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Organometallic derivatives of Ni(II) with poly(pyrazolyl)borate ligands [1]

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Abstract

The reaction of the alkyl or aryl derivatives $Ni(R)X(PMe_3)_2$ ($R = CH_2SiMe_3$, CH_2CMe_3, C_6H_5; X = Cl, Br) with the potassium salt of the Bp ligand (Bp = dihydrobis(pyrazolyl)borate anion) forms the corresponding compounds $BpNi(R)(PMe_3)$. In contrast, the reaction of the aryl derivatives $Ni(C_6H_4$-*p*-$X)Br(PMe_3)_2$ (X = H, Me, OMe, NMe_2) with the Bp^{tBu} anion (Bp^{tBu} = dihydrobis(3-*t*-butylpyrazolyl)borate) proceeds with formation of complexes of composition $Bp^{tBu}Ni(C_6H_4$-*p*-$X)(PMe_3)_2$, in which the polydentate ligand is bound to the metal through only one pyrazolyl group. The Tp anion leads to only aryl derivatives; the phenyl complex $TpNi(C_6H_5)(PMe_3)$ has been obtained, and the reaction of the alkyl complex $Ni(CH_2CMe_2Ph)Cl(PMe_3)_2$ with KTp furnishes the aryl $TpNi(C_6H_4$-*o*-$Bu^t)(PMe_3)$, by means of a rearrangement of the neophyl ligand. The Tp ligand in these complexes is bonded in the η^2 fashion, although an X-ray analysis carried out for $TpNi(Ph)(PMe_3)$ reveals the existence of an important Ni...N interaction with the third *pz* ring. Upon reaction with the bulky hydrotris(3-*t*-butylpyrazolyl)borate anion, the aryl derivatives $Ni(C_6H_4$-*p*-$X)Br(PMe_3)_2$ (X = H, Me, OMe, NMe_2) form complexes of composition $Tp^{tBu}Ni(C_6H_4$-*p*-$X)(PMe_3)_2$, in which the polydentate ligand is once more bound to the metal through only one pyrazolyl group. These complexes represent the first examples of η^1 coordination of poly(pyrazolyl)borate-type ligands. The acyl and aroyl complexes $BpNi(COR)(PMe_3)$ ($R = CH_2SiMe_3$, CH_2CMe_3) and $TpNi(COPh)(PMe_3)$ have been obtained by carbonylation of the parent compounds. The aroyls $Tp^{tBu}Ni(COC_6H_4$-*p*-$X)(PMe_3)_2$ have also been obtained from the derivatives $Ni(COC_6H_4$-*p*-$X)Br(PMe_3)_2$ although they evolve CO slowly in solution. An X-ray analysis carried out with $Tp^{tBu}Ni(C_6H_4$-*p*-$Me)(PMe_3)_2$ confirms the η^1-coordination mode of the Tp^{tBu} ligand, which was deduced from NMR studies.

Keywords: Ligands; Anion; Aryl derivatives

1. Introduction

The coordination chemistry of the poly(pyrazolyl)borates has been extensively developed since the ligands were initially synthesised and the first compounds prepared, about 30 years ago [1a,1b,1c,1d]. Several reviews on the subject are available [2a,2b,2c,2d,2e,2f,2g,3a,3b]. Most of the papers published refer to the use of tris(pyrazolyl)borates, although in some cases the coordination is through only two of the three N atoms available. In some cases, maximum coordination of the Tp ligand may be disfavoured on steric grounds [4a,4b,4c,4d], although the incidence of low coordination numbers in complexes of these ligands appears to be restricted to late members of the transition series such as Ag, Au, and Hg, the tendency for complexes of these metals to low coordination numbers being well-documented. Although a number of poly(pyrazolyl)borate complexes of Pd(II) and Pt(II) have been prepared [5], related studies involving nickel derivatives are very scarce [6a,6b,6c,6d,6e,6f,6g,6h,7a,7b,7c] [7d,7e,7f,8]. In this paper, we report on the reactivity of alkyl and aryl derivatives of Ni(II), towards poly(pyrazolyl)borate an-

* Corresponding author.
[1] Dedicated to Prof. P.M. Maitlis, a great teacher and imaginative researcher, on the occassion of his 65th birthday.
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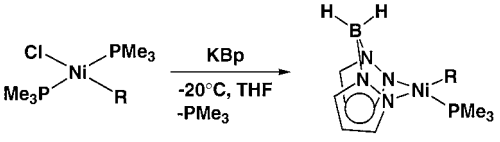
ions. In the case of the tris(pyrazolyl)borate derivatives, the effect of changes in the steric properties of the potentially tridentate ligand upon its mode of coordination and upon the characteristic reactivity of the complexes have been explored. Part of this work has been briefly communicated [9].

2. Results and discussion

2.1. Synthesis of complexes

2.1.1. Alkyl and aryl derivatives

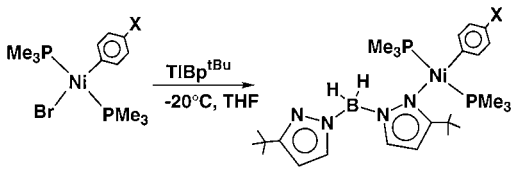
The displacement of a halide by an anionic ligand from the coordination sphere of a metal complex is a commonly employed route to the synthesis of further species, and, if the anion employed possesses potentially chelating properties, a donating ligand present in the original complex is usually eliminated together with the halide, or otherwise the coordination number is increased. Both possibilities can in principle be expected when a poly(pyrazolyl)borate is employed. The reaction between the Ni(II) compounds $Ni(R)Cl(PMe_3)_2$ ($R = CH_2SiMe_3$, CH_2CMe_3, C_6H_5) and KBp, proceeds smoothly at low temperatures to give complexes of formula $BpNi(R)(PMe_3)$ (**1**), as depicted in Eq. (1).



(1)

R = CH_2SiMe_3 (1a), CH_2CMe_3 (1b), C_6H_5 (1c)

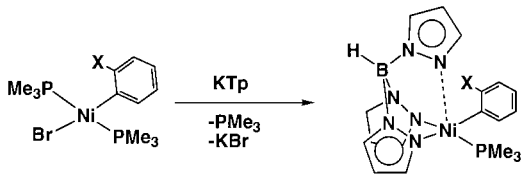
Compounds **1** can be isolated as reddish crystals, which are soluble in most common organic solvents. The microanalytical and spectroscopic data are consistent with the formulation proposed. In contrast with that, the reaction of the aryl derivatives $Ni(C_6H_4\text{-}p\text{-}X)Br(PMe_3)_2$ (X = H, Me, OMe, NMe_2) with the thallium salt of the dihydrobis(3-*t*-butylpyrazolyl)borate anion, Bp^{tBu}, yields crystalline materials whose elemental analyses reveal the composition $Bp^{tBu}Ni(C_6H_4\text{-}p\text{-}X)(PMe_3)_2$ (**2**) (Eq. (2)), that is, no PMe_3 is lost during the reaction.



(2)

X = H (2a), Me (2b), OMe (2c), NMe_2 (2d)

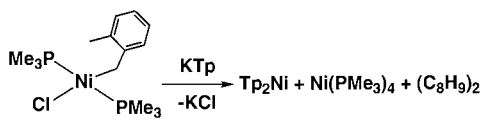
Also, the reaction of complexes $Ni(C_6H_4\text{-}o\text{-}X)Br(PMe_3)_2$ (X = H, Me) with KTp proceeds with loss of 1 equiv of PMe_3 and formation of complexes $TpNi(C_6H_4\text{-}o\text{-}X)(PMe_3)$ (X = H, **3a**; Me, **3b**), as brown crystalline materials (Eq. (3)). Analytical and spectroscopic data (see below) are in agreement with the formulation proposed.



(3)

X = H (3a), Me (3b)

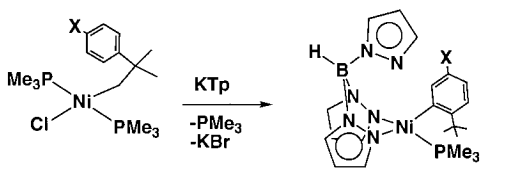
Surprisingly, we have been unable to synthesise other derivatives of composition $Tp Ni(R)(PMe_3)$, in which R is an alkyl group. Thus, when the complexes $Ni(R)X(PMe_3)_2$ ($R = CH_2SiMe_3$, CH_2CMe_3, $CH_2C_6H_4\text{-}o\text{-}Me$; X = Cl or Br) are treated with KTp, following a similar procedure as described in Section 3 for complexes **1–3**, analogous changes in the colour together with formation of KX salts are observed, but when workup of the brownish orange solutions and product isolation are attempted, violet–pink crystals of the known $NiTp_2$ were obtained in all cases [6f]. For the case of $R = CH_2C_6H_4\text{-}o\text{-}Me$, the mother liquors were investigated by NMR, showing the presence of $Ni(PMe_3)_4$ and R–R as the only byproducts (Eq. (4)). The lower strength of the Ni-alkyl bond



(4)

compared with the Ni-aryl is invoked to explain the lack of stability of the attempted species. It is worth mentioning that the analogous Cp derivatives of composition $CpNi(R)(PMe_3)$ [10,11] are quite stable, which suggests that the Tp ligand labilises the Ni–C bond.

On conducting the reaction between KTp and the neophyl or the Me-neophyl derivatives of nickel, $Ni(CH_2CMe_2Ph)Cl(PMe_3)_2$ and $Ni(CH_2CMe_2C_6H_4\text{-}p\text{-}Me)Cl(PMe_3)_2$, complexes **3c** and **3d** are obtained, in which a rearrangement of the neophyl ligand has taken place (Eq. (5)).



