

Synthesis and Reactivity of Group 6 and 10 Complexes of the Bis(dialkylaminophosphanyl)imine $i\text{PrN}=\text{C}[\text{CH}_2\text{P}(\text{N}i\text{Pr}_2)_2]_2$

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The coordination behaviour of the readily prepared, potentially ambidentate, bis(α,α' -phosphanyl)imine ($i\text{Pr}_2\text{N}$)₂-PCH₂C(=NiPr)CH₂P(NiPr₂)₂ (**1**, **PNP**) has been investigated. Treatment of palladium(II), platinum(II), chromium(0), and molybdenum(0) sources with ligand **1** afforded complexes in which **1** was coordinated solely in a bidentate *P,N*-chelating

fashion with a non-coordinating bis(diisopropylamino)phosphanyl-substituted pendant arm. Ligand **1** and complexes [PdCl₂(**PNP**- $\kappa^2\text{P,N}$)] (**2**) and [Mo(CO)₄(**PNP**- $\kappa^2\text{P,N}$)] (**10**) were characterised in the solid state by X-ray crystallography. The preparation of cationic Pd^{II} derivatives of **PNP** is discussed.

Introduction

There is continued interest in hetero-bifunctional “hybrid” ligands, which possess two chemically distinct donor sites that are each able to interact to a different extent with a chelated metal centre (e.g. one soft and one hard donor).^[1] The asymmetry present in systems of this type offers a degree of selectivity in reactions occurring at the metal centre, due to the electronic and steric disparity between the two different donor groups. In addition, it has been suggested that ligands of this type confer a “flexible” coordination environment at the metal centre, such that a vacant coordination site can be generated reversibly, without complete dissociation of the ligand (so-called “hemilability”). This feature is of considerable importance in catalysis and, since phosphanes are essential components in numerous industrially relevant catalytic processes, it is perhaps not surprising that many of the best-studied “hybrid” systems contain a *P*-donor constituent.

Currently there is a considerable resurgence in the use of heteroatom substituents at phosphorus to “tune” the steric demands and basicity of phosphane ligands.^[2] This is due,

in part, to the ease with which phosphorus–heteroatom bonds can be formed, as exemplified by *P–O* and *P–N* moieties. Diaminophosphanes have been targeted for study as they exhibit enhanced σ -donor strength (basicity) when compared with arylphosphanes and even triaminophosphanes, yet are often more easily prepared than strongly basic alkylphosphanes.^[2h]

As the number of stoichiometric and catalytic applications involving hetero-bifunctional ligands increases,^[3,4] simple, high-yielding syntheses of such species are of particular interest. Recently, we have reported the simple, “one-pot” synthesis of the bis(α,α' -phosphanyl)-substituted imines, e.g. **PNP** (**1**; Figure 1).^[5] These compounds are rare examples of a potentially chelating diaminophosphane-containing “hybrid” ligand. However, the presence of one imino- and two phosphanyl-donor sites permits **1** to potentially adopt a number of different coordination modes, examples of which are outlined in Figure 1. Here we report preliminary studies of the coordination chemistry of this ligand, with particular emphasis placed on investigating its mode of binding.

Results and Discussion

Neutral Palladium(II) Derivatives

The dichloro complex [PdCl₂(**PNP**- $\kappa^2\text{P,N}$)] (**2**) is readily prepared through addition of **PNP** (**1**), prepared as reported previously,^[5] to a dichloromethane solution of [PdCl₂(NPh)₂] at ambient temperature, the reaction reaching completion within 1 h according to ³¹P{¹H} NMR spectroscopy (Scheme 1). Removal of volatile components

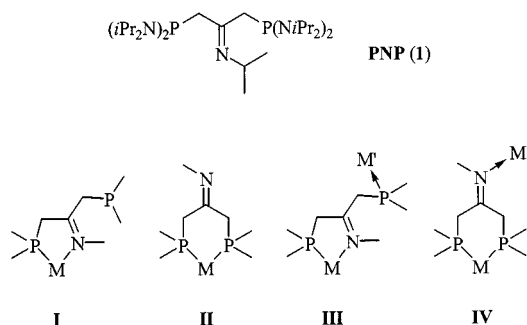
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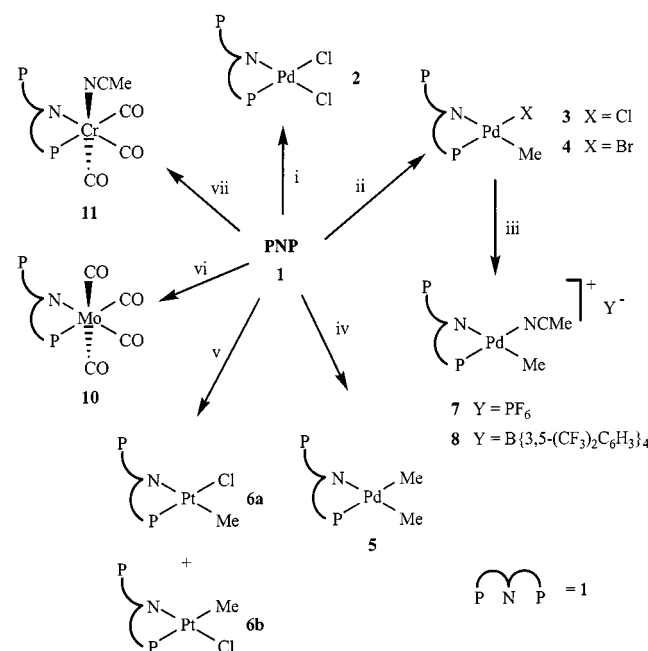
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Figure 1. Ligand **1** and its potential binding modes

in vacuo, followed by washing with dry hexane affords **2** as a yellow, air-stable, analytically pure powder in 90% yield, which exhibits a fragment ion at $m/z = 702$ $\{[\text{PdCl}(\text{PNP})]^+\}$ by mass spectrometry.



Scheme 1. Reagents and conditions: i: $\text{trans-}[\text{PdCl}_2(\text{NCPh})_2]$, CH_2Cl_2 , room temp., 2 h; ii: $[\text{PdX}(\text{Me})(\text{cod})]$ ($\text{X} = \text{Cl}, \text{Br}$), CH_2Cl_2 , room temp., 1 h; iii: NaY ($\text{Y} = \text{PF}_6$, $[\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$, CH_3CN , room temp., 3 d; iv: $[\text{PdMe}_2(\text{tmeda})]$, CH_2Cl_2 , room temp., 2 d; v: $[\text{PtCl}(\text{Me})(\text{cod})]$, CDCl_3 , room temp., 3 d; vi: $\text{cis-}[\text{Mo}(\text{CO})_4(\text{pip})_2]$, CH_2Cl_2 , room temp., 18 h; vii: $\text{fac-}[\text{Cr}(\text{CO})_3(\text{NCMe})_3]$, toluene, room temp., 2 d

