

# Fluoro aromatic imine nickel(0) complexes: Synthesis and structural studies

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## Abstract

The reaction of  $[\text{Ni}(\text{dippe})]_2(\mu\text{-H})_2$  with a series of fluoroaromatic imines affords nickel(0) complexes of the type  $[(\text{dippe})\text{Ni}(\eta^2\text{-C,N-PhHC=NR'Ph})]$ , dippe = 1,2-bis(diisopropylphosphine)ethane. Solution NMR experiments as well as X-ray diffraction studies confirmed the  $\pi$ -coordination of the ligand through the C=N moiety; the resulting complex found to adopt a distorted tetrahedral geometry around the nickel center. The compounds are thermally stable and decomposition is only observed after long periods of heating above 150 °C.

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**Keywords:** Nickel(0); Imines; Fluorinated ligands; Crystal structure

## 1. Introduction

The considerably low reactivity shown by C=N bond moieties towards nucleophilic addition reactions, as well as many other organic transformations makes them an attractive target for activation using transition metal complexes, and thus remains a challenge for the contemporary organometallic chemist [1]. In particular, imines (Schiff bases) are versatile ligands obtained from condensation reactions between aldehydes and primary amines and consequently the electronic and steric properties of the ligands can be modified in a straightforward fashion. The characteristic coordination modes of the imine ligands are illustrated in Fig. 1; and in this instance, a wealth of reviews covering this topic have appeared in a number of references [2,3]. Typically, the preferred bonding mode of Schiff bases is an  $\eta^1$ -fashion (*end on*), established through the lone pair of the terminal nitrogen ( $\sigma$  bonding). In sharp contrast, the  $\pi$ -binding (*side-on*) is rather unusual and only a handful of

reports are known; [4] *i.e.* Stone and co-workers [5] have synthesized a series of group 10 metal complexes with the general formula  $\text{L}_2\text{M-C}_2\text{N}_2(\text{CF}_3)_4$  where the C=N moiety of the azine is  $\eta^2$ -coordinated to the metal. Gabor et al. for their part, unexpectedly achieved  $\eta^2$ -binding of an imine to a Ni(0) carbene complex, while undergoing a series of substitution reactions, in which the olefin ligands had been displaced by chelating phosphines ( $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ ), the resulting complex rearranging into the  $\pi$ -complex. [6] More recently, heterobutadiene ligands that contain an imine moiety, were found to be  $\pi$ -bonded to Ni(0) by displacement reactions over  $\text{L}_2\text{Ni}(\text{COD})$  complexes. *Side-on* coordination was facilitated by the use of basic co-ligands such as  $\text{PMe}_3$  along with strong electron-withdrawing R-groups on the R-C=N-R' moiety [7].

On the other hand, in binuclear metal complexes (Fig. 1), it is proposed that a mixed  $\pi$ - $\sigma$  binding mode stabilizes this type of interaction: while one metal center  $\sigma$  binds, the other metallic center is more prone to accept  $\pi$  density from the C=N bond and  $\eta^2$  coordinate [8]. Hillhouse and co-workers have reported the oxidative addition reactions of *N*-tosylaziridines with Ni(0) ( $\text{bpy})\text{Ni}(\text{COD})$

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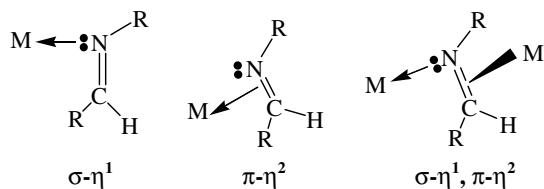


Fig. 1.  $\sigma$ -,  $\pi$ - and mixed  $\sigma, \pi$ -coordination modes of imines [8].

complexes to afford the corresponding Ni(II) azametallacyclobutane products [9].

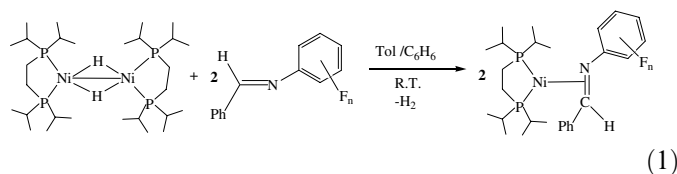
As a consequence of the low reactivity of the imine bond (*vide supra*) in comparison with other unsaturated substrates of the type  $C=X$  ( $X = C, O$ ), the number of reports regarding the activation of imine functionalities is rather small. For instance, in the case of imine hydrogenation the thermodynamic gain achieved within this process ( $-14$  kcal/mol) is small when compared with that obtained for the reduction of alkenes ( $-31$  kcal/mol). Here, the generally accepted mechanism for the hydrogenation of olefins mediated by transition metal complexes is well understood [10], and has shown the need of  $\pi$ -binding of the olefin to the metal center prior to the hydrogenation step. Thus, the fact that imines typically bind to the metal center in a  $\eta^1$  mode, results in a major drawback when its hydrogenation takes place.

For a number of years, our research group has been interested in the activation of  $C-CN$  bonds with the use of nickel(0) complexes, and reported the preparation of a variety of complexes bearing both alkyl-, aromatic- and heteroaromatic-substituents, such as cyanoquinolines and cyanopyridines [11–13]. In all cases, the  $\eta^2$ -coordination of the nitrile functionality to the nickel(0) moiety [(dippe)Ni] is observed to occur in place first; the oxidative cleavage of the  $C-CN$  bond of a variety of nitriles been observed to take place after mild heating. Only in the case of aromatic nitriles this process was found to be reversible [12]. The isomerization of cyanoolefins with (bis-diphenylphosphinoferrocene)Ni compounds has also been undertaken by our group recently [14]. Additionally, the functionalization of  $\eta^2$ -coordinated  $-CN$  bonds to nickel(0) was also addressed, hence a homogeneous catalytic hydration process for benzo- or acetonitrile [15] as well as for industrially important dinitriles such as 1,4-terephthalonitrile [15], was also attained. In general, the  $\eta^2$ -coordination is rather uncommon in nitrile hydration catalysis [16], the  $\eta^1$ -binding mode of the substrate to a metallic center been proposed to take place in most reaction mechanisms as a result of stoichiometric reactions generally pointing to a preferred *end on* coordination of the NCR moiety, particularly when electrophilic metal centers are used [16]. In this context, we have expanded this chemistry to other closely related substrates such as imines. Thus in this work we would like to describe our findings on the synthesis and characterization of Ni(0) complexes with aromatic monodentate Schiff base ligands ( $PhC=N-R'$ ) in which the electronic and steric environment can be modified by systematic fluorine substitution on the aniline moiety, thus allowing a fine tuning of both

the electronic and steric properties of the complexes and inducing significant changes in the overall reactivity of the coordinated molecule.

## 2. Results and discussion

Complexes of the type [(dippe)Ni( $\eta^2$ -( $C,N$ )-PhHC=NR')] were formed rapidly and in good yield upon reductive elimination of  $H_2$ , driven by the addition of 1 equiv. of the Nickel(I) dimer  $[Ni(dippe)]_2(\mu-H)_2$  in the presence of 2 equiv. of the corresponding imine (Table 1). The reactions were performed in all cases either in toluene or in  $C_6H_6$ , and are illustrated in reaction (1). In most cases, the starting solution was observed to change instantaneously from a wine-red coloured one to an even darker color. The resulting compounds were isolated from concentrated toluene/benzene solutions at low temperatures, or by vapor phase diffusion of THF/hexane. All of the complexes were characterized by their corresponding  $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{31}P\{^1H\}$  and  $^{19}F$  NMR spectroscopies. Single crystal X-ray structure determinations were also obtained for complexes **1**, **4\*THF**, **6**, **9** and **11**.



In general, the  $^{31}P$  NMR( $^1H$ ) spectrum of all complexes was found to exhibit two asymmetric doublets that are indicative of two types of phosphorus environments centered between 65.8–70.0 ppm and 61.8–66.6 ppm, respectively, the  $^2J_{P-P}$  coupling constant of each doublet being in the range of 58.5–50.9 Hz (see Table 1). The magnitude of the  $^2J_{P-P}$  constants observed within the series of complexes, varied depending on the nature of the R group present in each complex, either electron-withdrawing (EW) or electron donating (ED) in nature. The  $^2J_{P-P}$  coupling constant decreased on going from the electron rich  $-NH_2$  substituent to the electron poor  $-CN$ , in consistency with a trend observed in the case of the otherwise analogous [(dippe)Ni( $\eta^2$ -N,C-Ph-R)] Ni(0) nitrile complexes. Hence, the electron poor complexes **11** and **12** (4 and 5 fluorines over the coordinated imine ligand) (Table 1) displayed the smallest  $^2J_{P-P}$  coupling constants of the entire series and the largest one corresponding to compound **1** that is not fluorinated (Table 1) [11–13,17].

