

Preparation, structure, and dynamics of a nickel π -allyl cyanide complex

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Abstract

The complex $(\text{dippe})\text{Ni}(\eta^3\text{-allyl})(\text{CN})$ has been prepared and fully characterized (dippe = bis-(diisopropylphosphino)ethane), including X-ray diffraction studies, as a square pyramidal structure. The complex shows dynamic $^1\text{H-NMR}$ behavior consistent with substantial structural rearrangements upon π to σ allyl interconversion. A comparison is made with $(\text{dippe})\text{Ni}(\eta^3\text{-allyl})\text{Br}$, which also displays a square pyramidal structure.

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1. Introduction

π -Allyl complexes have been well-documented in the literature concerning the organometallic chemistry of nickel and palladium, largely because of their extensive use in organic synthesis [1]. Bis- π -allyl nickel complexes are known to dimerize propylene, giving new C_6 -olefin products [2]. Derivatives of the type $[\text{Ni}(\text{phosphine})_2(\eta^3\text{-allyl})]^+$ [3] and $\text{Ni}(\text{phosphine})_2(\eta^3\text{-allyl})(\text{halide})$ [4–7] are known, and a cyanide complex was mentioned in passing in an early report by Wilke [4]. The phosphines employed include PPh_3 , $\text{P}(\text{OPh})_3$, PEt_3 , dmpe, and diphos. In work related to the hydrocyanation of butadiene [8], DuPont workers have observed numerous allyl cyanide complexes of nickel during studies of the reaction of butadiene with HCN using $\text{Ni}[\text{P}(\text{OAr})_3]_4$ as catalyst, although these species were not generally isolated and characterized as stable complexes [9,10]. Herein is reported the synthesis and complete characterization of a new cyanide-containing π -allyl species, $(\text{dippe})\text{Ni}(\eta^3\text{-allyl})(\text{CN})$, along with its dynamic $^1\text{H-NMR}$ behavior.

2. Results and discussion

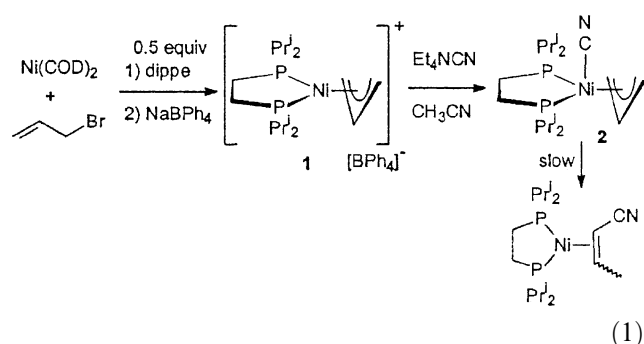
The synthesis of the cation $[(\text{dippe})\text{Ni}(\eta^3\text{-allyl})]^+$ (**1**) as the BPh_4^- salt was recently reported by reaction of $\text{Ni}(\text{cod})_2$ with allyl bromide, followed by dippe, and then NaBPh_4 [3]. Two resonances in the $^1\text{H-NMR}$ spectrum of this complex in acetone- d_6 were attributed to the π -allyl ligand: a quintet (1H) at δ 5.31 was assigned to the allyl methine proton while a doublet (4H) at 4.61 was assigned to the *syn* and *anti* protons at the terminus of the allyl ligand. These NMR data indicate that rapid π – σ interconversion, allowing interchange of the *syn* and *anti* protons, is occurring at ambient temperature. We found, however, that a $^1\text{H-NMR}$ spectrum of $[(\text{dippe})\text{Ni}(\eta^3\text{-allyl})]^+[\text{BPh}_4]^-$, prepared according to the literature protocol, actually contained three resonances in acetone- d_6 due to the π -allyl ligand: a septet at δ 5.31 (1H), a doublet at 4.61 (2H), and a doublet at 2.62 (2H). The two doublets were attributed to the *syn* and *anti* protons, respectively, of the allyl group. VT-NMR experiments confirmed that the *syn* and *anti* protons of this cationic complex do not coalesce even at 120 °C, indicating that π - to σ -allyl interconversion is not facile at room temperature in this cationic complex, in contrast to the behavior reported in the literature.