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2** exhibits two sharp resonances at $\delta = +100.9$ (s) and $+51.9$ (s). The considerable downfield shift of only one of the two resonances associated with **1** (Table 1) upon coordination ($\Delta\delta \approx 50$ ppm) suggests that in **2** the **PNP** ligand (**1**) is coordinated in a bidentate P,N -chelating bonding mode (**I**; Figure 1), with a pendant bis(diisopropylamino)phosphane arm.^[6] The lack of any detectable $^4J_{\text{PP}}$ coupling constant for **2** could result either from an alteration in the angle between the two phosphorus centres or from the change in hybridization of the phosphorus atom upon coordination.^[7] There is no evidence by NMR of any exchange between

the free and bound phosphane components of **2** over the temperature regime -80 to $+40$ °C. The ^1H NMR spectroscopic data for the **PNP** moiety are little changed following its coordination to the palladium centre with the two methylene resonances being obtained at $\delta = 2.94$ (s) and $\delta = 3.61$ (d, $^2J_{\text{PH}} = 11.6$, endocyclic CH_2), although the latter clearly exhibits a coupling to the phosphorus atom; both CH_2 groups appear as singlets in the ^1H NMR spectrum of **1**.^[5] Similarly, ^{13}C NMR spectroscopy clearly distinguishes the two different CH_2 environments: $\delta = 54.4$ (dd, $^1J_{\text{PC}} = 35.6$, $^3J_{\text{PC}} = 10.8$ Hz) and 38.5 (dd, $^1J_{\text{PC}} = 20.6$, $^3J_{\text{PC}} = 9.8$ Hz). The former has been assigned to the endocyclic methylene group based on its coordination chemical shift change ($\Delta\delta \approx 10$ ppm). As expected, the imine carbon atom appears as a doublet of doublets at $\delta = 176.6$ ($^2J_{\text{PC}} = 16.5$, 8.3 Hz), exhibiting a downfield shift compared with uncoordinated **1** [$\delta = 166.0$ (dd, $^2J_{\text{PC}} = 15.0$, 9.5 Hz)].

Table 1. ^{31}P NMR spectroscopic data for **PNP** (**1**) and its complexes

Compound	Solvent	$^{31}\text{P}\{^1\text{H}\}$
1	CDCl_3	$+53.1$ (d, $^4J_{\text{PP}} = 14.5$ Hz), $+46.2$ (d, $^4J_{\text{PP}} = 14.5$ Hz) ^[a]
2	CDCl_3	$+100.9$ (s), $+51.9$ (s) ^[b]
3	CDCl_3	$+112.6$ (s), $+49.3$ (s) ^[c]
4	CDCl_3	$+114.5$ (s), $+49.8$ (s) ^[c]
5	CDCl_3	$+113.2$ (s), $+48.9$ (s) ^[b]
6	CDCl_3	$+82.1$ ($^1J_{\text{PPt}} = 6007.0$), $+49.0$ (s), $+70.2$ ($^1J_{\text{PPt}} = 4565.0$), $+51.3$ (s)
7	CDCl_3	$+108.4$ (s), $+52.8$ (s), -143.4 (sept, $^1J_{\text{PF}} = 706.5$, PF_6^-) ^[c]
8	CDCl_3	$+108.4$ (s), $+52.8$ (s) ^[c]
9	CDCl_3	$+108.4$ (s), $+52.9$ (s) ^[c]
10	C_6D_6	$+132.1$ (s), $+51.4$ (s) ^[d]
11	CDCl_3	$+158.3$ (s), $+50.3$ (s) ^[d]

[a] 81.0 MHz. [b] 122.0 MHz. [c] 101.3 MHz. [d] 109.4 MHz.

Preparation of **2** through reaction of **1** with $[\text{PdCl}_2(\text{cod})]$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) was considerably slower (ca. 2 d) than with $[\text{PdCl}_2(\text{NCPh})_2]$. This observation is presumed to reflect the higher barrier to dissociation of the chelating cod ligand, compared with that for benzonitrile, and is consistent with the observation that $[\text{PdCl}_2(\text{tmeda})]$ does not react with **PNP**.

In contrast, **1** reacted rapidly at room temperature with dichloromethane solutions of $[\text{PdX}(\text{Me})(\text{cod})]$ to afford $[\text{PdX}(\text{Me})(\text{PNP-}\kappa^2P,N)]$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**)] quantitatively within 1 h, according to ^{31}P NMR spectroscopy (Scheme 1). Complexes **3** and **4** could be isolated as air-stable, cream solids in 85 and 72% yields, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra suggest that ligand **1** again adopts a P,N -chelating bonding mode (**I**; Figure 1), with the formation of a single isomer in each case [e.g. **3**: δ : $+112.6$ (s), $+49.3$ (s)] (Table 1). In contrast with **2**, the endocyclic CH_2 resonance from **3** now displays both $^2J_{\text{PH}}$ and $^4J_{\text{PH}}$ couplings (overlapping resonances obscure the signal for **4**). The presence of one methyl ligand environment was confirmed

by both ^1H [e.g. **3**: $\delta = 0.71$ (s)] and ^{13}C [e.g. **3**: $\delta = 0.8$ (d)] NMR spectroscopy. The ^1H NMR chemical shifts associated with the methyl ligand are comparable to those observed for related $[\text{PdCl}(\text{Me})(P',N')]$ complexes (ca. 0.7 ppm).^[8,9] Resonances corresponding to the exo- and endocyclic CH_2 groups are readily detected by ^{13}C NMR spectroscopy for **3** and **4**. Again, neither **3** nor **4** showed any evidence for exchange of the free and bound phosphane moieties.

The small magnitudes of the $^2J_{\text{P-Pd-C}}$ coupling constants associated with the methyl ligands (**3**: 7.3 Hz; **4**: 9.0 Hz) suggest that both complexes **3** and **4** adopt a structure in which the strongly *trans*-influencing methyl group lies *trans* to the weakly *trans*-influencing imine *N*-atom, i.e. the thermodynamically favoured form.^[10] This is consistent with data from other palladium complexes possessing a *P,N*-ligand.^[11] However, Boersma has indicated that caution must be used when spectroscopic methods are employed to assign *cis/trans* configurations about Pd for these types of complex.^[8] The geometric assignment for complex **3** is strongly supported by a combination of COSY and NOE NMR experiments.

Attempts were made to prepare the corresponding dimethyl complex, $[\text{PdMe}_2(\text{PNP-}\kappa^2P,N)]$, by methylation of complexes **2**, **3**, and **4** with Me_2LiCu , MeLi , or MeMgBr at low temperatures by analogy with previous work.^[12] In each case, an inseparable mixture of products, including some resulting from deprotonation of the coordinated PNP ligand methylene backbone, was obtained on warming to room temperature. There was no evidence for the generation of any Pd–Me species.

In contrast, treating a dichloromethane solution of the known $[\text{PdMe}_2(\text{tmeda})]$ complex with 1 equiv. of ligand **1** cleanly afforded a single new product, which has tentatively been assigned as $[\text{PdMe}_2(\text{PNP-}\kappa^2P,N)]$ (**5**), according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy [$\delta = +113.2$ (s), $+48.9$ (s)] in 77% yield (Scheme 1).^[9] Complete displacement of tmeda by PNP occurred within 2 d at room temperature. The exchange is presumably aided by the strong *trans* influence of the two methyl groups that facilitate dissociation of the diamine.

Problems were encountered, however, with the ^1H and ^{13}C NMR spectra associated with **5**. In both cases, only a single resonance attributable to a palladium-bound methyl ligand could be detected [^1H : $\delta = 0.73$ (d, $^3J_{\text{PH}} 0.9$ Hz); ^{13}C : $\delta = -0.6$ (d, $^2J_{\text{PC}} 7.8$ Hz)]. Variable-temperature, T_1 , and correlated $^1\text{H}/^{13}\text{C}$ NMR spectra were obtained but did not aid identification.