Long-range coupling with fluorine was observed for complexes **2**, **6–8** and **12** with  $J_{H-F}$  in the range 1.5–6.6 Hz, exhibiting a 2,6-doubly fluorinated ligand [18]. For compounds **9** and **11** a small coupling to fluorine by one of the phosphorus atom was observed. In the solid state, the crystal structure (see Supporting Information) of **11** reveals that P1 is closer to fluorine atoms F1 and F2 (see Fig. 6). Assuming the latter conformation is also stable in solution, then this could explain the reason for an heteronuclear through-space coupling to P1; a result

Table 1  
Relevant NMR data for compounds **1–12** in Toluene-*d*<sub>8</sub>

R'	Complex	<sup>1</sup> H NMR free <sup>b</sup> ligand	<sup>1</sup> H NMR CH=N <sup>c*</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR free ligand <sup>b</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR CH=N <sup>d*</sup>	<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>e*</sup>
C <sub>6</sub> H <sub>5</sub>	( <b>1</b> )	8.09	5.21	159.7	59.90	69.7 (d, <sup>2</sup> J <sub>P-P</sub> 58.6 Hz); 63.8 (d, <sup>2</sup> J <sub>P-P</sub> 58.6 Hz)
2F-C <sub>6</sub> H <sub>4</sub>	( <b>2</b> ) <sup>a</sup>	8.10	5.10	163.1	58.35	69.6 (dd, <sup>2</sup> J <sub>P-P</sub> 55.4, 2.5 Hz); 65.2 (dd, <sup>2</sup> J <sub>P-P</sub> 55.4, 5.8 Hz)
3F-C <sub>6</sub> H <sub>4</sub>	( <b>3</b> ) <sup>a</sup>	7.98	5.08	163.3	58.08	69.7 64.9
4F-C <sub>6</sub> H <sub>4</sub>	( <b>4</b> ) <sup>a</sup>	8.06	5.25	160.0	59.90	69.7 63.7
3,5F-C <sub>6</sub> H <sub>3</sub>	( <b>5</b> )	7.77	4.79	161.6	57.00	70.0 65.8
2,4F-C <sub>6</sub> H <sub>3</sub>	( <b>6</b> )	7.99	5.21	162.6	58.90	67.9 (dt, <sup>2</sup> J <sub>P-P</sub> 56.4, 2.6 Hz); 63.4 (dd, <sup>2</sup> J <sub>P-P</sub> 56.4, 4.6 Hz)
2,3F-C <sub>6</sub> H <sub>3</sub>	( <b>7</b> )	8.01	5.12	163.4	57.45	69.9 (dd, <sup>2</sup> J <sub>P-P</sub> 53.2, 2.3 Hz); 66.0 (dd, <sup>2</sup> J <sub>P-P</sub> 52.9, 6.4 Hz)
2,6F-C <sub>6</sub> H <sub>3</sub>	( <b>8</b> ) <sup>a</sup>	8.19 (t, <sup>5</sup> J <sub>H-F</sub> 1.5 Hz)	6.08	167.3	61.13 (dt, <sup>2</sup> J <sub>P-C</sub> 19.8, 7.0 Hz)	67.6 (dt, <sup>2</sup> J <sub>P-P</sub> 56.3, 2.7 Hz); 66.0 (dd, <sup>2</sup> J <sub>P-P</sub> 56.3, 4.3 Hz)
2,4,6F-C <sub>6</sub> H <sub>2</sub>	( <b>9</b> )	8.16	5.92	166.1	61.43 (dt, <sup>2</sup> J <sub>P-C</sub> 19.8, 6.9 Hz)	67.8 (dd, <sup>2</sup> J <sub>P-P</sub> 57.5, 2.6 Hz); 66.1 (d, <sup>2</sup> J <sub>P-P</sub> 57.5 Hz)
2,4,5F-C <sub>6</sub> H <sub>2</sub>	( <b>10</b> ) <sup>a</sup>	7.82	4.99	163.4	57.90	70.0 66.6
2,3,5,6F-C <sub>6</sub> H	( <b>11</b> ) <sup>a</sup>	7.97	5.78–5.83 (m)	168.8	57.6 (dt, <sup>2</sup> J <sub>P-C</sub> 21.5, 6.4 Hz)	68.4 66.5 (dt, <sup>2</sup> J <sub>P-P</sub> 50.8, 6.3 Hz)
2,3,4,5,6F-C <sub>6</sub>	( <b>12</b> ) <sup>a</sup>	8.03	5.69–5.72 (m)	168.9	58.1 (dt, <sup>2</sup> J <sub>P-C</sub> 21.5, 6.5 Hz)	68.4 (dd, <sup>2</sup> J <sub>P-P</sub> 50.9, 2.5 Hz), 66.6 (dt, <sup>2</sup> J <sub>P-P</sub> 50.9, 5.1 Hz)

\* for more details see Section 5.

<sup>a</sup> <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} in C<sub>6</sub>D<sub>6</sub>.

<sup>b</sup> Multiplicity: singlets, unless otherwise noted, unpublished results[19].

<sup>c\*</sup> Multiplicity (dd, 1H) except when noted.

<sup>d\*</sup> Multiplicity (d, CH=N) except when noted.

<sup>e\*</sup> Multiplicity (d, <sup>2</sup>J<sub>P-P</sub>) except when otherwise noted.

that is consistent with the F–F through-space coupling that has been observed for fluoro(2'-fluorophenyl) ethanes [18].

The proton NMR spectra allowed the assignment of nearly all signals. The coordination of the ligand to the electron rich Ni(dippe) fragment, causes a considerable upfield shift of the aldimine proton compared with the uncoordinated ligand (*i.e.* entry **1**, 5.21 ppm vs. 8.09 ppm, Table 1), thus substantially diminishing the sp<sup>2</sup> character of the CH=N bond, due to donation from the metal center. The H–C=N signal was also resolved in to a doublet of doublets (in the range of 4.79–6.08 ppm), that is due to coupling with non-equivalent phosphorus with <sup>3</sup>J<sub>P-H</sub> of an average 7.0, 3.1 Hz. Furthermore, in complexes **11** and **12** the proton signal is further resolved giving rise to a multiplet which is due to coupling with the polyfluorinated aniline moieties (see Section 5).

The aliphatic portion of the spectrum at room temperature showed different methyl group resonances for the majority of the complexes, perhaps associated to the formation of chiral center at the imine carbon upon coordination, which renders them diastereotopic and/or certain degree of hindered rotation. The distinctive <sup>3</sup>J<sub>H-H</sub> and <sup>3</sup>J<sub>H-P</sub> for the complexes averaging 7.0 and 15.0 Hz, respectively are observed [17]. In contrast, only two sets of signals are assigned to the methyne protons for most of the compounds (Section 5). These assignments were confirmed by DEPT and HETCOR NMR experiments.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectra showed similar features as those observed in the <sup>1</sup>H NMR: the signal corresponding to the aldimine carbon appearing 100 ppm upfield, compared with that of the uncoordinated ligand (*i.e.* entry **1**, 159.7 ppm vs. 59.9 ppm, Table 1). The imine carbon in general appears as a doublet since it couples to phosphorus across the metal center, the corresponding <sup>2</sup>J<sub>C-P</sub> being in the range of 20 Hz. For compounds **8**, **9**, **11**, **12** (*o*-positions), the signals are further resolved, presumably due to long-range coupling to fluorine across the nickel center, provided that in the free ligand this multiplicity is absent [19]. In the <sup>19</sup>F NMR spectra, the fluorine signals were shifted upfield Δδ = 9 ppm compared to the uncoordinated ligand [19], a feature that is possibly due to electron donation from the low valent nickel center and withdrawal of electron density onto the fluorine atoms enhancing the polarization of the ring [20].

*Crystal structure studies.* The structure of compound **1** was fully characterized by X-ray crystallography (Fig. 2). Suitable crystals were grown from a concentrated solution of toluene at –30°C. Crystallographic and structure refinement data for complex **1** are given in Table 2. The coordination geometry around Ni is a distorted tetrahedron, showing a considerable lengthening (0.135 Å) of the η<sup>2</sup> coordinated imine (1.368 Å) compared with that of the free ligand (1.233 Å) [21], due to the side-on coordination and to Ni(0) back bonding in to the C=N \*π orbitals, which con-

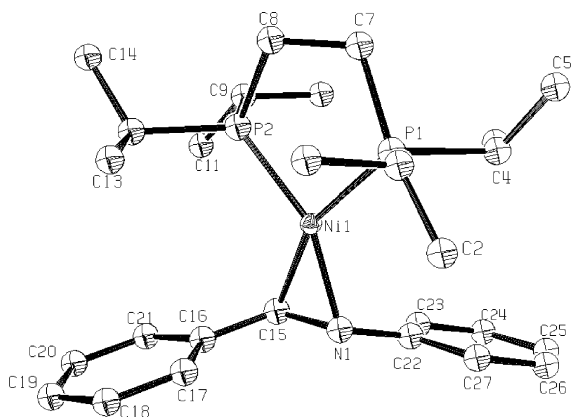


Fig. 2. ORTEP drawing of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-Ph-N=CHPh})]$  (**1**). Ellipsoids are shown at the 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): Ni–P1 2.1609(8), Ni–P2 2.1493(8), Ni–N 1.921(2), Ni–C15 1.931(2), N–C15 1.368(3); Selected angles (°): C15–Ni–N 41.61(10), C15–Ni–P2 111.18(8), N–Ni–P1 115.42(7), P2–Ni–P1 91.77(3), C15–Ni–P1 156.79(8), N–Ni–P2 152.79(7).

firm the partial loss of double bond character observed by  $^1\text{H}$  NMR. As a result, the structure has a significant contribution from the nickelacyclopropane canonical form [13]. Accordingly, Ni–P bond distances are the shortest reported for these sort of complexes: 2.1493(8), 2.1609(8) Å in  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-Ph-N=CHPh})]$ ; 2.165(1), 2.188(1) Å in  $[(\text{dippe})\text{Ni}(\eta^2\text{-}t\text{-Bu-N=CHPh})]$  [6]; 2.1742(8), 2.1944(8) Å in  $[(\text{PMe}_3)_2\text{Ni}\eta^2\text{-Ph-C(N-Mes)-N=C(CF}_3)_2]$ , respectively, which is also indicative of back donation from the electron rich metal center [7]; an evidence of the greater  $\pi$ -

accepting nature of the coordinated ligand. The almost equidistant Ni–P1 and Ni–P2 bond lengths suggest that the Ni(dippe) fragment is symmetrically bonded [17].

The coordinated ligand in **1**, adopted an *E* configuration with respect to the C=N bond. The imine moiety was essentially planar with the benzaldehyde aromatic ring with a C16–C15–N1 angle of 119.69°. Torsion angles (C21–C16–C15–N1 149.6° and C23–C22–N1–C15 164.6°) suggest that the ligand is not entirely planar, although the interplanar angles are smaller ( $\alpha$  30.4,  $\beta$  –15.1) than the ones reported for the free ligand ( $\alpha$  55.2,  $\beta$  –10.3) [21]. Additionally, the aromatic aniline ring is bent out of the plane with a dihedral angle of 26.82° defined by the planes C17–C21–C18 and C22–C27–C25, which can be assigned to the ligand binding requirements upon coordination with the (dippe)Ni fragment.