(5)

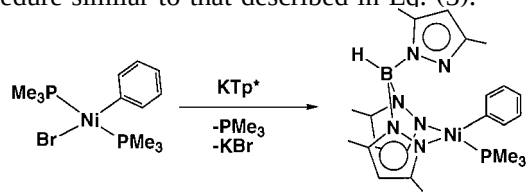
X = H, Me

X = H (3c), Me (3d)

This was deduced from NMR studies of the products, to be described below. This type of ligand rearrangement

has been reported [12a,12b,12c,12d,12e] on previous occasions, indeed, one nickel complex apparently undergoes an analogous transformation forming the isomer $CpNi(C_6H_4$-*o*-$CMe_3)PPh_3$ as a byproduct when $CpNi(CH_2CMe_2Ph)(PPh_3)$ is prepared from $CpNiCl(PPh_3)$ by reaction with Mg(neophyl)Cl [12b]. However, in the cases described herein only the rearranged aryl derivatives were observed. The instability of the Ni–C(alkyl) bond in this class of complex appears to preclude the formation of the expected products, rendering them susceptible to isomerisation via an intramolecular C–H bond activation process.

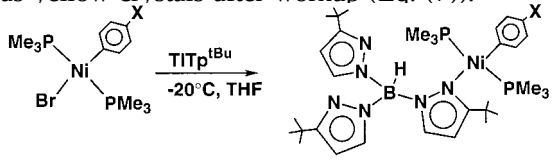
We have also prepared and studied an analogous phenyl derivative containing the Me-substituted Tp^* ligand, $Tp^*Ni(C_6H_5)(PMe_3)$ (**4**) which is obtained (Eq. (6)) as a red–brown crystalline material, following a procedure similar to that described in Eq. (3).



(6)

4

Finally on that respect, the reaction of the aryl complexes $Ni(C_6H_4$-*p*-$X)Br(PMe_3)_2$ with the thallium salt of the $HB(3\text{-}Bu^t pz)_3$ anion, Tp^{tBu}, proceeds smoothly at low temperatures affording $Tp^{tBu}Ni(C_6H_4$-*p*-$X)(PMe_3)_2$ (**5**) as yellow crystals after workup (Eq. (7)).

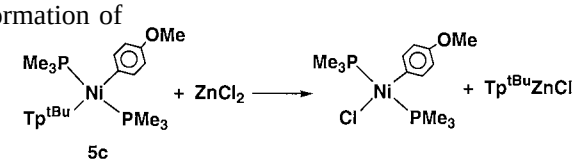


(7)

X = H (5a), Me (5b)
OMe (5c), NMe_2 (5d)

Once more, elemental analyses reveal the presence of two molecules of PMe_3 on the complexes. Moreover, NMR and X-ray studies to be described below reveal the monohapto coordination of the potentially tridentate ligand.

The reaction of derivative **5c** with $ZnCl_2$ has been carried out, in an attempt to remove one equivalent of PMe_3 and thus force the Tp^{tBu} ligand to bind η^2 to the nickel atom. However, this did not meet with success, the reaction proceeding as depicted in Eq. (8), with formation of



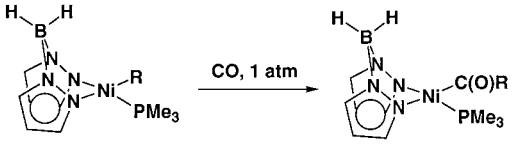
(8)

5c

the known $Tp^{tBu}ZnCl$ [13]. Also, attempts to protonate the unbound *pz* rings [14a,14b] with HBF_4 caused fragmentation of the Tp^{tBu} ligand and byproducts containing ^{t}Bu-pyrazole were obtained.

2.1.2. Carbonylation reactions. Synthesis of acyl and aroyl derivatives

Compounds **1a, b** undergo insertion reactions with CO (Eq. (9)) at



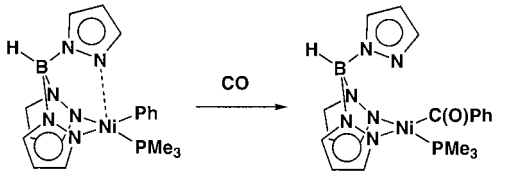
(9)

R = CH_2SiMe_3 (6a)
CH_2CMe_3 (6b)

room temperature and 1 atmosphere of pressure to give the corresponding acyl complexes $BpNi[C(O)R](PMe_3)$ (R = CH_2SiMe_3 (**6a**), R = CH_2CMe_3 (**6b**)).

These complexes are crystalline materials and, as expected [11,15a,15b,15c] they are somewhat less soluble than the parent alkyls. In their IR spectra, the CO stretching frequencies are observed in the region 1650–1670 cm^{-1}.

We have previously shown that the 18-electron complexes $CpNi(R)(PMe_3)$ [10,11] do not react with CO to form the acyl derivatives $CpNi(COR)(PMe_3)$. This was thought to be due to the poor dissociative ability of the PMe_3 group which precludes access to an unsaturated 16-electron intermediate which would be able to interact with CO. However, upon exposing a solution of **3a** to CO at room temperature, the acyl insertion product $TpNi[C(O)C_6H_5](PMe_3)$ (**7**) is obtained (Eq. (10)). This



(10)

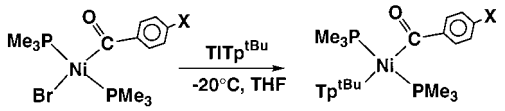
3a 7

is in accord with a mechanism that involves initial release of the weakly coordinated *pz* group from the

metal's coordination sphere, followed by trapping of the resultant 16 electron square planar intermediate by CO, the migratory insertion reaction to CO then follows affording the acyl product. Attempts to carbonylate complex TpNi(C_6H_4-*o*-Bu^t)(PMe_3) (**3c**) by a similar treatment with CO lead to an appropriate change of colour. Moreover, the solid obtained after evaporating the solution displays an infrared absorption at 1610 cm^{-1}, which can be assigned to ν(C–O) of an acyl ligand, suggesting that an analogous insertion of CO has occurred for **3c**. However, upon workup and attempted crystallisation of the product, only complex **3c** is obtained. This indicates that the putative acyl product is unstable with respect to the reverse deinsertion and subsequent elimination of CO.

An alternative route to the acyl derivatives was explored, in which the acyl ligand is in place prior to treatment with Tp′ anions. Thus, the complex Tp* Ni[C(O)C_6H_5](PMe_3) (**8**) was prepared by displacement of the halide from the parent Ni[C(O)C_6H_5]Br(PMe_3)$_2$.

Similarly, the corresponding aroyls **9** can be obtained as depicted in Eq. (11), and they also contain an η^1-Tp^{tBu} ligand.



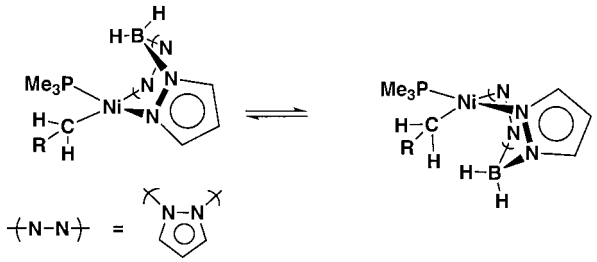
(11)

Complexes **9** slowly evolve CO in solution at room temperature, but display sufficient kinetic stability for full spectroscopic characterisation.

2.2. Spectroscopic studies

2.2.1. Alkyl and aryl derivatives

The NMR data for complexes **1** are consistent with a formulation involving a pseudo square-planar geometry in which the bidentate N-donor ligand occupies two mutually *cis* coordination positions [16a,16b]. As expected, the two *pz* rings of **1a** and **1b** exhibit separate resonances, indicating that these moieties are not exchanging their positions at room temperature. Nevertheless, the equivalence of the two methylenic protons of the alkyl group in each compound indicates that a fluxional process is occurring on the NMR time scale. The equivalence of these methylenic protons would require the coordination plane to be an effective plane of symmetry, and it can be proposed that this occurs via inversion of the boat configuration of the NiN_4B cycle (Scheme 1). The process depicted in Scheme 1 has been proposed to occur in complexes containing analogous bis(pyrazolyl)-methane [17] and -borate derivatives [18a,18b,18c,18d,18e].



Scheme 1.

In contrast, the complex BpNi(Ph)(PMe_3) (**1c**) is shown, by ^{1}H and ^{13}C{^{1}H} NMR, to exhibit a more complicated behaviour at room temperature with only one *pz* environment and lack of coupling between the Ni–*C* and the P nuclei. We propose that an associative [19] exchange of PMe_3 is occurring at room temperature, which is strongly supported from the fact that the ^{31}P{^{1}H} chemical shift at −8.0 moves to higher field, after addition of free PMe_3 to solutions of complex **1c**.

As expected, on lowering the temperature to −60°C, the exchange of phosphine can be suppressed. The quaternary aromatic carbon bound to nickel is then coupled to the phosphorus nucleus (d, $^2J_{CP} = 51$ Hz), and both *pz* rings are now inequivalent. Interestingly, the signals due to the four *C*H nuclei in the *o*- and the *m*- positions of the phenyl ring also resolve into separate peaks indicating that all important fluxional processes that may occur in the molecule are frozen under these conditions, included the boat-to-boat rearrangement observed in complexes **1**.

In the case of the Tp derivative **3a**, NMR studies reveal again the existence of only one set of pyrazole resonances at room temperature. In addition, the complex displays the same type of phosphine exchange mentioned above, as indicated by the observation of a

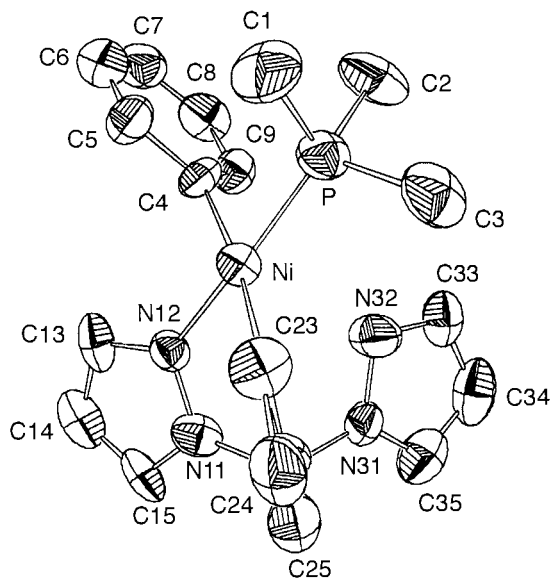
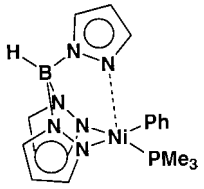


Fig. 1. The molecular structure of compound **3a**.

broad singlet in its ^{13}C NMR spectrum assigned to Ni–*C*.

