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# Nickel organometallic compounds containing optically active Schiff bases. A chiral carbon atom as a sensor of structural features †

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The reaction of $[Ni(cod)_2]$ with optically active *ortho*-halogeno-substituted imines, (*R*)-$C_6H_nR_{5-n}CH{=}NCH(Me)Ph$ (C–N), in the presence of an aromatic amine (L = 2,4,6-trimethylpyridine or 2,4-dimethylpyridine or dimethylphenylphosphine as stabilizing ligand, gave either five-membered metallacycles [Ni(C–N)XL] or the metallated compounds $[NiX(C{-}N)(PMe_2Ph)_2]$ through oxidative addition of one of the *ortho* C–X bonds (X = Br or Cl) of the imine. When the reaction was performed with the imines (*R*)-2,3,6-$Cl_3C_6H_2CH{=}NCH(Me)Ph$ and 2,3,6-$Cl_3C_6H_2CH{=}NCH_2Ph$, in the presence of dimethylphenylphosphine, a mixture of compounds coming from nucleophilic attack at C–Cl in 2 or 6 position was obtained, but when the stabilizing ligand was an aromatic amine only attack at C–Cl in position 2 occurred. The oxidative addition of one of the *ortho* C–F bonds of the imine (*R*)-$C_6F_5CH{=}NCH(Me)Ph$ to $[Ni(cod)_2]$ was also observed under mild conditions and compounds (*R*)-$[NiBr\{C_6F_4CH{=}NCH(Me)Ph\}\{2,4,6\text{-}Me_3(C_5H_2N)\}]$ and (*R*)-$[NiBr\{C_6F_4CH{=}NCH(Me)Ph\}(PMe_2Ph)_2]$ were obtained when the reaction was performed in the presence of LiBr and 2,4,6-trimethylpyridine or $PMe_2Ph$ respectively. The presence of a chiral carbon atom provides information about the structural features of the compounds here described.

The study of nickel complexes with polydentate ligands is especially interesting because of their reactivity and catalytic activity. Nickel compounds with anionic (P–O) ligands are highly active and selective catalysts in the oligomerization of ethylene to linear α-olefins[1] and nickel complexes containing neutral (N–N) ligands are used as catalysts in the polymerization of ethene and α-olefins to high molecular-weight polymers.[2] van Koten and co-workers have reported the synthesis and reactivity of many nickel complexes containing monoanionic ligands, potentially terdentate (N–C–N),[3] one of which is an effective catalyst in the Karasch addition.[4] In contrast, few nickelocycles containing bidentate anionic N–C ligands have been described, and there is no systematic way to obtain them.[5] This is surprising bearing in mind that a large number of cyclopalladated or cycloplatinated derivatives with N-donor ligands are known.[6] Furthermore, few optically active nickelocycles have been prepared and the synthesis and reactivity of enantiopure proline-based $Ni^{II}$ and $Ni^{III}$ (N–C–N) derivatives have been reported only recently.[7]

We have described the synthesis of five-membered nickelocycles by oxidative addition of $[Ni(cod)_2]$ and *ortho*-halogeno-substituted amines or imines, in the presence of heterocyclic amines or $PPhMe_2$ as stabilizing ligands.[8] We now extend our studies to optically active imines derived from (*R*)-(+)-α-methylbenzylamine. This reaction appears to be quite general and it permits the synthesis of the corresponding metallacycles, containing the enantiopure N–C ligands, in good yield.

The activation of C–F bonds by transition-metal compounds is a matter of interest; these bonds have long been considered among the least reactive of those capable of undergoing oxidative addition to metal centers. Recently, it has been shown that several low-valent transition-metal complexes can be inserted into an aromatic carbon–fluorine bond of N-donor ligands[9] but there are very few reports of activation of C–F bonds by nickel compounds.[8,9b,d] Here we report new examples of the activation of C–F bonds by a $Ni^0$ complex under mild conditions.