Suitable crystals for X-ray diffraction studies were obtained of complexes **4**\*THF, **6** and **9** (Figs. 3–5). Crystallographic and structure refinement data are summarized in Table 2. In general, the structures exhibit disorder around the coordinated ligand (imine bond and aromatic fluorine positions) *i.e.* one half of the molecules crystallized in one preferred orientation while the other half crystallized in the opposite direction; a consequence of the presence of a center of inversion in these structures. In the case of **4**\*THF, half molecule of THF was found in the unit cell, which accounts for the empirical formula of  $\text{C}_{29}\text{H}_{46}\text{FNiO}_{0.50}\text{P}_2$ . In this case, bond distances [Å] and angles [°] are similar to the ones reported for complex **1** (see Figs. 2–5). As a consequence of

Table 2  
Summary of crystallographic results for compounds **1**, **4**, **6**, **9**, and **11**

	<b>1</b>	<b>4</b> *THF	<b>6</b>	<b>9</b>	<b>11</b>
Formula	$\text{C}_{27}\text{H}_{43}\text{NNiP}_2$	$\text{C}_{29}\text{H}_{46}\text{FNiO}_{0.50}\text{P}_2$	$\text{C}_{27}\text{H}_{41}\text{F}_2\text{NNiP}_2$	$\text{C}_{27}\text{H}_{37}\text{F}_3\text{NNiP}_2$	$\text{C}_{27}\text{H}_{39}\text{F}_4\text{NNiP}_2$
FW	502.27	556.32	538.26	553.23	574.24
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	11.2086(17)	11.224(6)	11.263(3)	11.1929(17)	16.5127(15)
<i>b</i> (Å)	14.935(2)	15.749(8)	15.112(4)	15.378(2)	10.2374(9)
<i>c</i> (Å)	16.185(3)	16.587(10)	16.243(5)	16.183(3)	16.6960(15)
$\alpha$ (°)	90	90	90	90	90
$\beta$ (°)	95.140(3)	93.936(11)	93.870(5)	96.301(3)	93.301(2)
$\gamma$ (°)	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	2698.5(7)	2925(3)	2758.4(14)	2768.6(7)	2816.1(4)
<i>Z</i>	4	4	4	4	4
$\rho$ (Mg/m <sup>3</sup> )	1.236	1.263	1.296	1.327	1.354
Crystal size (mm)	0.46 × 0.33 × 0.27	0.21 × 0.17 × 0.13	0.32 × 0.21 × 0.16	0.23 × 0.18 × 0.15	0.31 × 0.27 × 0.12
$\theta$ Range (°)	1.82–24.99	1.79–25.08	1.81–25.08	1.83–25.09	2.34–25.07
Numbers of reflections collected	12629	9753	14149	15109	14133
Numbers of independent reflections [ $R_{\text{int}}$ ]	4727 [0.0441]	5003 [0.0408]	4879 [0.0728]	4915 [0.0276]	4973 [0.0274]
Refinement method	FLSQ on $F^2$	FLSQ on $F^2$	FLSQ on $F^2$	FLSQ on $F^2$	FLSQ on $F^2$
Data/restraints/parameters	4727/0/288	5003/0/415	4879/0/325	4915/0/343	4973/0/324
Goodness-of fit on $F^2$	1.007	1.027	1.190		1.026
<i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0406$ , $wR_2 = 0.0875$	$R_1 = 0.0445$ , $wR_2 = 0.1112$	$R_1 = 0.0591$ , $wR_2 = 0.1157$	$R_1 = 0.0392$ , $wR_2 = 0.1131$	$R_1 = 0.0348$ , $wR_2 = 0.0919$
<i>R</i> indices (all data)	$R_1 = 0.0591$ , $wR_2 = 0.0938$	$R_1 = 0.0572$ , $wR_2 = 0.1175$	$R_1 = 0.0946$ , $wR_2 = 0.1248$	$R_1 = 0.0420$ , $wR_2 = 0.1162$	$R_1 = 0.0399$ , $wR_2 = 0.0945$
Largest difference in peak and hole (e Å <sup>−3</sup> )	0.561 and −0.411	0.749 and −0.363	0.814 and −0.376	0.676 and −0.219	0.565 and −0.197



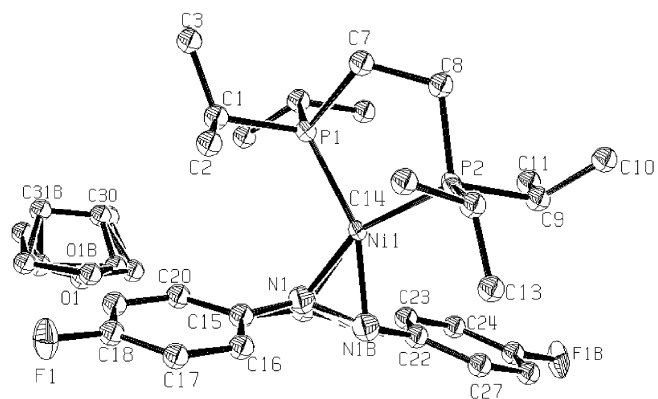


Fig. 3. ORTEP drawing of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-4F-C}_6\text{H}_3\text{-N=CHPh})] \cdot 4\text{*THF}$  (**9**). Ellipsoids are shown at the 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): Ni–P1 2.1576 (11), Ni–P2 2.1619 (13), Ni–N(1) 1.87(2), Ni–C(28) 1.928(19), C18–F 1.302(5), C25–F1B 1.317(5), N(1)–C(28) 1.39(2), N(1B)–C(28B) 1.36(4); selected angles (°): C28–Ni–P2 114.8(6), N1–Ni–P1 111.2(5), P2–Ni–P1 91.97(5), C28–Ni–P1 153.2(6), N–Ni–P2 156.8(5), F1–C18–C19 116.9(3), F1B–C25–C26 116.4(4).

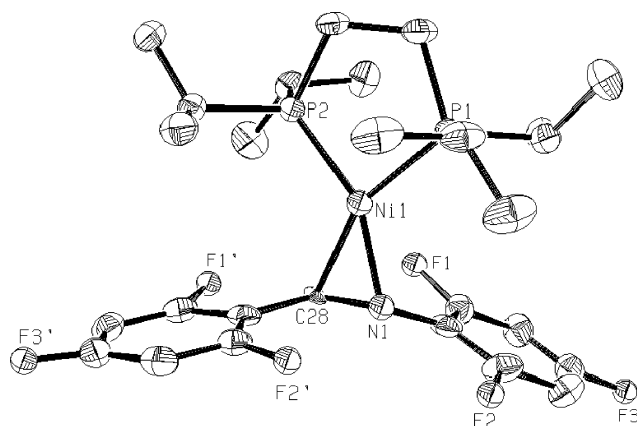


Fig. 5. ORTEP drawing of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-2,4,6F-C}_6\text{H}_2\text{-N=CHPh})]$  (**9**). Ellipsoids are shown at the 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): Ni–P1 2.1612 (8), Ni–P2 2.1443 (7), Ni–N(1) 1.902(2), Ni–C(28) 1.939(2), C16–F1 1.395(3), C18–F3 1.335(3), C20–F2 1.330(4), N(1)–C(28) 1.367(4); selected angles (°): C28–Ni–P2 113.38(9), N1–Ni–P1 113.08(8), P2–Ni–P1 91.89(3), C28–Ni–P1 154.73(9), N–Ni–P2 154.92(8), F1–C15–C16 119.7(2), F3–C18–C19 119.3(3), F2–C20–C15 119.3(3).

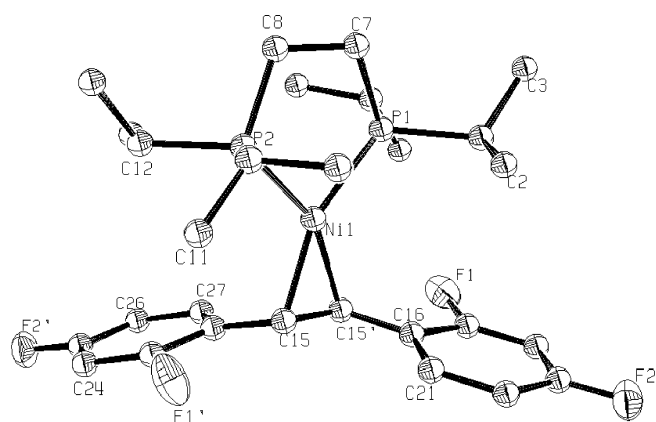


Fig. 4. ORTEP drawing of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-2,4F-C}_6\text{H}_3\text{-N=CHPh})]$  (**6**). Ellipsoids are shown at the 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): Ni–P1 2.155 (13), Ni–P2 2.1598(13), Ni–N(15B) 1.923(4), Ni–C(15A) 1.939(4), C19–F 1.248(7), C21–F1B 1.249(7); selected angles (°): C15B–Ni–P2 115.22(15), C15A–Ni–P1 112.29(15), P2–Ni–P1 91.78(5), C15B–Ni–P1 152.91(15), N–Ni–P2 155.76(15), F2B–C19–C20 123.8(6), F1B–C19–C20 126.0(6).

the  $\eta^2$ -binding to the Ni(dippe) fragment, a shortening of the C–F bond in all the structures was also observed, the average C–F bond distances in the structures being of 1.309, 1.282, and 1.324 Å, for **4\*THF**, **6**, and **9**, respectively. The C–F distance in an analogous structure of the uncoordinated ligand is in the order of 1.354 Å [22]. This is in contrast to the behavior reported for a related Ni(0) complex, Ni(dtbpe) = 1,2-bis(diterbutylphosphine)-ethane( $\eta^6\text{-C}_6\text{F}_6$ ) [23] where the C–F bond (1.37 Å) is slightly lengthened (0.03 Å) as a result of the coordination of the arene ( $\text{C}_6\text{F}_6$ , 1.34 Å) to the (dtbpe)Ni(0) fragment. Perutz and co-workers ascribe this effect to the loss of  $\pi$ -conjugation with the F lone pairs [24]. As the C–F bond in the cited complexes shortens, this suggests that is plausible that there be an enhancement of the  $\pi$  conjugation, thus allocating more electron density into

the F atoms which could cause a shortening of the bond. A proof to these premises was provided by a high field shift in the  $^{19}\text{F}$  NMR of the coordinated ligand (–133 ppm, **4**, see Section 5), compared to the free ligand (–121 ppm) [19].

