# **Pyrazolyl- and Hydrocarbyl-Bridged Binuclear Complexes of Nickel**

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The binuclear nickel complex Ni<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>- $\sigma$ -C<sub>6</sub>H<sub>4</sub>) (1) reacts with pyrazolyllithium (LiPz) to give the  $\mu$ -pyrazolyl  $\mu$ -hydrocarbyl compound Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br( $\mu_2 - \eta^3 : \eta^1 - \eta^3$  $CH_2$ -o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -Pz) (2). X-ray studies show a short Ni–Ni distance (2.710(2) Å) which suggests the existence of some bonding interaction. The bromide ligand of compound 2 can be replaced by anionic ( $N_3^-$ , 2,5-dimethylpyrrolide) or neutral (PMe<sub>3</sub>, Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) ligands. Other related complexes containing methyl or *tert*-butyl substituents on the 3-position or on the 3- and 5-positions of the pyrazolate ligand can be obtained using the corresponding pyrazolylthallium derivatives. The monosubstituted pyrazole complexes exist in solution as equilibrium mixtures of two isomers which differ in the relative position of the pyrazolate substituent. However, only one isomer has been isolated in the solid state.

## Introduction

The study of hydrocarbon- and hydrocarbyl-bridged di- or polynuclear complexes is a rapidly developing field of research in organometallic chemistry.<sup>1</sup> Much of the interest in these compounds arises in ascertaining whether the coordination of an organic fragment to two or more metal centers may allow the observation of new reactivity patterns, significantly different from those present in the related mononuclear complexes. Because of the possible cooperative effects between the two metal atoms, the chemical properties of the hydrocarbonbridged binuclear complexes have been recognized as midway between those of mononuclear species and of high-nuclearity clusters.<sup>1a,c</sup>

In recent publications, we have described the chemistry of the binuclear nickel complex 1, which contains the bridging  $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub> unit.<sup>2</sup> The coupling of



acyl and iminoacyl functionalities, and the migration of an inserted iminoacyl group, observed during the



course of these studies,<sup>2d</sup> are very likely caused by the mutual action of the two reactive nickel centers. The bonding mode of the  $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub> unit was found to be very sensitive to the number and nature of the coligands attached to the nickel atoms. Thus, 1 can add a fourth PMe<sub>3</sub> ligand in solution, giving rise to the labile species  $(Me_3P)_2Ni(Br)(\mu_2-\eta^1:\eta^1-CH_2-o-C_6H_4)Ni(Br)(P-$ Me<sub>3</sub>)<sub>2</sub>,<sup>2b</sup> or react with 2 equiv of bis(dimethylphosphino)methane (dmpm) to yield Ni<sub>2</sub>( $\mu_2$ -dmpm)<sub>2</sub>( $\mu_2$ - $\eta^1$ : $\eta^1$ -CH<sub>2</sub>o-C<sub>6</sub>H<sub>4</sub>).<sup>2a</sup> In these two complexes, the benzylic moiety acts as a  $\eta^1$  ligand.

As a continuation of these studies, we have probed the coordination chemistry of pyrazolate-type ligands in this system. Pyrazole and pyrazolate units have attracted much attention due to their versatile coordination chemistry.<sup>3</sup> These ligands were judged to be especially attractive for this study, for they can firmly hold two metal atoms at short distances, thereby allowing extensive electron delocalization between the two centers. The pyrazolate (Pz<sup>-</sup>) group can be monodentate,<sup>4</sup> or it can act as a bridging ligand. In the latter case, two Pz rings can bind two identical5a-d (I, Chart 1) or less frequently two different<sup>5e-h</sup> metal fragments

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(II). Complexes containing only one bridging Pz-type ligand are less common and contain usually another bridging group (III).<sup>5i-k</sup> In this paper we describe the synthesis and properties of some complexes of nickel of type III, in which a hydrocarbyl chain is the second bridging ligand.

### **Results and Discussion**

Synthesis and Structural Characterization of the Pyrazolate Complex Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -Pz) (2). The reaction of the binuclear complex 1 with 1 equiv of pyrazolyllithium (LiPz) in THF leads to the formation of the red crystalline material 2, which can be isolated in 73% yield (eq 1).



Analytical data and NMR studies show the incorporation of the Pz ring with concomitant dissociation of one of the PMe<sub>3</sub> ligands of **1**. Thus, the  ${}^{31}P{}^{1}H{}$  NMR spectrum of 2 consists of a weakly coupled AX spin system ( $J_{PP} = 4.5$  Hz), while the <sup>1</sup>H and the <sup>13</sup>C{<sup>1</sup>H} NMR spectra display two doublets of equal intensity in the region due to the PMe<sub>3</sub> ligands (see Experimental Section). The Pz ring is responsible for three <sup>1</sup>H multiplets at  $\delta$  5.91, 6.77, and 7.83 ppm that are integrated for a single proton each, while the CH<sub>2</sub> protons of the o-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> unit give an AB system in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum ( $\delta$  2.20 and 2.33 ppm, <sup>2</sup>J<sub>HH</sub> = 3.4 Hz), which further splits by coupling to only one <sup>31</sup>P nucleus ( $J_{H_{A}P} = 7.4$ ;  $J_{H_{B}P} = 3.4$  Hz). In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the CH<sub>2</sub> carbon appears at lower field than expected for a Ni $-\eta^1$ -benzyl unit (30.5 vs 0–20  $ppm^{2a,6,7}$ ) and it is also coupled to only one <sup>31</sup>P nucleus  $(J_{CP} = 10 \text{ Hz})$ . All these data taken together with the value of 152 Hz found for the  ${}^{1}J_{CH}$  coupling constant<sup>6</sup> suggest the presence in the molecule of **2** of an  $(\eta^3$ benzyl)nickel moiety and of a bridging pyrazolate ligand. This assumption has been confirmed by X-ray studies. Figure 1 shows an ORTEP view of the molecules of this

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Figure 1. ORTEP view and atom-labeling scheme of compound 2.

Table 1. Selected Bond Distances and Angles for 2

Bond Distances (Å)			
Ni1-P1	2.132(4)	Ni2-P2	2.154(4)
Ni1-N1	1.90(1)	Ni2-N2	1.91(1)
Ni1-C1	2.13(1)	Ni2-C1	1.91(1)
Ni1-C2	2.08(1)	N1-N2	1.36(1)
Ni1-C7	1.93(1)	Cl-C2	1.43(2)
Ni2-Br	2.381(3)	C2-C7	1.46(2)
Ni1 –Ni2	2.710(2)		
Bond Angles (deg)			
C2-Ni1-C7	42.3(5)	P2-Ni2-N2	170.2(3)
C1-Ni1-C7	73.4(5)	Br-Ni2-C1	176.7(4)
C1-Ni1-C2	39.7(5)	Br-Ni2-N2	91.4(3)
N1-Ni1-C7	158.4(5)	Br-Ni2-P2	91.0(1)
N1-Ni1-C2	123.2(5)	Ni1-N1-N2	104.8(7)
N1-Ni1-C1	87.0(4)	Ni2-N2-N1	116.0(8)
P1 -Ni1 -C7	95.0(4)	Ni1-C1-Ni2	84.2(4)
P1-Ni1-C2	134.8(3)	Ni2-C1-C2	128.1(9)
P1-Ni1-C1	162.9(3)	Ni1-C1-C2	68.4(7)
P1-Ni1-N1	101.9(3)	Ni1-C2-C1	71.9(7)
N2-Ni2-C1	89.1(5)	C1-C2-C7	115.0(1)
P2-Ni2-C1	88.9(4)	Ni1-C7-C2	74.2(7)

compound; selected bond distances and angles are listed in Table 1. The central core of the structure of this complex is composed of two Ni(II) units bridged by the pyrazolate and the hydrocarbyl  $CH_2$ -o- $C_6H_4$  ligand. Both nickel atoms are in square-planar environments, but the coordination of the benzyl-bound Ni atom deviates considerably from the ideal square-planar geometry due to its pseudoallylic coordination to the  $CH_2$ -o- $C_6H_4$  ligand.

An interesting structural feature of compound **2** is the coordination of the Ni1 atom to C1 instead of C3. Generally, in  $\eta^3$ -benzyl complexes that have an *ortho* substituent with respect to the CH<sub>2</sub> group, the  $\eta^3$ -allylic coordination involves the less hindered unsubstituted *ortho* carbon,<sup>2a,6a,b</sup> as exemplified by the structure of **1**. The more encumbered coordination mode adopted may be a consequence of the intrinsic nature of the  $\mu_2$ -Pz ligand, which due to the shortness of the N–N bond cannot embrace two metal centers that are too far away from each other.