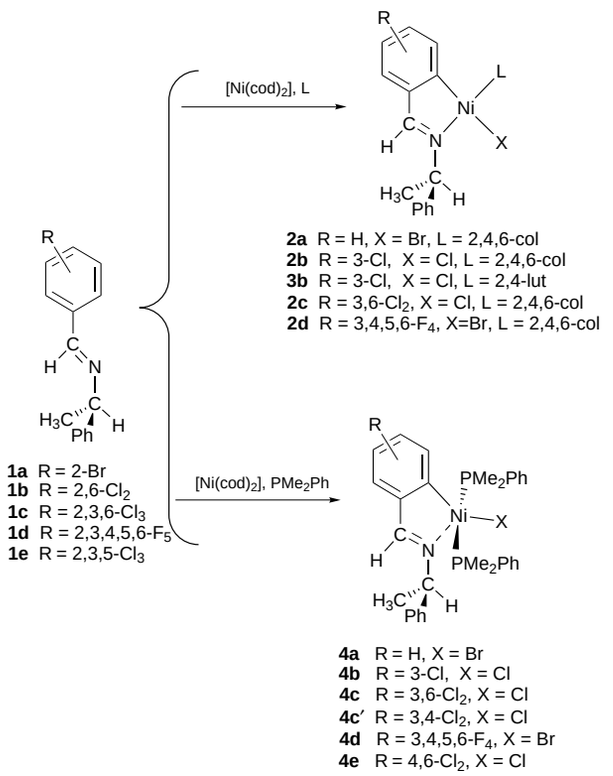
† Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

The presence of a chiral carbon atom in the two types of complex obtained, metallacycles containing aromatic amines as stabilizing ligands and metallated species containing two molecules of dimethylphenylphosphine per metal atom, provides new information about their structural features.

## Results and Discussion

The reaction of $[Ni(cod)_2]$ with optically active *ortho*-halogeno-substituted imines **1** in toluene, in the presence of 2,4-lutidine (2,4-lut, 2,4-dimethylpyridine), 2,4,6-collidine (2,4,6-coll, 2,4,6-trimethylpyridine) or dimethylphenylphosphine as stabilizing ligand, gave new organonickel complexes **2**, **3** and **4** through oxidative addition of one of the *ortho* C–X bonds (X = F, Cl or Br) of the imine (Scheme 1). It should be noted that this reaction permits the activation even of C–F bonds under mild conditions, but in this case correct elemental analyses were not obtained if the reactions were performed in the absence of LiBr. The tendency of the Ni–F bond to hydrolyze could explain this.[8] The compounds obtained were stable as dry solids or in benzene, toluene or tetrahydrofuran solutions under nitrogen, and they were characterized by elemental analyses, infrared and $^1H$ NMR spectra in $C_6D_6$ solution. Compounds **2c** and **4c**, which are oily materials, were characterized by $^1H$ NMR and positive FAB mass spectroscopy.

When the reaction was performed with the imines **1a**–**1d**, in the presence of 2,4-lutidine or 2,4,6-collidine, five-membered metallacycles [NiX(C–N)L], **2** and **3** were obtained. The $^1H$ NMR spectra of these compounds showed the signals of the *ortho*-methyl groups of the aromatic amines low-field shifted with respect to the free ligand, according to the occupation of the axial position of the co-ordination sphere;[10] the crystal structure of a closely related nickel collidine derivative confirms this.[8] The aromatic protons of both the heterocyclic amine and the metallated ring are high-field shifted, suggesting a *cis* arrangement of the two moieties. The methyl proton signal of the chiral carbon appears close to the shift of the free ligand but, in contrast, the *H*CMe proton appears low-field shifted in relation to the free ligand (Δδ 1.5–2.0), suggesting that these metallacycles adopt a conformation in which this proton is




**Scheme 1**

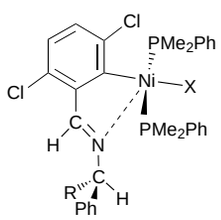
close to the metal atom, which minimizes steric repulsion. As a result of the fact that the rotation around the single carbon–nitrogen bond is hampered, conformational isomers have been reported for related palladium metallacycles.[11] The *ortho*-methyl protons of the collidine appear as two singlets at *ca.* δ 3.6, showing that these groups are in different environments because of the lack of a symmetry plane in these molecules. This lack is due to the presence of the chiral carbon atom and to the restricted rotation around the bond between the nickel and the nitrogen of the aromatic amine. For the same reasons two isomers, in a 1 : 1 ratio, were observed in the proton NMR spectrum of the 2,4-lutidine derivative **3b**.