Reaction of the pale yellow complex **1** with KCN or Et_4NCN leads to the formation of a new wine-red

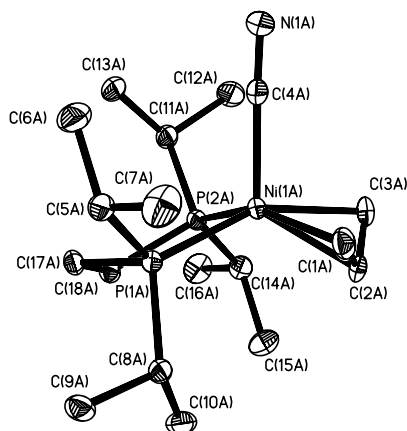
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species, $(\text{dippe})\text{Ni}(\eta^3\text{-allyl})(\text{CN})$ (**2**) (Eq. (1)). The synthesis of the complex required optimization to obtain the product in high yield, as choice of solvent, CN^- source, and stoichiometry were all found to be important. Reaction in THF is very slow (7–24 h), because neither KCN nor Et_4NCN is very soluble in THF. Also, the reaction in THF goes noticeably *faster* when the reaction mixture is more *dilute*, suggesting that increased dissociation of the cation/anion pair of the nickel reactant in dilute solutions may enhance its reactivity (the solution is always saturated with cyanide). Synthesis **2** in CH_3CN is much faster—instantaneously upon mixing for Et_4NCN —presumably because Et_4NCN is much more soluble in CH_3CN than in THF. While KCN is not as soluble, the reaction still goes to completion in 2 h in a suitably dilute solution. In addition to the fact that Et_4NCN is more soluble than KCN, the byproduct Et_4NBPh_4 of the Et_4NCN reaction is less soluble (and therefore easier to separate by filtration from the desired Ni product) than the byproduct KBPh_4 from the KCN reaction, making Et_4NCN superior to KCN as a cyanide source.

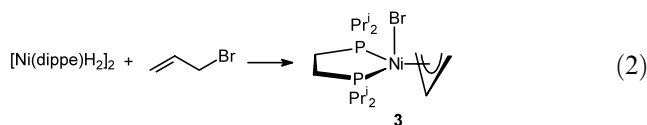


The amount of CN^- in these reactions is crucial and should be kept at the ideal 1:1 stoichiometry. With less than one equivalent, $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+[\text{BPh}_4]^-$ remains and is difficult to remove by recrystallization, since the salt is less soluble than the neutral product. With more than one equivalent of CN^- , however, dippe is displaced from Ni (free dippe is seen by NMR).



The reaction product **2** must be isolated promptly or it will transform into $(\text{dippe})\text{Ni}(\text{crotononitrile})$ [**11**](eq. 1). The byproduct Et_4NBPh_4 is fairly soluble in CH_3CN , so replacement of solvent by a 4:1 $\text{Et}_2\text{O}:\text{THF}$ mixture is required to dissolve the Ni product but not the salt. The product can be recrystallized from Et_2O at -30°C (small-scale preps) or from Et_2O containing a few drops of THF (large-scale preps), yielding red needles. The product is indefinitely stable at -30°C under nitrogen atmosphere as a solid. Upon standing in THF- d_8 solution at ambient temperature, **2** decomposes to a mixture of the Ni(0) η^2 -olefin complexes $(\text{dippe})\text{Ni}(\text{cis-crotononitrile})$ and $(\text{dippe})\text{Ni}(\text{trans-crotononitrile})$ with a half-life of ~ 12 h [11].