Compound **2** is a rare example of a binuclear complex containing  $\mu_2 \cdot \eta^3 : \eta^1$  allyl ligands of type **A** or **B**.<sup>1a</sup> On the assumption that there is no Ni–Ni bonding interaction, **2** would be the first example of a species with structure **A**; complexes of type **B** have been reported.<sup>8</sup>

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Pyrazolyl- and Hydrocarbyl-Bridged Complexes of Ni



Ni-Ni bonds can be found in a wide variety of binuclear compounds, in which the metal can have the oxidation state  $0,^{9a}$  1+, $^{9b,c,10}$  or 2+. $^{9d-f}$  Although the nature of the metal-metal bonding in these compounds is in general not fully understood on theoretical grounds,<sup>11a</sup> the observed Ni-Ni bond lengths have been rationalized in terms of the electron count at the metal centers and of the type of bridging ligands.<sup>11b</sup> Ni-Ni bond lengths shorter than 2.4 Å<sup>12</sup> have been observed when both metal centers attain a 16-electron configuration (e.g. [Ni(Cl)(*u*-C(SiMe<sub>3</sub>)(PMe<sub>3</sub>))]<sub>2</sub>, 2.28(1) Å<sup>9c</sup>), but Ni-Ni bond lengths as long as 2.788 Å<sup>9f</sup> have been found in binuclear complexes of nickel with 18-electron counts on both metal centers. Although the relatively short Ni-Ni distance in 2, 2.710 Å, which is shorter than twice the van der Waals radius of Ni (1.60 Å<sup>13</sup>), could be indicative of a weak bonding interaction, the metal centers could be also brought into close contact by the proximity of the N atoms of the bridging pyrazolate ligand<sup>14</sup> and by conformational restrictions arising from the pseudoallylic fragment. In order to ascertain the hypothetical metal-metal distance in the absence of the above ligand strain or bonding effects, we have constructed a molecular model<sup>15</sup> of the Ni( $\mu$ -C<sub>6</sub>H<sub>7</sub>)Ni core using bond lengths and angles derived from  $Ni(\eta^3$ -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-o-CH<sub>3</sub>)(PMe<sub>3</sub>)(Cl)<sup>6a</sup> for the pseudoallyl unit and from the related binuclear complex Ni(Br)(PMe<sub>3</sub>)<sub>2</sub>- $(\mu - \eta^1: \eta^1 - C_6H_4 - p - CH_2)Ni(Br)(PMe_3)_2^{6b}$  for the Ni-aryl bond length (Figure 2). As can be seen, there is only a minor structural change on going from the model to 2. However, the Ni-Ni distance predicted by the model is 0.13 Å longer than in 2, indicating that some forces overcome any steric repulsions between the metal fragments.

Since the Ni2-C1 distance used in the model (1.881 Å) is close to that of **2** (1.91(1) Å), the shorter Ni–Ni distance of the latter must be attributed to differences in the pseudoallylic units. Within these, comparison of the Ni1-C2 or the Ni1-C7 distances of the model and **2** reveals that they are the same within the experimen-



**Figure 2.** Experimental and modeled Ni(*u*-C<sub>6</sub>H<sub>7</sub>)Ni core of 2.

tal error. However, Ni1-C1 is significantly shorter in 2; therefore, one reaches the conclusion that it is the distortion of the pseudoallylic unit of 2 which allows both nickel atoms to approach. It would appear reasonable that the distortion of the pseudoallylic unit is a consequence of electronic effects rather than the imposition of ligand constraints. Since it has been proposed that for high-electron-count metals a bridging,  $\pi$ -acceptor ligand can increase the metal-metal bonding order by accepting electron density from the metal-metal antibonding orbitals, 9a, 10, 16 the relatively short Ni1-C1 distance could be explained as a consequence of the reinforcement of the retrodonation component of this bond. Thus, a weak Ni-Ni interaction seems a likely proposal.

Analogous Complexes with Substituted Pyrazolate Ligands. As shown in Scheme 1, complexes 3, which are similar to 2 but contain pyrazolate groups with Me or t-Bu substituents in the ring 3- or 3,5positions, can be readily prepared by the reaction of 1 with the thallium salt of the appropriate pyrazole. Since thallium pyrazolates can be generated *in situ* by addition of TIOEt to a THF solution of the pyrazole,<sup>17</sup> this is a simple and convenient synthetic procedure for the generation of the corresponding thallium pyrazolates. Not unexpectedly, in the case of the monosubstituted 3-methyl (Pz') and 3-tert-butyl (Pz\*) pyrazolates, the reaction results in a mixture of two isomers, 3a/3b and 3d/3e, respectively.

The Me-substituted pyrazolate (Pz' and Pz") complexes 3a/3b and 3c are red-brown crystalline solids, with physical appearance similar to that of 2, while the tert-butyl pyrazolate (Pz\* and Pz\*\*) derivatives form dark purple, nearly black crystals. However, they all exhibit NMR features similar to those of 2. For instance, they display chemically inequivalent methylene protons which give rise to two multiplets in the 1.8-2.5 ppm range in the proton NMR spectra, which arise from the mutual coupling of these protons and from coupling to one of the phosphorus nuclei. The corresponding <sup>13</sup>C methylene resonance appears at a chemical shift similar to that of 2 (27-30 ppm); large values of  ${}^{1}J_{CH}$  (145–157 Hz) and small values of  ${}^{2}J_{HH}$  (3.3–

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<sup>(14)</sup> Bridging pyrazole ligands allow long metal–metal distances. For example, in the anionic complex  $[{\rm Ni}(C_6F_5)_2](\mu$ -OH)( $\mu$ -Pz)],  $^{5f}$  the long Ni–Ni distance (3.263 Å) rules out metal–metal bonding.

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Figure 3. Phosphine-pyrazole NOE interaction in compound 2.



3.9 Hz) for this methylene group also support the pseudoallylic coordination of the benzylic fragment. From the <sup>13</sup>C{<sup>1</sup>H} NMR spectra it can also be inferred that the pseudoallylic Ni atom is situated as well on the substituted side of the aromatic ring, i.e. close to the arylic nickel unit, since only the pyrazole C(4)Hresonance can be found in the 95-120 ppm region. Long-range through-ligand PP coupling ( $J_{PP} = 5-6$  Hz) was also observed in the  ${}^{31}P{}^{1}H{}$  NMR spectra of **3a**f.

As mentioned before, the reaction of 1 with the monosubstituted thallium pyrazolates TlPz' and TlPz\* affords mixtures of two isomers which differ in the position of the pyrazole substituent. The assignation of a precise structure to each isomer can be done with a combination of chemical shift analysis of the proton NMR signals of the pyrazole substituents and NOE experiments.

As shown in Figure 3, a NOE intensity enhancement of one of the pyrazole proton signals of compound 2 is to be expected when the phosphine proton resonance becomes saturated. A similar effect was also detected on the minor isomer of the 3a/3b mixture, for which structure **3b** can be therefore proposed. Interestingly, <sup>1</sup>H and <sup>13</sup>C signals corresponding to the substituents on the 3-position of the pyrazolate ligands of 2 and 3a/

3b are significantly shifted upfield as compared to those on the 5-position (e.g. 7.83 ppm for H(3) in 3b vs 6.77 ppm for H(5) in **3a**). Similar observations on the chemical shifts of the analogous signals of the 3d/3e mixture indicate that the major isomer is 3d. Therefore, the bulkier pyrazole substituent is bonded to the C atom closer to the  $\eta^3$ -benzyl-Ni fragment (Ni1, Figure 1), avoiding in this way the repulsion with the also sterically demanding Br ligand bonded to the other Ni atom (Ni2).

The NMR spectra of the **3a/b** and **3d/e** mixtures are sharp at room temperature, and therefore no isomer exchange takes place on the NMR time scale under these conditions. Since the 3a/3b and 3d/3e isomer ratios appear to be constant from one preparation to other, it would appear likely that these isomers are in equilibrium (eq 2). While the rate of exchange is too



slow to allow line-broadening observation, it is fast enough to be detected by spin saturation transfer (SST) experiments.<sup>18a</sup> Thus, saturation at room temperature of the Pz' methyl signal of one of the isomers of the 3a/ **3b** mixture causes a ca. 10% intensity decrease of the analogous signal on the other isomer. In order to directly observe the transformation between **3a** and **3b**, a solid sample obtained by crystallization of a solution of the isomeric mixture was redissolved in cold CD<sub>2</sub>Cl<sub>2</sub>  $(-80 \degree C)$  and its <sup>1</sup>H NMR spectrum registered at various temperatures. Below -30 °C, pure solutions of **3a** were observed, but at 0 °C, smooth isomerization to 3b occurs, until the equilibrium concentrations are reached. This process follows first-order kinetics with  $k_1 = 5.3 \times 10^{-4}$  ${
m s}^{-1}$  and  $k_{-1}=9.8$  imes 10<sup>-4</sup>  ${
m s}^{-1}.^{18b}$ 

In a formal sense, the exchange between 3a/3b and 3d/3e isomers can be viewed as a rotation of the bridging pyrazole ligand through an axis that bisects the N-N bond, and it can also be detected on those derivatives that contain symmetrically substituted pyrazolate ligands (e.g. 3c) by means of SST experiments. This type of exchange has also been observed previously in the Pd complexes  $[{(C_6F_5)_2Pd}_2(\mu-L)]_2^{2-}$  (L = Pz, Pz', triazolate, indazolate).<sup>5c</sup> In donor solvents, the analogous Ni compounds<sup>5f</sup> dissociate into two  $[(C_6F_5)_2N_1]$ (Pz)(S)<sup>-</sup> units (S = CD<sub>3</sub>COCD<sub>3</sub>), which then undergo fast Pz ligand exchange even at -70 °C. Due to the fact that in complexes with  $\eta^1$ -pyrazolate,  $\eta^1$ -pyridazine, and other related ligands the metal atom can readily jump from one nitrogen atom to the adjacent one,<sup>19</sup> it would appear likely that a similar, solvent-mediated dissociation process could be responsible for the dynamic

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behavior detected in the Pd complexes. However, for Ni and Pd, dissociation of the Pz ligand from one of the metal centers usually requires an associative process,<sup>20</sup> with participation of a donor molecule to complete the 16-electron shell of the metal center. Since the isomerization kinetics of **3a** and **10a** was measured in CD<sub>2</sub>-Cl<sub>2</sub>, one has to speculate that either the solvent fulfills these improbable donor requirements or the exchange requires at some stage an additional electron output from the benzyl ligand.<sup>21</sup> While we have not pursued this problem any further, we have studied the influence of added PMe<sub>3</sub> on this isomerization reaction (see below).