In all the compounds containing a chlorine substituent in an *ortho* position on the aromatic ring (**2b**, **3b**, **2c**) the HC=N proton signal appears at lower fields than in the non-substituted derivative **2a**, indicating an intramolecular interaction between the atoms, as has been found for related palladium and platinum metallacycles. It has been found, by crystal structure determination, that the distance between the *ortho*-chlorine substituent and the HC=N proton in free imines and in palladium or platinum metallacycles is shorter (*ca.* 2.5–2.7 Å) than the sum of the van der Vaals radii (3.0 Å).[12]

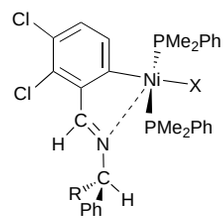
Imine **1c** could afford two different metallacycles as a result of the oxidative addition process, but the chemical shift of the aromatic protons of the metallated ring shows that the metallation occurred selectively at position 2,[13] which has a chlorine group at the adjacent carbon atom. This result can be explained by the electron-withdrawing ability of the chlorine substituent which activates the adjacent C–Cl bond towards the nucleophilic attack of the metal and shows that, in this case, the nucleophilic attack of the metal is controlled by electronic effects. Preliminary charge calculations confirm the larger positive charge of $C^2$.

The reaction of [Ni(cod)$_2$] with *ortho*-halogeno-substituted imines **1** in toluene in the presence of dimethylphenylphosphine gave the compounds [NiX(C–N)(PMe$_2$Ph)$_2$] **4**. The $^{31}$P-{$^1$H} NMR spectra of these complexes display a singlet at δ *ca.* −14 to −18, showing that the two phosphorus atoms are chemically equivalent. The aromatic protons of the metallated ring appear high-field shifted, showing that this metallated ring is adjacent to the phosphine molecules. All the spectroscopic evidence points to a five-co-ordinated geometry for these compounds, as has been found for related nickel derivatives.[8] Analogous palladium complexes with imine ligands adopt this geometry, as has been shown by X-ray studies.[14] In an NOE difference experiment, performed in an $(CD_3)_2CO$ solution of **4e** at 300 MHz, strong NOE was observed from the HC=N proton to the aromatic proton of the metallated ring in *ortho* position in relation to the C=N group. This confirms the structure proposed for **4e** (see Scheme 1), in which the nitrogen atom is close to the metal atom.

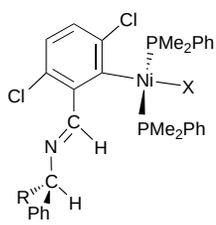
When this reaction was performed with the imine **1c**, three isomers were observed. In the two major isomers the protons of the metallated ring appear as two doublets at δ 6.48 and 6.17 for one isomer and at δ 6.41 and 6.39 for the other. The HC=N protons appear low-field shifted at δ 9.08, overlapped for both isomers, showing the existence of an intramolecular interaction between this proton and the *ortho*-chlorine atom (see above). The *H*CMe proton appears low-field shifted, and also shows the proximity of this proton to the metal atom in these isomers. These data suggest that, in this case, the nucleophilic attack of the nickel occurs in both *ortho*-chlorine groups of the imine **1c**, affording the complexes **4c** and **4c′** (see below).



**4f** R = H
**4c** R = $CH_3$



**4f′** R = H
**4c′** R = $CH_3$



**4f″** R = H
**4c″** R = $CH_3$

The chemical shift of the *Me*CH and *H*CMe protons of the third minor isomer ‡ (δ 4.42 and 1.60 respectively) are similar to those of the free ligand. In addition the HC=N proton appears at δ 8.12, showing the lack of interaction between this proton and the *ortho*-chlorine atom. The aromatic proton signals of this complex appear as two doublets at δ 6.68 and 6.64. These data indicate the structure **4c″** for this isomer, in which the nitrogen atom of the ligand is far from the metal atom (see above). van Koten and co-workers have shown by X-ray structure analysis that the Ni···N distance in the related amine derivative [NiBr{2,6-[$CH_2N$(Ph)Me]$_2C_6H_3$}($PEt_3$)$_2$] is greater than 4 Å.[3b] When (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3,6-$Cl_2C_6H_2$}{2,4,6-$Me_3(C_5H_2N)$}] **2c** was treated with PMe$_2$Ph in toluene at room temperature the substitution of the collidine by the phosphine occurred in high yield and the two isomers **4c** and **4c″** were also obtained. This confirms that **4c″** comes from a compound formed when the oxidative addition reaction takes place at position 2 and rules out the possibility that this isomer