We have determined the X-ray structure of **3a**, which will be discussed below, and, as can be observed in Fig. 1, complex **3a** is tetracoordinated in the solid state, with a square planar geometry, although an important interaction between the Ni atom and the third *pz* ring (Ni–N(32) 2.57 Å) exists. Although the complex is highly fluxional in solution, we suggest that the structure found in the solid state is maintained in solution, and hence **3a** is a 16 e^- species, although the existence of the weak interaction could not be ruled out with the data available.



3a (12)

As with the Bp derivative **1c**, at −60°C the ^{13}C NMR singlet at 154.3 ppm (Ni–C) splits into a doublet, ($^2J_{CP} = 55$ Hz) attesting to the fact that the PMe_3 exchange is slow on the NMR time-scale at this temperature. The resonances due to the *pz* rings remain unchanged at this temperature, but at −90°C, they become broadened although a clear separation is not observed.

The observance of only one *pz* environment is indicative of rapid exchange of coordinated and uncoordinated groups [20a,20b,20c,20d,20e,20f,20g,2c] and this feature has been described as a "tumbling" process [1c].

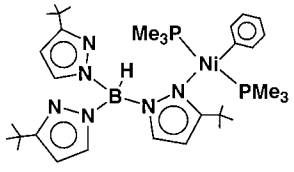
In contrast to the behaviour of **3a**, the PMe_3 exchange in **3b** was slow on the NMR time-scale at room temperature, as indicated by the presence of a doublet at 152.8 ppm ($^2J_{CP} = 49$ Hz) for the Ni–*C* nucleus. Presumably, the presence of the Me group at the *ortho* position of the phenyl ring blocks the axial coordination site, thus preventing the coordination of free PMe_3 at this site and thus hindering the exchange pathway.

Spectroscopic studies of **3c** and **3d** in solution at room temperature show the three pyrazole rings to be inequivalent. The presence of the very bulky ^{t}Bu retards significantly all the fluxional processes observed for the related Ph derivative **3a**.

In the case of the Tp* derivative **4**, PMe_3 exchange is judged to be slow by $^{13}C\{^1H\}$ NMR, as suggested by the doublet seen at 152 ppm ($^2J_{CP} = 45$ Hz) which arises from the nickel-bound aryl carbon atom. Taking into account the exchange of PMe_3 found for the Tp-containing complex **3a**, the methyl in the 3 position of the *pz* rings presumably hinders the interchange of phosphine. Further, the other interchange processes involving the *pz* groups, which were observed to be very fast in the case of **3a**, are now slowed down, giving C–H pyrazolyl resonances in a 1:2 ratio, which separate into three peaks each at −60°C. We presume that the complex has a square planar structure, with one non-bonded or weakly interacting *pz** ring.

A selective exchange between the unbound and one of the coordinated *pz* rings is invoked in order to explain the observed 1:2 intensities of the NMR signals for the *pz** moieties at room temperature. A related exchange has been recently proposed for a Tp*–Rh compound [21]. Considering the great *trans* effect [22] of the PR_3 group as compared with the phenyl, it can be proposed that the exchange takes place between the uncoordinated and the pyrazolyl *trans* to the phosphine ligand.

NMR studies on complex **5a** provide interesting information about its solution structure. In the ^1H NMR, the appearance of a virtually coupled triplet [23] shows the presence of two mutually *trans* PMe_3 groups in the molecule. This contrasts with the results obtained for the parent Tp and Tp* described above, for which a PMe_3 is lost during the reaction. In addition, two distinct sets of pyrazolyl resonances are observed, in a 1:2 ratio. These observations, together with the strong tendency of Ni(II) to form four coordinate square-planar structures in complexes of this type, suggests that the borate ligand in complex **5a** is behaving as a monohapto, i.e., as an one electron donor fragment. The



5a (13)

coordinated and uncoordinated *pz* groups do not exchange on the NMR time scale at the temperatures studied.

Several cases have been reported previously in which a Tp′ or Bp′ is bound asymmetrically, with a strong M . . . N bond and a weaker M...N interaction [24a,24b,24c]. Such cases are usually motivated by the electronic requirements at the metal centre, specifically those which display a pronounced tendency to low coordination numbers. The complexes reported in this paper represent the first examples of a strict η^1 coordination of poly(pyrazolyl)borate-type ligands.

$^{13}C\{^1H\}$ NMR data also provides information about the existence of a high barrier of rotation of the phenyl ring, and six separate resonances are found for this group at room temperature.

NMR data for derivatives **5b–d** are in agreement with them having a square planar structure analogous to **5a**. This has been confirmed by means of an X-ray

study, carried out with complex **5b**, to be described below, which confirms the square planar structure shown.

NMR features for complexes **2** are very similar to those encountered for the Tp^{tBu} derivatives. For instance, complex **2a** presents a virtually coupled triplet for the two equivalent PMe_3 ligands, pz^{tBu} resonances in 1:1 ratio and five singlets for the *C*H nuclei of the phenyl, in the $^{13}C\{^1H\}$ NMR spectra. All other spectroscopic data obtained for these complexes are in agreement with the structure proposed and need no further comment.

2.2.2. Acyl and aroyl complexes

In contrast with their parent alkyls, ^1H and $^{13}C\{^1H\}$ NMR studies demonstrate that the two acyl complexes **6a** and **6b** do not possess rigid stereochemistry at room temperature. Thus, the pyrazole rings are now magnetically equivalent, giving rise to just one set of signals and the *C*OR carbon produces a broad singlet at 255 ppm in the $^{13}C\{^1H\}$ NMR spectrum. This last observation is suggestive of an intermolecular exchange process involving traces of PMe_3 present in solution, and in accord with this, in the presence of additional PMe_3 at room temperature, the signal in the $^{31}P\{^1H\}$ NMR spectrum of compound **6b**, at -11.0 ppm shifts to higher fields, a single resonance being observed for both the free and bound PMe_3. On cooling to -80°C, a splitting of the mentioned ^{13}C acyl resonance occurs (d, $^2J_{CP} = 31$ Hz) indicating that at this temperature this process has been stopped on the NMR timescale.

In the case of the aroyl $TpNi[C(O)C_6H_5](PMe_3)$ (**7**), NMR studies again reveal that a dynamic process is taking place at room temperature with equivalence of the three *pz* rings. Cooling down to -80°C, has no effect on the signals corresponding to the *pz* rings. In contrast, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy show **8** to be a rigid square-planar complex with the Tp^* ligand bound in a dihapto (η^2) mode at room temperature with no appreciable exchange processes taking place under these conditions.

Like their parent aryl derivatives **5**, the aroyls **9** have two *trans* PMe_3 groups and an η^1-Tp^{tBu}. The spectroscopic data are collected in Section 3 and need no further comment.

2.3. Structural studies

Single crystal X-ray studies have been carried out for compounds **3a** and **5b**. Figs. 1 and 2 show ORTEP [25] representations for them while Tables 1 and 2 collect relevant structural data. As may be seen, the molecules of **3a** have a distorted square planar structure in the solid state with the Tp ligand coordinated through only two of the three *pz* rings. Notewhorty, the distance 2.57(1) Å for the Ni–N(32) contact in **3a** is out of the

Table 1
Crystal and refinement data for complexes **3a** and **5b**

Compound	**3a**	**5b**
Formula	$C_{18}H_{27}BN_6NiP$	$C_{34}H_{59}BN_6NiP_2$
Formula weight	427.9	683.34
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a (Å)	10.271(1)	12.626(4)
b (Å)	8.218(2)	24.298(3)
c (Å)	24.960(8)	13.413(3)
β (°)		102.43(3)
V (Å^3)	2106(8)	4018(2)
Z	4	4
Crystal dimensions (mm^3)	$0.15 \times 0.15 \times 0.15$	$0.2 \times 0.3 \times 0.4$
D_{calc} (g cm^{-3})	1.35	1.13
μ (cm^{-1})	10.13	5.90
Temperature (K)	295	
Diffractometer	Enraf-Nonius	
Monochromator	graphite	
Radiation	Mo Kα ($\lambda = 0.71069$ Å)	
Scan technique	$\omega - 2\theta$	$\omega/2\theta$
θ	$1 < \theta < 30$	$1 < \theta < 25$
Data collected	(0,0,0) to (14,11,35)	(-15,0,0) to (15,28,16)
Unique data	3470	7360
Unique data $(I) > 2\sigma(I)$	1410	–
Unique data $(I) > 3\sigma(I)$	–	3169
$R = \Sigma\lvert\Delta^2F\rvert/\Sigma\lvert F_0\rvert$	5.0	6.2
$R_w = (\Sigma\omega\Delta^2F/\Sigma\omega\lvert F_0\rvert^2)^{1/2}$	5.4	6.6