Some Chemical Properties of Compounds 2 and **3.** We have considered the possibility of derivatizing compounds 2 and 3a - e by replacing the bromine atom with other substituents. The halide anion can be easily substituted by other halides or pseudohalides  $(N_3^-)$ , or azolate ligands such as 2,5-dimethylpyrrolyl, giving rise to compounds 4 and 5 (Scheme 2). NMR data for these complexes are similar to those already discussed for 2 and merit no further comment, except perhaps to note that in compound 5 restricted rotation around the Ni-N bond of the Ni-pyrrolyl linkage makes the two methyl groups inequivalent. Several attempts aimed at the preparation of alkyl, aryl, and alkynyl derivatives have proved unsuccessful, but the reaction of 2 with NaCp or TlCp gives rise to the bis(cyclopentadienylnickel) complex 6, independent of the reagent ratio (Scheme 2). The latter behavior contrasts with that of compound **1**, which selectively reacts with 1 equiv of NaCp to give Ni(Cp)(PMe<sub>3</sub>)(*u*-CH<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>)Ni(PMe<sub>3</sub>)<sub>2</sub>Br.<sup>6b</sup> Compound 6 can also be obtained from 1 using 2 equiv of NaCp and prolonged reaction times.

Compound **2** reacts with an excess of PMe<sub>3</sub>, at room temperature, to give the known binuclear species [Ni- $(Br)(PMe_3)_2(\mu$ -C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)]<sub>2</sub><sup>6b</sup> (**7**), together with other uncharacterized products (eq 3). Binuclear **7** has been reported to form in the reaction of and **1** and PMe<sub>3</sub><sup>2c</sup> as a result of a disproportionation process which appears to be characteristic of nickel benzyl complexes.<sup>6a</sup> However, the low-temperature reaction (-60 °C) of **2** and equimolecular amounts of PMe<sub>3</sub> can be shown by <sup>31</sup>P-



{<sup>1</sup>H} NMR spectroscopy to produce a new species, **8**, which has been isolated as the BPh<sub>4</sub><sup>-</sup> salt (Scheme 3). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **8** are very similar to those of **2**, except for the presence of a new PMe<sub>3</sub> ligand, which is for example evidenced by the observation of a nickel  $\sigma$ -bonded quaternary aromatic carbon signal as a doublet of doublet of doublets, with the largest constant (<sup>2</sup>*J*<sub>CP</sub> = 72 Hz) being indicative of a *trans*-type coupling. Three signals (intensity ratio 1:1:1) are observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum: two doublets ( $\delta$  -7.7, *J*<sub>PP</sub> = 6 Hz;  $\delta$  -16.4, *J*<sub>PP</sub> = 49 Hz) and a doublet of doublets ( $\delta$  -10.0, *J*<sub>PP</sub> = 6 and 49 Hz). Interestingly enough, these cationic species can delocalize the positive charge on both metal centers, as described by resonance forms **C** and **D**.



A related cationic complex, 9 (Scheme 3), can be obtained by the reaction of **2** with the chelating diphosphine 1,2-bis(dimethylphosphino)ethane (dmpe), and it is best isolated in a pure, crystalline form, following substitution of the Br<sup>-</sup> counterion by BPh<sub>4</sub><sup>-</sup>. In a similar manner, treatment of CD<sub>2</sub>Cl<sub>2</sub> solutions of 3a/ **3b** with PMe<sub>3</sub> results in the formation of the corresponding cationic complexes, once again isolated as BPh<sub>4</sub><sup>-</sup> salts. Complexes **10a** and **10b** also interconvert in solution, but their interchange is somewhat slower than that observed for the 3a/3b couple, no magnetization transfer being detected between the methyl signals of the former pair of isomers. The crystalline solid obtained from 10a/10b solutions contains only one of the isomers, for which structure 10a can be proposed on the basis of the chemical shift arguments discussed previously. If a sample of solid **10a** is dissolved in CD<sub>2</sub>-Cl<sub>2</sub> and its proton NMR spectrum is immediately recorded, only pure 10a is observed. A smooth isomerization process ensues at room temperature, which leads to the isomeric mixture with 10a and 10b in a ca. 1.1:1 ratio (eq 4). The rate constants for this process have



values of  $k_1 = 2.3 \times 10^{-4}$  and  $k_{-1} = 2.8 \times 10^{-4} \text{ s}^{-1}$  at 20 °C and are not affected by the presence of the PMe<sub>3</sub> scavenger PdCp( $\eta^3$ -C<sub>3</sub>H<sub>7</sub>). It is worth mentioning at this stage that the rate of exchange between **3a** and **3b**,

<sup>(20)</sup> Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1987.

<sup>(21)</sup> The ability of the benzyl ligand to compensate highly electrondeficient situations is well-documented. For a recent example see: Pellechia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773.



Scheme 4



measured at 0 °C, increases markedly in the presence of PMe<sub>3</sub>; the addition of 0.009 mmol of PMe<sub>3</sub> makes the interconversion fast enough to prevent the determination of the reaction rate by the above-described method, while line broadening in the NMR spectra due to the presence of the free ligand makes the use of SST methods unreliable. A similar observation holds for isomerization of 10a into 10b. A variety of Ni complexes containing the PMe<sub>3</sub> ligand are known to undergo fast ligand exchange catalyzed by small amounts of PMe<sub>3</sub>.<sup>22</sup> On these grounds, the pyrazolate "rotation" can be proposed to proceed as depicted in Scheme 4, at least in the case of the  $10a \Rightarrow 10b$  interconversion. Added PMe<sub>3</sub> can displace the bridging Pz' ligand from one of the Ni atoms; the monodentate Pz' group then readily undergoes a facile N1-N2 shift. Rotation about the Ni<sub>a</sub>-N bond, followed by coordination of the second N atom of the Pz' ligand to Nib, would render the other isomer. As for the  $3a \Rightarrow 3b$  isomerization, a similar mechanism could be proposed in which the Br<sup>-</sup> ligand displaced by the added PMe<sub>3</sub> would induce the bidentate to monodentate change in the coordination of the added Pz' ligand. However, neither the isomerization rate of 3a nor that of 10a is affected by the presence of CpPd- $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>), an efficient phosphine sponge.<sup>10</sup> Thus, different mechanisms seem to operate in the presence and the absence of added PMe<sub>3</sub>. So far, we are unable to propose a mechanism for the second situation, but the difference between the  $3a \rightleftharpoons 3b$  and the  $10a \rightleftharpoons 10b$  exchange rates indicates that the nature of the second-ary ligands on the arylic nickel atom can influence the rate of isomerization. Clearly, more detailed research on the effect of different neutral and anionic coligands and on the solvent effect will be required to unravel the nature of this interesting process.

#### **Experimental Section**

Microanalyses were performed by Pascher Microanalytical Laboratory, Remagen, Germany, and the Analytical Service of the University of Seville. The spectroscopic instruments used were Perkin-Elmer Models 577 and 684 for IR spectra and Bruker AMX-300 and AMX-500 for NMR spectroscopy. The <sup>13</sup>C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to SiMe<sub>4</sub>. The  ${}^{13}C{}^{1}H$  NMR assignments were helped in most cases with the use of gate decoupling techniques. <sup>31</sup>P{<sup>1</sup>H} NMR shifts are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40-60 °C. Lithium pyrazolate was obtained by reacting *n*-BuLi with pyrazole, and NaCp was prepared from NaH and freshly cracked dicyclopentadiene. Compound 1 was prepared according to the reported procedure.2b

Synthesis of Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>) (2). To a cold (-60 °C) solution of 1 (0.6 g, 1 mmol) in THF (50 mL) was added lithium pyrazolate (1 mmol, 2 mL of a 0.5 M solution in THF). The original red color of 1 changed to purple. The cooling bath was removed, and when it was warmed, the solution developed a red coloration again. After it was stirred at room temperature for 5 min, the reaction mixture was taken to dryness and the residue extracted with toluene. This operation was repeated twice, and after filtration, concentration, addition of some petroleum ether, and cooling to -20 °C, compound 2 was obtained as red crystals. Yield: 73%. Anal. Calcd for C<sub>16</sub>H<sub>27</sub>N<sub>2</sub>BrP<sub>2</sub>Ni<sub>2</sub>: C, 37.9; H, 5.3; N, 5.5. Found: C, 38.2; H, 5.3; N, 4.7. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  0.99 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.2 Hz, PMe<sub>3</sub>), 1.42 (d, 9 H,  ${}^{2}J_{\rm HP} = 9.2$  Hz, PMe<sub>3</sub>), 2.20 (dd, 1 H,  ${}^{2}J_{\rm HH} = 3.4$ ,  ${}^{3}J_{\rm HP} = 7.8$  Hz, CH<sub>2</sub>), 2.33 (pt, 1 H,  ${}^{2}J_{\rm HH} \approx {}^{3}J_{\rm HP} = 3.8$  Hz, CH<sub>2</sub>), 5.91 (dd, 1 H,

<sup>(22)</sup> Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883.