‡ Selected NMR data for complex **4c″**. $^1$H NMR ($C_6D_6$): δ 8.12 (s, 1 H, HC=N), 7.53 [d, 2 H, $^3J$(HH) = 7.6, H$^7$, H$^{11}$), 6.68 [d, 1 H, $^3J$(HH) = 7.2, imine], 6.64 [d, 1 H, $^3J$(HH) = 7.2, imine], 4.42 (q, 1 H, C*H*Me), 1.60 [d, 3 H, $^3J$(HH) = 6.7, *Me*CH].

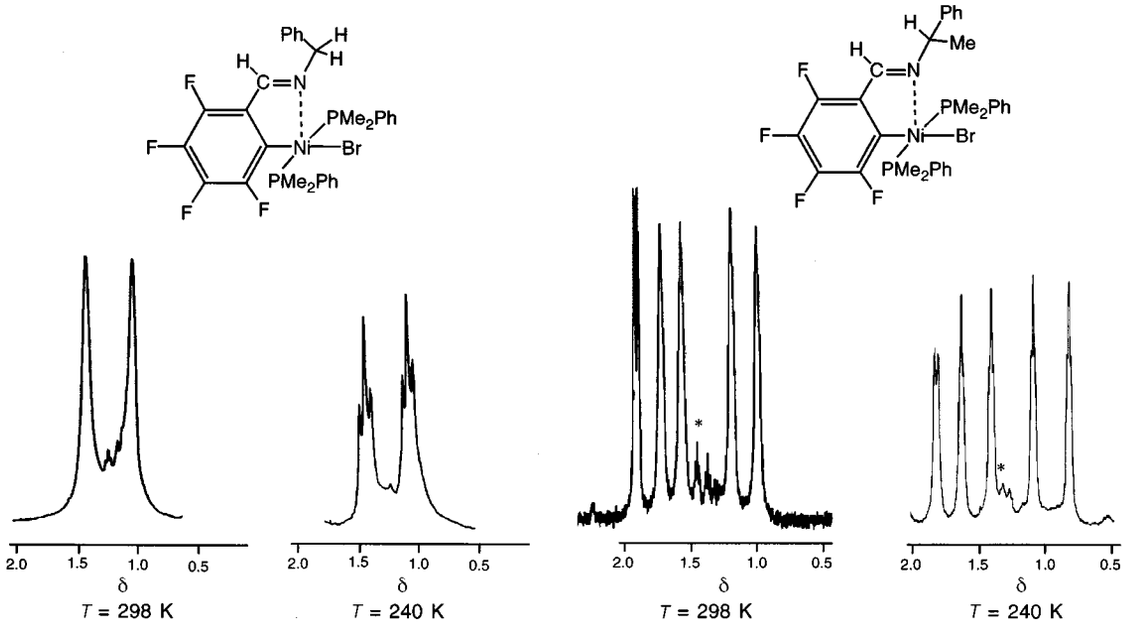



**Fig. 1** * Impurities

comes from the nickel attack on another C–Cl bond of the imine.

When the oxidative addition reaction was performed with imine 2,3,6-$Cl_3C_6H_2CH{=}NCH_2Ph$ **1f**, analogous results were obtained; the nucleophilic attack of the nickel complex takes place in both *ortho* C–Cl bonds and the formation of the isomer **4f′** was detected in low yield.§

Dimethylphenylphosphine has been used as a sensor of the symmetry of transition-metal complexes.[15] The observation of two triplets due to the Me-P protons in organometallic nickel compounds containing two $PMe_2Ph$ ligands, in *trans* position, has been taken as an indication that one asymmetric ligand breaks the symmetry plane defined by the metal co-ordination sphere, as has been found for [NiBr($C_6F_4CH{=}NCH_2Ph$)-($PMe_2Ph)_2$].[8]

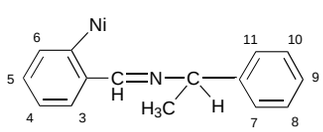
Four signals corresponding to Me-P protons were observed in the proton NMR spectra of **4e** and **4d** at 298 K, and a triplet fine structure, due to the virtual coupling,[16] was detected at 240 K. These results confirm the interaction between the nitrogen and nickel atoms and show also that the symmetry plane perpendicular to the co-ordination plane is lost because of the presence of the chiral carbon atom (see Fig. 1). It is noteworthy that to perform this type of testing in co-ordination compounds containing one chiral ligand, the racemic mixture can be used.