The correct formulation of **5** as $[\text{PdMe}_2(\text{PNP-}\kappa^2P,N)]$ was suggested by mass spectrometry, which exhibited ions at $m/z = 681$ and 695 corresponding to the species $[\text{PdH}(\text{Me})(\text{PNP})]^+$ and $[\text{PdMe}_2(\text{PNP})]^+$, respectively. Elemental analyses were irreproducible and inconclusive, possibly as a result of the lack of long-term thermal stability of the dimethyl complex. However, further support for the formation of the desired species was obtained by treating a sample of **5** with 1 equiv. of dppe in dichloromethane. This cleanly afforded the known $[\text{PdMe}_2(\text{dppe})]$ complex ($\delta =$

$+55.7$) with concomitant liberation of ligand **1**, according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.^[12]

Neutral Platinum(II) Derivatives

Attempts were made to prepare the analogous platinum(II) complexes of PNP. Somewhat surprisingly, no reaction was observed between either $[\text{PtCl}_2(\text{cod})]$ or $[\text{PtCl}_2(\text{NCR})_2]$ ($\text{R} = \text{Me}, \text{Ph}$) and ligand **1** in chlorinated solvents even at elevated temperatures (under rigorously dry and anaerobic conditions). In each case, **1** could be recovered unchanged. However, displacement of cod from unsymmetrical $[\text{PtCl}(\text{Me})(\text{cod})]$ by **1** proved more facile (vide supra). After 3 d at room temp., $[\text{PtCl}(\text{Me})(\text{PNP-}\kappa^2P,N)]$ (**6a,b**) was obtained as a mixture of *trans* and *cis* isomers according to ^{31}P NMR spectroscopy (20:1) in CDCl_3 , the product in which the phosphorus atom lies *trans* to the chloride ion (**6a**) being the major species ($^1J_{\text{PtP}} = 6007.0$ Hz). No interconversion of isomers was observed on prolonged heating.

Cationic Palladium(II) Derivatives

Part of our interest in group 10 complexes of the sterically demanding ligand PNP, arises from their potential to serve as precursors to the corresponding cationic Pd^{II} salts for application in olefin oligomerisation and polymerisation.^[14,15] Initial, unsuccessful attempts to prepare the desired alkyl cations focussed on halide abstraction from acetonitrile solutions of the dichloro and chloro(methyl) complexes **2** and **3**, respectively, using a variety of silver salts. In each case, oxidation and subsequent decomposition of the *P,N*-ligand accompanied by precipitation of colloidal palladium was observed.

In contrast, halide abstraction from **3** using 1 equiv. of NaY ($\text{Y} = \text{PF}_6$, $[\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$) proceeded cleanly in acetonitrile at room temperature to afford the monocationic acetonitrile adducts $[\text{PdMe}(\text{NCCH}_3)(\text{PNP-}\kappa^2P,N)]\text{Y}$ ($\text{Y} = \text{PF}_6$ (**7**); $\text{Y} = [\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ (**8**)) (Table 1, Scheme 1), which could be isolated as moisture-sensitive, yellow/brown solids. Elemental analyses and variable-temperature ^1H NMR spectroscopy confirmed the presence of acetonitrile in both complexes. At 300 K complex **7** presents a broadened resonance at $\delta = 2.33$ ($\nu_{1/2} = 11$ Hz), which is replaced by two singlets ($\delta = 2.45$ and 2.04) in a 50:1 ratio at 243 K, corresponding to bound and a trace of residual free CH_3CN , respectively. [Pure acetonitrile displays a single resonance at $\delta = 2.04$ by ^1H NMR spectroscopy (400.1 MHz, CDCl_3) at 243 K.] This behaviour has been attributed to the CH_3CN ligand of **7** undergoing slow exchange with any residual CH_3CN at 300 K, a process that no longer occurs at lower temperatures. Similarly, complex **8** exhibits a single resonance at $\delta = 2.23$ (300 K), which is resolved into two signals at 243 K ($\delta = 2.30$ and 2.04) corresponding to bound and free CH_3CN , respectively.

Surprisingly, treatment of **3** with NaBPh_4 under identical reaction conditions resulted in the formation of the acetonitrile-free salt $[\text{PdMe}(\text{NCCH}_3)(\text{PNP-}\kappa^2P,N)][\text{BPh}_4]$ (**9**), as confirmed by both elemental analyses and variable-temper-

ature ^1H NMR spectroscopy. Indeed, the room-temperature ^1H NMR spectrum of a freshly prepared CDCl_3 solution of **9** shows no evidence of free or bound acetonitrile. On lowering the temperature to 243 K, a small resonance corresponding to a trace of residual unbound CH_3CN was detected ($\delta = 2.04$), despite extended drying of the solid sample of **9** under high vacuum. There was no indication of bound acetonitrile. Addition of 1.1 equiv. of CH_3CN to this sample, followed by cooling to 243 K, merely increased the intensity of the signal corresponding to unbound CH_3CN .

The coordination of the tetraphenylborate anion to electron-deficient metal centres is now well documented.^[16] Thus, it seems reasonable to suggest that the formation of complex **9** as a base-free species has to be attributed to the presence of the $[\text{BPh}_4]^-$ anion presumably as a result of ion pairing. However, variable-temperature ^1H NMR spectroscopy, over the temperature regime 243–300 K, could not establish the nature of the cation–anion interaction for **9**. The possibility of intermolecular coordination of the pendant diaminophosphane arm or a monomer/dimer equilibrium was, however, clearly ruled out by ^{31}P NMR spectroscopy (243–300 K).

Salts **7** and **8** are stable in acetonitrile solution and in the solid state under nitrogen (months). Complex **8** is also stable in CDCl_3 solution, but both **7** and **9** decompose slowly in dry chlorinated solvents (24 h at room temp.). Despite the differences in structure, complexes **7**–**9** exhibit virtually identical ^{31}P NMR spectra, in both CD_3CN and CDCl_3 . As for the neutral Pd^{II} derivatives, ^{13}C NMR spectroscopy readily distinguishes two CH_2 environments for the cationic derivatives **7**–**9**. Just as was observed for **3** the ^1H NMR spectra of these complexes display both $^2J_{\text{PH}}$ and $^4J_{\text{PH}}$ couplings to the endocyclic CH_2 resonance.

In the olefin polymerisation arena, high catalytic activities have been achieved by combining sterically encumbered metal alkyl cations with a noncoordinating anion such as the perfluorinated analogue of BPh_4 , $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.^[17] Hence, a number of attempts were made to prepare the palladium **PNP** salts of this anion. Both halide elimination from **3**, using $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$, and alkyl abstraction from the proposed dimethyl complex **5** by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, led to intractable mixtures of largely unidentifiable but similar products according to NMR spectroscopy, when performed under rigorously dry and anaerobic conditions. However, for the latter reaction, the formation of Ph_3CH was evident presumably as a result of hydride abstraction by the trityl cation. There was no evidence of C_6F_5 -group transfer to the metal centre.

Carbonylmetal Coordination Chemistry

The potential for ligand **1** to adopt a number of different coordination modes is readily apparent (Figure 1). Thus, in order to probe the coordination behaviour of **PNP** (**1**), substitution reactions between **1** and a number of group 6 carbonyl complexes were undertaken. Subsequently, examination of the metal–carbonyl stretching frequencies from the resulting complexes can be used to assess the relative basi-

city of the chelating ligand **1**, although some caution must be observed when comparing carbonyl stretching frequencies of unsymmetrical chelate complexes.^[2c,2h]

Treating a dichloromethane solution of $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ (pip = piperidine) with an equimolar amount of chelate **1** cleanly afforded the six-coordinate carbonylmolybdenum complex $[\text{cis-Mo}(\text{CO})_4(\text{PNP-}\kappa^2P,N)]$ (**10**) in 64% yield after 18 h at room temperature. The complex was isolated, after workup, as an air-stable crystalline solid. Data from both $^{31}\text{P}\{^1\text{H}\}$ NMR and infrared spectroscopy are consistent with ligand **1** being coordinated in a bidentate, P,N fashion [$\delta = +132.1$ (s), $+51.4$ (s)] (mode **I**; Figure 1). A compound which possesses identical spectroscopic data to those obtained for **10** was isolated in low yield (28%) from the reaction of **1** with $[\text{Mo}(\text{CO})_3(\text{cht})]$ (cht = η^6 -cycloheptatriene). In the latter case, the formation of **10** is believed to result from carbon monoxide scrambling.