 ${}^{3}J_{HH} = 2.0, J_{HP} = 3.2$  Hz, H(4) pyraz), 6.77 (d, 1H,  ${}^{3}J_{HH} = 0.9$ Hz, H pyraz), 6.84 (dm, 1 H,  ${}^{3}J_{HH} = 6.8$  Hz, aromatic), 7.03 (m, 2 H, aromatics), 7.79 (m, 1 H,  ${}^{3}J_{HH} = 6.6$  Hz, aromatic), 7.83 (d, 1 H,  ${}^{3}J_{HH} = 2.0$  Hz, H pyraz).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AX spin system,  $\delta_{A} = -11.8, \delta_{X} = -9.8, J_{AX} = 5$  Hz.  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  15.8 (d,  ${}^{1}J_{CP} = 32$  Hz, PMe<sub>3</sub>), 15.8 (d,  ${}^{1}J_{CP} = 27$  Hz, PMe<sub>3</sub>), 30.4 (d,  ${}^{2}J_{CP} = 10, {}^{1}J_{CH} = 152$  Hz, CH<sub>2</sub>), 103.4 (s, C(4)H pyraz), 122.8 (dd,  ${}^{2}J_{CP} = 19$  and 42 Hz, C<sub>q</sub> arom-Ni), 124.0, 124.7, 128.8, 144.7 (s, CH aromatics), 126.8 (d,  ${}^{2}J_{CP} = 5$  Hz, C<sub>q</sub> arom), 140.0 (s, CH pyraz).

Synthesis of Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ - $N_2C_3HRR'$ ) (R = H, R' = Me, 3a,b; R = R' = Me, 3c; R = H,  $\mathbf{R}' = \mathbf{B}\mathbf{u}^{\mathsf{t}}, \mathbf{3d}, \mathbf{e}; \mathbf{R} = \mathbf{R}' = \mathbf{B}\mathbf{u}^{\mathsf{t}}, \mathbf{3f}$ . The preparation of these compounds involves the reaction of 1 with the corresponding thallium pyrazolate salts. A representative example of the experimental procedure employed to synthesize 3a(b) is as follows: Thallium 2-methylpyrazolate was generated by the reaction of 2-methylpyrazole (0.12 mL, 1.5 mmol) with thallium ethoxide (1.5 mmol, 1.5 mL of a 1 M solution in THF) in THF at low temperature (-40 °C). The cooling bath was then removed, and the mixture was stirred until it reached room temperature and added to a stirred solution of 1 (0.9 g, 1.5 mmol) in THF (50 mL) cooled to -60 °C. The resulting red suspension was slowly warmed and stirred at room temperature for 30 min. The solvent was removed under vacuum and the residue extracted with Et<sub>2</sub>O. After centrifugation and concentration of the solution, cooling to -30 °C furnished red crystals of complex 3a in 86% yield. Dissolution of these crystals at room temperature affords equilibrium mixtures of 3a and 3b.

The complexes **3c** and **3d/3e** were similarly prepared and isolated as dark red crystals in 70% and 90% yield, respectively. The more soluble compound **3f** was crystallized from petroleum ether as purple crystals in 60% yield.

**Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br(\mu\_2-\eta^3:\eta^1-CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)(\mu\_2-N<sub>2</sub>C<sub>3</sub>H<sub>2</sub>Me) (3a/b). Anal. Calcd for C<sub>17</sub>H<sub>29</sub>N<sub>2</sub>BrP<sub>2</sub>Ni<sub>2</sub>: C, 39.2; H, 5.6; N, 5.4. Found: C, 39.3; H, 5.8; N, 5.7.** 

**3a**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  0.99 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.0 Hz, PMe<sub>3</sub>), 1.44 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.2 Hz, PMe<sub>3</sub>), 1.74 (s, 3 H, Me pyraz), 2.12 (m, 1 H, CH<sub>2</sub>), 2.14 (m, 1 H, CH<sub>2</sub>), 5.68 (m, 1 H, H(4) pyraz), 6.90 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, aromatic), 7.0 (m, 2 H, aromatics), 7.70 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 1.5 Hz, H pyraz), 7.70 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, aromatic); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) AX spin system,  $\delta_A = -12.1$ ,  $\delta_X = -10.3$ ,  $J_{AX} = 5$  Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  13.1 (s, Me pyraz), 15.8 (d, <sup>1</sup>J<sub>CP</sub> = 26 Hz, PMe<sub>3</sub>), 16.2 (d, <sup>1</sup>J<sub>CP</sub> = 23 Hz, PMe<sub>3</sub>), 29.2 (d, <sup>2</sup>J<sub>CP</sub> = 11, <sup>1</sup>J<sub>CH</sub> = 145 Hz, CH<sub>2</sub>), 103.3 (s, C(4)H pyraz), 124.8, 125.1, 128.5, 144.4 (s, CH aromatics), 141.2 (s, CH pyraz), 148.4 (s, C<sub>q</sub> pyraz).

**3b**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  1.02 (d, 9 H, <sup>2</sup>*J*<sub>HP</sub> = 10.1 Hz, PMe<sub>3</sub>), 1.53 (d, 9 H, <sup>2</sup>*J*<sub>HP</sub> = 9.3 Hz, PMe<sub>3</sub>), 2.12 (m, 1 H, CH<sub>2</sub>), 2.29 (pt, 1 H, <sup>2</sup>*J*<sub>HH</sub>  $\approx$  <sup>3</sup>*J*<sub>HP</sub> = 3.7 Hz, CH<sub>2</sub>), 2.56 (s, 3 H, Me pyraz), 5.67 (m, 1 H, H(4) pyraz), 6.60 (d, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 1.6 Hz, H pyraz), 6.80 (dm, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, aromatic), 7.0 (m, 2 H, aromatics), 7.49 (dm, 1 H, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, aromatic); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) AX spin system,  $\delta_A = -13.6$ ,  $\delta_X = -8.6$ , *J*<sub>AX</sub> = 4 Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  14.7 (s, Me pyraz), 15.6 (d, <sup>1</sup>*J*<sub>CP</sub> = 32 Hz, PMe<sub>3</sub>), 16.0 (d, <sup>1</sup>*J*<sub>CP</sub> = 22 Hz, PMe<sub>3</sub>), 29.0 (d, <sup>2</sup>*J*<sub>CP</sub> = 10 Hz, CH<sub>2</sub>), 104.0 (s, CH pyraz), 124.3, 125.1, 128.6, 144.6 (s, CH aromatics), 139.8 (s, CH pyraz), 149.0 (s, C<sub>9</sub> pyraz).

**Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br(\mu\_2-\eta^3:\eta^1-CH<sub>2</sub>-\sigma-C<sub>6</sub>H<sub>4</sub>)(\mu\_2-N<sub>2</sub>C<sub>3</sub>HMe<sub>2</sub>) (3c). Anal. Calcd for C<sub>18</sub>H<sub>31</sub>N<sub>2</sub>BrP<sub>2</sub>Ni<sub>2</sub>: C, 40.4; H, 5.8; N, 5.2. Found: C, 40.0; H, 5.9; N, 4.9. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ 1.03 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.1 Hz, PMe<sub>3</sub>), 1.55 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.4 Hz, PMe<sub>3</sub>), 1.69 (s, 3 H, Me pyraz), 2.05 (m, 2 H, CH<sub>2</sub>), 2.53 (s, 3 H, Me pyraz), 5.46 (s, 1 H, H(4) pyraz), 6.86 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, aromatic), 6.97 (m, 2 H, aromatics), 7.41 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AX spin system, \delta\_A = -13.5, \delta\_X = -8.9, J\_{AX} = 5 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): \delta 13.2 (s, Me pyraz), 14.9 (s, Me pyraz), 15.7 (d, <sup>1</sup>J<sub>CP</sub> = 31 Hz, PMe<sub>3</sub>), 16.6 (d, <sup>1</sup>J<sub>CP</sub> = 27 Hz, PMe<sub>3</sub>), 27.9 (d,**   ${}^{2}J_{CP} = 11$ ,  ${}^{1}J_{CH} = 149$  Hz, CH<sub>2</sub>), 104.1 (s, C(4)H pyraz), 125.2, 125.5, 128.4, 144.0 (s, CH aromatics), 129.1 (dd,  ${}^{2}J_{CP} = 17$  and 42 Hz, C<sub>q</sub> arom–Ni), 147.8 (s, C<sub>q</sub> pyraz), 149.1 (d,  $J_{CP} = 3$  Hz, C<sub>q</sub> pyraz).

**Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br(\mu\_2-\eta^3:\eta^1-CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)(\mu\_2-N<sub>2</sub>C<sub>3</sub>H<sub>2</sub>Bu<sup>4</sup>) (3d/e). Anal. Calcd for C<sub>20</sub>H<sub>35</sub>N<sub>2</sub>BrP<sub>2</sub>Ni<sub>2</sub>: C, 42.7; H, 6.2; N, 5.0. Found: C, 42.4; H, 6.4; N, 5.1.** 

**3d**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  0.90 (s, 9 H, CMe<sub>3</sub>), 1.02 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.0 Hz, PMe<sub>3</sub>), 1.48 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.1 Hz, PMe<sub>3</sub>), 1.88 (dd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.6, <sup>3</sup>J<sub>HP</sub> = 6.4 Hz, CH<sub>2</sub>), 2.08 (dd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.6, <sup>3</sup>J<sub>HP</sub> = 6.2 Hz, CH<sub>2</sub>), 5.72 (dd, 1 H, <sup>3</sup>J<sub>HH</sub> = 1.9, J<sub>HP</sub> = 0.7 Hz, H(4) pyraz), 7.38 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, aromatic), 6.9–7.0 (m, 3 H, aromatics), 7.64 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 1.9 Hz, H pyraz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  –12.4 (s, 2 PMe<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  16.2 (d, <sup>1</sup>J<sub>CP</sub> = 30 Hz, 2 PMe<sub>3</sub>), 27.4 (d, <sup>2</sup>J<sub>CP</sub> = 9 Hz, CH<sub>2</sub>), 30.7 (s, CMe<sub>3</sub>), 31.3 (s, CMe<sub>3</sub>), 101.1 (s, C(4)H pyraz), 122.3 (s, C<sub>q</sub> arom), 125.1, 126.5, 127.9, 143.7 (s, CH aromatics), 131.0 (dd, <sup>2</sup>J<sub>CP</sub> = 17 and 46 Hz, C<sub>q</sub> arom– Ni), 140.0 (c, CH pyraz), 162.6 (s, C<sub>q</sub> pyraz).

**3e**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  1.02 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.0 Hz, PMe<sub>3</sub>), 1.60 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.5 Hz, PMe<sub>3</sub>), 1.82 (s, 9 H, CMe<sub>3</sub>), 2.13 (ddd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.9, <sup>3</sup>J<sub>HP</sub> = 7.1, <sup>5</sup>J<sub>HP</sub> = 1.2 Hz, CH<sub>2</sub>), 2.49 (pt, 1 H, <sup>2</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HP</sub> = 3.9 Hz, CH<sub>2</sub>), 5.72 (m, 1 H, H(4) pyraz), 6.60 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, H pyraz), 6.66 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, aromatic), 6.9–7.0 (m, 3 H, aromatics); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) AX spin system,  $\delta_A = -16.2$ ,  $\delta_X = -8.1$ ,  $J_{AX} = 6$  Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  16.3 (d, <sup>1</sup>J<sub>CP</sub> = 27 Hz, 2 PMe<sub>3</sub>), 28.8 (d, <sup>2</sup>J<sub>CP</sub> = 10 Hz, CH<sub>2</sub>), 32.1 (s, CMe<sub>3</sub>), 32.2 (s, CMe<sub>3</sub>), 101.4 (s, C(4)H pyraz), 124.1, 126.5, 128.5, 144.3 (s, CH aromatics), 139.5 (s, CH pyraz), 163.5 (s, C<sub>q</sub> pyraz).

Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Br( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>- $\sigma$ -C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -N<sub>2</sub>C<sub>3</sub>HBu<sup>t</sup><sub>2</sub>) (3f). Anal. Calcd for C<sub>24</sub>H<sub>43</sub>N<sub>2</sub>BrP<sub>2</sub>Ni<sub>2</sub>: C, 46.6; H, 7.0; N, 4.5. Found: C, 46.1; H, 7.0; N, 4.6. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ 0.89 (s, 9 H, CMe<sub>3</sub>), 1.02 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.1 Hz, PMe<sub>3</sub>), 1.67 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.6 Hz, PMe<sub>3</sub>), 1.88 (s, 9 H, CMe<sub>3</sub>), 2.03 (m, 1 H, CH<sub>2</sub>), 2.07 (dd, 1 H, <sup>2</sup>J<sub>HH</sub> = 3.4, <sup>3</sup>J<sub>HP</sub> = 7.0 Hz, CH<sub>2</sub>), 5.56 (d, 1 H, <sup>3</sup>J<sub>HP</sub> = 0.7 Hz, H(4) pyraz), 6.79–6.90 (m, 4 H, aromatics). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AX spin system,  $\delta_A$  = −18.5,  $\delta_X$  = −11.1,  $J_{AX}$  = 6 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ 16.1 (d, <sup>1</sup>J<sub>CP</sub> = 31 Hz, PMe<sub>3</sub>), 16.2 (d, <sup>1</sup>J<sub>CP</sub> = 27 Hz, PMe<sub>3</sub>), 26.4 (d, <sup>2</sup>J<sub>CP</sub> = 11, <sup>1</sup>J<sub>CH</sub> = 157 Hz, CH<sub>2</sub>), 30.8, 32.3 (s, CMe<sub>3</sub>), 31.0, 32.0 (s, CMe<sub>3</sub>), 99.7 (s, C(4)H pyraz), 122.5 (d, <sup>2</sup>J<sub>CP</sub> = 5 Hz, C<sub>q</sub> arom), 125.5, 126.1, 127.6, 142.1 (s, CH aromatics), 127.9 (dd, <sup>2</sup>J<sub>CP</sub> = 15 and 46 Hz, C<sub>q</sub> arom–Ni), 161.5, 162.7 (s, C<sub>q</sub> pyraz).

Synthesis of Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>) (4). To a solution of 2 (0.5 g, 1 mmol) in THF (50 mL) was added 1 g of solid sodium azide (15 mmol). The mixture was stirred at room temperature overnight and then taken to dryness. Extraction with toluene, filtration, concentration of the filtrate, and addition of some petroleum ether provided red crystals of the complex after cooling to -30 °C for several hours. Yield: 60%. Anal. Calcd for C16H27N5P2-Ni<sub>2</sub>: C, 41.0; H, 5.8; N, 14.9. Found: C, 40.4; H, 5.8; N, 14.1. IR (Nujol mull): 2046 cm<sup>-1</sup> ( $\nu$ (N<sub>3</sub>)). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  0.90 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 10.2 Hz, PMe<sub>3</sub>), 1.41 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.2 Hz, PMe<sub>3</sub>), 2.19 (br s, 1 H, CH<sub>2</sub>), 2.26 (br s, 1 H, CH<sub>2</sub>), 5.97 (s, 1 H, H(4) pyraz), 6.80 (s, 1 H, H pyraz), 6.81 (d, 1 H,  ${}^{3}J_{HH} =$ 7.0 Hz, aromatic), 7.03 (m, 2 H, aromatics), 7.64 (s, 1 H, H pyraz), 7.83 (d, 1 H,  ${}^{3}J_{HH} = 7.6$  Hz, aromatic).  ${}^{31}P{}^{1}H$  NMR  $(CD_2Cl_2, 20 \ ^{\circ}C): \ \delta \ -10.1 \ (br \ s, \ PMe_3), \ -9.4 \ (br \ s, \ PMe_3).$ <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  15.2 (d, <sup>1</sup>*J*<sub>CP</sub> = 25 Hz, PMe<sub>3</sub>), 17.4 (d,  ${}^{1}J_{CP} = 28$  Hz, PMe<sub>3</sub>), 32.3 (s, CH<sub>2</sub>), 105.2, (s, C(4)H pyraz), 125.3, 126.3, 130.6, 146.8 (s, CH aromatics), 128.8 (s, C<sub>q</sub> arom), 139.8, 142.1 (s, CH pyraz).