In sharp contrast with the previous discussed complexes, no disorder was present in the crystal structure of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-2,3,5,6F-C}_6\text{H-N=CHPh})]$  (**11**). However, the tetrahedral coordination environment around nickel is more distorted in this structure, resulting in a more asymmetrically bound [dippe]Ni(0) fragment (Fig. 6). As

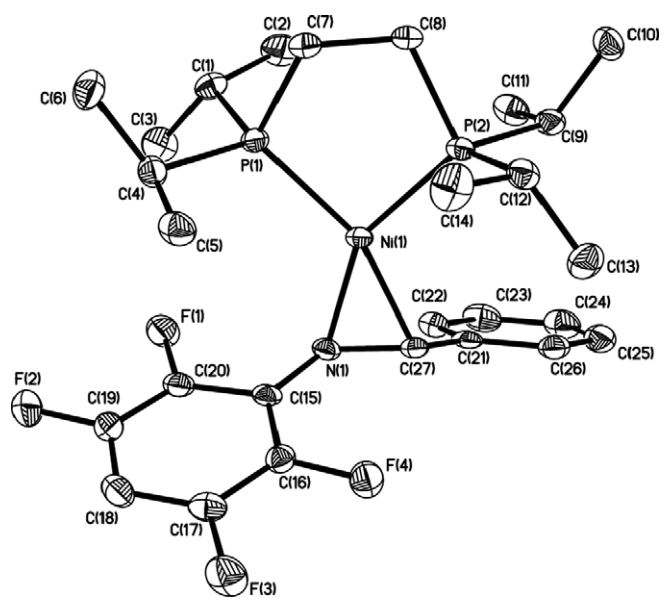


Fig. 6. ORTEP drawing of  $[(\text{dippe})\text{Ni}(\eta^2\text{-(C,N)-2,3,5,6F-C}_6\text{H-N=CHPh})]$  (**11**). Ellipsoids are shown at the 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): Ni–P1 2.1893 (6), Ni–P2 2.1429 (6), Ni–N(1) 1.9139(17), Ni–C(27) 1.945(2), C20–F1 1.350(3), C17–F3 1.347(3), N(1)–C(27) 1.387(3); selected angles (°): C27–Ni–P2 107.61(6), N1–Ni–P1 118.31(6), P2–Ni–P1 91.64(2), C27–Ni–P1 160.10(6), N–Ni–P2 149.61(6), F3–C17–C18 119.2(2), F1–C20–C15 117.8(2).

expected, the lengthening (0.163 Å) [19] of the C=N bond upon coordination to the metallic center (1.387 Å) is 0.135 Å longer than its non-fluorinated counterpart **1** (*vide supra*), thus indicative of a stronger backbonding from the Ni(0) center, due to the greater  $\pi$  accepting capability of the perfluorinated ligand. This behavior is similar to that reported for Rh(II) isonitrile complexes with EW substituents [24]. However, contrasting with the behavior showed by the former complexes (*vide supra*), the average C–F bond distance (1.35 Å) of the coordinated ligand appears elongated (0.019 Å; see Fig. 6), when it is compared to that of the free tetrafluorinated ligand (1.332 Å); [19] yet smaller than the one proposed as necessary for a typical C–F bond activation [23].

### 3. Thermal stability

As confirmed upon the use of sealed NMR tubes under argon, all complexes studied herein were found to be thermally stable in the range from 40 to 150 °C. From the latter temperature and higher, the compounds suffer ligand disproportionation. Monitoring of the corresponding  $^1\text{H}$  NMR integrals of the coordinated imine moiety at room temperature and also after heating to 150 °C, showed that the integral value after heating was decreased. At the same time, the signal corresponding to the free ligand (imine proton) increased as was also the case for the decomposition of the phosphine. The  $^{31}\text{P}\{^1\text{H}\}$  NMR, exhibited signals that were assigned to both Ni(dippe) $_2$  and free phosphine, which are typical decomposition products [13]. Metallic nickel particles were also observed upon heating above 150 °C. The fact that no decomposition was observed under 150 °C suggests that the imine compounds prepared are in fact quite stable. No evidence of oxidative addition was observed; a fact that contrasts with the typical reactivity found in other Ni(0) complexes bearing aromatic nitriles [12]. Furthermore, no C–F bond activation products were detected; albeit this type of activation been observed earlier with similar ligands and Ni(0) or Pt(II) compounds [25–27]. The elongation of the C–F bond in  $\text{C}_6\text{F}_6[\text{Ni}(\text{dtbpe})(\eta^6\text{-C}_6\text{F}_6)]$  (*vide supra*) after coordination was considered significant for the following insertion of Ni into the C–F arene bond [24]. This is in sharp contrast to the behavior observed for complexes **4**<sup>\*</sup>THF, **6**, and **9**, which may be one of the reasons for the stability in the present systems. Additionally, the lack of thermal C–F oxidation in the related Ni(0) complex Ni(PEt $_3$ ) $_2(\eta^2\text{-CH}_2\text{=CHC}_6\text{F}_5)$  was attributed to the structure of the ligand, this being the tightly bound  $\eta^2$ -pentafluorostyrene ligand [18].

On the other hand, in unsaturated moieties (*i.e.* alkenes, arenes, isonitriles) with EW atoms like F, CN (electron deficient), it is expected a stronger back bonding from the metallic center be present, and a relatively greater reactivity displayed as a result of it as compared with that of the unsubstituted ligand [24]. Therefore, compounds **11** and **12** are expected to be more reactive under such basis, and be more prone to nucleophilic attack, provided that the

perfluorinated imines moieties exhibiting a strong EW ability be present. (Table 1) [24]. Studies are currently underway to assess the reactivity and susceptibility of these complexes towards oxidative addition reactions.

### 4. Conclusions

A series of nickel(0) complexes with an imine coordinated in a  $\eta^2$  fashion have been synthesized and their spectroscopic and structural features studied. Results show that the fluorine substitution pattern over the coordinated ligand, has a direct influence over the chemical shift in the CH=N moiety. The geometry around nickel is pseudo-tetrahedral, the coordinated ligand in the complexes found to exhibit an *E* arrangement. All the compounds are thermally stable up to a temperature of 150 °C, at which time ligand disproportionation occurs yielding free phosphine, imine and other decomposition products. The latter is attributed to the preference showed by the starting imines to bind in a  $\pi$ -fashion towards an electron rich metallic center. Further work is underway to assess their potential in catalytic reactions.

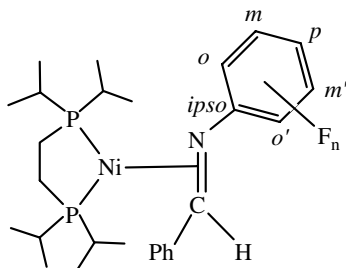
### 5. Experimental

#### 5.1. General methods

All manipulations were carried out using standard Schlenk type and glove box techniques under argon (Praxair 99.998). Toluene was dried by standard methods and stored over molecular sieves 4 Å, under argon. THF and hexane were dried and distilled from dark purple solutions of sodium/benzophenone ketyl. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in an MBraun glove box (<1 ppm H $_2$ O and O $_2$ ). [Ni(dippe) $_2(\mu\text{-H})_2$ ] was prepared by the procedure reported in the literature [28].  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{19}\text{F}$  NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in toluene- $d_8$  or C $_6$ D $_6$ .  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts ( $\delta$ ) are reported relative to the residual proton resonances in the deuterated solvent. All  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded relative to external 85% H $_3$ PO $_4$ , and  $^{19}\text{F}$  NMR  $\delta$  were recorded relative to external standard CF $_3$ COOH. Coupling constants (*J* values) are given in Hz. All elemental analysis of Ni(0) complexes were performed by USAI-UNAM, however, results showed these to be irreproducible due to the high air sensitivity of the complexes.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra for compounds **1–12** are included in the Supporting Information.

All NMR spectra and thermal stability studies were carried out using thin wall (0.38 cm) WILMAD NMR tubes with J. Young valves. A Bruker APEX CCD diffractometer with monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) was used for the X-ray structure determinations. Crystals of **1**, **4**, **6**, **9** and **11** were mounted under Paratone 8277 on a glass fiber and immediately placed under a cold stream

of nitrogen. Mass determinations (FAB<sup>+</sup>) were performed using a JEOL SX-102 A, in a nitrobenzolic alcohol matrix.