As was observed for the palladium–**PNP** derivatives, complex **10** is rigid on the NMR timescale, with no interconversion of the free and bound phosphane components being detectable. The infrared spectroscopic data from complex **10** reveal that the presence of the diisopropylamino substituents on the phosphane component does render ligand **1** slightly more basic when compared with the values of the range of carbonyl stretching frequencies observed for similar P,N -ligands bearing a diphenylphosphane moiety bound to the $\text{Mo}(\text{CO})_4$ fragment (Table 2). However, ligand **1** remains considerably less basic than the strongly σ -donating bis(pyrrolyl)-substituted diphosphane, $(\text{pyrrolyl})_2\text{P}(\text{CH}_2)_2\text{P}(\text{pyrrolyl})_2$ [$\tilde{\nu}_{\text{CO}} = 2044, 1970, 1916 \text{ cm}^{-1}$], which possesses related diamino phosphane components, as a result of aromatic delocalisation of the nitrogen lone pair in the latter.^[2b]

Table 2. Representative metal–carbonyl stretching frequencies observed for $[\text{Mo}(\text{CO})_4(\kappa^2P,N)]$ complexes

κ^2 ligand	$\tilde{\nu}_{\text{CO}}$	Ref.
1	2009, 1897, 1882, 1822	This work
 PPh_2 R = Me	2014, 1905, 1887, 1853	[18]
 PPh_2 R = H	2020, 1910, 1870, 1843	[19]
 PPh_2	2018, 1911, 1897, 1850	[20]
 PPh_2	2020, 1905, 1850	[21]
 PPh_2	2013, 1909, 1878, 1820	[22]

Treatment of a toluene solution of *fac*- $[\text{Cr}(\text{CO})_3(\text{NCCH}_3)_3]$ with 1 mol-equiv. of **1** afforded a single phosphorus-containing product according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy [$\delta = +158.3$ (s) and $+50.3$ (s)] after 2 d at room temp. Cooling (-30°C , 12 h) of a concentrated

toluene/pentane solution of the crude mixture produced yellow/orange microcrystals in a low yield (23%).

The ^{31}P , ^1H , and ^{13}C NMR spectroscopic data are consistent with the formulation of this product as the mono(acetonitrile) adduct, *fac*-[Cr(CO) $_3$ (NCCH $_3$)(PNP- $\kappa^2\text{P},\text{N}$)] (**11**), with **1** again adopting a mode **I** coordination (Figure 1).

In the IR spectrum of **11**, recorded under rigorously dry, anaerobic conditions (KBr, Nujol), no C–N absorption corresponding to bound CH $_3$ CN could be detected. For comparison, an IR spectrum of an authentic sample of *fac*-[Cr(CO) $_3$ (NCMe) $_3$] [C $_9$ H $_9$ N $_3$ O $_3$ Cr (259.18): calcd. C 41.71, H 3.50, N 16.21; found C 41.79, H 3.39, N 16.09] was recorded under identical conditions. In contrast to the original work,^[40] no CN absorption was detectable at 2280 cm $^{-1}$, despite the carbonyl regions being identical [experimentally observed IR (Nujol): $\tilde{\nu}$ = 1915, 1782 cm $^{-1}$]. Neither decomposition nor the appearance of free CH $_3$ CN was observed over a period of approximately 30 min.

The isolation of an octahedral group 6, tricarbonyl/mono(acetonitrile) complex bearing a bidentate ligand is not without precedent.^[23] The formation of a bridged species of the type [{Cr(CO) $_5$] $_2$ (PNP- $\kappa^2\text{P},\text{P}$)], resulting from CO scrambling, is clearly ruled out by ^{31}P NMR spectroscopy.^[24] Both the ^1H and ^{13}C NMR spectra show some line broadening, which appears temperature-independent (–45 to +40 °C). This suggests the presence of traces of a paramagnetic chromium species rather than any fluxionality associated with **11**. Such an explanation is reinforced by the broadened signals observed for the residual protio impurities of the deuterated NMR solvents. All attempts to further purify **11** were unsuccessful and resulted in decomposition. Prolonged cooling of the reaction mixture containing **11** eventually yielded inseparable mixtures of Cr(CO) $_6$ and **11**. Simply heating a toluene solution containing equimolar amounts of **1** and hexacarbonylchromium resulted in the formation of an intractable mixture of unidentified products with no evidence consistent with the formation of **11**.

Investigation of the Reactivity of the Pendant Diaminophosphane Arm

Since complexes **2**–**11** all possess a pendant, non-coordinating diaminophosphane moiety, it was of interest to investigate the reactivity of this group. Preliminary studies employing [PdCl $_2$ (PNP- $\kappa^2\text{P},\text{N}$)] (**2**) are somewhat surprising. In dry dichloromethane solution, no reaction was observed at either of the two phosphorus centres with molecular oxygen, sulfur, BH $_3$ (THF), Me $_3$ SiN $_3$, or [Mo(CO) $_5$ (THF)]. In contrast, **1** reacted rapidly with elemental sulfur.^[5] A similar lack of reactivity towards boranes or chalcogens was noted for the free phosphane arm of **10**.

It is noteworthy that despite the well-documented reactivity of P–N bonds towards protic reagents, complexes **2**, **3**, and **4** were found stable to alcoholysis, even in neat anhydrous methanol.^[25] However, when solutions of complex **2** were treated with 1 equiv. of either methyl iodide or benzyl bromide (CH $_2$ Cl $_2$, –30 °C), many unidentifiable products

were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Similar reactivity is observed when the oxidative addition of alkyl halides is attempted with **1**.

Molecular Structure Determinations

Surprisingly few metal complexes of chelating ligands bearing a diaminophosphane unit rather than a dialkyl- or diarylphosphane have been structurally characterised.^[2c,26,27] This prompted an investigation of the molecular structures of ligand **1** and complexes **2** and **10** in the solid state.

The crystal structure of **1** revealed that the geometric parameters associated with the imine moiety [C=N 1.268(4) Å, C(3)–N(1)–C(4) 122.8(2)°, sum of angles about C(3) = 360.0°] are typical of this functionality (Figure 2, Table 3).^[2c] A staggered conformation is adopted such that the lone pair of phosphorus atom P(1) is directed away from those on both the imine nitrogen N(1) and the second phosphorus atom P(2). As is observed for many aminophosphanes, the four P–N bond lengths are significantly shorter than that associated with a true P–N single bond, the sums of angles about nitrogen atoms N(2) to N(5) [358.4, 359.9, 360.0, 360.0°, respectively] indicating significant sp 2 character;^[28] together this suggests there is a degree of lone pair donation from the nitrogen atom to the phosphorus atoms.