The single crystal X-ray structure of **2** revealed that the complex is square pyramidal with the cyanide ligand in the axial position, as shown in Fig. 1. The π -allyl unit in the complex is symmetrically bound, with Ni–C distances of 2.090(3), 1.997(3), and 2.084(3) Å for the three allyl carbons. The Ni–CN bond is fairly long, at 1.994(3) Å. The Ni–CN distance in the related Ni(II) complex $(\text{dippe})\text{Ni}(\text{Ph})(\text{CN})$ is only 1.877(3) Å [12], and 1.879(4) Å is observed in $\text{Ni}(\text{Ph}_2\text{PCH}=\text{CHPh}_2)(\text{CN})_2$ [13]. For comparison, the related bromide derivative $(\text{dippe})\text{Ni}(\eta^3\text{-allyl})\text{Br}$ (**3**) was also synthesized by the reaction of $[\text{Ni}(\text{dippe})\text{H}]_2$ with allyl bromide (Eq. (2)), and its structure determined. Complex **3** is also square pyramidal with axial bromide, and was found to have similar Ni–C distances within the π -allyl unit and similar Ni–P distances (Table 1). The bromide appears to be slightly more bent towards the dippe ligand compared with the cyanide ligand. Note that bromo complex **3** does *not* react with KCN in THF to give cyano complex **2**.



The ^{31}P -NMR spectrum of **2** in THF- d_8 consists of a singlet at δ 80.8. The ^1H -NMR spectrum at 20°C shows

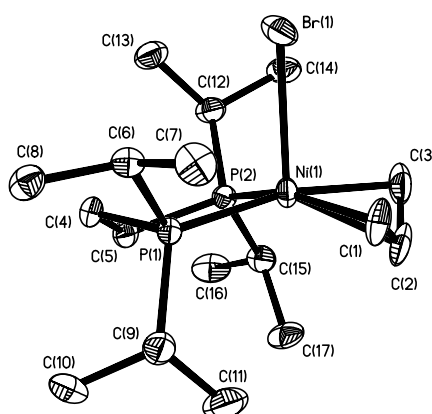


Fig. 1. ORTEP drawing of **2** and **3** showing 30% probability ellipsoids.

Table 1
Selected distances (Å) and angles (°) in (dippe)Ni(allyl)(CN) (**2**) and (dippe)Ni(allyl)Br (**3**)

Atoms	2 ^a	3
<i>Bond lengths</i>		
Ni(1A)–C(1A)	2.090(3), 2.098(3)	2.080(7)
Ni(1A)–C(2A)	1.997(3), 1.990(3)	2.012(7)
Ni(1A)–C(3A)	2.084(3), 2.078(3)	2.054(7)
Ni(1A)–X ^b	1.994(3), 1.983(3)	2.6409(12)
Ni(1A)–P(1A)	2.1916(8), 2.1847(8)	2.1936(19)
Ni(1A)–P(2A)	2.1894(9), 2.1899(8)	2.187(2)
<i>Bond angles</i>		
P(1)–Ni(1)–P(2)	88.72(3), 89.06(3)	89.90(7)
P(1)–Ni(1)–X	107.18(9), 106.56(9)	95.57(6)
P(2)–Ni(1)–X	106.23(10), 108.03(9)	104.39(6)

^a Two molecules in asymmetric unit.

^b For **2**, X = C(4A); for **3**, X = Br(1).

a quintet of triplets at δ 4.73 ($J = 9.0, 2.4$ Hz) for the methine proton (a) and a doublet at 2.97 ($J = 9.0$ Hz) for the combined *syn* and *anti* protons (b and c) of the allyl group. The dippe ligand gives resonances for two types of methyl groups at δ 1.27 and 1.12, each a doublet of doublets due to coupling to the adjacent methine and phosphorus nuclei. Only one kind of isopropyl methine is observed. The above data are consistent with rapid π -to σ -allyl interconversion in **2**, resulting in observation of a very symmetric time-averaged spectrum, similar to that reported for the related chloride (dippe)Ni(η^3 -methallyl)Cl [5]. ^{13}C labeled **2** was prepared by reaction of cation **1** with K^{13}CN in CH_3CN . While the yields were not as high, the labeled cyanide ligand could easily be identified in the ^{13}C -NMR spectrum at δ 154.8 as a triplet with a ^{13}C -P coupling of 10.3 Hz. This coupling clearly indicates that ^{13}C is coordinated to the Ni center in **2**, rather than simply acting as a counterion. Consistent with this observation, **2** also displays a CN stretch at 2096 cm^{-1} in an IR spectrum taken in THF solution, which is 20 cm^{-1} higher than that observed for free CN^- (KCN in THF solution).