Synthesis of Ni<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>(NC<sub>4</sub>H<sub>2</sub>Me<sub>2</sub>)( $\mu_2$ - $\eta^3$ : $\eta^1$ -CH<sub>2</sub>- $\sigma$ -C<sub>6</sub>H<sub>4</sub>)-( $\mu_2$ -N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>) (5). *n*-BuLi (1 mmol, 0.62 mL of a 1.6 M solution in hexanes) was added to a cold (-40 °C) solution of 2,5dimethylpyrrole (0.1 mL, 1 mmol) in THF (10 mL). After the cooling bath was removed, the mixture was warmed to room temperature and stirred for 15 min. This solution was added to a cooled (-60 °C) solution of 2 (0.5 g, 1 mmol) in THF (50 mL). The suspension was stirred at room temperature for 2 h. The solvent was stripped off and the residue extracted with toluene and centrifuged. After partial evaporation of the solvent, cooling of the resulting solution to -30 °C furnished dark red crystals of 5 in 60% yield. Anal. Calcd for C<sub>22</sub>H<sub>35</sub>N<sub>3</sub>P<sub>2</sub>-Ni<sub>2</sub>: C, 50.7; H, 6.7; N, 8.1. Found: C, 51.2; H, 6.9; N, 8.1. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  0.66 (d, 9 H,  ${}^{2}J_{\text{HP}} = 9.8$  Hz, PMe<sub>3</sub>), 1.38 (d, 9 H,  ${}^{2}J_{HP} = 9.0$  Hz, PMe<sub>3</sub>), 2.25 (dd, 1 H,  ${}^{2}J_{HH} = 3.5$ ,  ${}^{3}J_{\rm HP} = 7.9$  Hz, CH<sub>2</sub>), 2.37 (d, 1 H,  ${}^{2}J_{\rm HH} = 3.5$  Hz, CH<sub>2</sub>), 2.89, 2.97 (s, s, 3 H, 3 H, Me pyrrole), 5.68 (s, 1 H, H(4) pyraz), 5.77, 5.81 (s, s, 1 H, 1 H, H pyrrole), 6.59, 6.82 (s, s, 1 H, 1 H, H pyraz), 6.87 (d, 1 H,  ${}^{3}J_{HH} = 7.5$  Hz, aromatic), 7.12 (m, 2 H, aromatics), 8.26 (d, 1H,  ${}^{3}J_{\text{HH}} = 7.1$  Hz, aromatic).  ${}^{31}P{}^{1}H{}$ NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AX spin system,  $\delta_A = -11.5$ ,  $\delta_X = -10.2$ ,  $J_{AX} = 13$  Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  14.5 (d, <sup>1</sup> $J_{CP} =$ 29 Hz, PMe<sub>3</sub>), 16.0 (d,  ${}^{1}J_{CP} = 27$  Hz, PMe<sub>3</sub>), 17.5, 18.1 (s, Me pyrrole), 31.0 (d, <sup>2</sup>J<sub>CP</sub> = 10 Hz, CH<sub>2</sub>), 103.2 (s, C(4)H pyraz), 105.5, 105.7 (s, CH pyrrole), 122.9 (dd,  ${}^{2}J_{CP} = 20$  and 39 Hz, Cq arom-Ni), 123.3, 124.3, 128.9, 145.8 (s, CH aromatics), 128.7 (d,  ${}^{2}J_{CP} = 4$  Hz, C<sub>q</sub> arom), 131.2, 133.4 (s, C<sub>q</sub> pyrrole), 138.3 (d,  $J_{CP} = 3$  Hz, CH pyraz), 140.8 (d,  $J_{CP} = 3$  Hz, CH pyraz).

Synthesis of [CpNi(PMe<sub>3</sub>)]<sub>2</sub>( $\mu_2$ - $\eta^1$ : $\eta^1$ -CH<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>) (6). Method a. A solution of 2 (0.36 g, 0.71 mmol) in THF (50 mL) cooled to -80 °C was treated with NaCp (1.4 mmol, 3.5 mL of a 0.4 M solution in THF). The resulting mixture was stirred at room temperature for 30 min and taken to dryness. Extraction with a mixture of petroleum ether and Et<sub>2</sub>O (1:1), centrifugation, and concentration provided crystals of **6** as green needles after cooling to -30 °C. Yield: 22%.

**Method b.** CpTl (0.54 g, 2 mmol) was added to a cooled (-80 °C) solution of **2** (0.47 g, 0.9 mmol). After the suspension was warmed to room temperature, the stirring was continued overnight. The workup of the reaction mixture was similar to that in method a. Compound **6** was obtained as green crystals in 28% yield.

**Method c.** To a cold (-80 °C) stirred solution of 1 (0.74 g, 1.25 mmol) in THF (50 mL) was added CpNa (2.5 mmol, 6.2 mL of a 0.4 M solution in THF). The color of the solution changed to deep green, and upon gentle warming a further change to a reddish coloration was observed. The mixture was stirred at room temperature for 6 h. The solvent was evaporated under vacuum and the residue extracted with Et<sub>2</sub>O. After centrifugation, concentration, and cooling to -20 °C, compound **6** was obtained as green crystals in 48% yield.

Anal. Calcd for  $C_{23}H_{34}P_2Ni_2$ : C, 56.4; H, 7.0. Found: C, 56.2; H, 7.3. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  1.01 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.6 Hz, PMe<sub>3</sub>), 1.33 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.1 Hz, PMe<sub>3</sub>), 2.10 (t, 1 H, <sup>2</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HP</sub> = 10 Hz, CH<sub>2</sub>), 2.13 (t, 1 H, <sup>2</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HP</sub> = 10 Hz, CH<sub>2</sub>), 2.13 (t, 1 H, <sup>2</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HP</sub> = 10 Hz, CH<sub>2</sub>), 4.79 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 5.44 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 6.41 (tm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, aromatic), 6.57 (tm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, aromatic), 6.57 (tm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, aromatic), 7.20 (dm, 1 H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, H aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): -3.2 (s, PMe<sub>3</sub>), -2.4 (s, PMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  9.6 (d, <sup>2</sup>J<sub>CP</sub> = 20 Hz, CH<sub>2</sub>), 17.7 (d, <sup>1</sup>J<sub>CP</sub> = 28 Hz, PMe<sub>3</sub>). 18.6 (d, <sup>1</sup>J<sub>CP</sub> = 30 Hz, PMe<sub>3</sub>), 90.0, 91.3 (s, C<sub>5</sub>H<sub>5</sub>), 119.2, 121.7, 127.4, 142.8 (s, CH aromatics), 140.7 (d, <sup>2</sup>J<sub>CP</sub> = 37 Hz, C<sub>q</sub> arom-Ni), 164.2 (s, C<sub>q</sub> arom).

**Reaction of Compound 2 with Excess PMe<sub>3</sub>.** To a solution of **2** (0.33 g, 0.56 mmol) in THF (50 mL) cooled to -80 °C was added an excess of PMe<sub>3</sub> (0.3 mL, 3 mmol). After the solution was warmed to room temperature, the stirring was continued overnight. The solvent was stripped off and the yellow residue extracted with toluene. This solution was filtered and the filtrate evaporated to dryness. The resulting yellow microcrystalline residue, identified as [Ni(PMe<sub>3</sub>)<sub>2</sub>Br]<sub>2</sub>-[ $\mu_2$ -(C<sub>6</sub>H<sub>4</sub>-o-CH<sub>2</sub>)<sub>2</sub>] (7), was washed with petroleum ether and dried under vacuum. Yield: 84%. Complex 7 has been previously prepared by using another synthetic method.<sup>2b</sup>

Synthesis of  $[Ni_2(PMe_3)_3(\mu_2-\eta^3:\eta^1-CH_2-o-C_6H_4)(\mu_2-N_2C_3H_3)]$ -BPh<sub>4</sub> (8). Solid 2 (0.24 g, 0.47 mmol) and NaBPh<sub>4</sub> (0.17 g, 0.5 mmol) were mixed and cooled down to -80 °C, THF (10 mL) was introduced into the flask, and after dissolution of the reagents, PMe<sub>3</sub> (0.5 mmol, 0.5 mL of a 1 M solution in THF) was added. The mixture was stirred at -80 °C for 15 min and then warmed to room temperature. The solvent was evaporated under reduced pressure and the solid residue extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solution was filtered and the filtrate partially concentrated. After addition of some Et<sub>2</sub>O and cooling to 0 °C for 3 days, compound 8 was obtained as red-brown crystals. Yield: 72%. Anal. Calcd for C43H56N2-BP<sub>3</sub>Ni<sub>2</sub>: C, 62.8; H, 6.9; N, 3.4. Found: C, 62.7; H, 7.1; N. 2.9. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  0.95 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.8 Hz, PMe<sub>3</sub>), 1.27 (d, 9 H,  ${}^{2}J_{HP} = 8.1$  Hz, PMe<sub>3</sub>), 1.46 (d, 9 H,  ${}^{2}J_{HP} =$ 9.2 Hz, PMe<sub>3</sub>), 2.41 (t, 1 H,  ${}^{2}J_{\rm HH} \approx {}^{3}J_{\rm HP} = 3.8$  Hz, CH<sub>2</sub>), 2.44 (dd, 1 H,  ${}^{2}J_{HH} = 3.8$ ,  ${}^{3}J_{HP} = 7.3$  Hz, CH<sub>2</sub>), 6.16 (pq, 1 H,  ${}^{3}J_{HH}$  $\approx$   $^4J_{\rm HP}$  = 2.1 Hz, H(4) pyraz), 6.92 (d, 1 H,  $^3J_{\rm HH}$  = 2.1 Hz, H pyraz), 6.96 (m, 4 H, arom BPh<sub>4</sub>), 7.11 (m, 8 H, arom BPh<sub>4</sub>), 7.15 (m, 1 H, arom), 7.20 (m, 1 H, arom), 7.40 (m, 8 H, arom BPh<sub>4</sub>), 7.58 (d, 1 H,  ${}^{3}J_{HH} = 2.1$  Hz, H pyraz).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AMX spin system,  $\delta_A = -9.9$ ,  $\delta_M = -12.0$ ,  $\delta_X$ = -18.6,  $J_{AM}$  = 6.2,  $J_{MX}$  = 48.6 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  14.6 (d, <sup>1</sup> $J_{CP}$  = 24 Hz, PMe<sub>3</sub>), 15.8 (d, <sup>1</sup> $J_{CP}$  = 28 Hz, PMe<sub>3</sub>), 16.7 (dd,  ${}^{1}J_{CP} = 29$ ,  ${}^{3}J_{CP} = 4$  Hz, PMe<sub>3</sub>), 32.0 (d,  ${}^{2}J_{CP} =$ 10 Hz, CH2), 105.7 (s, C(4)H pyraz), 122.0, 125.9, 136.2 (s, CH arom BPh<sub>4</sub>), 124.6, 126.9, 130.6, 144.1 (d, s, s, and s,  $J_{CP} = 5$ Hz, CH arom), 126.5 (pt,  $J_{CP}(app) = 5$  Hz,  $C_q$  arom), 127.0 (ddd,  $J_{CP} = 72$ , 37, and 21 Hz, C<sub>q</sub> arom–Ni), 139.6, 141.7, (s, CH pyraz), 164.6 (m, C<sub>q</sub> arom BPh<sub>4</sub>).