## 5.2. Synthesis of Ni(0) complexes

All the Ni(0) complexes were prepared in the following manner, using compound **1** as an example: ligand (0.017 g, 0.093 mmol) was added to a 5 mL THF/toluene solution of the dimer [Ni(dippe)]<sub>2</sub>(μ-H)<sub>2</sub> (0.030 g, 0.046 mmol), in the glove box, and the resulting solution stirred for 5 min until complete evolution of H<sub>2(g)</sub>. The solvent was removed *in vacuo*, and the solid dried for 5 h to afford **1** as bright orange-red crystals. Yield (0.030 g, 76.9%), NMR spectra in toluene-d<sub>8</sub>, <sup>1</sup>H: δ (ppm) 7.66 (d, *J* 7.8 Hz, 2 H), 7.31 (d, *J* 7.8 Hz, 2H), 7.12–7.16 (m, 5H), 6.77 (t, *J* 7.1 Hz, 1H), 5.21 (dd, <sup>3</sup>J<sub>P-H</sub> 7.4 Hz, 2.6 Hz, 1H, CH=N), 1.54–1.56 (m, 2CH), 1.62–1.71 (m, 2CH), 1.30 (dd, <sup>3</sup>J<sub>H-H</sub> 6.8 Hz, <sup>3</sup>J<sub>P-H</sub> 15.5 Hz, 3H), 1.12 (dd, <sup>3</sup>J<sub>H-H</sub> 7.0 Hz, <sup>3</sup>J<sub>P-H</sub> 14.9 Hz, 3H), 0.96 (dd, <sup>3</sup>J<sub>H-H</sub> 6.8 Hz, <sup>3</sup>J<sub>P-H</sub> 14.6 Hz, 3H), 0.82 (d, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, 3H), 0.76 (t, <sup>3</sup>J<sub>H-H</sub> 8.0 Hz, 3H), 0.64 (d, <sup>3</sup>J<sub>H-H</sub> 7.9 Hz, 3H), 0.60 (t, <sup>3</sup>J<sub>H-H</sub> 7.4 Hz, 3H), 0.28 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 15.5 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H}: δ (ppm) 157.4 (d, <sup>1</sup>J<sub>P-C</sub> 2.7 Hz, *ipso*), 149.1 (d, <sup>3</sup>J<sub>P-C</sub> 4.0 Hz), 131.6, 126.4, 121.9 (d, <sup>4</sup>J<sub>P-C</sub> 1.7 Hz), 118.1 (d, <sup>4</sup>J<sub>P-C</sub> 4.7 Hz, *o,o'*), 59.9 (d, <sup>2</sup>J<sub>P-C</sub> 18.8 Hz, CH=N), 26.7 (dd, <sup>1</sup>J<sub>C-P</sub> 19.9, <sup>3</sup>J<sub>C-P</sub> 2.2 Hz, CH), 26.07 (dd, <sup>1</sup>J<sub>C-P</sub> 15.5, <sup>3</sup>J<sub>C-P</sub> 1.7 Hz, CH), 23.4 (dd, <sup>1</sup>J<sub>C-P</sub> 17, <sup>3</sup>J<sub>C-P</sub> 5 Hz, CH), 23.03 (dd, <sup>1</sup>J<sub>C-P</sub> 12.8, <sup>3</sup>J<sub>C-P</sub> 4.6 Hz, CH), 20.6 (dd, *J* 10.0, 6.8 Hz, 2CH<sub>3</sub>), 19.8 (dd, *J* 12.5, 9.0 Hz, 2CH<sub>3</sub>), CH<sub>2</sub> under CH<sub>3</sub> resonances 20.6 (dd, *J* 18.2, 4.6 Hz, CH<sub>2</sub>), 19.8 (dd, *J* 19.1, 2.7 Hz, CH<sub>2</sub>), 18.8 (d, *J* 6.9 Hz, 2CH<sub>3</sub>), 16.7 (t, *J* 5.5 Hz, 2CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: δ (ppm) 69.7 (d, <sup>2</sup>J<sub>P-P</sub> 58.6 Hz), 63.8 (d, <sup>2</sup>J<sub>P-P</sub> 58.6 Hz). FAB<sup>+</sup>: 502(M<sup>+</sup>). Single crystals of **1**, suitable for X-ray diffraction studies were obtained from a concentrated toluene solution, stored at –30 °C within the dry box.

**2.** Yield: (0.052 g, 88.1%), bright orange crystals. NMR spectra in C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H: δ (ppm) 7.49 (d, *J* 7.2 Hz, 3H), 6.89 (t, *J* 7.5 Hz, 2H), 6.72 (t, *J* 7.2 Hz, 1H, *m*), 6.56–6.66 (m, 1H, *o'*), 6.49–6.54 (m, 1H, *p*), 6.36 (dd, *J* 12.0, 7.2 Hz, 1H, *m'*), 5.10 (dd, <sup>3</sup>J<sub>P-H</sub> 6.9, 3.3 Hz, 1H, CH=N), 1.83–1.91 (m, 2CH), 1.43–1.56 (m, 2CH), 1.23 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 14.7 Hz, 3H), 0.81 (dd, <sup>3</sup>J<sub>H-H</sub> 7.1 Hz, <sup>3</sup>J<sub>P-H</sub> 14.9 Hz, 3H), 0.67 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 13.8 Hz, 3H), 0.49 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 15.0 Hz, 3H), 0.43 (d, <sup>3</sup>J<sub>H-H</sub> 8.1 Hz,

3H), 0.32 (t, <sup>3</sup>J<sub>H-H</sub> 8.1 Hz, 3H), 0.27 (t, <sup>3</sup>J<sub>H-H</sub> 7.1 Hz, 3H), 0.1 (dd, <sup>3</sup>J<sub>H-H</sub> 7.2 Hz, <sup>3</sup>J<sub>P-H</sub> 16.5 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H}: δ (ppm) 157.6 (d, <sup>1</sup>J<sub>C-F</sub> 244.4 Hz, *o*), 148.8 (d, <sup>2</sup>J<sub>C-F</sub> 3.1 Hz, *ipso*), 145.0, 129.7, 129.2, 125.4, 127.0 (d, <sup>3</sup>J<sub>C-F</sub> 7.7 Hz, *o'*), 125.4, 123.4, 117.8 (d, <sup>3</sup>J<sub>C-F</sub> 7.1 Hz, *p*), 119.1, 115.9 (d, <sup>2</sup>J<sup>C-F</sup> 19.8 Hz, *m*), 58.4 (d, <sup>2</sup>J<sub>P-C</sub> 19.7 Hz, CH=N), 26.4 (dd, <sup>1</sup>J<sub>C-P</sub> 23.7, <sup>3</sup>J<sub>C-P</sub> 18.2 Hz, CH), 23.9 (d, <sup>1</sup>J<sub>C-P</sub> 13.1, CH), 23.4 (dd, <sup>1</sup>J<sub>C-P</sub> 17.2, <sup>3</sup>J<sub>C-P</sub> 5.0 Hz, CH), CH<sub>2</sub> under CH<sub>3</sub> resonances, 19.2 (d, *J* 6.7 Hz, 2CH<sub>3</sub>), 17.7 (d, *J* 5.4 Hz, 2CH<sub>3</sub>), 17.1 (d, *J* 5.7 Hz, 2CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: δ (ppm) 69.6 (dd, <sup>2</sup>J<sub>P-P</sub> 55.4 Hz, <sup>5</sup>J<sub>P-F</sub> 2.5 Hz), 65.2 (d, <sup>2</sup>J<sub>P-P</sub> 55.4, <sup>5</sup>J<sub>P-F</sub> 5.8 Hz); <sup>19</sup>F: δ (ppm) –123.2 (s, 1F, *o*). FAB<sup>+</sup>: 520 (M<sup>+</sup>).

**3.** Yield: (0.031 g, 82.9%), bright red-orange crystals. NMR spectra in C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H: δ (ppm) 7.71 (d, *J* 8.1 Hz, 1H), 7.10–7.24 (m, 3H), 7.0–7.07 (m, 3H), 6.47 (t, *J* 7.8 Hz, 1H, *m'*), 5.08 (dd, <sup>3</sup>J<sub>P-H</sub> 7.5, 2.7 Hz, 1H, CH=N), 2.14 (qd, *J* 7.2, 2.4 Hz, CH), 1.50–1.74 (m, 3CH), 1.42 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 15.6 Hz, 3H), 1.09 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 15.2 Hz, 3H), 0.96 (dd, <sup>3</sup>J<sub>H-H</sub> 6.6 Hz, <sup>3</sup>J<sub>P-H</sub> 14.4 Hz, 3H), 0.32 (dd, <sup>3</sup>J<sub>H-H</sub> 7.2 Hz, <sup>3</sup>J<sub>P-H</sub> 15.5 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H}: δ (ppm) 165.4 (d, <sup>1</sup>J<sub>C-F</sub> 241.1 Hz, *m*), 159.9 (d, <sup>3</sup>J<sub>C-F</sub> 9.3 Hz, *ipso*), 148.9 (t, *J* 3.7 Hz), 130.2 (d, *J* 10.4 Hz, *m'*), 128.8 (d, *J* 1.7 Hz), 125.2 (d, *J* 2.0 Hz, *o'*), 123.4 (d, *J* 1.7 Hz), 117.2, 108.0 (dd, <sup>2</sup>J<sub>C-F</sub> 21.7, 2.3 Hz, *p*), 103.9 (d, <sup>2</sup>J<sub>C-F</sub> 21.8 Hz, *o*), 58.1 (d, <sup>2</sup>J<sub>P-C</sub> 20.1 Hz, CH=N), 26.5 (dd, <sup>1</sup>J<sub>C-P</sub> 20.5, <sup>3</sup>J<sub>C-P</sub> 2.0 Hz, CH), 25.9 (d, <sup>1</sup>J<sub>C-P</sub> 16.1 Hz, CH), 22.0 (dd, <sup>1</sup>J<sub>C-P</sub> 13.3, <sup>3</sup>J<sub>C-P</sub> 4.6 Hz, CH), CH<sub>2</sub> under CH<sub>3</sub> resonances 20.8 (dd, <sup>1</sup>J<sub>C-P</sub> 21.1, <sup>3</sup>J<sub>C-P</sub> 4.0 Hz, CH<sub>2</sub>), 20.1 (dd, <sup>1</sup>J<sub>C-P</sub> 21.5, <sup>3</sup>J<sub>C-P</sub> 6.1 Hz, CH<sub>2</sub>), 20.9 (t, *J* 7.0 Hz, 2CH<sub>3</sub>), 19.1 (d, *J* 6.7 Hz, 2CH<sub>3</sub>), 17.2 (t, *J* 6.4 Hz, 2CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: δ (ppm) 69.7 (d, <sup>2</sup>J<sub>P-P</sub> 54.8 Hz), 64.9 (d, <sup>2</sup>J<sub>P-P</sub> 54.8 Hz); <sup>19</sup>F: δ (ppm) –115.6–115.7 (s, 1F, *m*). FAB<sup>+</sup>: 520 (M<sup>+</sup>).