Lowering the temperature of a solution of **2** resulted in decoalescence of its ^1H -NMR spectrum as shown in Fig. 2. Two observations can be made. First, the resonance at δ 2.97 for the *syn* and *anti* protons b and c collapses and reappears as two broad resonances at δ 3.21 and 2.59 (2H each) for the independent sets of protons. Therefore, π - σ allyl interconversion has been slowed at low temperature. In addition, the isopropyl methyl groups now give rise to four distinct resonances, indicating that the molecule now has a mirror plane of symmetry coincident with the P–Ni–P plane. Note that simply freezing out π - σ interconversion in this square pyramidal complex is expected to produce eight, rather than four, distinct methyl resonances in the ^1H -NMR spectrum as the methyl groups above and below the P–Ni–P plane are rendered inequivalent by the axial

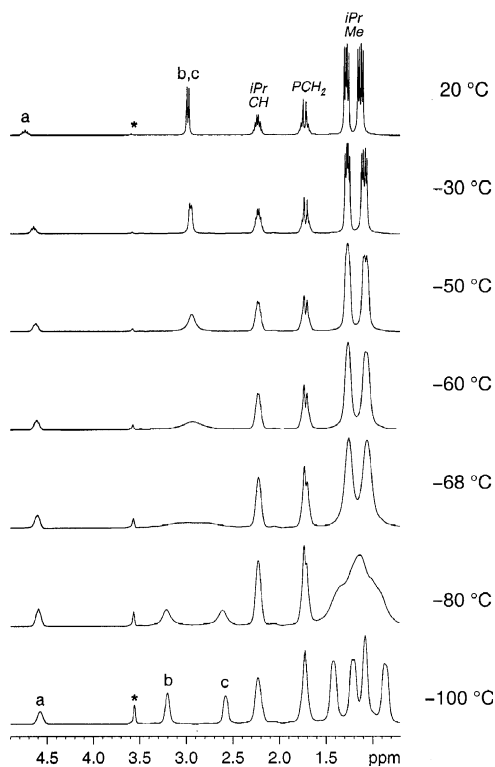
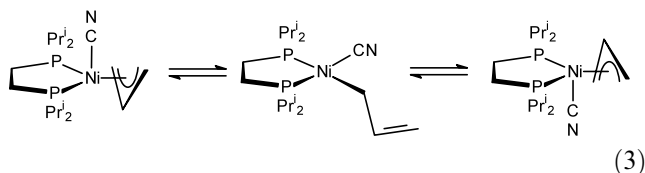


Fig. 2. VT ^1H -NMR spectra for (dippe)Ni(η^3 -allyl)(CN) (* = THF-d8).

cyanide ligand. Since only four resonances are observed, it is proposed that as the allyl group changes from η^3 to η^1 coordination, the cyanide moves into the basal plane to give a square planar Ni(II) intermediate, which has planar symmetry (Eq. (3)). Upon conversion back to the η^3 -allyl coordination mode, the cyano group may then end up on either side of the P–Ni–P plane, interconverting the ‘above’ and ‘below’ dippe methyl groups. From the separation of the allylic resonances (248 Hz), the barrier for interconversion at the coalescence temperature (-68 °C) can be estimated to be $\Delta G^\ddagger = 9.3\text{ kcal mol}^{-1}$. The chloro derivative (dippe)Ni(η^3 -methallyl)Cl was reported to behave similarly [5].



3. Conclusion

In summary, a new π -allyl derivative of nickel has been prepared with cyanide as the apical ligand. There is no evidence for ionization to give the cation in polar solvents. The bromo and cyano derivatives display similar structures. Rapid π - σ allyl interconversion is

observed at ambient temperature; coalescence of the *syn* and *anti* protons of the allyl group is observed at $-68\text{ }^{\circ}\text{C}$, leading to estimation of the barrier for this process as $\Delta G^{\ddagger} = 9.3\text{ kcal mol}^{-1}$.