In contrast, the P-Me proton signals appear as broad multiplets, partially overlapped, in the spectra of compounds **4a** and **4b**, suggesting that the rotation around the Ph–C=N and Ni–C single bonds has a smaller rotation barrier. This can be related to the greater electronegativity of the metallated phenyl group of the imine ligands **1d** and **1e**, that increases the electrophilicity of the nickel atom,[8,15] as well as with the presence in **4e** and **4d** of an atom X (Cl or F) in the second axial position of the square-planar co-ordination sphere that constrains the rotation around the Ni–C bond. A different mechanism, consisting of the previous dissociation and subsequent co-ordination of the phosphine, could also explain the broad P-Me proton signals in these compounds, but this phosphine exchange has not been detected in the $^{31}P$ NMR spectra, which shows only one sharp singlet even at room temperature.

§ Selected $^1H$ NMR data for complex **4f′**. $^1H$ NMR ($C_6D_6$): δ 8.2 (s, 1 H, HC=N), 6.7 (m, 2 H, aromatic), 4.71 (s, 2 H, $CH_2N$).

## Experimental

The $^1H$, $^{31}P$-{$^1H$} and $^{19}F$ NMR spectra were obtained in $C_6D_6$ solutions using Varian XL-200 (200 MHz), Bruker 250 DRX (250.1 MHz) and Varian XL300 FT (282.2 MHz) instruments, respectively. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for $^1H$, to 85% $H_3PO_4$ for $^{31}P$ and to $CFCl_3$ for $^{19}F$. Coupling constants in Hz; numbering as shown below. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and by the Serveis Científico-Tècnics de la Universitat de Barcelona. The samples were introduced in a matrix of 2-nitrobenzyl alcohol for FAB analysis and then subjected to bombardment with caesium atoms.



### Materials and synthesis

All manipulations of the organonickel compounds were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Diethyl ether and toluene were distilled over sodium–benzophenone, under nitrogen, before use. The complex [Ni(cod)$_2$] was prepared according to a procedure described elsewhere.[17]

**Imines 1a–1e.** (*R*)-(+)-α-Methylbenzylamine (2.5 mmol) and the appropriate aldehyde (2.5 mmol) were dissolved in ethanol (20 $cm^3$) and the resulting solution was refluxed for 2 h. The solution was concentrated to dryness on a rotary evaporator. The oils obtained contain the imines, nearly in pure form, and were used without further purification.

**(*R*)-[NiBr{2-[CH=NCH(Me)Ph]$C_6H_4$}{2,4,6-$Me_3(C_5H_2N)$}] 2a; (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3-$ClC_6H_3$}{2,4,6-$Me_3(C_5H_2N)$}] 2b; (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3,6-$Cl_2C_6H_2$}{2,4,6-$Me_3(C_5H_2N)$}] 2c; (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3-$ClC_6H_3$}{2,4-$Me_2(C_5H_3N)$}] 3b.** To a suspension of [Ni(cod)$_2$] (0.65 g, 2.40 mmol) in toluene (25 $cm^3$) at −78 °C was added the corresponding imine (2.40 mmol) and the substituted pyridine (2.40 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 4 h under these condi-