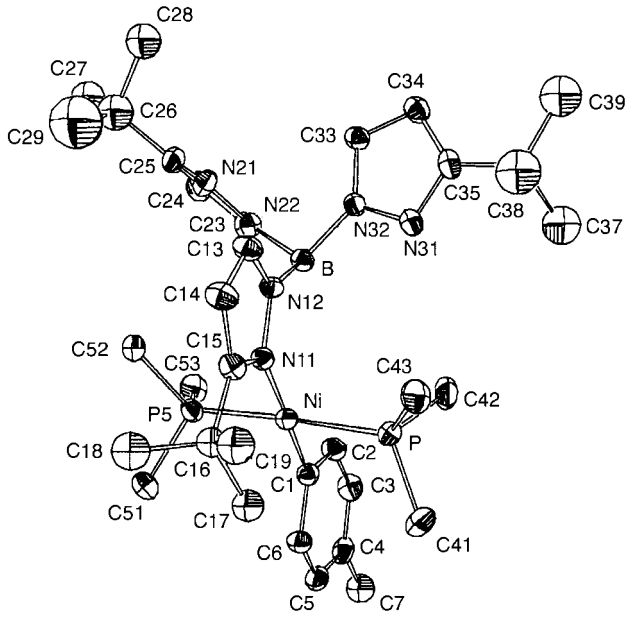
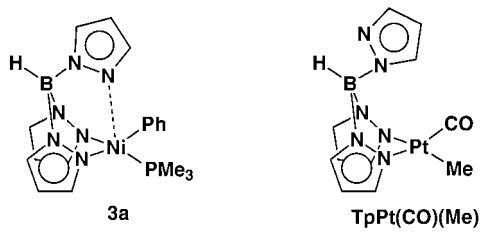


Fig. 2. The molecular structure of compound **5b**.

normal bonding range (1.938(8) and 1.970(9) for the other two distances in **3a**), but reflects the existence of an important Ni · · · N interaction. Although the behaviour of the complex in solution (see above) is in agreement with a 16 electron unsaturated structure, the geometry in the solid state could be defined as square pyramidal, in which the square plane defined by C, P and two pyrazolyl N atoms is capped by the third pyrazolyl N atom, the latter interaction being weaker than the two Ni-N equatorial bonds. The existence of an axial *pz* weakly coordinated to the metal has been reported previously [26]. The distance Ni–P for **3a** (2.141(3) Å) fall into the range found for other Ni(II)–PMe_3 examples [11,15a,20a,20b,20c,20d,20e,20f,20g]. The same is true of the Ni–C distance, of 1.87(1) Å,

Table 2
Selected bond distances (Å) and angles (°) for compounds **3a** and **5b**

3a			
Ni–P	2.141(3)	N(32)–Ni–C(4)	106.9(4)
Ni–N(12)	1.938(8)	N(22)–Ni–C(4)	170.6(4)
Ni–N(22)	1.979(9)	N(22)–Ni–N(32)	82.2(4)
Ni–N(32)	2.57(1)	N(12)–Ni–C(4)	89.9(4)
Ni–C(4)	1.87(1)	N(12)–Ni–N(32)	85.7(3)
		N(12)–Ni–N(22)	88.5(4)
		P–Ni–C(4)	86.3(4)
		P–Ni–N(32)	92.8(2)
		P–Ni–N(22)	95.7(3)
		P–Ni–N(12)	175.3(3)
5b			
Ni–P(4)	2.207(2)	C(1)–Ni–N(11)	178.6(3)
Ni–P(5)	2.214(2)	P(5)–Ni–N(11)	93.5(2)
Ni–C(1)	1.891(8)	P(5)–Ni–C(1)	86.1(2)
Ni–N(11)	1.947(6)	P(4)–Ni–N(11)	93.6(2)
		P(4)–Ni–C(1)	86.8(2)
		P(4)–Ni–P(5)	172.7(1)



Scheme 2.

close to other examples (1.93(1)° for the Ni-aryl bond of $Ni(CH_2CMe_2-o-C_6H_4)(PMe_3)_2$ [17] or 1.951(12)° for complex $Ni(CH_2CH_2C_6H_4\text{-}o)(Cy_2PCH_2CH_2PCy_2)$ [27a,27b]).

A comparison can be drawn between the structural geometry of compound **3a** and the complexes TpPt(L)(R) which are square planar in the solid state but have been proposed to be pentacoordinate in solution, by means of NMR studies [28a,28b]. As can be seen in Scheme 2, the N atom of the non-bonded *pz* is oriented away from the Pt atom, unlike in complex **3a**.

The nickel centre of complex **5b** lies in a slightly distorted square plane, with the phenyl ring being perpendicular to the coordination plane and, as expected, the two phosphine ligands in mutually *trans* positions. The borate moiety is coordinated to the nickel through only one nitrogen, with the other two *pz* rings oriented away from the metal centre. The distance Ni–N(11), of 1.947(6) Å is in the range found for complex **3a**. Finally, the distance Ni–C(1) (1.891(8) Å) is also within the expected range of values for a Ni-aryl bond [16a,27a,27b].

3. Experimental details

3.1. General considerations

Mycroanalyses were performed by the Microanalytical Service of the University of Seville. Perkin–Elmer Models 577 and 684 spectrometers were used for IR spectra, and a Varian XL-200 instrument was used for NMR studies. The ^{13}C resonance of the solvent was used as an internal reference, but chemical shifts are reported with respect to $SiMe_4$. ^{31}P NMR shifts are relative to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenck techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60°C. The compounds $Ni(CH_2SiMe_3)Cl(PMe_3)_2$ [15a], $Ni(CH_2CMe_3)Cl(PMe_3)_2$ [10] and $Ni(CH_2CMe_2Ph)Cl(PMe_3)_2$ [15a] were obtained by published methods, as well as the ligands $KH_2B(pz)_2$ [6f,29], $KHB(pz)_3$ [6f,31], $KHB(3,5\text{-}Me_2pz)_3$ [1d], $TlH_2B(3\text{-}Bu^tpz)_2$ [7d], and $TlHB(3\text{-}Bu^tpz)_3$ [7d]. The

syntheses of Ni(C_6H_4-*o*-Me)Br(PMe_3)$_2$, and Ni(C_6H_4-*p*-X)Br(PMe_3)$_2$ were carried out following the procedure described previously for the phenyl derivative Ni(C_6H_5)Br(PMe_3)$_2$ [30], using THF as the solvent, at 60°C. The corresponding aroyl derivatives were prepared by reaction of solutions of the parent aryls with 1 atm of CO. The Cp derivative (Cp)Ni(C_6H_5)(PMe_3) was synthesised from Ni(C_6H_5)Br(PMe_3)$_2$ by reaction with NaCp in THF and isolated as dark red crystals.

(Cp)Ni(C_6H_5)(PMe_3): ^{1}H NMR (20°C, C_6D_6) δ 0.66 (d, 9 H, $^2J_{HP}$ = 9.6 Hz, PMe_3), 5.18 (s, 5 H, Cp), 6.97 (t, 1 H, $^3J_{HH}$ = 7.0 Hz, *p*-CH), 7.03 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, *m*-CH), 7.57 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, *o*-CH); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 17.8 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 89.9 (s, Cp), 122.1, 126.0, 143.0 (s, 1, 2, 2 CH), 144.2 (d, $^2J_{CP}$ = 39 Hz, Cq); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −3.56.

$ClCH_2CMe_2C_6H_4$-*p*-Me was prepared as reported for neophyl chloride [31] using toluene instead of benzene. Ni($CH_2CMe_2C_6H_4$-*p*-Me)Cl(PMe_3)$_2$ was synthesised as follows: to a solution of $NiCl_2(PMe_3)_2$ (0.56 g, 2 mmol) in Et_2O (30 ml) cooled to −60°C, Mg($CH_2CMe_2C_6H_4$-*p*-Me)Cl is added (1.66 ml of a solution 1.2 M in Et_2O, 2 mmol). The mixture is stirred for 40 min at low temperature and a further period of 24 h at room temperature. The solvent is evaporated under vacuum and the mixture extracted with petroleum ether (40 ml). The resulting solution is concentrated and cooled to −20°C, to yield brown–yellow needles of the expected product in about 20% yield.

Ni($CH_2CMe_2C_6H_4$-p-Me)Cl(PMe_3)$_2$: ^{1}H NMR (20°C, CD_3COCD_3) δ 0.72 (t, 2 H, $^3J_{HP}$ = 13.4 Hz, Ni–CH_2), 1.15 (br s, 18 H, PMe_3), 1.56 (s, 6H, Me_2), 2.25 (s, 3 H, Me), 7.06 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, 2 CH), 7.79 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, 2 CH); ^{13}C{^{1}H} NMR (20°C, CD_3COCD_3) δ 13.9 (pt, $J_{CP(app)}$ = 12.5 Hz, PMe_3), 17.5 (t, $^2J_{CP}$ = 22.4 Hz, CH_2), 20.9 (s, *p*-Me), 33.1 (s, Me_2), 41.6 (s, *C*Me_2), 126.6, 129.1 (s, 2, 2 CH), 134.6, 150.6 (s, 2 C_q); ^{31}P{^{1}H} NMR (20°C, CD_3COCD_3) δ −18.5 (s).

Ni(C_6H_4-o-Me)Br(PMe_3)$_2$: ^{1}H NMR (20°C, C_6D_6) δ 0.82 (pt, 18 H, $J_{HP(app)}$ = 3.7 Hz, PMe_3), 2.66 (s, 3H, Me), 6.8–7.3 (m, 4 H, C_6H_4); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 13.5 (pt, $J_{CP(app)}$ = 14 Hz, PMe_3), 25.9 (s, CH_3), 121.8, 124.0, 127.5, 134.1 (s, CH), 141.9 (t, $^3J_{CP}$ = 4 Hz, *C*Me), 157.8 (t, $^2J_{CP}$ = 34 Hz, Ni–C).

Ni(C_6H_4-p-Me)Br(PMe_3)$_2$: ^{1}H NMR (20°C, C_6D_6) δ 0.85 (pt, 18 H, $J_{HP(app)}$ = 3.6 Hz, PMe_3), 2.16 (s, 3H, Me), 6.82, 6.86, 7.21, 7.25 (br, 4 H, C_6H_4); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 13.3 (pt, $J_{CP(app)}$ = 13 Hz, PMe_3), 20.6 (s, CH_3), 127.9 (s, 2 CH), 135.5 (s, 2 CH); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −14.9 (s). Anal. Calcd. for $C_{13}H_{25}BrNiP_2$: C, 40.9; H, 6.6. Found: C, 40.1; H, 7.0.