4. Experimental

4.1. General methods

Et_4NCN and K^{13}CN were purchased from Aldrich and dried in vacuo overnight before use. The ligand dippe [14] and the complexes $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+[\text{BPh}_4]^-$ [3] and $[\text{Ni}(\text{dippe})\text{H}]_2$ [14] were prepared by literature protocols. All solvents, including THF- d_8 , were distilled or vacuum transferred from Na/benzophenone and stored in a Vacuum Atmospheres glove box; all reactions were performed in this glove box. Solvent removal in vacuo was performed either in the box or on a Schlenk line using standard techniques. Room temperature $^{31}\text{P}\{^1\text{H}\}$ and ^1H -NMR spectra were recorded on a Bruker AMX400 instrument; low temperature $^{31}\text{P}\{^1\text{H}\}$, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker Avance400 spectrometer. Chemical shifts are given in parts per million and referenced to residual solvent peaks (^1H and ^{13}C -NMR) or to an external standard (85% H_3PO_4 , ^{31}P -NMR). IR spectra were recorded in THF solution on a Mattson Instruments 6020 GALAXY Series FT spectrophotometer. Crystallographic data were collected using a Siemens SMART diffractometer with CCD detection. Elemental analysis was performed by Desert Analytics, Tucson, Arizona.

4.2. $(\text{dippe})\text{Ni}(\pi\text{-allyl})\text{CN}$ (2)

In an N_2 -filled glove box, a solution of NEt_4CN (53.4 mg, 342 μmol) in 5 ml CH_3CN was added to a pale yellow solution of $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+[\text{BPh}_4]^-$ (223.1 mg, 327 μmol) in 25 ml CH_3CN . The reaction mixture immediately turned wine-red. ^{31}P -NMR (unlocked, in CH_3CN) of an aliquot taken after 15 min showed 99% conversion to $(\text{dippe})\text{Ni}(\pi\text{-allyl})\text{CN}$, along with 1% free dippe. The volume of the reaction solution was reduced to 10 ml in vacuo, and white precipitate (the byproduct NEt_4BPh_4) appeared, which was removed by filtration through Celite. The filtrate was evaporated to dryness in vacuo, leaving red–orange solid. The residue was dissolved in 50 ml of a 4:1 mixture of Et_2O and THF, giving a wine-red solution that still contained white solid NEt_4BPh_4 , which was again removed by filtration through Celite. Concentration of the filtrate in vacuo to 5 ml resulted in formation of red microcrystals of product. After addition of 20 ml of pentane to the solution, the crystals were isolated by filtration and dried in vacuo (90.0 mg, 70.8% yield). $^{31}\text{P}\{^1\text{H}\}$ -NMR

(162 MHz, THF- d_8 , $20\text{ }^{\circ}\text{C}$) $\delta = 80.8$; ^1H -NMR (400 MHz, THF- d_8 , $20\text{ }^{\circ}\text{C}$) $\delta = 4.73$ (quin of t, $J = 9.0\text{ Hz}$, 2.4 Hz, 1H, π -allyl H_a), 2.97 (d, $J = 9.0\text{ Hz}$, 4H, π -allyl H_b , H_c), 2.22 (sext, $J = 7.2\text{ Hz}$, 4H, $^i\text{PrCH}$), 1.72 (m, $J = 9.2\text{ Hz}$, 26.1 Hz, 4H, PCH_2), 1.27 (dd, $J = 7.2\text{ Hz}$, 12.8 Hz, 12H, $^i\text{PrCH}_3$), 1.12 (dd, $J = 7.2\text{ Hz}$, 15.2 Hz, 12H, PrCH_3); IR (THF) $\nu_{\text{CN}} = 2096\text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{18}\text{H}_{37}\text{P}_2\text{NNi}$: C, 55.70; H, 9.61; N, 3.61. Found: C, 55.55; H, 9.79; N, 3.72%.

