{HH}$ = 7.7 Hz, 2 H, CH_2-CH_2-CH_2), 2.02 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2-CH_2-CH_3), 2.06 (s, 3 H, *p*-CH_3), 2.70 (s, 6 H, *o*-CH_3), 2.77 (m, 4 H, CH_2-C=C + CH_2-N-C), 6.17 (s, 2 H, mes-H), 7.28 (m, 15 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, room temp.): δ = 13.6, 18.4, 20.0, 21.0, 25.3, 38.1, 40.0, 61.9, 80.9, 100.1, 126.0, 127.7 (d, J_{PC} = 10 Hz), 129.8, 130.8, 131.2, 132.6, 134.3 (d, J_{PC} = 10 Hz), 142.1, 170.4, 186.7 ppm. ^{31}P{^{1}H} NMR (81.01 MHz, CD_2Cl_2, room temp.): δ = 25.9 ppm. ^{31}P{^{1}H} NMR (81.01 MHz, C_6D_6, room temp.): δ = 26.4 ppm. MS (MALDI, CH_3OH): *m*/*z* = 381 [PPh_3+mes]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3052 (m, C–$H_{aromat.}$) 2960 (m, C–$H_{aliphat.}$) 2196 (vs, C≡N) 1573 (vs, C=O) 1478 (vs, C=C) 1434 (m, P–C) cm^{-1}. $C_{37}H_{39}N_2NiOP$ (617.39): calcd. C 71.98, H 6.37, N 4.54; found C 72.22, H 6.06, N 4.40.

(R_P)/(S_P)-(*SP*-4-3)-[Ni(L^3)(2-tol)(PPh_3)] (7): 3-Oxo-2-pyrrolidin-(2*Z*)-ylidene-3-undecafluorocyclohexylpropionitrile (HL^3) (250 mg, 0.6 mmol) was dissolved in toluene (30 mL). Then, sodium bis(trimethylsilyl)amide (1.0 mL, 0.6 mmol, 0.6 M in toluene) was added, and the mixture was stirred overnight. A solution of (*SP*-4-3)-[NiBr(2-tol)(PPh_3)$_2$] (**1**) (452 mg, 0.6 mmol) in toluene (30 mL) was added dropwise with stirring. After complete addition, stirring was continued overnight, and the reaction mixture was filtered through Celite. The solvent was removed in vacuo, and pentane (20 mL) was added to the residue. After stirring overnight, the yellow precipitate was filtered, washed with pentane and dried in vacuo to yield 352 mg (71%) of **7**. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of a mixture of pentane/hexane (1:1) into a concentrated solution of the complex in toluene. ^{1}H NMR (500.13 MHz, C_6D_6, room temp.): δ = 0.81 (m, 2 H, CH_2-CH_2-CH_2), 2.43 (m, 2 H, CH_2-C=C), 2.59, 2.70 (m, 2 H, CH_2-N-C), 2.62 (s, 3 H, CH_3), 6.39 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, *2-tol* 3-H), 6.53, 6.62 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, *2-tol* 4,5-H), 6.95 (m, 10 H, *2-tol* 6-H + PPh_3), 7.49 (m, 6 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, room temp., only aliphatic ring protons): δ = 26.5 (CH_2-C=C), 40.1 (CH_2-CH_2-CH_2), 64.5 (CH_2-N-C) ppm. ^{19}F NMR (470.54 MHz, C_6D_6, room temp., ppm): δ = –116.4 (d, $^2J_{FF}$ = 293 Hz, 1 F, 6-CF_{ax}), –117.8 (d, $^2J_{FF}$ = 294 Hz, 1 F, 2-CF_{ax}), –121.9 (d, $^2J_{FF}$ = 281 Hz, 1 F, 5-CF_{ax}), –122.1 (d, $^2J_{FF}$ = 279 Hz, 1 F, 3-CF_{ax}), –123.5 (d, $^2J_{FF}$ = 283 Hz, 1 F, 4-CF_{ax}), –131.4 (d, $^2J_{FF}$ = 292 Hz, 1 F, 6-CF_{eq}), –132.3 (d, $^2J_{FF}$ = 294 Hz, 1 F, 2-CF_{eq}), –139.7 (d, $^2J_{FF}$ = 279 Hz, 2 F, 3,5-CF_{eq}), –142.2 (d, $^2J_{FF}$ = 283 Hz, 1 F, 4-CF_{eq}), –174.1 (hept, $^4J_{FF}$ = 37, $^5J_{FF}$ = 18 Hz, 1 F, C(O)CF) ppm. ^{19}F NMR (470.54 MHz, CD_2Cl_2, room temp., ppm): δ = –116.3 (d, $^2J_{FF}$ = 293 Hz, 1 F, 6-CF_{ax}), –117.7 (d, $^2J_{FF}$ = 294 Hz, 1 F, 2-CF_{ax}), –121.8 (d, $^2J_{FF}$ = 281 Hz, 1 F, 5-CF_{ax}), –122.0 (d, $^2J_{FF}$ = 279 Hz, 1 F, 3-CF_{ax}), –123.3 (d, $^2J_{FF}$ = 283 Hz, 1 F, 4-CF_{ax}), –131.2 (d, $^2J_{FF}$ = 292 Hz, 1 F, 6-CF_{eq}), –132.2 (d, $^2J_{FF}$ = 294 Hz, 1 F, 2-CF_{eq}), –139.5 (d, $^2J_{FF}$ = 279 Hz, 2 F, 3,5-CF_{eq}), –141.9 (d, $^2J_{FF}$ = 283 Hz, 1 F, 4-CF_{eq}), –173.9 (hept, $^4J_{FF}$ = 37, $^5J_{FF}$ = 18 Hz, 1 F, C(O)CF) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6, room temp.): δ = 27.5 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 27.2 ppm. IR (KBr disk): $\tilde{\nu}$ = 3054 (m, C–$H_{aromat.}$) 2981 (m, C–$H_{aliphat.}$) 2212 (vs, C≡N) 1584 (vs, C=O) 1506 (vs, C=C) 1435 (m, P–C) 1242 (s, C–F) cm^{-1}. MS (ESI, MeOH): *m*/*z* = 849 [M + Na]$^+$. $C_{38}H_{28}F_{11}N_2NiOP{\cdot}C_7H_8$ (919.44): calcd. C 58.79, H 3.95, N 3.05; found C 58.51, H 3.75, N 3.23.