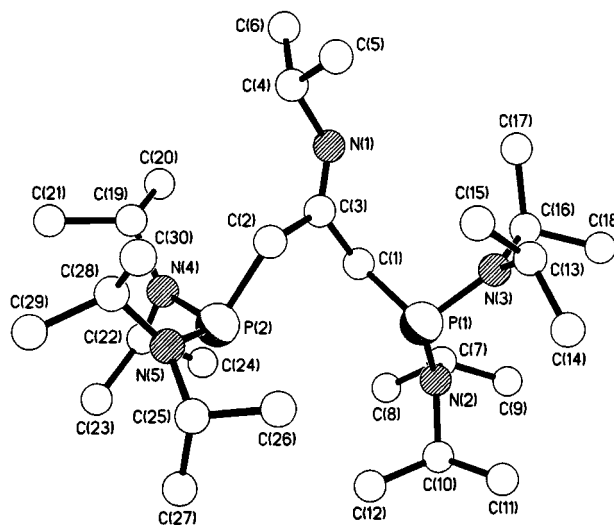


Figure 2. Molecular structure of PNP (**1**)

Table 3. Selected bond lengths [Å] and angles [°] for ligand PNP (**1**)

P(1)–N(3)	1.691(2)	P(1)–N(2)	1.698(2)
P(1)–C(1)	1.870(3)	P(2)–N(5)	1.703(2)
P(2)–N(4)	1.687(2)	P(2)–C(2)	1.857(3)
N(1)–C(3)	1.268(4)	C(1)–C(3)	1.502(4)
C(2)–C(3)	1.509(4)		
N(3)–P(1)–N(2)	110.0(1)	N(3)–P(1)–C(1)	102.6(1)
N(2)–P(1)–C(1)	99.5(1)	N(5)–P(2)–N(4)	109.7(1)
N(5)–P(2)–C(2)	100.7(1)	N(4)–P(2)–C(2)	102.3(1)
C(3)–N(1)–C(4)	122.8(2)	C(3)–C(1)–P(1)	114.8(2)
C(3)–C(2)–P(2)	117.1(2)	N(1)–C(3)–C(2)	126.9(2)
N(1)–C(3)–C(1)	117.0(2)	C(2)–C(3)–C(1)	116.1(2)

The molecular structure determination of complex **2** (Figure 3, Table 4) revealed a near square-planar geometry, the palladium centre and its four coordinated atoms being co-planar to within 0.049 Å, with a *cis*-PdCl₂ arrangement. No inter- or intramolecular interaction of the pendant phosphane P(2) was observed, the closest intermolecular contact being 4.93 Å to Cl(2). The P(1)–Pd and N(1)–Pd bond lengths of 2.197(2) and 2.112(7) Å, respectively, and the P(1)–Pd–N(1) angle of 81.7(2)° are entirely consistent with those reported for similar Pd^{II} complexes.^[11,29] The non-equivalence observed for the two palladium–chlorine

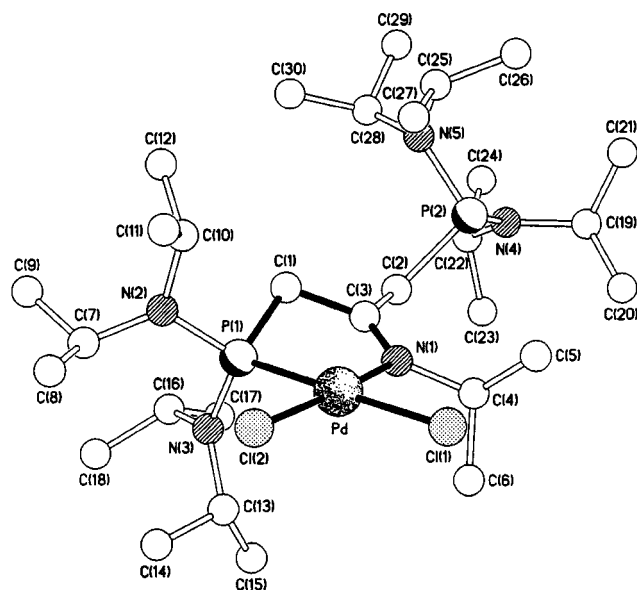


Figure 3. Molecular structure of $[\text{PdCl}_2(\text{PNP-}\kappa^2\text{P,N})]$ (**2**)

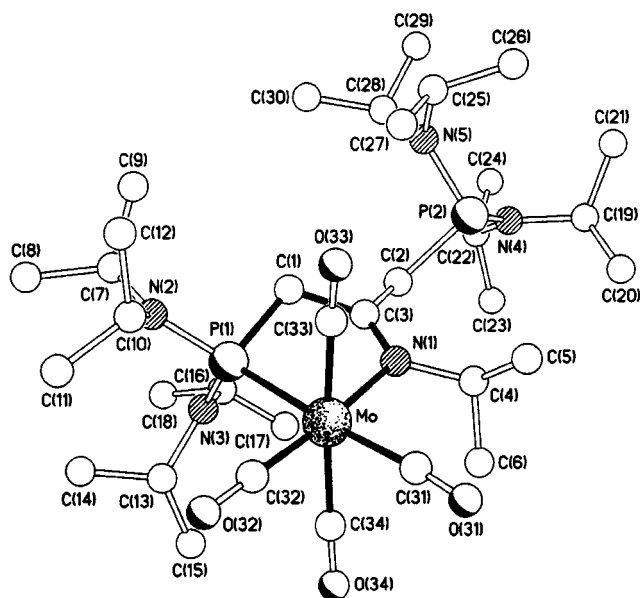
Table 4. Selected bond lengths [Å] and angles [°] for complex **2**

Pd–N(1)	2.112(7)	Pd–P(1)	2.197(2)
Pd–Cl(2)	2.306(3)	Pd–Cl(1)	2.412(2)
P(1)–N(3)	1.647(7)	P(1)–N(2)	1.669(6)
P(1)–C(1)	1.838(8)	P(2)–N(5)	1.690(8)
P(2)–N(4)	1.697(8)	P(2)–C(2)	1.880(8)
N(1)–C(3)	1.293(11)	C(1)–C(3)	1.518(10)
C(2)–C(3)	1.504(12)		
N(1)–Pd–P(1)	81.7(2)	N(1)–Pd–Cl(2)	171.4(2)
P(1)–Pd–Cl(2)	90.12(9)	N(1)–Pd–Cl(1)	100.8(2)
P(1)–Pd–Cl(1)	176.86(8)	Cl(2)–Pd–Cl(1)	87.51(9)
N(3)–P(1)–N(2)	109.5(4)	N(3)–P(1)–C(1)	109.0(4)
N(2)–P(1)–C(1)	104.1(4)	N(3)–P(1)–Pd	111.7(3)
N(2)–P(1)–Pd	121.7(3)	C(1)–P(1)–Pd	99.4(3)
N(5)–P(2)–N(4)	111.3(4)	N(5)–P(2)–C(2)	102.8(4)
N(4)–P(2)–C(2)	98.2(4)	C(3)–N(1)–C(4)	119.2(7)
C(3)–N(1)–Pd	119.6(5)	C(4)–N(1)–Pd	121.1(5)
C(3)–C(1)–P(1)	107.5(6)	C(3)–C(2)–P(2)	113.1(6)
N(1)–C(3)–C(2)	127.0(7)	N(1)–C(3)–C(1)	117.9(7)
C(2)–C(3)–C(1)	115.1(7)		

bond lengths Pd–Cl(1) and Pd–Cl(2) of 2.412(2) and 2.306(3) Å, respectively, reflects the larger *trans* influence of phosphorus compared to nitrogen.^[30]