4.3. $(\text{dippe})\text{Ni}(\pi\text{-allyl})^{13}\text{CN}$

Method A in THF: In an N_2 -filled glove box, a suspension of K^{13}CN (7.2 mg, 108.9 μmol) in 5 ml THF was added to a vigorously stirred, pale yellow solution of $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+[\text{BPh}_4]^-$ (50.0 mg, 73.4 μmol) in 20 ml THF. The reaction solution turned slowly orange, then red. ^{31}P -NMR (unlocked, in THF) of an aliquot taken after 5 h showed 49% conversion to $(\text{dippe})\text{Ni}(\pi\text{-allyl})^{13}\text{CN}$, while 66% conversion was observed after 9 h. After 24 h, ^{31}P -NMR revealed that no starting material remained, but 14% of the product had decomposed to $(\text{dippe})\text{Ni}(\text{crotononitrile})$. The reaction solution was filtered through Celite to remove the byproduct KBPh_4 , and the filtrate was concentrated to dryness in vacuo, leaving a red–orange solid. A solution of the red solid in Et_2O was filtered again through Celite and allowed to stand at $-30\text{ }^{\circ}\text{C}$; after 24 h, red crystals of product were isolated, dried in vacuo, and used for ^{13}C -NMR. *Method B in CH_3CN :* Following the same procedure as for the non-labeled complex $(\text{dippe})\text{Ni}(\pi\text{-allyl})\text{CN}$, when 153.8 mg of $[(\text{dippe})\text{Ni}(\pi\text{-allyl})]^+[\text{BPh}_4]^-$ (226 μmol) and 17.9 mg of K^{13}CN (271 μmol) were used, 51.4 mg of red microcrystals were obtained (59% yield). $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, THF- d_8 , $-20\text{ }^{\circ}\text{C}$) $\delta = 80.8$ (d, $J = 9.7\text{ Hz}$); ^1H -NMR (400 MHz, THF- d_8 , $-20\text{ }^{\circ}\text{C}$) same as non-labeled complex; $^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, THF- d_8 , $-20\text{ }^{\circ}\text{C}$) $\delta = 154.8$ (t, $J_{\text{C-P}} = 10.3\text{ Hz}$, ^{13}CN), 89.7 (t, $J_{\text{C-P}} = 6.5\text{ Hz}$, π -allyl C_a), 53.7 (t, $J_{\text{C-P}} = 9.0\text{ Hz}$, π -allyl C_b), 26.6 (d, $J_{\text{C-P}} = 18.5\text{ Hz}$, $^i\text{PrCH}$), 22.1 (t, $J_{\text{C-P}} = 20.4\text{ Hz}$, PCH_2), 19.0 (d, $J_{\text{C-P}} = 3.7$, $^i\text{PrCH}_3$), 18.1 (s, $^i\text{PrCH}_3$).

4.4. Variable temperature NMR of $(\text{dippe})\text{Ni}(\pi\text{-allyl})\text{CN}$

$(\text{dippe})\text{Ni}(\pi\text{-allyl})\text{CN}$ was dissolved in THF- d_8 (17.7 mg/0.5 ml) producing a wine-red solution. To prevent decomposition to crotononitrile complexes, the solution was frozen in liquid N_2 until the start of the experiment. $^{31}\text{P}\{^1\text{H}\}$ and ^1H spectra were then recorded on a Bruker Avance400 instrument at $5\text{ }^{\circ}\text{C}$ intervals between -110 and $20\text{ }^{\circ}\text{C}$. All $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra consisted of a sharp singlet, which shifted progressively downfield as the temperature was lowered (6.6 ppm difference between $\delta(-100\text{ }^{\circ}\text{C})$ and $\delta(20\text{ }^{\circ}\text{C})$), while the ^1H -

NMR spectra varied with temperature as shown in Fig. 2. Additional ^1H -NMR spectra were collected at -67 , -68 and -69 °C in order to precisely identify the temperature at which the *syn* and *anti* protons on the terminal carbon of the π -allyl group coalesce (determined to be -68 °C).