Ni(C_6H_4-p-OMe)Br(PMe_3)$_2$: ^{1}H NMR (20°C, C_6D_6) δ 0.85 (pt, 18 H, $J_{HP(app)}$ = 3.7 Hz, PMe_3), 3.38 (s, 3H, OMe), 6.72, 6.77, 7.13, 7.17 (br, 4 H, C_6H_4); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 13.4 (pt, $J_{CP(app)}$ = 14 Hz, PMe_3), 54.3 (s, OCH_3), 113.6 (s, 2 *m*-CH), 135.4 (t, $^3J_{CP}$ = 4 Hz, 2 *o*-CH), 142.3 (t, $^2J_{CP}$ = 34 Hz, Ni–C), 156.4 (s, *C*OMe); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −14.8 (s). Anal. Calcd. for $C_{13}H_{25}BrNiOP_2$: C, 39.2; H, 6.3. Found: C, 38.3; H, 6.6.

Ni(C_6H_4-p-NMe_2)Br(PMe_3)$_2$: ^{1}H NMR (20°C, C_6D_6) δ 0.89 (pt, 18 H, $J_{HP(app)}$ = 3.7 Hz, PMe_3), 2.58 (s, 6H, NMe_2), 6.60, 6.64, 7.15, 7.16 (br, 4 H, C_6H_4); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 13.4 (br, PMe_3), 40.6 (s, NMe_2), 113.8 (s, 2 CH), 135.6 (s, 2 CH); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −15.0 (s).

3.2. Synthesis of complexes

3.2.1. BpNi(CH_2SiMe_3)(PMe_3) (**1a**)

To a stirred solution of Ni(CH_2SiMe_3)Cl(PMe_3)$_2$ (0.29 g, 0.88 mmol) in THF (20 ml) at −20°C, was added $KH_2B(pz)_2$ (0.17 g, 0.91 mmol) in THF (10 ml). A turbid yellow solution was obtained which was stirred for 4 h at room temperature. It was then evaporated in vacuo to give a brownish solid which was extracted with 20 ml of petroleum ether, centrifuged to remove KCl and concentrated. Cooling to −20°C provided cream-coloured crystals; yield 0.24 g (74%). IR (Nujol, cm^{-1}): ν_{B-H} 2460–2280, ν_{C-N} 1500; ^{1}H NMR (20°C, C_6D_6) δ 0.63 (d, 9 H, $^2J_{HP}$ = 9.2 Hz, PMe_3), −0.42 (d, 2 H, $^3J_{HP}$ = 11.2 Hz, CH_2), 0.22 (s, 3 H, CH_3), 5.79, 5.87, 6.94, 7.40, 7.46, 7.51 (s br, 6 H, CH_{pz}); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 14.2 (d, $^1J_{CP}$ = 29 Hz, PMe_3), −4.2 (d, $^2J_{CP}$ = 33 Hz, CH_2), 2.7 (s, CH_3), 104.2, 104.6, 135.2, 135.5, 138.7, 139.7 (s, CH_{pz}); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −10.2. Anal. Calcd. for $C_{13}H_{28}N_4BNiPSi$: C, 42.3; H, 7.6; N, 15.2. Found: C, 42.3; H, 7.6; N, 15.0.

3.2.2. BpNi(CH_2CMe_3)(PMe_3) (**1b**)

This complex was prepared in the same manner as compound **1a** using 0.16 g (0.44 mmol) of Ni(CH_2CMe_3)Br(PMe_3)$_2$ and 0.09 g (0.46 mmol) of $KH_2B(pz)_2$. The product was obtained as reddish–brown crystals; yield 0.85 g, 55%. IR (Nujol, cm^{-1}): ν_{B-H} 2480–2280, ν_{C-N} 1500; ^{1}H NMR (20°C, C_6D_6) δ 0.68 (d, 9 H, $^2J_{HP}$ = 8.8 Hz, PMe_3), 0.83 (d, 2 H, $^3J_{HP}$ = 10.7 Hz, CH_2), 1.20 (s, 3 H, CH_3), 5.80, 5.90, 6.98, 7.49 (s br, 4 H, CH_{pz}), 7.55 (s br, 2 H, CH_{pz}); ^{13}C{^{1}H} NMR (20°C, C_6D_6) δ 14.4 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 22.9 (d, $^2J_{CP}$ = 34 Hz, CH_2), 33.7 (s, CH_3), 34.4 (s, *C*Me_3), 104.2, 104.5, 135.4, 139.2, 139.7 (s, CH_{pz}); ^{31}P{^{1}H} NMR (20°C, C_6D_6) δ −11.8. Anal. Calcd. for $C_{14}H_{28}N_4BNiP$: C, 47.7; H, 7.9; N, 15.9. Found: C, 47.7; H, 8.2; N, 16.0.

3.2.3. BpNi(C_6H_5)(PMe_3) (**1c**)

Following the same procedure as for complexes **1a** and **1b**, 0.66 g (1.8 mmol) of Ni(C_6H_5)Cl(PMe_3)$_2$ was reacted with 0.34 g (1.8 mmol) of $KH_2B(pz)_2$ in THF yielding complex **1c** as a brown crystalline material;

yield 0.49 g (71%). IR (Nujol, cm^{-1}): ν_{B-H} 2430–2170, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.55 (d, 9 H, $^2J_{HP} = 7.3$ Hz, PMe_3), 5.80 (t, 2 H, $^3J_{HH} = 2.1$ Hz, CH_{pz}), 6.86 (d, 2 H, $^3J_{HH} = 2.1$ Hz, CH_{pz}), 6.94–7.55 (m, 7 H, CH_{pz} and CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.6 (d, $^1J_{CP} = 26$ Hz, PMe_3), 104.3, 135.0, 140.6, 139.7 (s, CH_{pz}), 122.6, 126.3, 136.6 (s, CH_{Ar}), 154.3 (s, Cq_{Ar}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −11.5. Anal. Calcd. for $C_{15}H_{22}N_4BNiP$: C, 50.2; H, 6.2; N, 15.6. Found: C, 50.1; H, 6.3; N, 15.9.

3.2.4. $Bp^{tBu}Ni(C_6H_4\text{-}p\text{-}X)(PMe_3)_2$

The Bp^t derivatives can be prepared in 65–80% yields as orange crystalline materials following the procedure described above for complexes **1**.

3.2.4.1. $Bp^{tBu}Ni(C_6H_5)(PMe_3)_2$ ***(2a)***. ^1H NMR (20°C, C_6D_6) δ 0.76 (pt, 18 H, $J_{HP(app)} = 3.8$ Hz, PMe_3), 1.54 (s, 9 H, CMe_3), 1.58 (s, 9 H, CMe_3), 5.87, 6.37, 7.25, 8.0 (d, $^3J_{HH} = 2.2$ Hz, 1, 1, 1 and 1 H, CH_{pz}), 6.8–7.4 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.5 (s, C*Me*$_3$), 99.3, 104.3, 134.8, 135.5 (s, 1, 1, 1, 1 CH_{pz}), 122.1 (s), 125.6 (s), 125.7 (s), 138.5 (s), 139.1 (s) (5 CH_{Ph}), 151.5 (t, $^2J_{CP} = 38$ Hz, Ni–C), 158.3, 162.2 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −16.4 (s). Anal. Calcd. for $C_{26}H_{47}N_4BNiP_2$: C, 57.1; H, 8.6; N, 10.2. Found: C, 57.0; H, 8.8; N, 10.1.

3.2.4.2. $Bp^{tBu}Ni(C_6H_4\text{-}p\text{-}Me)(PMe_3)_2$ ***(2b)***. ^1H NMR (20°C, C_6D_6) δ 0.78 (pt, 18 H, $J_{HP(app)} = 3.7$ Hz, PMe_3), 1.48 (s, 9 H, CMe_3), 1.53 (s, 9 H, CMe_3), 2.16 (s, 3H, Me), 5.87, 6.37, 7.23, 7.98 (br s, 1, 1, 1 and 1 H, CH_{pz}), 6.7–7.4 (m, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 20.6 (s, Me), 31.3 (s, C*Me*$_3$), 99.3, 104.3, 134.7, 135.3 (s, 1, 1, 1, 1 CH_{pz}), 126.8 (s), 127.2 (s), 138.4 (s), 138.9 (s) (C_6H_4), 130.9 (br s, *C*Me), 145.5 (t, $^2J_{CP} = 38$ Hz, Ni–C), 158.3, 162.2 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −16.7 (s). Anal. Calcd. for $C_{27}H_{49}N_4BNiP_2$: C, 57.8; H, 8.7; N, 10.0. Found: C, 58.4; H, 9.3; N, 9.8.

3.2.4.3. $Bp^{tBu}Ni(C_6H_4\text{-}p\text{-}OMe)(PMe_3)_2$ ***(2c)***. ^1H NMR (20°C, C_6D_6) δ 0.77 (pt, 18 H, $J_{HP(app)} = 3.7$ Hz, PMe_3), 1.54 (s, 9 H, CMe_3), 1.59 (s, 9 H, CMe_3), 3.37 (s, 3H, OMe), 5.87, 6.37, 7.25, 8.00 (d, $^3J_{HH} = 2.2$ Hz, 1, 1, 1 and 1 H, CH_{pz}), 6.6–7.4 (m, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.4 (s, C*Me*$_3$), 54.1 (s, OMe), 99.4, 104.3, 134.8, 135.5 (s, 1, 1, 1, 1 CH_{pz}), 112.1 (s), 113.1 (s), 138.4 (br s), 139.0 (br s) (C_6H_4), 157.0, 158.3, 159.6 (s, Cq); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −16.8 (s).