Following its complexation to the PdCl₂ fragment, ligand **1** adopts a folded envelope conformation with C(3) and C(1) lying 0.37 and 0.88 Å, respectively, “above” the coordination plane a geometry that results from the presence of the planar C=N moiety. There is little perturbation of the metrical parameters for the imine fragment [C(3)–N(1) 1.293(11) Å, C(3)–N(1)–C(4) 119.2(7)°, sums of angles at C(3) and N(1) 360.0 and 359.9°, respectively]. Similarly, the geometry around each of the four amino nitrogen atoms N(2) to N(5) remains essentially planar (sum of angles 359.4, 359.9, 359.5, and 359.3°, respectively). The P–N bond lengths in the non-coordinated aminophosphane moiety [P(2)–N(4) 1.697(8); P(2)–N(5) 1.690(8) Å] are both marginally longer than their counterparts [P(1)–N(2) 1.669(6), P(1)–N(3) 1.647(7) Å] in the metal-bound component. As in the free ligand **1**, these distances are significantly shorter than the values quoted for a P–N single bond,^[28] but are in line with those of other structurally characterised coordinated aminophosphanes.^[2c,26,27,31]

For comparison, the crystal structure of **10** was also determined and is presented in Figure 4 with selected bond lengths and angles given in Table 5. The comparatively small P–N “bite angle” [P(1)–Mo–N(1) 75.96(9)°] of ligand **1** results in a distorted octahedral geometry about the molybdenum centre. The metal atom lies only 0.011 Å from the equatorial plane formed by atoms P(1), N(1), and the two carbonyl ligands C(31) and C(32), which are coplanar to within 0.042 Å. The contracted geometry at the molybdenum centre caused by the small bite angle of the chelating ligand is compensated in the equatorial plane by an increase in both the adjacent angles P(1)–Mo–C(32) and N(1)–Mo–C(31) to 95.8(2) and 100.4(2)°, respectively. The two pseudo-axial carbonyl ligands bend slightly away from the chelating ligand [C(33)–Mo–C(34) 171.8(2)°]. As was observed for the palladium complex **2**, the P–N-metallacycle adopts a folded envelope conformation with C(3) and C(1) lying 0.25 and 0.77 Å, respectively, “above” the coordination plane. Again the metric parameters of the imine fragment [N(1)–C(3) of 1.287(5) Å, C(3)–N(1)–C(4) 117.9(4)°] differ little from those for the free ligand **1**, with both N(1) and C(3) remaining essentially planar (sums of angles around both atoms 360°). Similarly, the P(1)–N bond lengths, and the geometries about N(2) and N(3), show little alteration from those of the free ligand. The Mo–N(1) bond length [2.356(4) Å] is comparable with other Mo–N σ-donor bonds.^[29,31] The greater *trans* influence of phosphorus over nitrogen is reflected in the molybdenum–carbonyl bond lengths of the equatorial carbonyl ligands with that to C(31) being significantly longer than that to C(32) [Mo–C(31) 1.987(6) Å, Mo–C(32) 1.940(6) Å]. The molybdenum–phosphorus bond length of 2.5367(11) Å [P(1)–Mo] is unremarkable.^[22,29,33] There are no short inter- or intramolecular interactions involving the pendant phosphane P(2), the closest intermolecular contact being 5.46 Å to O(32).

Table 5. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for complex **10**

Mo-C(32)	1.940(6)	Mo-C(31)	1.987(6)
Mo-C(34)	2.026(5)	Mo-C(33)	2.052(5)
Mo-N(1)	2.356(4)	Mo-P(1)	2.5367(11)
P(1)-N(2)	1.687(4)	P(1)-N(3)	1.692(3)
P(1)-C(1)	1.843(4)	P(2)-N(5)	1.680(4)
P(2)-N(4)	1.694(4)	P(2)-C(2)	1.890(4)
N(1)-C(3)	1.287(5)	C(1)-C(3)	1.497(5)
C(2)-C(3)	1.516(5)		
C(32)-Mo-C(31)	87.9(3)	C(32)-Mo-C(34)	84.4(3)
C(31)-Mo-C(34)	84.0(3)	C(32)-Mo-C(33)	92.3(2)
C(31)-Mo-C(33)	88.4(3)	C(34)-Mo-C(33)	171.8(2)
C(32)-Mo-N(1)	171.3(2)	C(31)-Mo-N(1)	100.4(2)
C(34)-Mo-N(1)	93.8(2)	C(33)-Mo-N(1)	90.5(2)
C(32)-Mo-P(1)	95.8(2)	C(31)-Mo-P(1)	176.1(2)
C(34)-Mo-P(1)	97.8(2)	C(33)-Mo-P(1)	90.1(2)
N(1)-Mo-P(1)	75.96(9)	N(2)-P(1)-N(3)	108.2(2)
N(2)-P(1)-C(1)	104.0(2)	N(3)-P(1)-C(1)	104.8(2)
N(2)-P(1)-Mo	121.6(2)	N(3)-P(1)-Mo	118.20(14)
C(1)-P(1)-Mo	96.70(13)	N(5)-P(2)-N(4)	111.7(2)
N(5)-P(2)-C(2)	101.7(2)	N(4)-P(2)-C(2)	98.3(2)
C(3)-N(1)-C(4)	117.9(4)	C(3)-N(1)-Mo	121.2(3)
C(4)-N(1)-Mo	120.9(3)	C(3)-C(1)-P(1)	113.5(3)
C(3)-C(2)-P(2)	112.7(2)	N(1)-C(3)-C(1)	118.6(3)
N(1)-C(3)-C(2)	125.8(4)	C(1)-C(3)-C(2)	115.6(3)

Together, these observations suggest that the easily prepared, chelating *P,N*-ligand **1** makes an interesting partner for a range of metals. The straightforward synthesis and now predictable coordination geometry of bis(phosphanyl)imine **1** offers considerable scope for further “tuning” the

The apparent lack of reactivity of the pendant, non-coordinated, diaminophosphane unit warrants additional study. If the reactions at this site can be controlled, then this "arm" could be exploited as a means of "immobilising" these complexes on insoluble support materials such as silica or cross-linked polystyrenes. Further coordination chemistry and catalysis studies are on-going.

All manipulations were performed under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Solvents were freshly distilled under nitrogen from sodium/benzophenone (tetrahydrofuran, diethyl ether, toluene), from calcium hydride (dichloromethane, acetonitrile), from sodium (hexane, pentane), or from P_2O_5 (C_6D_6 , CD_3CN , and $CDCl_3$) and degassed prior to use. Elemental analyses were performed by the microanalytical services of Imperial College or by S. Boyer at the University of North London. NMR spectra were recorded with a Bruker AC200, AM 250, AMX 300, AMX 400, or JEOL 270; chemical shifts were referenced to residual protio impurities in the deuterated solvent (1H), to the deuterated solvent (^{13}C), external $CFCl_3$ (^{19}F), or to external aqueous 85% H_3PO_4 (^{31}P). All spectra were obtained at ambient probe temperatures unless stated otherwise. Infrared spectra were recorded [Nujol mulls (KBr windows), KBr discs, or in solution (KBr windows)] with either Perkin–Elmer 1600 or Mattson Research Series 1 spectrophotometers; Nujol was dried over sodium wire. Mass spectra were recorded with either Kratos Concept 1H or AutospecQ instruments and are reported in (*m/z*). **PNP** (**1**),^[5] *cis*-[Mo(CO)₄(pip)₂],^[34] *fac*-[Cr(CO)₃(NCCH₃)₃],^[35] *trans*-[PdCl₂(NCPh)₂],^[36] [PdCl₂(cod)],^[37] [PdCl₂(tmeda)], [PdMe₂(tmeda)],^[9] [PdCl(Me)(cod)],^[38] [PtCl(Me)-(cod)],^[11b] and Na[B{4,5-(CF₃)₂C₆H₃}₄]^[39] were prepared according to literature procedures. [PdBr(Me)(cod)] was prepared using a procedure based on that used for the preparation of [PdCl(Me)-(cod)] but starting with [PdBr₂(cod)]. All other chemicals were obtained commercially and used as received. Melting points were obtained in sealed glass tubes under nitrogen, using a Gallenkamp melting point apparatus and are uncorrected. A variable-temperature 1H NMR study of the various cationic palladium systems reported is recorded in the electronic Supporting Information in addition to ORTEP views for each of the molecular structures determined by X-ray crystallography.