**4.** Yield: (0.034 g, 70.0%), dark-red-orange crystals. NMR spectra in C<sub>6</sub>D<sub>6</sub>, <sup>1</sup>H: δ (ppm) 7.72 (d, *J* 7.8 Hz, 1H), 7.13–7.18 (m, 4H), 7.02 (t, *J* 7.2 Hz, 1H, *o*), 6.92–6.94 (m, 2H, *m, o'*), 6.84 (t, *J* 8.4 Hz, 1H, *m'*), 5.16 (dd, <sup>3</sup>J<sub>P-H</sub> 7.2, 2.7 Hz, 1H, CH=N), 1.86 (qd, *J* 7.4, 2.7 Hz, CH), 1.44–1.67 (m, 3CH), 1.38 (dd, <sup>3</sup>J<sub>H-H</sub> 5.1 Hz, <sup>3</sup>J<sub>P-H</sub> 14.4 Hz, 3H), 1.10 (dd, <sup>3</sup>J<sub>H-H</sub> 7.1 Hz, <sup>3</sup>J<sub>P-H</sub> 14.9 Hz, 3H), 1.06 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 15.0 Hz, 3H), 0.91 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 14.4 Hz, 3H), 0.69–0.91 (m, 3H), 0.56 (dd, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, <sup>3</sup>J<sub>P-H</sub> 10 Hz, 3H), 0.50 (dd, <sup>3</sup>J<sub>H-H</sub> 7.5 Hz, <sup>3</sup>J<sub>P-H</sub> 16 Hz, 3H), 0.26 (dd, <sup>3</sup>J<sub>H-H</sub> 7.5 Hz, <sup>3</sup>J<sub>P-H</sub> 16.4 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H}: δ (ppm) 156.6 (d, <sup>1</sup>J<sub>C-F</sub> 234.7 Hz, *p*), 153.7 (*ipso*), 148.8 (t, <sup>4</sup>J<sub>C-F</sub> 3.7 Hz), 137.7, 129.4, 129.2, 125.1 (d, <sup>3</sup>J<sub>C-F</sub> 1.7 Hz, *o'*), 122.1 (d, <sup>3</sup>J<sub>C-F</sub> 2.4 Hz, *o*), 115.7 (d, <sup>2</sup>J<sub>C-F</sub> 21.5 Hz, *m, m'*), 59.9 (d, <sup>2</sup>J<sub>P-C</sub> 18.8 Hz, CH=N), 26.4 (dd, <sup>1</sup>J<sub>C-P</sub> 20.2, <sup>3</sup>J<sub>C-P</sub> 2.0 Hz, CH), 25.9 (dd, <sup>1</sup>J<sub>C-P</sub> 15.8, <sup>3</sup>J<sub>C-P</sub> 2.0 Hz, CH), 23.4 (dd, <sup>1</sup>J<sub>C-P</sub> 16.1, <sup>3</sup>J<sub>C-P</sub> 5.5 Hz, CH), 22.0 (dd, <sup>1</sup>J<sub>C-P</sub> 13.3, <sup>3</sup>J<sub>C-P</sub> 4.6 Hz, CH), CH<sub>2</sub> under CH<sub>3</sub> resonances, 20.6–21.1 (m, 2CH<sub>3</sub>), 19.8–20.3 (m, 2CH<sub>3</sub>), 19.2 (d, *J* 6.8 Hz, 2CH<sub>3</sub>), 17.2 (d, *J* 5.7 Hz, 2CH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}: δ (ppm) 69.7 (d, <sup>2</sup>J<sub>P-P</sub> 58.5 Hz), 63.7 (d, <sup>2</sup>J<sub>P-P</sub> 58.5 Hz); <sup>19</sup>F: δ (ppm) –133.2 (s, 1F, *p*). FAB<sup>+</sup>: 520 (M<sup>+</sup>). Single crystals of **4**\*THF, suitable for

X-ray diffraction studies were obtained by vapor phase diffusion of a THF solution of this complex into hexane, at room temperature, in the glove box.

**5.** Yield: (0.039 g, 63%), dark-red crystals. NMR spectra in toluene- $d_8$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.52 (d,  $J$  7.8 Hz, 2H), 7.10 (t,  $J$  7.7 Hz, 3H), 6.74 (d,  $J$  9.3 Hz, 2H,  $o,o'$ ), 6.18 (t,  $J$  9.0 Hz, 1H,  $p$ ), 4.79 (dd,  $^3J_{\text{P-H}}$  7.05, 3.3 Hz, 1H,  $\text{CH}=\text{N}$ ), 1.57–1.66 (m, 2CH), 1.43–1.54 (m, 2CH), 1.33 (dd,  $^3J_{\text{H-H}}$  6.9,  $^3J_{\text{P-H}}$  15.6 Hz, 3H), 1.03 (dd,  $^3J_{\text{H-H}}$  6.9 Hz,  $^3J_{\text{P-H}}$  15.0 Hz, 3H), 0.85–0.93 (m, 6H), 0.77–0.79 (m, 6H), 0.58 (dd,  $^3J_{\text{H-H}}$  7.2 Hz,  $^3J_{\text{P-H}}$  10.2 Hz, 3H), 0.46 (dd,  $^3J_{\text{H-H}}$  7.1 Hz,  $^3J_{\text{P-H}}$  16.4 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta$  (ppm), 165.3 (dd,  $^1J_{\text{C-F}}$  241.9 Hz,  $^3J_{\text{C-F}}$  16.4 Hz,  $m,m'$ ), 148.4 (t,  $^3J_{\text{C-F}}$  11.8 Hz,  $ipso$ ), 132.3, 123.6, 103.5 (d,  $^2J_{\text{C-F}}$  23.9 Hz,  $o,o'$ ), 92.1 (t,  $^2J_{\text{C-F}}$  26.7 Hz,  $p$ ), 57.00 (d,  $^2J_{\text{P-C}}$  20.7 Hz,  $\text{CH}=\text{N}$ ), 26.7 (d,  $^1J_{\text{C-P}}$  20.9 Hz, CH), 25.9 (d,  $^1J_{\text{C-P}}$  20.9 Hz, CH), 23.2 (m, 2CH), 21.3 (t,  $^2J_{\text{P-C}}$  19.1 Hz, 2CH<sub>3</sub>), 19.2 (d,  $J$  6.4 Hz, 2CH<sub>3</sub>), 17.1 (m, 4CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  (ppm) 70.0 (d,  $^2J_{\text{P-P}}$  52.2 Hz); 65.8 (d,  $^2J_{\text{P-P}}$  52.2 Hz);  $^{19}\text{F}$ :  $\delta$  (ppm) –113.3 (t,  $^3J_{\text{F-H}}$  9.0 Hz, 1F), –116.8 (t,  $^3J_{\text{F-H}}$  9.0 Hz, 1F). FAB+: 538 ( $\text{M}^+$ ).

**6.** Yield: (0.042 g, 95.0%), bright reddish crystals. NMR spectra in toluene- $d_8$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.66 (d,  $J$  7.5 Hz, 2H), 7.13 (d,  $J$  7.2 Hz, 2H), 6.98 (q,  $J$  9.0 Hz, 1H), 6.86 (dd,  $J$  9.1 Hz, 6.1 Hz, 1H,  $o'$ ), 6.67 (m, 1H,  $m'$ ), 6.55 (m, 1H,  $m$ ), 5.21 (dd,  $^3J_{\text{P-H}}$  7.0 Hz, 3.3 Hz, 1H,  $\text{CH}=\text{N}$ ), 1.98–2.02 (m, CH), 1.70–1.78 (m, CH), 1.51–1.62 (m, 2CH), 1.44 (ddd,  $^3J_{\text{H-H}}$  7.1 Hz,  $^3J_{\text{P-H}}$  15.8 Hz, 3H), 1.12 (dd,  $^3J_{\text{H-H}}$  7.1 Hz,  $^3J_{\text{P-H}}$  14.9 Hz, 6H), 0.93 (dd,  $^3J_{\text{H-H}}$  7.1 Hz,  $^3J_{\text{P-H}}$  15.2 Hz, 6H), 0.62 (dd,  $^3J_{\text{H-H}}$  7.2 Hz, Hz, 3H), 0.49 (dd,  $^3J_{\text{H-H}}$  7.2 Hz,  $^3J_{\text{P-H}}$  16.5 Hz, 3H), 0.24 (dd,  $^3J_{\text{H-H}}$  7.2 Hz,  $^3J_{\text{P-H}}$  15.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta$  (ppm) 156.3 (dd,  $^1J_{\text{C-F}}$  251.3 Hz,  $^3J_{\text{C-F}}$  11.0 Hz,  $p$ ), 155.7 (dd,  $^1J_{\text{C-F}}$  237.2 Hz,  $^3J_{\text{C-F}}$  10.5 Hz,  $o$ ), 148.4 (t,  $J_{\text{C-F}}$  3.5 Hz,  $ipso$ ), 141.5, 132.1, 129.0, 123.4, 118.4 (s,  $o'$ ), 110.8 (d,  $^2J_{\text{P-C}}$  20.8 Hz,  $m$ ), 104.4 (t,  $^2J_{\text{C-F}}$  24.8 Hz,  $m'$ ), 58.9 (d,  $^2J_{\text{P-C}}$  19.3 Hz,  $\text{CH}=\text{N}$ ), 26.8 (dd,  $J$  20.0, 2.0 Hz, CH), 26.5 (d,  $J$  15.8 Hz, CH), 24.0 (dt,  $J$  13.1, 3.9 Hz, CH), 23.6 (dd,  $J$  17.3, 5.2 Hz, CH), 21.1 (d,  $J$  5.4 Hz, CH<sub>3</sub>), CH<sub>2</sub> under CH<sub>3</sub> resonances 21.2 (dd,  $J_{\text{P-C}}$  19.0, 3.7 Hz, CH<sub>2</sub>), 20.4 (dd,  $J_{\text{P-C}}$  18.3, 3.8 Hz, CH<sub>2</sub>), 20.3 (t,  $^3J_{\text{P-C}}$  7.4 Hz, 2CH<sub>3</sub>), 19.2 (d,  $J$  6.7 Hz, 2CH<sub>3</sub>), 17.6 (d,  $J$  5.5 Hz, 2CH<sub>3</sub>), 17.1 (d,  $J$  5.4 Hz, 2CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  (ppm) 67.9 (dt,  $^2J_{\text{P-P}}$  56.4 Hz,  $^7J_{\text{P-F}}$  2.6 Hz), 63.4 (dd,  $^2J_{\text{P-P}}$  56.4 Hz,  $^5J_{\text{P-F}}$  4.6 Hz);  $^{19}\text{F}$ :  $\delta$  (ppm) –120.5 (s, 1F,  $o$ ), –129.2 (d,  $^3J_{\text{F-H}}$  6.2 Hz, 1F,  $p$ ). FAB+: 537 ( $\text{M}^+-1$ ). Single crystals of **6**, suitable for X-ray diffraction studies were obtained from a concentrated toluene solution, stored at  $-30^\circ\text{C}$  within the dry box.