Synthesis of  $[Ni_2(PMe_3)(Me_2PCH_2CH_2PMe_2)(\mu_2-\eta^3:\eta^1 CH_2$ -o-C<sub>6</sub>H<sub>4</sub>)( $\mu_2$ -N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>)]BPh<sub>4</sub> (9). To a cooled (-80 °C) solution of 2 (0.23 g, 0.46 mmol) in THF (30 mL) was added a solution of  $NaBPh_4^-$  (0.34 g, 0.46 mmol) and dmpe (0.08 mL, 0.48 mmol) in THF (30 mL). When the temperature was gently raised to -10 °C, the solvent was removed in vacuo and the residue extracted twice with CH<sub>2</sub>Cl<sub>2</sub> and a mixture of THF and Et<sub>2</sub>O, respectively. The resulting suspension was centrifuged and the solution concentrated and cooled to -30 °C. Compound 9 was obtained as red-orange crystals in 31% yield. Anal. Calcd for C43H54N2BP3Ni2: C, 63.3; H, 7.0; N, 3.1. Found: C, 62.4; H, 7.2; N, 2.5. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$ 0.87 (d, 3 H,  ${}^{2}J_{HP} = 11.1$  Hz, P–Me), 1.13 (d, 3 H,  ${}^{2}J_{HP} = 10.3$ Hz, P-Me), 1.40–1.70 (bm, 4 H, P-CH<sub>2</sub>), 1.41 (d, 9 H,  ${}^{2}J_{HP} =$ 9.2 Hz, PMe<sub>3</sub>), 1.52 (d, 3 H,  ${}^{2}J_{HP} = 9.1$  Hz, P–Me), 1.65 (d, 3 H,  ${}^{2}J_{\text{HP}} = 9.2$  Hz, P–Me), 2.08 (t, 1 H,  ${}^{2}J_{\text{HH}} \approx {}^{3}J_{\text{HP}} = 3.9$  Hz, CH<sub>2</sub>), 2.40 (dd, 1 H,  ${}^{2}J_{\text{HH}} = 3.9$ ,  ${}^{3}J_{\text{HP}} = 7.8$  Hz, CH<sub>2</sub>), 6.20 (br s, 1 H, H(4) pyraz), 6.98 (m, 4 H, arom BPh<sub>4</sub>), 7.07 (d, 1 H,  ${}^{3}J_{\rm HH} = 7.9$  Hz, arom), 7.13 (m, 8 H, arom BPh<sub>4</sub>), 7.27 (t, 1 H,  ${}^{3}J_{\rm HH} = 7.4$  Hz, arom), 7.30 (t, 1 H,  ${}^{3}J_{\rm HH} = 7.0$  Hz, arom), 7.42 (m, 8 H, arom BPh<sub>4</sub>), 7.59 (d, 1 H,  ${}^{3}J_{HH} = 1.9$  Hz, H pyraz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): AMX spin system,  $\delta_A = -9.7$ ,  $\delta_{\rm M} = 32.7, \ \delta_{\rm X} = 36.4, \ J_{\rm AM} = 6, \ J_{\rm MX} = 29 \ {\rm Hz}.$  <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C):  $\delta$  11.4 (d, <sup>1</sup>J<sub>CP</sub> = 21 Hz, P-Me), 11.5 (d, <sup>1</sup>J<sub>CP</sub> = 23 Hz, P-Me), 12.4 (d,  ${}^{1}J_{CP}$  = 32 Hz, P-Me), 13.0 (d,  ${}^{1}J_{CP}$ = 33 Hz, P–Me), 15.7 (d,  ${}^{1}J_{CP}$  = 28 Hz, PMe<sub>3</sub>), 24.8 (dd,  ${}^{1}J_{CP}$ = 32,  ${}^{2}J_{CP}$  = 11 Hz, P–CH<sub>2</sub>), 28.4 (dd,  ${}^{1}J_{CP}$  = 31,  ${}^{2}J_{CP}$  = 18 Hz, P-CH<sub>2</sub>), 31.9 (d,  ${}^{2}J_{CP} = 11$  Hz, CH<sub>2</sub>), 105.2 (s, C(4)H pyraz), 122.2, 126.0, 136.3, (s, CH arom BPh<sub>4</sub>), 124.5, 126.5, 130.6, 143.6 (d, s, s, and s,  $J_{CP} = 5$  Hz, CH arom), 124.7 (ddd,  $J_{CP} = 70, 34$ , and 21 Hz, C<sub>q</sub> arom–Ni), 128.1 (pt,  $J_{CP}(app) = 5$ Hz, Cq arom), 140.3, 141.7 (s, CH pyraz), 164.3 (m, Cq arom BPh<sub>4</sub>).

Synthesis of  $[Ni_2(PMe_3)_3(\mu_2-\eta^3:\eta^1-CH_2-o-C_6H_4)(\mu_2-N_2C_3-H_2Me)]BPh_4$  (10a,b). Complex 3a/3b (0.46 g, 0.89 mmol) and NaBPh\_4 (0.30 g, 0.89 mmol) were cooled to 0 °C, and THF (20 mL) and PMe\_3 (1 mmol, 1 mL of a 1 M solution in THF) were added. The mixture was stirred at room temperature for 15 min and then taken to dryness. The residue was extracted with CH\_2Cl\_2, the suspension filtered and the filtrate evaporated under vacuum and extracted with a mixture of Me\_2CO and petroleum ether (1:1) to afford red crystals of 10a in 63% yield. Dissolution of these crystals at room temperature affords solutions that contain equilibrium mixtures of 10a and



**Figure 4.** Plot of the **3a** Pz' Me <sup>1</sup>H NMR signal decay at 0 °C (A) and representation of  $\ln((C(t) - C_e)/(C_0 - C_e))$  vs time (B).

**10b.** Anal. Calcd for  $C_{44}H_{58}N_2BP_3Ni_2$ : C, 63.2; H, 7.0. Found: C, 63.3; H, 7.0.

**10a**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  0.93 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.8 Hz, PMe<sub>3</sub>), 1.32 (d, 9 H,  ${}^{2}J_{HP} = 8.1$  Hz, PMe<sub>3</sub>), 1.43 (d, 9 H,  ${}^{2}J_{HP} =$ 9.0 Hz, PMe<sub>3</sub>), 1.76 (s, 3 H, Me pyraz), 2.20 (t, 1 H,  $^2J_{\rm HH}\approx$  ${}^{3}J_{\text{HP}} = 4.0$  Hz, CH<sub>2</sub>), 2.29 (dd, 1 H,  ${}^{2}J_{\text{HH}} = 4.0$ ,  ${}^{3}J_{\text{HP}} = 7.3$  Hz, CH<sub>2</sub>), 5.90 (br s, 1 H, H(4) pyraz), 6.92 (m, 4 H, arom BPh<sub>4</sub>), 7.05 (m, 8 H, arom BPh<sub>4</sub>), 7.09-7.18 (m, 2 H, arom), 7.33 (m, 8 H, arom BPh<sub>4</sub>), 7.43 (d, 1 H,  ${}^{3}J_{HH} = 2.0$  Hz, H pyraz);  ${}^{31}P{}^{1}H{}$ NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) AMX spin system,  $\delta_A = -10.4$ ,  $\delta_M =$  $-12.0, \delta_{\rm X} = -18.7, J_{\rm AM} = 7, J_{\rm MX} = 47$  Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>-Cl<sub>2</sub>, 20 °C)  $\delta$  14.2 (s, Me pyraz), 14.9 (d,  ${}^{1}J_{CP} = 24$  Hz, PMe<sub>3</sub>), 16.3 (d,  ${}^{1}J_{CP} = 28$  Hz, PMe<sub>3</sub>), 16.4 (dd,  ${}^{1}J_{CP} = 31$ ,  $J_{CP} = 4$  Hz, PMe<sub>3</sub>), 30.7 (d,  ${}^{2}J_{CP} = 10$  Hz, CH<sub>2</sub>), 105.3 (s, C(4)H pyraz), 122.0, 125.9, 136.3, (s, CH arom BPh<sub>4</sub>), 125.4, 127.0, 130.6, 143.3 (d, s, s, and s,  $J_{CP} = 5$  Hz, CH arom), 125.6 (t,  ${}^{2}J_{CP} = 5$ Hz, C<sub>q</sub> arom), 128.7 (ddd,  $J_{CP} = 75$ , 38, and 19 Hz, C<sub>q</sub> arom-Ni), 140.3, (s, CH pyraz), 149.6 (s, C<sub>q</sub> pyraz), 164.4 (m, C<sub>q</sub> arom BPh<sub>4</sub>).