Synthesis of [PdCl₂(PNP-*κ*-P,N)] (2): A dichloromethane (10 mL) solution of **1** (0.32 g, 0.57 mmol) was added to a solution of [PdCl₂(NCPPh₂)] (0.22 g, 0.57 mmol) in dichloromethane (10 mL) at -30 °C. The mixture was allowed to warm to room temp. and

stirred for 2 h, affording a red-orange solution. Removal of solvent under reduced pressure gave a yellow-orange solid that was washed with Et_2O (3×10 mL) yielding a pale yellow analytically pure sample of **2** (0.38 g, 90% yield). Single crystals suitable for study by X-ray diffraction were obtained following prolonged cooling (-30 °C) of a concentrated $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution, m.p. > 225 °C (dec.). $\text{C}_{30}\text{H}_{67}\text{Cl}_2\text{N}_5\text{P}_2\text{Pd}$ (737.16): calcd. C 48.88, H 9.18, N 9.50; found C 49.02, H 9.02, N 9.48. MS (FAB^+ , NBA matrix): $m/z = 702$ [$\text{M} - \text{Cl}$]. ^1H NMR (270.1 MHz, CDCl_3): $\delta = 1.08$ [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.16 [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.28 [d, 12 H, $^3J_{\text{H,H}} = 6.9$, $\text{PNCH}(\text{CH}_3)_2$], 1.45 [d, 12 H, $^3J_{\text{H,H}} = 6.9$, $\text{PNCH}(\text{CH}_3)_2$], 1.65 [d, 6 H, $^3J_{\text{H,H}} = 6.7$, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 2.94 (s, 2 H, CH_2), 3.35 (m, 4 H, PNCH), 3.61 (d, 2 H, $^2J_{\text{PH}} = 11.6$, CH_2), 4.07 (sept, 4 H, $^3J_{\text{H,H}} = 6.9$, PNCH), 4.28 (sept, 1 H, $^3J_{\text{H,H}} = 6.7$, $\text{C}=\text{NCH}$). ^{13}C $\{^1\text{H}\}$ NMR (68.0 MHz, CDCl_3): $\delta = 23.1$ [s, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 24.4 [d, $^3J_{\text{CP}} = 6.2$, $\text{PNCH}(\text{CH}_3)_2$], 25.2 [d, $^3J_{\text{CP}} = 7.2$, $\text{PNCH}(\text{CH}_3)_2$], 25.7 [s, $\text{PNCH}(\text{CH}_3)_2$], 38.5 (dd, $^1J_{\text{CP}} = 20.6$, $^3J_{\text{CP}} = 9.8$, exocyclic PCH_2), 47.7 (d, $^2J_{\text{CP}} = 10.3$, PNCH), 50.0 (d, $^2J_{\text{CP}} = 7.2$, PNCH), 54.4 (dd, $^1J_{\text{CP}} = 35.6$, $^3J_{\text{PC}} = 10.8$, endocyclic PCH_2), 59.0 (s, $\text{C}=\text{NCH}$), 176.6 (dd, $^2J_{\text{CP}} = 8.3$, 16.5, $\text{C}=\text{N}$).

Synthesis of $[\text{PdCl}(\text{Me})(\text{PNP-}\kappa^2\text{P,N})]$ (3**):** A dichloromethane solution (10 mL) of **1** (0.72 g, 1.28 mmol) was added to a solution of $[\text{PdCl}(\text{Me})(\text{cod})]$ (0.34 g, 1.28 mmol) in dichloromethane (10 mL) at -30 °C. The mixture was allowed to warm to room temp. and stirred for 1 h, affording a red solution. Removal of solvent under reduced pressure gave a yellow-orange solid that was washed with Et_2O (3×10 mL) yielding **3** as a cream powder that was used without further purification (0.78 g, 85% yield), m.p. > 200 °C (dec.). $\text{C}_{31}\text{H}_{70}\text{ClN}_5\text{P}_2\text{Pd}$ (716.74): calcd. C 54.64, H 10.38, N 10.28; found C 55.01, H 10.10, N 10.20. MS (FAB^+ , NBA matrix): $m/z = 717$ [M^+], 702 [$\text{M}^+ - \text{Me}$], 681 [$\text{M}^+ - \text{Cl}$]. ^1H NMR (400.1 MHz, CDCl_3): $\delta = 0.71$ (s, 3 H, $\text{Pd}-\text{CH}_3$), 1.11 [d, 12 H, $^3J_{\text{H,H}} = 6.6$, $\text{PNCH}(\text{CH}_3)_2$], 1.20 [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.30 [24 H, overlapping d, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.60 [d, 6 H, $^3J_{\text{H,H}} = 6.5$, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 2.85 (s, 2 H, CH_2), 3.31 (dd, 2 H, $^2J_{\text{PH}} = 10.0$, $^4J_{\text{PH}} = 1.5$, CH_2), 3.39 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, $^3J_{\text{PH}} = 11.1$, PNCH), 3.92 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, PNCH), 4.10 (sept, 1 H, $^3J_{\text{H,H}} = 6.5$, $\text{C}=\text{NCH}$). ^{13}C $\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 0.75$ (d, $^2J_{\text{CP}} = 7.3$, $\text{Pd}-\text{CH}_3$), 22.9 [s, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 24.9 [d, $^3J_{\text{CP}} = 7.1$, $\text{PNCH}(\text{CH}_3)_2$], 24.4 [d, $^3J_{\text{CP}} = 6.4$, $\text{PNCH}(\text{CH}_3)_2$], 24.6 [d, $^3J_{\text{CP}} = 2.4$, $\text{PNCH}(\text{CH}_3)_2$], 26.1 [d, $^3J_{\text{CP}} = 2.1$, $\text{PNCH}(\text{CH}_3)_2$], 37.3 (dd, $^1J_{\text{CP}} = 19.7$, $^3J_{\text{CP}} = 5.7$, exocyclic PCH_2), 46.9 (d, $^2J_{\text{CP}} = 10.9$, PNCH), 47.8 (d, $^2J_{\text{CP}} = 9.3$, PNCH), 50.6 (dd, $^1J_{\text{CP}} = 26.5$, $^3J_{\text{CP}} = 7.3$, endocyclic PCH_2), 56.0 (s, $\text{C}=\text{NCH}$), 171.2 (dd, $^2J_{\text{CP}} = 5.7$, 16.1, $\text{C}=\text{N}$).