3.2.4.4. $Bp^{tBu}Ni(C_6H_4\text{-}p\text{-}NMe_2)(PMe_3)_2$ ***(2d)***. ^1H NMR (20°C, C_6D_6) δ 0.82 (pt, 18 H, $J_{HP(app)} = 3.8$ Hz, PMe_3), 1.54 (s, 9 H, CMe_3), 1.62 (s, 9 H, CMe_3), 2.57 (s, 6H, NMe_2), 5.88, 6.36, 7.26, 8.00 (d, $^3J_{HH} = 2.2$ Hz, 1, 1, 1 and 1 H, CH_{pz}), 6.5–7.25 (br m, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.3 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.5 (s, C*Me*$_3$), 40.4 (s, NMe_2), 99.3, 104.1, 134.8, 135.5 (s, CH_{pz}), 112.7 (s), 112.7 (s), 135.5 (s), 139.1 (s) (C_6H_4), 130.1 (t, $^2J_{CP} = 38$ Hz, Ni–C), 147.5 (s, $CNMe_2$), 158.3, 162.3 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −17.0 (s). Anal. Calcd. for $C_{28}H_{52}N_5BNiP_2$: C, 57.0; H, 8.9; N, 11.8. Found: C, 57.6; H, 9.5; N, 11.2.

3.2.5. $TpNi(C_6H_5)PMe_3$ ***(3a)***

To a stirred solution of $Ni(C_6H_5)Cl(PMe_3)_2$ (0.2 g, 0.54 mmol) in THF (20 ml) at −20°C, was added $KHB(pz)_3$ (0.14 g, 0.56 mmol) in THF (10 ml). The reaction mixture was stirred for 4 h at room temperature. The solvent was then evaporated in vacuo to give a brownish solid which was extracted with 20 ml of petroleum ether, centrifuged to remove KCl and concentrated. Cooling to −20°C provided brown crystals of complex **3a**; yield 0.14 g (61%). IR (Nujol, cm^{-1}): ν_{B-H} 2450, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.64 (s br, 9 H, PMe_3), 5.94 (s br, 3 H, CH_{pz}), 7.25 (s br, 3 H, CH_{pz}), 7.55 (s br, 3 H, CH_{pz}), 6.9–7.7 (m, 5 H, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.6 (d, $^1J_{CP} =$ 26 Hz, PMe_3), 104.3, 135.0, 140.6, 139.7 (s, CH_{pz}), 122.6, 126.3, 136.6 (s, CH_{Ar}), 154.3 (s, Cq_{Ar}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −11.5. Anal. Calcd. for $C_{18}H_{24}N_6BNiP$: C, 50.9; H, 5.7; N, 19.8. Found: C, 51.0; H, 5.6; N, 19.8.

3.2.6. $TpNi(C_6H_4\text{-}o\text{-}CH_3)PMe_3$ ***(3b)***

The reaction procedure followed was the same as for compound **3a** using 0.46 g (1.2 mmol) of $Ni(C_6H_4\text{-}o\text{-}CH_3)Br(PMe_3)_2$ and 0.3 g (1.2 mmol) of $KHB(pz)_3$. The product was obtained as a light orange crystalline material; yield 0.28 g (56%). IR (Nujol, cm^{-1}): ν_{B-H} 2450, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.61 (s br, 9 H, PMe_3), 2.96 (s, 3 H, CH_3), 6.0 (s br, 3 H, CH_{pz}), 6.87–7.65 (m, 10 H, CH_{pz} and CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 14.0 (d, $^1J_{CP} = 31$ Hz, PMe_3), 25.4 (s, CH_3), 104.5, 135.0, 140.7 (s, CH_{pz}), 126.7, 126.8, 137.6 (s, CH_{Ar}), 143.4 (s, Cq_{Ar}–Me), 152.8 (d, $^2J_{CP} =$ 51 Hz, Cq_{Ar}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −12.2. Anal. Calcd. for $C_{19}H_{26}N_6BNiP$: C, 52.0; H, 6.0; N, 19.1. Found: C, 51.8; H, 6.4; N, 19.1.

3.2.7. $TpNi(C_6H_5\text{-}o\text{-}CMe_3)(PMe_3)_2$ ***(3c)***

To a solution of $Ni(CH_2CMe_2Ph)Cl(PMe_3)_2$ (0.15 g, 0.39 mmol) in THF (20 ml) at −20°C, was added a solution of $KHB(pz)_3$. A turbid, orange solution was obtained which was left stirring at room temperature for 3 h, after which the solvent was evaporated under vacuum. The solid residue was extracted with petroleum ether (20 ml) and centrifuged. On concentration of the solution, and cooling to −20°C overnight, yellow–orange crystals were obtained; yield 0.12 g (64%). IR

(Nujol, cm^{-1}): ν_{B-H} 2444, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.43 (d, 9 H, $^2J_{HP} = 10.0$, PMe_3), 2.05 (s, 9 H, CH_3), 5.63, 5.96, 6.40, 7.56, 7.12, 7.41, 6.66, 7.70 (s br, 9 H, CH_{pz}), 6.8–7.9 (m, 4 H, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.9 (d, $^1J_{CP} = 29$ Hz, PMe_3), 33.9 (s, CH_3), 36.5 (s, CMe_3), 104.4, 104.6, 105.0, 133.2, 136.3, 137.8, 140.7, 142.0, 142.8 (s, CH_{pz}), 123.0, 123.2, 126.5, 137.0 (s, CH_{Ar}), 146.3 (d, $^2J_{CP} = 47$ Hz, C_{Ar}–CMe_3), 155.5 (s, Cq_{Ar}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −16.4. Anal. Calcd. for $C_{22}H_{32}N_6BNiP$: C, 54.7; H 6.7; N 17.1. Found: C, 54.9; H 6.7; N 17.5.

3.2.8. $TpNi(1\text{-}C_6H_4\text{-}2\text{-}CMe_3\text{-}5\text{-}Me)PMe_3$ (3d)

Using the same method as for **7** and **8**, 0.14 g (0.36 mmol) of $Ni(CH_2C(CH_3)_2C_6H_4\text{-}p\text{-}CH_3)Cl(PMe_3)_2$ was reacted with 0.09 (0.36 mmol) of $KHB(pz)_3$ giving **3d** as red–brown crystals; yield 0.2 g (67%). IR (Nujol, cm^{-1}): ν_{B-H} 2450, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.48 (d, 9 H, $^2J_{HP} = 9.7$ Hz, PMe_3), 2.05 (s, 9 H, $C(CH_3)_3$), 2.10 (s, 3 H, C_{Ar}–CH_3), 5.63–7.89 (br s, 10 H, CH_{pz} and 1 CH_{Ar}), 6.74 (d, 1H, $^3J_{HH} = 7.4$, CH_{Ar}), 7.08 (d, 1H, $^3J_{HH} = 7.4$, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.9 (d, $^1J_{CP} = 30$ Hz, PMe_3), 31.1 (s, $C(Me)_2$), 34.0 (s, $C(CH_3)_3$), 36.1 (s, CMe_3), 104.3, 104.6, 105.0, 133.4, 136.3, 138.2, 140.7, 142.0, 142.9 (s, CH_{pz}), 124.1, 126.3, 137.0 (3 CH_{Ar}), 131.4, 152.5 (s, C_q), 145.8 (d, $^2J_{CP} = 50$ Hz, Ni–C); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −17.9 s. Anal. Calcd. for $C_{23}H_{34}N_6BNiP$: C, 56.0; H 6.7; N 17.0. Found: C, 55.9; H 7.0; N 17.1.

3.2.9. $Tp^*Ni(C_6H_5)(PMe_3)$ (4)

To a stirred solution of $Ni(C_6H_5)Cl(PMe_3)_2$ (0.31 g, 0.84 mmol) in THF (20 ml) at −20°C, was added $KHB(pz^*)_3$ (0.28 g, 0.84 mmol) in THF (10 ml). The reaction mixture was stirred for 4 h at room temperature. It was then evaporated in vacuo to give a brownish solid which was extracted with 20 ml of petroleum ether, centrifuged to remove KCl and concentrated. Cooling to −20°C provided red–brown crystals of complex **4**; yield 0.14 g (61%). IR (Nujol, cm^{-1}): ν_{B-H} 2460, ν_{C-N} 1550; ^1H NMR (20°C, C_6D_6) δ 0.57 (d, 9 H, $^2J_{HP} = 10.3$, PMe_3), 1.45, 2.16, 2.19, 1.32 (s, 18 H, Me_{pz}), 5.33, 5.84, 7.14 (s, 3 H, CH_{pz}), 6.9–7.6 (m, 5 H, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.4 (d, $^1J_{CP} = 30$ Hz, PMe_3), 12.4, 13.3, 13.9, 14.6 (s, Me_{pz}), 105.9, 106.9 (s, CH_{pz}), 122.4, 125.2, 139.0 (s, CH_{Ar}), 144.8, 147.3, 150.6 (s, Cq_{pz}), 151.3 (d, $^2J_{CP} = 54$ Hz, Cq_{Ar}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −13.6. Anal. Calcd. for $C_{24}H_{36}N_6BNiP$: C, 56.6; H, 7.1; N, 16.5. Found: C, 56.8; H, 7.4; N, 16.4.

3.2.10. $Tp^{tBu}Ni(C_6H_4\text{-}p\text{-}X)(PMe_3)_2$ (5)

These complexes were prepared starting from the aryls $Ni(C_6H_4\text{-}p\text{-}X)Br(PMe_3)_2$ following the procedure described below for the phenyl derivative:

To a solution of $Ni(C_6H_5)Br(PMe_3)_2$ (0.19 g, 0.51 mmol) in THF (20 ml) cooled to −20°C was added $TlTp^{tBu}$ (0.30 g, 0.51 mmol) dissolved in THF (10 ml). A white precipitate of TlBr was formed immediately. The mixture was stirred for 4 h at room temperature and the solvent was evaporated under vacuum. The residue was extracted with petroleum ether (20 ml), the suspension centrifuged and the resulting solution concentrated under vacuum and cooled to −20°C overnight. Yellow needles (0.21 g, 65% yield) of complex **5a** were obtained.