tions. The solution was filtered to remove some metallic nickel, and the filtrate was evaporated to dryness. The addition of ether affords **2a**, **2b** and **3b**, in the solid state in 50–70% yield. Compound **2c** was obtained as an oily material. Data for **2a** (Found: C, 59.5; H, 5.6; N, 6.0. Calc. for $C_{23}H_{25}BrN_2Ni$: C, 59.02; H, 5.38; N, 5.98%). $^1$H NMR: δ 7.57 (s, 1 H, HC=N), 7.47 [d, $^3J$(HH) = 7.0, 2 H, H$^7$, H$^{11}$], 7.18–7.0 (br m, 3 H, imine), 6.90–6.60 (m, 4 H), 6.24 (s, 1 H, col), 6.21 (s, 1 H, col), 5.42 [d, $^3J$(HH) = 7.0, 1 H, H$^6$], 3.74 (s, 3 H, col), 3.62 (s, 3 H, col), 1.71 (s, 3 H, col), 1.66 [d, $^3J$(HH) = 6.8, 3 H, *Me*CH]. Data for **2b** (Found: C, 60.4; H, 5.5; N, 6.1. Calc. for $C_{23}H_{24}Cl_2N_2Ni$: C, 60.31; H, 5.29; N, 6.11%). $^1$H NMR: δ 8.31 (s, 1 H, HC=N), 7.50 [d, $^3J$(HH) = 7.2, 2 H, H$^7$, H$^{11}$], 7.35–7.20 (br m, 3 H, imine), 6.85 [d, $^3J$(HH) = 7.0, 1 H, H$^4$], 6.60–6.45 (br m, 2 H, imine), 6.30 (s, 1 H, col), 6.26 (s, 1 H, col), 5.35 [d, $^3J$(HH) = 7.2, 1 H, H$^6$], 3.74 (s, 3 H, col), 3.61 (s, 3 H, col), 1.78 (s, 3 H, col), 1.68 [d, $^3J$(HH) = 6.8, 3 H, *Me*CH]. Data for **2c**. $^1$H NMR: δ 8.20 (s, 1 H, HC=N), 7.45–7.20 (br m, 5 H, imine), 6.70 (br, 2 H, H$^4$, H$^5$), 6.24 (m, 3 H, col, *H*CMe), 3.74 (s, 3 H, col), 3.62 (s, 3 H, col), 1.71 (s, 3 H, col), 1.66 [d, $^3J$(HH) = 6.8, 3 H, *Me*CH]. Oily material. MS: *m*/*z* 492 (*M*). Data for **3b** (mixture of two isomers) (Found: C, 59.6; H, 5.2; N, 6.1. Calc. for $C_{22}H_{22}Cl_2N_2Ni$: C, 59.51; H, 4.99; N, 6.31%). $^1$H NMR: δ 8.79 (br s, 1 H, lut), 8.71 (br s, 1 H, lut), 8.25 (br s, 2 H, CH=N), 7.45–6.80 (br m, 12 H), 6.60–6.20 (m, 8 H, lut, H$^5$, H$^4$, *H*CMe), 5.32 (br s, 2 H, H$^6$), 3.49 (br s, 3 H, lut), 3.43 (br s, 3 H, lut), 1.70–1.45 (br m, 12 H, lut, *Me*CH).

**(*R*)-[NiBr{2-[CH=NCH(Me)Ph]-3,4,5,6-F$_4$C$_6$}{2,4,6-Me$_3$-(C$_5$H$_2$N)}] 2d.** To a suspension of [Ni(cod)$_2$] (0.65 g, 2.40 mmol) in a 1:1 mixture of toluene and tetrahydrofuran (30 cm$^3$) at −78 °C was added the corresponding imine (2.40 mmol), LiBr (0.21 g, 2.40 mmol) and 2,4,6-collidine (2.40 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 6 h under these conditions. The solution was filtered and the solvent was removed under vacuum. An orange solid was obtained after addition of hexane. Recrystallization from toluene–hexane gave **2d** in 30% yield. Data for **2d** (Found: C, 51.1; H, 4.0; N, 5.1. Calc. for $C_{23}H_{21}BrF_4N_2Ni$: C, 51.15; H, 3.92; N, 5.19%). $^1$H NMR: δ 7.31 (s, 1 H, CH=N), 6.95 [d, $^3J$(HH) = 6.9, 2 H, H$^7$, H$^{11}$], 6.86–6.77 (br m, 3 H, Ph), 6.03 [q, $^3J$(HH) = 6.9, 1 H, *H*CMe], 3.44 (s, 3 H, col), 3.34 (s, 3 H, col), 1.33 (s, 3 H, col), 1.02 [d, $^3J$(HH) = 6.9, 3 H, *Me*CH]. $^{19}$F NMR: δ −138.2 [dd, $J$(FF)$_{para}$ = 26.0, $J$(FF)$_{ortho}$ = 16.0, F$^6$], −143.6 (m, F$^5$), −152.9 [ddd, $J$(FF)$_{para}$ = 26.0, $J$(FF)$_{ortho}$ = 18.0, $J$(FF)$_{meta}$ = 3.1, F$^3$], −164.0 [t, $J$(FF)$_{ortho}$ = 20.0, F$^4$].