(*SP*-4-3)-[Ni(L^3)(mes)(PPh_3)] (8): The synthesis was carried out as for **7**, except that (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**) (469 mg, 0.6 mmol) was used. Yield: 436 mg (85%). ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 1.65 (qt, $^3J_{HH}$ = 7.9 Hz, 2 H, CH_2-CH_2-CH_2), 2.01 (s, 3 H, *p*-CH_3), 2.76 (s, 6 H, *o*-CH_3), 2.85 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2-C=C), 2.93 (t, $^3J_{HH}$ = 8.3 Hz, 2 H, CH_2-N-C), 6.11 (s, 2 H, mes), 7.29 (m, 15 H, PPh_3) ppm. ^{1}H NMR (500.13 MHz, C_6D_6, room temp.): δ = 0.83 (qt, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2-CH_2-CH_2), 2.08 (s, 3 H, *p*-CH_3), 2.47 (t, $^3J_{HH}$ = 8.0 Hz, 2 H, CH_2-C=C), 2.63 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, CH_2-N-C), 2.85 (s, 6 H, *o*-CH_3), 6.19 (s, 2 H, mes), 7.09 (m, 15 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $C_6D_5CD_3$, room temp., only aliphatic ring protons): δ = 26.5 (CH_2-C=C), 40.2 (CH_2-CH_2-CH_2), 64.4 (CH_2-N-C) ppm. ^{19}F NMR (470.52 MHz, C_6D_6, room temp., ppm): δ = –116.6 (d, $^2J_{FF}$ = 294 Hz, 2 F, 2,6-CF_{ax}), –121.6 (d, $^2J_{FF}$ = 272 Hz, 2 F, 3,5-CF_{ax}), –123.2 (d, $^2J_{FF}$ = 283 Hz, 1 F, 4-CF_{ax}), –131.2 (d, $^2J_{FF}$ = 293 Hz, 2 F, 2,6-CF_{eq}), –139.3 (d, $^2J_{FF}$ = 279 Hz, 2 F, 3,5-CF_{eq}), –141.7 (d, $^2J_{FF}$ = 282 Hz, 1 F, 4-CF_{eq}), –173.3 (hept, $^4J_{FF}$ = 17 Hz, 1 F, C(O)CF) ppm. ^{19}F NMR (470.54 MHz, CD_2Cl_2, room temp., ppm): δ = –117.4 (d, $^2J_{FF}$ = 292 Hz, 2 F, 2,6-CF_{ax}), –122.7 (d, $^2J_{FF}$ = 280 Hz, 2 F, 3,5-CF_{ax}), –123.9 (d, $^2J_{FF}$ = 281 Hz, 1 F, 4-CF_{ax}), –132.4 (d, $^2J_{FF}$ = 282 Hz, 2 F, 2,6-CF_{eq}), –140.1 (d, $^2J_{FF}$ = 280 Hz, 2 F, 3,5-CF_{eq}), –142.6 (d, $^2J_{FF}$ = 282 Hz, 1 F, 4-CF_{eq}), –174.7 (hept, $^5J_{FF}$ = 17 Hz, 1 F, C(O)CF) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 24.6 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, $C_6D_5CD_3$, room temp.): δ = 24.8 ppm. MS (MALDI, CH_3OH): *m*/*z* = 877 [M + Na]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3058 (m, C–$H_{aromat.}$) 2965 (m, C–$H_{aliphat.}$) 2213 (vs, C≡N) 1584 (vs, C=O) 1506 (vs, C=C) 1436 (m, P–C) 1238 (s, C–F) cm^{-1}. $C_{40}H_{32}F_{11}N_2NiOP$ (855.35): calcd. C 56.17, H 3.77, N 3.28; found C 56.36, H 3.57, N 2.99.