3.2.10.1. $Tp^{tBu}Ni(C_6H_5)(PMe_3)_2$ (5a)

IR (Nujol, cm^{-1}): ν_{B-H} 2330, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.64 (pt, 18 H, $J_{HP(app)} = 3.8$ Hz, PMe_3), 1.48 (s, 18 H, CMe_3), 1.54 (s, 9 H, CMe_3), 5.88, 6.22, 7.40, 7.64 (d, $^3J_{HH} = 2.2$ Hz, 1, 2, 2 and 1 H, CH_{pz}), 6.91 (br m, 3H, Ph), 7.22 (br d, 1 H, $^3J_{HH} = 7.5$ Hz, Ph), 7.63 (br d, 1 H, $^3J_{HH} = 7.5$ Hz, Ph); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.3 (s, CMe_3), 31.8 (s, CMe_3), 32.2 (s, $2CMe_3$), 100.2, 104.5, 133.2, 137.5 (s, 2, 1, 2, 1 CH_{pz}), 122.2 (s), 125.6 (s), 126.0(s), 138.3(br s), 139.1 (br s) (5 CH_{Ph}), 150.8 (t, $^2J_{CP} = 37$ Hz, Ni–C), 159.8, 162.1 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −18.3 (s). Anal. Calcd. for $C_{33}H_{57}N_6BNiP_2$: C, 59.2; H, 8.6; N, 12.6. Found: C, 60.0; H, 8.6; N, 13.3.

3.2.10.2. $Tp^{tBu}Ni(C_6H_4\text{-}p\text{-}Me)(PMe_3)_2$ (5b)

IR (Nujol, cm^{-1}): ν_{B-H} 2330, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.66 (pt, 18 H, $J_{HP(app)} = 3.8$, PMe_3), 1.49 (s, 18 H, CMe_3), 1.55 (s, 9 H, CMe_3), 2.17 (s, 3H, Me), 5.88, 6.22, 7.41, 7.65 (d, $^3J_{HH} = 2.2$ Hz, 1, 2, 2 and 1 H, CH_{pz}), 6.84 (br m, 2H, C_6H_4), 7.16 (br s, 1 H, C_6H_4), 7.54 (br d, 1H, $^3J_{HH} = 7.8$ Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 20.6 (s, Me), 31.3 (s, CMe_3), 32.2 (s, CMe_3), 100.3, 104.5, 133.2, 137.5 (s, 2, 1, 2, 1 CH_{pz}), 126.8 (s), 127.2 (s), 138.1 (br s), 139.0 (br s) (C_6H_4), 131.2 (br s, CMe), 144.9 (t, $^2J_{CP} = 40$ Hz, Ni–C), 159.8, 162.1 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −18.5 (s). Anal. Calcd. for $C_{34}H_{59}N_6BNiP_2$: C, 59.8; H, 8.7; N, 12.3. Found: C, 59.7; H, 8.8; N, 12.3.

3.2.10.3. $Tp^{tBu}Ni(C_6H_4\text{-}p\text{-}OMe)(PMe_3)_2$ (5c)

IR (Nujol, cm^{-1}): ν_{B-H} 2330, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.65 (pt, 18 H, $J_{HP(app)} = 3.7$, PMe_3), 1.49 (s, 18 H, CMe_3), 1.55 (s, 9 H, CMe_3), 3.37 (s, 3H, OMe), 5.88, 6.22, 7.41, 7.63 (d, $^3J_{HH} = 2.2$ Hz, 1, 2, 2 and 1 H, CH_{pz}), 6.71 (m, 2H, C_6H_4), 7.05 (br d, 1 H, $^3J_{HH} = 8.1$ Hz, C_6H_4), 7.44 (br d, 1H, $^3J_{HH} = 8.0$ Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.2 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.2 (s, CMe_3), 31.3 (s, CMe_3), 31.8 (s, CMe_3), 32.2 (s, CMe_3), 54.2 (s, OMe), 100.2, 104.5, 133.2, 137.5 (s, 2, 1, 2, 1 CH_{pz}), 112.4 (s), 113.0 (s), 138.1 (br s), 139.0 (br s) (C_6H_4), 135.3 (t, $^2J_{CP} = 39$

Hz, Ni–C), 157.1 (s, *C*OMe), 159.8, 162.2 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −18.5 (s). Anal. Calcd. for $C_{34}H_{59}N_6BNiOP_2$: C, 58.4; H, 8.5; N, 12.0. Found: C, 57.6; H, 8.9; N, 11.8.

*3.2.10.4. $Tp^{tBu}Ni(C_6H_4$-p-$NMe_2)(PMe_3)_2$ (**5d**).* IR (Nujol, cm^{-1}): ν_{B-H} 2340, ν_{C-N} 1500; ^1H NMR (20°C, C_6D_6) δ 0.69 (pt, 18 H, $J_{HP(app)} = 3.7$, PMe_3), 1.46 (s, 18 H, CMe_3), 1.59 (s, 9 H, CMe_3), 2.58 (s, 6 H, NMe_2), 5.88, 6.18, 7.37, 7.61 (d, $^3J_{HH} = 2.2$ Hz, 1, 2, 2 and 1 H, CH_{pz}), 6.57 (m, 2 H, C_6H_4), 7.01 (br d, 1 H, $^3J_{HH} = 8.1$ Hz, C_6H_4), 7.42 (br, 1 H, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.4 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 31.3 (s, C*Me*$_3$), 31.4 (s, C*Me*$_3$), 31.8 (s, *C*Me_3), 32.2 (s, *C*Me_3), 40.4 (s, NMe_2), 100.1, 104.4, 133.1, 137.3 (s, 2, 1, 2, 1 CH_{pz}), 112.4 (s), 112.9 (s), 138.2 (br s), 139.1 (br s) (C_6H_4), 147.5 (s, $C_q(C_6H_4)$), 159.8, 162.0 (s, Cq_{pz}); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −18.6 (s). Anal. Calcd. for $C_{35}H_{62}N_7BNiP_2$: C, 59.0; H, 8.8; N, 13.7. Found: C, 59.2; H, 9.0; N, 13.6.

*3.2.10.5. Reaction of complex **5c** with $ZnCl_2$.* To a solution of complex **5c** (0.07 g, 0.1 mmol) in Et_2O (15 ml) a solution of $ZnCl_2$ (0.06 ml, 1 M solution in Et_2O, 0.06 mmol) was added. A white precipitate was formed and after 1 h of stirring, the solution was filtered and the solvent evaporated under vacuum. The residue was extracted with Et_2O, concentrated and cooled at −20°C to yield orange crystals of the complex Ni(C_6H_4-*p*-OMe)Cl(PMe_3)$_2$. From the mother liquors a white solid identified as Tp^{tBu}ZnCl was crystallised. Anal. Calcd. for $C_{21}H_{34}N_6BZnCl$: C, 52.3; H, 7.1; N, 17.4. Found: C, 52.5; H, 7.4; N, 17.6.

*3.2.11. BpNi[C(O)CH_2SiMe_3](PMe$_3$) (**6a**)*

A solution of **1a** (0.24 g, 0.65 mmol) in 30 ml of petroleum ether was bubbled with CO for 5 min at room temperature during which the appearance of a yellow microcrystalline solid was observed. The solvent was evaporated under reduced pressure leaving a yellow solid residue which crystallised from a 1:1 petroleum ether/diethyl ether mixture at −20°C to give an orange crystalline material in essentially quantitative yield. IR (Nujol, cm^{-1}): ν_{B-H} 2460–2280, ν_{C-N} 1500, ν_{C-O} 1625; ^1H NMR (20°C, C_6D_6) δ 0.67 (d, 9 H, $^2J_{HP} = 9.3$ Hz, PMe_3), 2.83 (s, CH_2), −0.06 (s, 9 H, CH_3), 5.81 (t, 2H, CH_{pz}), 7.18, 7.50 (d, 4 H, $^3J_{HH} = 2.1$ Hz, CH_{pz}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.9 (d, $^1J_{CP}$ = 28 Hz, PMe_3), 43.6 (s, CH_2), −0.9 (s, CH_3), 34.4 (s, *C*Me_3), 104.4, 135.4, 139.7 (s, CH_{pz}), 255.5 (s br, C = O); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −10.6. Anal. Calcd. for $C_{14}H_{28}N_4BNiOPSi$: C, 42.4; H, 7.1; N, 14.1. Found: C, 42.7; H, 7.0; N, 14.3.

*3.2.12. BpNi[C(O)CH_2CMe_3](PMe$_3$) (**6b**)*

Employing the same method for compound **6a**, 0.16 g (0.45 mmol) of BpNi(CH_2CMe_3)(PMe_3) underwent insertion with CO to give the product as yellow crystals in nearly quantitative yield. IR (Nujol, cm^{-1}): ν_{B-H} 2480–2280, ν_{C-N} 1500, ν_{C-O} 1600; ^1H NMR (20°C, C_6D_6) δ 0.66 (d, 9 H, $^2J_{HP} = 9.0$ Hz, PMe_3), 2.96 (s, CH_2), 0.91 (s, 9 H, CH_3), 5.82 (d, 2H, $^3J_{HH} = 2.1$ Hz, CH_{pz}), 7.12 (s br, 2 H, CH_{pz}), 7.49 (d, 2 H, $^3J_{HH} = 2.1$ Hz, CH_{pz}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.3 (d, $^1J_{CP} = 28$ Hz, PMe_3), 63.2 (s, CH_2), 29.2 (s, CH_3), 30.9 (s, *C*Me_3), 104.5, 135.3, 139.6 (s, *C*H_{pz}), 256.9 (s br, C = O); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −11.0. Anal. Calcd. for $C_{15}H_{28}N_4BNiOP$: C, 47.3; H, 7.4; N, 14.7. Found: C, 47.4; H, 7.6; N, 14.9.