**7.** Yield: (0.042 g, 66%), dark-red crystals. NMR spectra in toluene- $d_8$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.61 (d,  $J$  7.8 Hz, 2H), 7.1 (t,  $J$  7.5 Hz, 3H), 6.72 (t,  $J$  7.7 Hz, 1H,  $o'$ ), 6.53–6.60 (m, 1H,  $p$ ), 6.36–6.48 (m, 1H,  $m'$ ), 5.12 (dd,  $^3J_{\text{P-H}}$  7.05, 3.3 Hz, 1H,  $\text{CH}=\text{N}$ ), 1.66–1.78 (m, 2CH), 1.47–1.55 (m, 2CH), 1.40 (ddd,  $^3J_{\text{H-H}}$  6.9, 1.5 Hz,  $^3J_{\text{P-H}}$  16.2 Hz, 3H), 1.07 (dd,  $^3J_{\text{H-H}}$  7.2 Hz,  $^3J_{\text{P-H}}$  14.9 Hz, 3H), 0.74–0.92 (m, 9H), 0.66–0.73 (m, 3H), 0.52–0.62 (m, 3H), 0.21 (dd,  $^3J_{\text{H-H}}$

7.5 Hz,  $^3J_{\text{P-H}}$  16.2 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta$  (ppm) 153.1 (dd,  $^1J_{\text{C-F}}$  241.9 Hz,  $^3J_{\text{C-F}}$  11.7 Hz,  $m$ ), 148.5 (dd,  $J_{\text{C-F}}$  4.4 Hz, 2.7 Hz,  $ipso$ ), 145.4 (dd,  $^1J_{\text{C-F}}$  241.9 Hz,  $^3J_{\text{C-F}}$  13.0 Hz,  $o$ ), 132.4, 129.8, 129.2, 125.3 (d,  $^3J_{\text{C-F}}$  1.6 Hz,  $m'$ ), 124.2 (q,  $^3J_{\text{C-F}}$  5.0 Hz,  $o'$ ), 104.9 (d,  $^2J_{\text{C-F}}$  17.8 Hz,  $p$ ), 57.5 (d,  $^2J_{\text{P-C}}$  20.4 Hz,  $\text{CH}=\text{N}$ ), 26.6 (dd,  $^1J_{\text{C-P}}$  18.8,  $^3J_{\text{C-P}}$  2.0 Hz, CH), 26.2 (d,  $^1J_{\text{C-P}}$  16.1 Hz, CH), 24.1 (dt,  $J$  13.8, 3.7 Hz, CH), 23.4 (dd,  $^1J_{\text{C-P}}$  15.3,  $^3J_{\text{C-P}}$  5.3 Hz, CH), CH<sub>2</sub> under CH<sub>3</sub> resonances, 19.9–21.0 (m, 2CH<sub>3</sub>), 19.2 (d,  $J$  6.4 Hz, 2CH<sub>3</sub>), 17.7 (d,  $J$  5.4 Hz, 2CH<sub>3</sub>), 17.1 (d,  $J$  5.4 Hz, 2CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  (ppm) 69.9 (dd,  $^2J_{\text{P-P}}$  53.2, 2.3 Hz); 66.0 (dd,  $^2J_{\text{P-P}}$  52.9, 6.4 Hz);  $^{19}\text{F}$ :  $\delta$  (ppm) –141.9 (dd,  $^3J_{\text{F-F}}$  19.2,  $^3J_{\text{F-H}}$  9.0 Hz, 1F,  $m$ ), –148.8 (d,  $^3J_{\text{F-F}}$  15.2 Hz, 1F,  $o$ ). FAB+: 538 ( $\text{M}^+$ ).

**8.** Yield: (0.040 g, 87.5%), dark-red crystals. NMR spectra in  $\text{C}_6\text{D}_6$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.74–7.80 (m, 2H), 7.00–7.20 (m, 3H), 6.60–6.74 (m, 2H,  $m, m'$ ), 6.34 (pq,  $J$  7.1 Hz, 1H,  $p$ ), 6.08 (dd,  $^3J_{\text{P-H}}$  6.6, 3.0 Hz, 1H,  $\text{CH}=\text{N}$ ), 1.70–1.83 (m, 2CH), 1.53–1.65 (m, 2CH), 1.45 (dd,  $^3J_{\text{H-H}}$  6.9,  $^3J_{\text{P-H}}$  15.0 Hz, 3H), 1.20 (dd,  $^3J_{\text{H-H}}$  6.8 Hz,  $^3J_{\text{P-H}}$  15.0 Hz, 3H), 0.87–1.06 (m, 9H), 0.72 (dd,  $^3J_{\text{H-H}}$  6.9 Hz,  $^3J_{\text{P-H}}$  16.8 Hz, 3H), 0.62 (dd,  $^3J_{\text{H-H}}$  6.9 Hz,  $^3J_{\text{P-H}}$  16.5 Hz, 3H), 0.29 (dd,  $^3J_{\text{H-H}}$  7.5 Hz,  $^3J_{\text{P-H}}$  15.9 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta$  (ppm) 159.1 (dd,  $^1J_{\text{C-F}}$  248.8 Hz,  $^3J_{\text{C-F}}$  8.8 Hz,  $o,o'$ ), 149.4 ( $ipso$ ), 134.8, 129.7, 123.3, 116.8 (t,  $^3J_{\text{C-F}}$  10.1 Hz,  $p$ ), 112.3 (dd,  $^2J_{\text{C-F}}$  16.3, 9.6 Hz,  $m,m'$ ), 61.13 (dt,  $^2J_{\text{P-C}}$  19.8, 6.9 Hz), 26.8 (d,  $^1J_{\text{C-P}}$  20.1 Hz, CH), 25.9 (d,  $^1J_{\text{C-P}}$  15.5 Hz, CH), 24.2 (d,  $^1J_{\text{C-P}}$  13.0 Hz, CH), 25.9 (dd,  $^1J_{\text{C-P}}$  15.1, 6.7 Hz, CH), 21.0 (t,  $^2J_{\text{P-C}}$  20.7 Hz, CH<sub>3</sub>), 19.2 (d,  $^2J_{\text{P-C}}$  6.8 Hz, CH<sub>3</sub>), 18.0 (d,  $^2J_{\text{P-C}}$  5.4 Hz, 2CH<sub>3</sub>), 17.1 (d,  $^2J_{\text{P-C}}$  5.4 Hz, CH<sub>3</sub>), 19.8–20.7 (m, 4CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  (ppm) 67.6 (dt,  $^2J_{\text{P-P}}$  56.3, 2.7 Hz); 66.0 (dd,  $^2J_{\text{P-P}}$  56.3, 4.3 Hz);  $^{19}\text{F}$ :  $\delta$  (ppm) –123.5 (s, 2F). FAB+: 538 ( $\text{M}^+$ ).

**9.** Yield: (0.029 g, 78%), amber red crystals. NMR spectra in toluene- $d_8$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.68 (d,  $J$  7.2 Hz, 2H), 7.05–7.14 (m, 2H), 6.97 (pt,  $J$  6.8 Hz, 1H), 6.38 (t,  $J$  9.0 Hz, 1H,  $m$ ), 6.27 (t,  $J$  8.6 Hz, 1H,  $m'$ ), 5.92 (d,  $^3J_{\text{P-H}}$  6.6 Hz, 1H,  $\text{CH}=\text{N}$ ), 1.66–1.76 (m, 2CH), 1.53–1.63 (m, 2CH), 1.36 (dd,  $^3J_{\text{H-H}}$  7.1,  $^3J_{\text{P-H}}$  15.2 Hz, 3H), 1.20 (dd,  $^3J_{\text{H-H}}$  6.9 Hz,  $^3J_{\text{P-H}}$  15.0 Hz, 3H), 0.88–1.05 (m, 9H), 0.62–0.73 (m, 3H), 0.55 (dd,  $^3J_{\text{H-H}}$  7.5 Hz,  $^3J_{\text{P-H}}$  15.9 Hz, 3H), 0.24 (dd,  $^3J_{\text{H-H}}$  7.2 Hz,  $^3J_{\text{P-H}}$  16.2 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$ :  $\delta$  (ppm) 158.7 (d,  $^1J_{\text{C-F}}$  245.9 Hz,  $o$ ), 156.6 (d,  $^1J_{\text{C-F}}$  239.0 Hz,  $p$ ), 149.2 ( $ipso$ ), 137.8, 132.4, 100.8 (q,  $^2J_{\text{C-F}}$  28.0 Hz,  $m,m'$ ), 61.4 (dt,  $^2J_{\text{P-C}}$  19.8, 6.9 Hz,  $\text{CH}=\text{N}$ ), 26.9 (d,  $^1J_{\text{C-P}}$  19.8 Hz, CH), 25.9 (d,  $^1J_{\text{C-P}}$  15.5 Hz, CH), 24.2 (dd,  $^1J_{\text{C-P}}$  13.1,  $^3J_{\text{C-P}}$  5.0 Hz, CH), 23.5 (dd,  $^1J_{\text{C-P}}$  17.5,  $^3J_{\text{C-P}}$  5.1 Hz, CH), 19.7–21.6 (m, 2CH<sub>3</sub>), 19.2 (d,  $J$  6.4 Hz, 2CH<sub>3</sub>), 17.0 (d,  $J$  5.4 Hz, 2CH<sub>3</sub>), 16.3 (d,  $J$  21.5 Hz, 2CH<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  (ppm) 67.8 (dd,  $^2J_{\text{P-P}}$  57.5 Hz, 2.6 Hz); 66.1 (d,  $^2J_{\text{P-P}}$  57.5 Hz);  $^{19}\text{F}$ :  $\delta$  (ppm) –113.6 (s, 1F,  $p$ ), –121.4 (s, 2F,  $o$ ). FAB+: 556 ( $\text{M}^+$ ). Single crystals of **9**, suitable for X-ray diffraction studies were obtained by vapor phase diffusion of a THF solution of this complex into hexane, at room temperature, in the glove box.