4.5. (dippe)Ni(π -allyl)Br (**3**)

In an N_2 -filled glove box, allyl bromide (4.2 μl , 48.5 μmol) was added to a very dark red solution of [(dippe)Ni(μ -H)]₂ (15.7 mg, 24.4 μmol) in THF-*d*₈. The reaction mixture immediately turned bright red, evolution of H_2 gas was observed, and some bright red–orange precipitate formed. $^{31}\text{P}\{^1\text{H}\}$ and ^1H -NMR spectra showed that the solution contained predominantly (dippe)Ni(π -allyl)Br. KCN (4.4 mg, 67.6 μmol) was then added to the solution in the glove box, and the mixture was sonicated for 1 h, then heated to 55 °C for 3 h, and finally allowed to stand at RT for 4 days. However, no conversion to (dippe)Ni(π -allyl)CN was observed. Filtration of the reaction mixture followed by evaporation of solvent from the filtrate yielded red-brown powder, which was washed with pentane and recrystallized from THF/pentane at -30 °C; dark red crystals of the product were obtained in low yield (< 50%) and characterized by X-ray diffraction. $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, THF-*d*₈, 21 °C) $\delta = 71.5$; ^1H -NMR (400 MHz, THF-*d*₈, 21 °C) $\delta = 4.73$ (quin, $J = 10.0$ Hz, 1H, π -allyl H_a), 3.86 (very br s, 2H, π -allyl H_b), 3.39 (very br s, 2H, π -allyl H_c), 2.8–2.0 (very br m, 4H, $^i\text{PrCH}$), 1.80 (br d, $J = 14.4$ Hz, 4H, PCH_2), 1.5–0.9 (very br m, 24H, $^i\text{PrCH}_3$).

In a separate experiment, the red–orange precipitate formed during this reaction was isolated by filtration, recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, and identified through X-ray crystallographic analysis as (dippe)NiBr₂. An organic byproduct of the reaction, propene, was also identified by comparison of its ^1H -NMR spectrum (obtained after vacuum transfer of the volatiles from the reaction mixture into a clean NMR tube) with that of an authentic sample.

4.6. Experimental details of X-ray structural determinations

Single crystals of **2** and **3** were mounted under Paratone-8277 on glass fibers and immediately placed in a cold nitrogen stream at -80 °C on the X-ray diffractometer. The X-ray intensity data were collected with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s per frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of

56.54°). Frames were integrated with the Siemens SAINT program to 0.75 Å. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three dimensional centroids of > 5000 reflections. Data were corrected for absorption using the program SADABS [15]. Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on F^2 [16]. For both of the structures, the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions giving data:parameter ratios greater than 10:1. There was nothing unusual about the solution or refinement of either of the structures, except that **2** contained two independent molecules in the asymmetric unit. Further experimental details of the X-ray diffraction studies are shown in Table 2, and positional parameters for all atoms, anisotropic thermal parameters, all bond lengths and angles, as well as fixed hydrogen positional parameters are given in the supporting information for both of the structures.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 207394 and 207395. Copies of

Table 2
Summary of crystallographic data for **2** and **3**

Crystal parameters	2	3
Chemical formula	$\text{C}_{18}\text{H}_{37}\text{NNiP}_2$	$\text{C}_{17}\text{H}_{37}\text{BrNiP}_2$
Formula weight	388.14	442.03
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Z	8	4
<i>a</i> (Å)	17.2805(9)	14.0186(12)
<i>b</i> (Å)	14.8588(7)	8.2869(7)
<i>c</i> (Å)	17.4578(8)	19.3198(16)
β (°)	112.2040(10)	109.7020(10)
<i>V</i> (Å ³)	4150.2(3)	2113.0(3)
ρ_{calc} (g cm ⁻³)	1.242	1.389
Crystal dimension (mm)	0.08 × 0.20 × 0.24	0.18 × 0.24 × 0.36
Temperature (°C)	−80	−80
μ (mm ⁻¹)	1.087	2.955
Absorption correction	Empirical (SADABS)	Empirical (SADABS)
2θ Range (°)	1.86–23.25	2.24–23.26
No. of data collected	18 188	9129
No. of unique data	5934	3036
No. of params varied	397	190
$R_1(F_o)$, $wR_2(F_o^2)$, ($I > 2\sigma(I)$)	0.0378, 0.0782	0.0702, 0.1310
$R_1(F_o)$, $wR_2(F_o^2)$, all data	0.0470, 0.0812	0.0741, 0.1322
Goodness of fit	1.134	1.501

this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supporting Information includes tables of collection parameters, distances, angles and coordinates for the structures.

Acknowledgements

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