**(*R*)-[NiBr{2-[CH=NCH(Me)Ph]C$_6$H$_4$}(PMe$_2$Ph)$_2$] 4a; (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3-ClC$_6$H$_3$}(PMe$_2$Ph)$_2$] 4b; (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-3,6-Cl$_2$C$_6$H$_2$}(PMe$_2$Ph)$_2$] 4c (mixture of isomers); (*R*)-[NiCl{2-[CH=NCH(Me)Ph]-4,6-Cl$_2$C$_6$H$_2$}(PMe$_2$Ph)$_2$] 4e; [NiCl{2-(CH=NCH$_2$Ph)-3,6-Cl$_2$C$_6$H$_2$}(PMe$_2$Ph)$_2$] 4f (mixture of isomers).** To a suspension of [Ni(cod)$_2$] (0.65 g, 2.40 mmol) in toluene or THF (40 cm$^3$) at −78 °C was added the corresponding imine (2.40 mmol) and dimethylphenylphosphine (4.80 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 2 h under these conditions. The solvent was removed under vacuum. Compounds **4a**, **4b**, **4e** and **4f** were precipitated in 50–80% yield on adding absolute ethanol and **4c** was obtained as an oily material. Data for **4a** (Found: C, 59.0; H, 6.0; N, 2.2. Calc. for $C_{31}H_{36}BrNNiP_2$: C, 59.75; H, 5.82; N, 2.25%). $^1$H NMR: δ 8.33 (s, 1 H, HC=N), 7.85 [d, $^3J$(HH) = 7.3, 2 H, H$^7$, H$^{11}$], 7.70 (br s, 4 H, PPh), 7.36–7.15 (br m, 9 H), 6.98 [d, $^3J$(HH) = 6.9, 1 H, H$^3$], 6.78 [t, $^3J$(HH) = 6.9, 1 H, H$^4$], 6.72–6.50 (m, 2 H, H$^5$, H$^6$), 5.32 (br m, 1 H, *H*CMe), 2.09 (d, $^3J$(HH) = 6.3, 3 H, *Me*CH), 1.2–0.5 (br, 12 H, PMe). $^{31}$P NMR: δ −15.4. Data for **4b** (Found: C, 60.1; H, 5.8; N, 2.3. Calc. for $C_{31}H_{35}Cl_2NNiP_2$: C, 60.71; H, 5.76; N, 2.28%). $^1$H NMR: δ 9.06 (s, 1 H, HC=N), 7.73 [d, $^3J$(HH) = 7.2, 2 H, H$^7$, H$^{11}$], 7.39 (br s, 4 H, PPh), 7.15–7.00 (br m, 9 H), 6.65 [d, $^3J$(HH) = 7.0, 1 H, H$^4$], 6.33 (m, 2 H, H$^5$, H$^6$), 5.30 (br m, 1 H, *H*CMe), 1.92 [d, $^3J$(HH) = 6.6, 3 H, *Me*CH], 1.2–0.5 (br, 12 H, P-Me). $^{31}$P NMR: δ −17.6. Data for **4c** (mixture of two isomers). $^1$H NMR: δ 9.08 (s, 2 H, HC=N), 7.79 [d, $^3J$(HH) = 7.2, 2 H, H$^7$, H$^{11}$], 7.62 [d, $^3J$(HH) = 7.1, 2 H, H$^7$, H$^{11}$], 7.40 (br s, 8 H, PPh), 7.15–7.00 (br m, 18 H), 6.48 [d, $^3J$(HH) = 7.2, 1 H], 6.41 [d, $^3J$(HH) = 7.2, 1 H], 6.39 [d, $^3J$(HH) = 7.2, 1 H], 6.17 [d, $^3J$(HH) = 7.2, 1 H], 5.29 (m, 2 H, *H*CMe), 2.02 [d, $^3J$(HH) = 6.7, 3 H, *Me*CH], 1.81 [d, $^3J$(HH) = 6.8, 3 H, *Me*-CH], 1.6–0.5 (br, 24 H, PMe). $^{31}$P NMR: δ −18.3. Oily material. MS: *m*/*z* 647 (*M*). Data for **4e** (Found: C, 57.0; H, 5.1; N, 2.0. Calc. for $C_{31}H_{34}Cl_3NNiP_2$: C, 57.49; H, 5.29; N, 2.16%). $^1$H NMR [(CD$_3$)CO]: δ 8.66 (s, 1 H, HC=N), 7.57 [d, $^3J$(HH) = 6.7, 2 H, H$^7$, H$^{11}$], 7.40–7.00 (br m, 13 H), 7.04 (s, 1 H, H$^3$), 6.72 (s, 1 H, H$^5$), 5.10 (br m, 1 H, *H*CMe), 1.73 [d, $^3J$(HH) = 6.6, 3 H, *Me*CH], 1.42 (br s, 3 H, PMe), 1.38 (br s, 3 H, PMe), 1.12 (br s, 3 H, PMe), 1.04 (br s, 3 H, PMe). $^1$H NMR (C$_6$D$_6$): δ 8.36 (s, 1 H, HC=N), 7.60 [d, $^3J$(HH) = 6.7, 2 H, H$^7$, H$^{11}$], 7.40–7.00 (br m, 15 H), 4.82 (br m, 1 H, *H*CMe), 1.73 [d, $^3J$(HH) = 6.7, 3 H, *Me*CH], 1.36 (s, 6 H, PMe), 1.16 (s, 3 H, PMe), 1.08 (s, 3 H, PMe). $^{31}$P NMR: δ −18.2. Data for **4f** (mixture of two isomers) (Found: C, 55.1; H, 5.2; N, 2.3. Calc. for $C_{30}H_{32}Cl_3NNiP_2$: C, 56.87; H, 5.09; N, 2.20%). $^1$H NMR: δ 8.94 (s, 1 H, HC=N), 8.87 (s, 1 H, HC=N), 7.68 [d, $^3J$(HH) = 6.6, 2 H, H$^7$, H$^{11}$], 7.55 [d, $^3J$(HH) = 6.6, 2 H, H$^7$, H$^{11}$], 7.40–7.10 (br s, 26 H, PPh), 6.54 [d, $^3J$(HH) = 8.0, 1 H], 6.47 (br s, 2 H), 6.25 [d, $^3J$(HH) = 8.0, 1 H], 5.20 (2, 2 H, CH$_2$N), 4.96 (2, 2 H, CH$_2$N), 1.45–1.0 (br, 24 H, PMe). $^{31}$P NMR: δ −19.1.