**10.** Yield: (0.040 g, 85.0%), bright orange-red crystals. NMR spectra in  $\text{C}_6\text{D}_6$ ,  $^1\text{H}$ :  $\delta$  (ppm) 7.68 (d,  $J$  7.1 Hz,



2H), 7.16 (d,  $J$  7.8 Hz, 2H), 7.02 (t,  $J$  6.9 Hz, 1H), 6.89 (dt,  $J$  13.2, 6.9 Hz, 1H,  $o'$ ), 6.67 (qd,  $J$  9.3, 3.0 Hz, 1H,  $m$ ), 4.99 (dd,  $^3J_{P-H}$  7.1, 3.5 Hz, 1H,  $CH=N$ ), 1.97–2.03 (m, 2CH), 1.66–1.76 (m, 2CH), 1.43 (ddd,  $^3J_{H-H}$  7.1 Hz,  $^3J_{P-H}$  15.9 Hz, 2.0 Hz, 3H), 1.02 (dd,  $^3J_{H-H}$  6.9 Hz,  $^3J_{P-H}$  15.0 Hz, 3H), 0.58 (t,  $^3J_{H-H}$  7.2 Hz, 3H), 0.53 (dd,  $^3J_{P-H}$  14.3 Hz,  $^3J_{H-H}$  7.1 Hz, 3H), 0.25 (dd,  $^3J_{H-H}$  7.0 Hz,  $^3J_{P-H}$  16.8 Hz, 3H);  $^{13}C\{^1H\}$ :  $\delta$  (ppm) 151.9 (d,  $^1J_{C-F}$  243.4 Hz,  $o$ ), 149.9 (d,  $^1J_{C-F}$  235.4 Hz,  $m'$ ), 148.0 (*ipso*), 142.0 (d,  $^1J_{C-F}$  240.1 Hz,  $p$ ), 141.9, 132.4, 125.3, 123.7, 106.0 (d,  $^2J_{C-F}$  17.8 Hz,  $o'$ ), 105.4 (t,  $^2J_{C-F}$  23.7 Hz,  $m$ ), 59.7 (d,  $^2J_{P-C}$  20.5 Hz,  $CH=N$ );  $^{31}P\{^1H\}$ :  $\delta$  (ppm) 70.0 (d,  $^2J_{P-P}$  53.1 Hz); 66.0 (d,  $^2J_{P-P}$  53.1 Hz);  $^{19}F$ :  $\delta$  (ppm) –124.3 (s, 1F,  $o$ ), –144.5 (m, 1F,  $p$ ), –151.7 (t,  $^3J_{F-H}$  11.6 Hz, 1F). FAB+: 555 ( $M^+-1$ ).

**11.** Yield: (0.054 g, 86%), bright light orange-red crystals. NMR spectra in  $C_6D_6$ ,  $^1H$ :  $\delta$  (ppm) 7.65 (d,  $^3J_{H-H}$  7.8 Hz, 2H), 7.09–7.14 (m, 2H), 6.96–7.05 (m, 1H), 6.01–6.14 (m, 1H,  $p$ ), 5.78–5.83 (m, 1H,  $CH=N$ ), 1.91 (dt,  $^3J_{P-H}$  18.2 Hz,  $^3J_{H-H}$  7.2 Hz,  $CH$ ), 1.70 (dt,  $^3J_{P-H}$  23.4 Hz,  $^3J_{H-H}$  7.2 Hz,  $CH$ ), 1.56–1.43 (m, 2CH), 1.33 (dd,  $^3J_{H-H}$  7.2 Hz,  $^3J_{P-H}$  15.9 Hz, 3H), 1.28 (dd,  $^3J_{H-H}$  7.2 Hz,  $^3J_{P-H}$  15.2 Hz, 3H), 1.05 (dd,  $^3J_{H-H}$  6.9 Hz,  $^3J_{P-H}$  15.0 Hz, 3H), 0.88–0.93 (m, 6H), 0.85–0.76 (m, 3H), 0.53 (dd,  $^3J_{H-H}$  6.9 Hz,  $^3J_{P-H}$  10.2 Hz, 3H), 0.21 (dd,  $^3J_{H-H}$  7.5 Hz,  $^3J_{P-H}$  16.4 Hz, 3H);  $^{13}C\{^1H\}$ :  $\delta$  (ppm), 148.5, 147.8 (dt,  $^1J_{C-F}$  256.3, 28.3 Hz,  $m, m'$ ), 142.8 (s,  $^1J_{C-F}$  229.4 Hz,  $o, o'$ ), 141.2 (*ipso*), 125.2, 123.9, 91.8 (t,  $^2J_{C-F}$  23.8 Hz,  $p$ ), 57.6 (dt,  $^2J_{P-C}$  21.5, 6.4 Hz,  $CH=N$ ), 26.7 (d,  $^1J_{C-P}$  21.2 Hz,  $CH$ ), 25.8 (d,  $^1J_{C-P}$  16.1 Hz,  $CH$ ), 24.3 (d,  $^1J_{C-P}$  11.0 Hz,  $CH$ ), 23.3 (dd,  $^1J_{C-P}$  17.8,  $^3J_{C-P}$  5.0 Hz,  $CH$ ),  $CH_2$  under  $CH_3$  resonances 19.7 (d,  $J$  5.6 Hz, 2CH<sub>3</sub>), 19.2 (d,  $J$  6.3 Hz, 2CH<sub>3</sub>), 17.9 (d,  $J$  3.3 Hz, 2CH<sub>3</sub>), 16.9 (d,  $J$  5.7 Hz, 2CH<sub>3</sub>);  $^{31}P\{^1H\}$ :  $\delta$  (ppm); 68.4 (d,  $^2J_{P-P}$  50.8 Hz), 66.5 (dt,  $^2J_{P-P}$  50.8 Hz, 6.3 Hz);  $^{19}F$ :  $\delta$  (ppm) –144.4 (m, 2F,  $m$ ), –153.7 (d,  $^3J_{F-F}$  13.81, 2F,  $o$ ). FAB+: 573 ( $M^+-1$ ). Single crystals of **11**, suitable for X-ray diffraction studies were obtained by vapor phase diffusion of a THF solution of this complex into hexane, at room temperature, in the glove box.

**12.** Yield: (0.055 g, 70%), bright light orange-red crystals. NMR spectra in  $C_6D_6$ ,  $^1H$ :  $\delta$  (ppm) 7.62 (d,  $J$  7.5 Hz, 2H), 7.07 (t,  $J$  7.5 Hz, 2H), 6.91–7.01 (m, 1H), 5.69–5.72 (m, 1H,  $CH=N$ ), 1.75–1.84 (m,  $CH$ ), 1.63–1.73 (m,  $CH$ ), 1.40–1.59 (m, 2CH), 1.25 (dd,  $^3J_{P-H}$  15.6 Hz,  $^3J_{H-H}$  7.2 Hz, 3H), 1.00 (dd,  $^3J_{P-H}$  14.9 Hz,  $^3J_{H-H}$  7.1 Hz, 3H), 0.82–0.96 (m, 9H), 0.627–0.638 (m, 3H), 0.53 (dd,  $^3J_{H-H}$  7.2 Hz,  $^3J_{P-H}$  15.6 Hz, 3H), 0.15 (dd,  $^3J_{H-H}$  7.2 Hz,  $^3J_{P-H}$  16.2 Hz, 3H);  $^{13}C\{^1H\}$ :  $\delta$  (ppm) 148.6, 143.2 (d,  $^1J_{C-F}$  245.1 Hz,  $o, o'$ ), 139.4 (d,  $^1J_{C-F}$  252.6 Hz,  $m, m'$ ), 133.5 (d,  $^1J_{C-F}$  230.2 Hz,  $p$ ), 133.2, 130.0, 129.6 (d,  $J_{P-C}$  6 Hz), 125.0, 123.9, 58.1 (dt,  $^2J_{P-C}$  21.5, 6.5 Hz,  $CH=N$ ), 26.7 (dd,  $^1J_{C-P}$  21.2,  $^3J_{C-P}$  2.3 Hz,  $CH$ ), 25.8 (d,  $^1J_{C-P}$  16.1 Hz,  $CH$ ), 24.3 (dd,  $^1J_{C-P}$  14.1,  $^3J_{C-P}$  4.7 Hz,  $CH$ ), 23.3 (dd,  $^1J_{C-P}$  18.2,  $^3J_{C-P}$  4.7 Hz,  $CH$ ),  $CH_2$  under  $CH_3$  resonances 20.9–20.1 (m, 2CH<sub>2</sub>), 19.8 (d,  $J$  7.7 Hz, 2CH<sub>3</sub>), 19.1 (d,  $J$  6.0 Hz, 2CH<sub>3</sub>), 17.9 (d,  $J$  3.4 Hz, 2CH<sub>3</sub>), 17.0

(d,  $J$  5.7 Hz, 2CH<sub>3</sub>);  $^{31}P\{^1H\}$ :  $\delta$  (ppm) 68.4 (dd,  $^2J_{P-P}$  50.9 Hz, 2.5 Hz), 66.6 (dt,  $^2J_{P-P}$  50.9 Hz, 5.1 Hz);  $^{19}F$ :  $\delta$  (ppm) –157.6 –157.8 (m, 2F,  $o$ ), –171.6 (t,  $^3J_{F-F}$  21.4 Hz, 2F,  $m$ ), –180.4 (t,  $^3J_{F-F}$  24.2 Hz, 1F,  $p$ ). FAB+: 515 ( $M^+-Ph$ ).

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## Appendix A. Supplementary material

CCDC 639444, 639445, 639446, 639447 and 639448 contain the supplementary crystallographic data for **1**, **4\*THF**, **6**, **9** and **11**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.04.026](https://doi.org/10.1016/j.jorganchem.2007.04.026).

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