**10b**: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  0.98 (d, 9 H, <sup>2</sup>J<sub>HP</sub> = 9.9 Hz, PMe<sub>3</sub>), 1.26 (d, 9 H,  ${}^{2}J_{HP} = 8.1$  Hz, PMe<sub>3</sub>), 1.46 (d, 9 H,  ${}^{2}J_{HP} =$ 9.2 Hz, PMe<sub>3</sub>), 2.20 (t, 1 H,  $^2J_{\rm HH}\approx {^3J_{\rm HP}}=$  4.0 Hz, CH<sub>2</sub>), 2.36 (dd, 1 H,  ${}^{2}J_{\rm HH}$  = 4.0,  ${}^{3}J_{\rm HP}$  = 7.7 Hz, CH<sub>2</sub>), 2.47 (s, 3 H, Me pyraz), 5.86 (bs, 1 H, H(4) pyraz), 6.75 (d, 1 H,  ${}^{3}J_{HH} = 1.8$  Hz, H pyraz), 6.92 (m, 4 H, arom BPh<sub>4</sub>), 7.05 (m, 8 H, arom BPh<sub>4</sub>), 7.09-7.18 (m, 2H, arom), 7.33 (m, 8 H, arom BPh<sub>4</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C) AMX spin system,  $\delta_A = -9.3$ ,  $\delta_M = -13.7$ ,  $\delta_{\rm X} = -19.0, J_{\rm AM} = 7, J_{\rm MX} = 47$  Hz; <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)  $\delta$  13.2 (s, Me pyraz), 14.9 (d,  $^1J_{\rm CP}=$  24 Hz, PMe\_3), 16.0 (d,  ${}^{1}J_{CP} = 29$  Hz, PMe<sub>3</sub>), 16.7 (dd,  ${}^{1}J_{CP} = 31$ ,  $J_{CP} = 4$  Hz, PMe<sub>3</sub>), 31.4 (d,  ${}^{2}J_{CP} = 10$  Hz, CH<sub>2</sub>), 105.8 (s, C(4)H pyraz), 122.0, 125.9, 136.3 (s, CH arom BPh<sub>4</sub>), 124.7, 127.0, 130.3, 143.9 (d, s, s, and s,  $J_{CP} = 5$  Hz, CH arom), 126.5 (t,  ${}^{2}J_{CP} = 4$  Hz, C<sub>q</sub> arom), 127.5 (ddd,  $J_{CP} = 75$ , 37, and 20 Hz,  $C_q$  arom-Ni), 142.1 (s, CH pyraz), 147.7 (d,  $J_{CP} = 4$  Hz, C<sub>q</sub> pyraz), 164.4 (m, C<sub>q</sub> arom BPh<sub>4</sub>).

Kinetic Measurements. A solid sample (10-20 mg) of 3a or 10a was placed in an NMR tube and weighed by difference. The tube was placed in a cooling bath (-80 °C for 3a and 0 °C for 10a) and the solvent (CD<sub>2</sub>Cl<sub>2</sub>, 0.6 mL) was added slowly from a syringe. The sample was shaken and cooled repeatedly until the solid completely dissolved and placed in the NMR probe at the experiment temperature (0 °C for 3a, 20 °C for 10a). When the kinetic measurement was carried out in the presence of  $(\eta^5$ -Cp)Pd $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>), this reagent was previously dissolved in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub> and added to the solid sample. PMe<sub>3</sub> was added from a GC syringe to the NMR tube immediately before the sample was placed in the probe. The intensity of the <sup>1</sup>H signal of the methyl substituent of the Pz' ligand was used to monitor the relative concentration of each isomer. Figure 4A shows the intensity decay of this signal for compound **3a**. Representation of  $\ln((C(t) - C_e)/(C_0 - C_e))$ vs time (*t*) (where C(t) is the relative intensity of the Pz' Me signal of **3a** or **10a** and  $C_0$  and  $C_e$  are the same intensities when t = 0 and  $t = \infty$ , respectively) gives a straight line with

	Weimemeine Dutu 101 \$	
formula	$C_{16}H_{27}BrN_2Ni_2P_2$	
mol wt	506.7	
cryst syst	monoclinic	
space group	$P2_1/n$	
cell dimens		
<i>a</i> , Å	14.970(4)	
<i>b</i> , Å	16.207(4)	
<i>c</i> , Å	9.074(2)	
$\beta$ , deg	104.96(2)	
Z	4	
<i>V</i> , Å <sup>3</sup>	2126.9(9)	
$D_{\rm calcd}$ , g cm <sup>-3</sup>	1.58	
F(000)	1032	
temp, K	295	
diffractometer	Enraf-Nonius	
radiation	graphite monochromated,	
	Mo Kα ( $\lambda = 0.710$ 69 Å)	
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	37.9	
crystal dimens, mm	0.1 imes 0.3 imes 0.08	
$2\check{ heta}$ range, deg	1-50	
scan technique	$\omega/2\theta$	
data collected	(-17,0,0) to $(17,19,11)$	
no. of unique data	3732	
no. of obsd rflns	1953	
$R_{\rm int}$ (%)	2.9	
decay, %	3	
std rflns	3/48	
weighting scheme	unit	
$R = \sum  \Delta^2 F  / \sum  F_0 $	6.3	
$R_{\rm w} = (\sum w  \Delta^2 F  / \sum w  Fo )^{1/2}$	6.8	
max shift/error	0.03	
abs corr range	0.72 - 1.34	

Table 9 Crystal and Refinement Data for 9

slope  $-(k_1 + k_{-1})$ .<sup>9b</sup> The graph corresponding to **3a** is shown in Figure 4B. Explicit values for the rate constant are obtained from the equilibrium constant.  $K_{eq}$  was optimized in each case for the best fit of the experimental points. The following experiments were carried out.

(a) Compound **3a** (20 mg, 0.04 mmol):  $k_1 + k_{-1} = [1.48(3)] \times 10^{-3} \text{ s}^{-1}$ ;  $K_{\text{eq}} = [\textbf{3a}]/[\textbf{3b}] = 1.95$ ;  $k_1 = 9.8 \times 10^{-4} \text{ s}^{-1}$ .

(b) Compound **3a** (18 mg, 0.034 mmol) in the presence of 0.03 mmol of  $(\eta^5$ -Cp)Pd $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>):  $k_1 + k_{-1} = [1.13(2)] \times 10^{-3}$  s<sup>-1</sup>;  $K_{eq} = [3a]/[3b] = 2.19$ ;  $k_{-1} = 7.8 \times 10^{-4}$  s<sup>-1</sup>.

(c) Compound **3a** (10 mg, 0.017 mmol) in the presence of PMe<sub>3</sub> (0.9  $\mu$ L, 0.009 mmol): equilibrium was reached before the first spectrum could be recorded.

(d) Compound **10a** (20 mg, 0.023 mmol):  $k_1 + k_{-1} = [7.96-(9)] \times 10^{-4}$ ;  $K_{eq} = [10a]/[10b] = 0.795$ ;  $k_{-1} = 3.5 \times 10^{-4} \text{ s}^{-1}$ .

(e) Compound **10a** (18 mg, 0.021 mmol) in the presence of 0.021 mmol of ( $\eta^5$ -Cp)Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>):  $k_1 + k_{-1} = [5.95(17)] \times 10^{-4}$  s<sup>-1</sup>;  $K_{eq} = [10a]/[10b] = 0.644$ ;  $k_{-1} = 2.3 \times 10^{-4}$  s<sup>-1</sup>.

(f) Compound **10a** (10 mg, 0.012 mmol) in the presence of PMe<sub>3</sub> (0.8  $\mu$ L, 0.008 mmol): equilibrium was reached before the first spectrum could be recorded.

**X-ray Structure Determination of Compound 2.** A summary of the fundamental crystal data is given in Table 2. A red crystal of prismatic shape was coated with epoxy resin

and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the  $\theta$  values of 25 reflections with a  $2\theta$  range of  $10-30^\circ$ . The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and Br were taken from ref 23. The structure was solved by Patterson and Fourier methods. An empirical absorption correction<sup>24</sup> was applied at the end of the isotropic refinements. A final refinement was undertaken with unit weight and anisotropic thermal motion for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in  $\Delta F$  vs  $F_0$  or  $(\sin\theta)/\lambda$  was observed. The final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system.<sup>25</sup>

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Supporting Information Available: Tables of fractional coordinates, H atom coordinates, thermal parameters, and bond lengths and angles for 2 (4 pages). Ordering information is given on any current masthead page.

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