*3.2.13. TpNi[C(O)C_6H_5]PMe$_3$ (**7**)*

A solution of TpNi(C_6H_5)(PMe_3) (0.12 g, 0.28 mmol) in 40 ml of a 1:1 mixture of diethylether/petroleum ether was bubbled with CO for 5 min at room temperature during which the solution took on an orange hue. The solvent was then removed under vacuum leaving an orange solid which was extracted with diethyl ether (15 ml). On cooling, orange crystals of **7** were obtained; yield 0.1 g (79%). IR (Nujol, cm^{-1}): ν_{B-H} 2450, ν_{C-N} 1510, ν_{C-O} 1620; ^1H NMR (20°C, C_6D_6) δ 0.68 (d, 9 H, $^2J_{HP} = 9.7$ Hz, PMe_3), 5.94, 7.25, 7.55 (m, 9 H, CH_{pz}), 7.0–8.4 (m, 5 H, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 14.1 (d, $^1J_{CP} = 30$ Hz, PMe_3), 104.3, 134.8, 141.1 (s, CH_{pz}), 128.0, 128.7, 131.1 (s, CH_{Ar}), 138.3 (s, Cq_{Ar}), 253.7 (s, C = O); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −10.5. Anal. Calcd. for $C_{19}H_{24}N_6BNiOP$: C, 50.4; H 5.3; N 18.6. Found: C, 50.6; H 5.3; N 18.6.

*3.2.14. Tp^*Ni[C(O)C_6H_5]PMe$_3$ (**8**)*

Following the same procedure as for **7**, 0.25 g (0.66 mmol) of the complex Ni[C(O)C_6H_5]Br(PMe_3)$_2$ was reacted with 0.23 g (0.68 mmol) of KHB(pz^*)$_3$ giving orange crystals of the expected product; yield 0.2 g (55%). IR (Nujol, cm^{-1}): ν_{B-H} 2460, ν_{C-N} 1530, ν_{C-O} 1610; ^1H NMR (20°C, C_6D_6) δ 0.78 (d, 9 H, $^2J_{HP} = 9.9$, PMe_3), 1.95 (s, 3 H, Me_{pz}), 2.17 (s, 6 H, Me_{pz}), 2.33 (s, 9 H, Me_{pz}), 5.21, 5.57 (s br, 3 H, CH_{pz}), 6.2–8.0 (m, 5 H, CH_{Ar}); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.4 (d, $^1J_{CP} = 29$ Hz, PMe_3), 12.6–15.0 (m, Me_{pz}), 105.3, 106.5, 107.1 (s, CH_{pz}), 127.9, 128.5, 131.0 (s, CH_{Ar}), 143.7, 145.7, 146.0, 146.8, 149.7 (s, Cq_{pz}), 139.0 (s, Cq_{Ar}), 254.0 (d, $^2J_{CP} = 38$ Hz, C = O); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −11.1. Anal. Calcd. for $C_{25}H_{36}N_6BNiOP$: C, 55.9; H, 6.7; N, 15.7. Found: C, 55.3; H, 6.9; N, 15.7.

3.2.15. $Tp^{tBu}Ni(COC_6H_4$-p-X)$(PMe_3)_2$

The aroyls **9** can be synthesised similarly. A typical procedure is as follows:

A solution of Ni(COC_6H_5)Br(PMe_3)$_2$ (0.17 g, 0.43 mmol) in THF (20 ml) cooled to −20°C, was treated with a solution of $TlTp^{tBu}$ (0.25 g, 0.43 mmol) dissolved in THF (10 ml). The mixture was stirred at low

temperature for 2 h. The solvent was removed in vacuo at 0°C and the residue extracted with petroleum ether (20 ml) and filtered off. After concentration and cooling at −20°C yellow crystals of complex **9a** were obtained (yield 67%).

*3.2.15.1. $Tp^{tBu}Ni(COC_6H_5)(PMe_3)_2$ (**9a**).* IR (Nujol, cm^{-1}): ν_{B-H} 2390, ν_{C-N} 1510, ν_{C-O} 1610; ^1H NMR (20°C, C_6D_6) δ 0.69 (pt, 18 H, $J_{HP(app)} = 3.6$ Hz, PMe_3), 1.47 (s, 18 H, CMe_3), 1.61 (s, 9 H, CMe_3), 5.85 (br s), 6.21 (br s), 7–8 (m) (1, 2 and 3 H, CH_{pz}), 7–8 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 12.9 (pt, $J_{CP(app)} = 13$ Hz, PMe_3), 31.2 (s, C*Me*$_3$), 31.4 (s, C*Me*$_3$), 32.1 (s, *C*Me$_3$), 100.4, 104.5, 132.9, 137.0 (s, 2, 1, 2, 1 CH_{pz}), 128.2 (s), 131.7 (s), 134.0 (s) (C_6H_5), 138.9 (t, $^3J_{CP} = 7$ Hz, CO*C*), 160.1, 162.2 (s, Cq_{pz}), 254.2 (t, $^2J_{CP} = 27$ Hz, CO); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −19.5 (s). Anal. Calcd. for $C_{34}H_{57}N_6BNiOP_2$: C, 58.6; H, 8.2; N, 12.1. Found: C, 58.6; H, 8.3; N, 12.1.

*3.2.15.2. $Tp^{tBu}Ni(COC_6H_4$-p-Me$)(PMe_3)_2$ (**9b**).* IR (Nujol, cm^{-1}): ν_{B-H} 2390, ν_{C-N} 1510, ν_{C-O} 1600; ^1H NMR (20°C, C_6D_6) δ 0.72 (pt, 18 H, $J_{HP(app)} = 3.9$ Hz, PMe_3), 1.99 (s, 3 H, Me), 1.47 (s, 18 H, CMe_3), 1.62 (s, 9 H, CMe_3), 5.86 (d), 6.23 (d), 7.49 (d), 7.52 (br s) ($^3J_{HH} = 2.2$ Hz, 1, 2, 2, 1 H, CH_{pz}), 7.0–7.7 (m, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.0 (pt, $J_{CP(app)} = 13$ Hz, PMe_3), 21.1 (s, Me), 31.2 (s, C*Me*$_3$), 31.5 (s, C*Me*$_3$), 31.7 (s, *C*Me$_3$), 32.2 (s, *C*Me$_3$), 100.3, 104.5, 132.9, 137.0 (s, 2, 1, 2, 1 CH_{pz}), 128.9 (br s, C_6H_4), 137.0 (s, C_q), 142.1 (s, C_q), 160.1 (s, Cq_{pz}), 162.1 (s, Cq_{pz}), 253.3 (t, $^2J_{CP} = 26$ Hz, CO); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −19.5 (s). Anal. Calcd. for $C_{35}H_{59}N_6BNiOP_2$: C, 59.1; H, 8.3; N, 11.8. Found: C, 58.9; H, 8.4; N, 11.6.

*3.2.15.3. $Tp^{tBu}Ni(COC_6H_4$-p-OMe$)(PMe_3)_2$ (**9c**).* IR (Nujol, cm^{-1}): ν_{B-H} 2390, ν_{C-N} 1510, ν_{C-O} 1605; ^1H NMR (20°C, C_6D_6) δ 0.74 (pt, 18 H, $J_{HP(app)} = 3.9$ Hz, PMe_3), 3.22 (s, 3H, OMe), 1.49 (s, 18 H, CMe_3), 1.63 (s, 9 H, CMe_3), 5.87 (d), 6.22 (d), 7.43 (d), 7.46 (br s) ($^3J_{HH} = 2.2$ Hz, 1, 2, 2, 1 H, CH_{pz}), 6.5–7.0 (m, C_6H_4); $^{13}C\{^1H\}$ NMR (20°C, C_6D_6) δ 13.7 (pt, $J_{CP(app)} = 14$ Hz, PMe_3), 54.8 (s, OMe), 31.3 (s, C*Me*$_3$), 31.4 (s, C*Me*$_3$), 31.7 (s, *C*Me$_3$), 32.2 (s, *C*Me$_3$), 100.4, 104.5, 132.9, 136.7 (s, 2, 1, 2, 1 CH_{pz}), 112–140 (br, C_6H_4), 133.3 (t, $^3J_{CP} = 6$ Hz, C(O)*C*), 162.6 (s, *C*OMe), 160.3 (s, Cq_{pz}), 162.2 (s, Cq_{pz}), 251.1 (t, $^2J_{CP} = 27$ Hz, CO); $^{31}P\{^1H\}$ NMR (20°C, C_6D_6) δ −19.3 (s). Anal. Calcd. for $C_{35}H_{59}N_6BNiO_2P_2$: C, 57.8; H, 8.2; N, 11.6. Found: C, 56.9; H, 8.0; N, 11.2.

*3.3. X-ray structure determinations of **3a** and **5b***

Crystals (red (**3a**) or yellow (**5b**)) of prismatic shape were coated with an epoxi resin and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and Pd were taken from the literature [32]. The structure was solved by Patterson and Fourier methods in the centrosymetric $P2_1/n$ space group. An empirical absorption correction [33] was applied at the end of the isotropic refinements. As can be seen in the values of the thermal parameters for **5b**, there exists some non resolvable disorder in the C atoms of the *t*-Butyl groups due to their thermal motions. A final refinement was undertaken with unit weight and anisotropic thermal motion for all atoms except the hydrogen atoms that have been refined isotropically. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in ΔF vs. F_o or sin θ/λ was observed. Final difference synthesis showed no significant electron density (no greater than 0.40 e $Å^{-3}$ for **5b**). Most of the calculations were carried out with the *X-Ray 80* system [34]. Atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographyc Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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