**(*R*)-[NiBr{2-[CH=NCH(Me)Ph]-3,4,5,6-F$_4$C$_6$}(PMe$_2$Ph)$_2$] 4d.** To a suspension of [Ni(cod)$_2$] (0.65 g, 2.40 mmol) in toluene (30 cm$^3$) at −78 °C was added the corresponding imine (2.40 mmol), LiBr (0.21 g, 2.40 mmol) and dimethylphenylphosphine (4.80 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 1 h under these conditions. The solvent was removed under vacuum and after addition of methanol a maroon solid was collected. Recrystallization from toluene–methanol gave **4d** in 70% yield. Data for **4d** (Found: C, 53.6; H, 4.8; N, 2.0. Calc. for $C_{31}H_{32}BrF_4NNiP_2$: C, 53.56; H, 4.64; N, 2.01%). $^1$H NMR: δ 8.61 (s, 1 H, CH=N), 7.68 [d, $^3J$(HH) = 7.5, 2 H, H$^7$, H$^{11}$], 6.90–7.35 (br m, 13 H, PPh, H$^8$, H$^9$, H$^{10}$), 5.11 (br q, 1 H, *H*CMe), 1.88 [d, $^3J$(HH) = 6.7, 3 H, *Me*CH], 1.71 (br s, 3 H, PMe), 1.56 (br s, 3 H, PMe), 1.19 (br s, 3 H, PMe), 1.01 (br s, 3 H, PMe). $^{31}$P NMR: δ −15.6. $^{19}$F NMR: δ −117.9 (m, F$^6$), −149.7 [t, $J$(FF)$_{ortho}$ = 17.0, F$^5$], −156.7 [dd, $J$(FF)$_{para}$ = 33.0, $J$(FF)$_{ortho}$ = 20.0, F$^3$] −168.1 [t, $J$(FF)$_{ortho}$ = 20.0, F$^4$].

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