(R_P)/(S_P)-(*SP*-4-3)-[Ni(L^4)(2-tol)(PPh_3)] (9): The synthesis was carried out as for **5**, except that 2-[1-amino-eth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxo-hexanenitrile (HL^4) (278 mg, 1 mmol) was used. Yield: 406 mg (59%) of **9**. ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 2.23 (s, 3 H, CH_3), 2.58 (s, 3 H, *2-tol* CH_3), 6.48 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, *2-tol* 3-H), 6.53, 6.63 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, *2-tol* 4,5-H), 7.20 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, *2-tol* 6-H), 7.32 (m, 15 H, PPh_3) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2, room temp.): δ = 25.5 (N-C-*C*H_3), 28.3 (*2-tol* CH_3), 85.4 (*C*-C≡N), 123.3, 123.4, 128.0, 128.1, 128.2, 128.8, 129.5, 129.8, 130.2, 134.1, 134.2, 135.8, 142.9, 149.4, 149.7 (N-*C*-CH_3), 170.0 (C=O) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 28.2 ppm. ^{19}F NMR (470.55 MHz, CD_2Cl_2, room temp.): δ = –81.5 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –115.5, –116.3 (dq, $^2J_{FF}$ = 270, $^4J_{FF}$ = 9 Hz, 2 F, C(O)CF_2), –126.6, –126.8 (d, $^2J_{FF}$ = 292 Hz, 2 F, C*F*$_2$-CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3306 (vs, N–H) 3057 (m, C–$H_{aromat.}$) 2962 (m, C–$H_{aliphat.}$) 2215 (vs, C≡N) 1592 (vs, C=O) 1494 (vs, C=C) 1435 (m, P–C) 1233 (s, C–F) cm^{-1}. MS (ESI, MeOH): *m*/*z* = 711 [M + Na]$^+$. MS (FAB): *m*/*z* = 689 [M]$^+$, 353 [PPh_3+2-tol]$^+$, 262 [PPh_3]$^+$. $C_{33}H_{26}F_7N_2NiOP$ (689.23): calcd. C 57.51, H 3.80, N 4.06; found C 57.19, H 3.63, N 3.98.

(*SP*-4-3)-[Ni(L^4)(mes)(PPh_3)] (10): The synthesis was carried out as for **10**, except that (*SP*-4-3)-[NiBr(mes)(PPh_3)$_2$] (**2**) (782 mg, 1 mmol) was used. Yield: 473 mg (66%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of a mixture of pentane/hexane (1:1) into a concentrated solution of the complex in toluene. ^{1}H NMR (500.13 MHz, CD_2Cl_2, room temp.): δ = 2.07 (s, 3 H, *p*-CH_3), 2.21 (s, 3 H, CH_3), 2.67 (s, 6 H, *o*-CH_3), 6.24 (s, 2 H, mes), 7.28 (m, 15 H, PPh_3) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, CD_2Cl_2, room temp.): δ = 25.6 ppm. ^{19}F NMR (470.55 MHz, CD_2Cl_2, room temp.): δ = –81.6 (t, $^4J_{FF}$ = 10 Hz, 3 F, CF_3), –115.7 (q, $^4J_{FF}$ = 9 Hz, 2 F, C(O)CF_2), –126.3 (s, 2 F, C*F*$_2$-CF_3) ppm. MS (MALDI, CH_3OH): *m*/*z* = 381 [PPh_3+mes]$^+$, 739 [M + Na]$^+$. IR (KBr disk): $\tilde{\nu}$ = 3310 (s, N–H) 3060 (m, C–$H_{aromat.}$) 2921 (m, C–$H_{aliphat.}$) 2212 (vs, C≡N) 1595 (vs, C=O) 1497 (vs, C=C) 1435 (m, P–C) 1234 (s, C–F) cm^{-1}. $C_{35}H_{30}F_7N_2NiOP{\cdot}0.5C_5H_{12}$ (753.37): calcd. C 59.79, H 4.82, N 3.72; found C 60.02, H 5.09, N 3.52.

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