Synthesis of $[\text{PdBr}(\text{Me})(\text{PNP-}\kappa^2\text{P,N})]$ (4**):** In a similar manner to the above, reaction of **1** (0.132 g, 0.24 mmol) in dichloromethane (25 mL) with a solution of $[\text{PdBrMe}(\text{cod})]$ (0.073 g, 0.24 mmol) in dichloromethane (15 mL) at -30 °C afforded **4**. Recrystallisation from a mixture of ether and dichloromethane (1:1) and prolonged cooling to -30 °C afforded **4** as yellow-orange microcrystals (0.14 g, 72% yield). A small (50 mg) sample of **4** was recrystallised a second time using the same combination to afford a microcrystalline material that afforded correct elemental analyses, m.p. > 195 °C (dec.). $\text{C}_{31}\text{H}_{70}\text{BrN}_5\text{P}_2\text{Pd}$ (761.32): calcd. C 48.92, H 9.27, N 9.20; found C 48.95, H 9.20, N 9.19. MS (FAB^+ , NBA matrix): $m/z = 761$ [M^+], 747 [$\text{M}^+ - \text{CH}_2$], 681 [$\text{M}^+ - \text{Br}$]. ^1H NMR (301.5 MHz, CDCl_3): $\delta = 0.71$ (s, 3 H, $\text{Pd}-\text{CH}_3$), 1.08 [d, 12 H, $^3J_{\text{H,H}} = 6.7$ Hz, $\text{PNCH}(\text{CH}_3)_2$], 1.18 [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.28 [m, 24 H, $\text{PNCH}(\text{CH}_3)_2$], 1.60 [d, 6 H, $^3J_{\text{H,H}} = 6.4$, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 2.84 (s, 2 H, CH_2), 3.35 (m, 6 H, PNCH and

CH_2), 3.90 (m, 4 H, PNCH), 4.08 (sept, 1 H, $^3J_{\text{H,H}} = 6.4$, $\text{C}=\text{NCH}$). ^{13}C $\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3): $\delta = -1.7$ (d, PdCH_3 , $^3J_{\text{PC}} = 9.0$), 21.9 [s, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 23.0 [d, $^3J_{\text{PC}} = 6.6$, $\text{PNCH}(\text{CH}_3)_2$], 23.2 (d, $J_{\text{PC}} = 3.0$), 23.5 [d, $^3J_{\text{PC}} = 7.2$, $\text{PNCH}(\text{CH}_3)_2$], 24.5 [d, $^3J_{\text{PC}} = 3.0$, $\text{PNCH}(\text{CH}_3)_2$], 36.4 (dd, $^1J_{\text{PC}} = 19.2$, $^3J_{\text{PC}} = 4.5$, exocyclic PCH_2), 46.1 (d, $^2J_{\text{PC}} = 10.8$, PNCH), 47.0 (d, $^2J_{\text{PC}} = 9.0$, PNCH), 49.2 (dd, $^2J_{\text{PC}} = 25.9$, 7.2, endocyclic PCH_2), 54.7 (s, $\text{C}=\text{NCH}$), 170.4 (m, $\text{C}=\text{N}$).

$[\text{PdMe}_2(\text{PNP-}\kappa^2\text{P,N})]$ (5**):** To a mixture of $[\text{PdMe}_2(\text{tmeda})]$ (0.48 g, 1.9 mmol) and **1** (1.07 g, 1.9 mmol) was added dichloromethane (30 mL) at room temp. The yellow reaction mixture was stirred for 48 h at room temp. before volatile components were removed in vacuo. The resulting off white solid was washed with Et_2O (3×10 mL). Complex **5** was dried under vacuum (1.02 g, 77% yield), m.p. > 180 °C (dec.). $\text{C}_{32}\text{H}_{73}\text{N}_5\text{P}_2\text{Pd}$ (696.46): calcd. C 55.18, H 10.59, N 10.06; found C 49.27, H 10.67, N 10.18. MS (FAB^+ , NBA matrix): $m/z = 696$ [M^+], 682 [$\text{M}^+ - \text{CH}_2$]. ^1H NMR (301.5 MHz, CDCl_3): $\delta = 0.73$ (d, 3 H, $^3J_{\text{PH}} = 0.9$, $\text{Pd}-\text{CH}_3$), 1.12 [d, 12 H, $^3J_{\text{H,H}} = 6.4$, $\text{PNCH}(\text{CH}_3)_2$], 1.22 [d, 12 H, $^3J_{\text{H,H}} = 6.4$, $\text{PNCH}(\text{CH}_3)_2$], 1.31 [d, 12 H, $^3J_{\text{H,H}} = 6.9$, $\text{PNCH}(\text{CH}_3)_2$], 1.34 [d, 12 H, $^3J_{\text{H,H}} = 7.1$, $\text{PNCH}(\text{CH}_3)_2$], 1.61 [d, 6 H, $^3J_{\text{H,H}} = 6.5$, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 2.87 (s, 2 H, CH_2), 3.33 (dd, 2 H, $^2J_{\text{PH}} = 13.7$, $^4J_{\text{PH}} = 3.8$, CH_2), 3.40 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, PNCH), 3.94 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, PNCH), 4.12 (sept, 1 H, $^3J_{\text{H,H}} = 6.5$, $\text{C}=\text{NCH}$). ^{13}C $\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3): $\delta = -0.6$ (d, $^2J_{\text{PC}} = 7.8$, $\text{Pd}-\text{CH}_3$), 22.7 [s, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 24.3 [d, $^3J_{\text{PC}} = 6.6$, $\text{PNCH}(\text{CH}_3)_2$], 24.4 [d, $^3J_{\text{PC}} = 3.0$, $\text{PNCH}(\text{CH}_3)_2$], 24.7 [d, $^3J_{\text{PC}} = 7.2$, $\text{PNCH}(\text{CH}_3)_2$], 25.9 [d, $^3J_{\text{PC}} = 2.4$, $\text{PNCH}(\text{CH}_3)_2$], 37.4 (dd, $^1J_{\text{PC}} = 19.0$, $^3J_{\text{PC}} = 5.7$, exocyclic PCH_2), 47.3 (d, $^2J_{\text{PC}} = 11.4$, PNCH), 48.1 (d, $^2J_{\text{PC}} = 9.0$, PNCH), 50.6 (dd, $^1J_{\text{PC}} = 27.1$, $^3J_{\text{PC}} = 8.4$, endocyclic PCH_2), 55.8 (s, $\text{C}=\text{NCH}$), 171.3 (dd, $^2J_{\text{PC}} = 16.0$, $^2J_{\text{PC}} = 5.7$, $\text{C}=\text{N}$).

$[\text{PtCl}(\text{Me})(\text{PNP-}\kappa^2\text{P,N})]$ (6**):** An NMR tube fitted with a J. Young's valve was charged with **1** (71 mg, 0.13 mmol), $[\text{PtCl}(\text{Me})(\text{cod})]$ (45 mg, 0.13 mmol) and CDCl_3 (0.5 mL) under nitrogen. After 3 d at room temp., no further evolution was observed according to ^{31}P NMR spectroscopy. Removal of volatile components in vacuo, followed by washing with Et_2O (2×2 mL) afforded a mixture of both *cis* and *trans* isomers of **6** as a white powder (0.10 g, 98% yield), m.p. > 230 °C (dec.). $\text{C}_{31}\text{H}_{70}\text{ClN}_5\text{P}_2\text{Pt}$ (805.53) calcd. C 46.22, H 8.78, N 8.71; found C 46.24, H 8.73, N 8.68. MS (FAB^+ , NBA matrix): $m/z = 805$ [M^+], 790 [$\text{M}^+ - \text{Me}$], 770 [$\text{M}^+ - \text{Cl}$]. ^1H NMR (301.5 MHz, CDCl_3), major isomer **6a** only: $\delta = 0.77$ (d, 3 H, $^3J_{\text{PH}} = 2.0$, $\text{Pt}-\text{CH}_3$), 1.12 [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.22 [d, 12 H, $^3J_{\text{H,H}} = 6.7$, $\text{PNCH}(\text{CH}_3)_2$], 1.31 [d, 12 H, $^3J_{\text{H,H}} = 7.0$, $\text{PNCH}(\text{CH}_3)_2$], 1.32 [d, 12 H, $^3J_{\text{H,H}} = 7.0$, $\text{PNCH}(\text{CH}_3)_2$], 1.64 [d, 6 H, $^3J_{\text{H,H}} = 6.4$, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 2.85 (s, 2 H, CH_2), 3.22 (dd, 2 H, $^2J_{\text{PH}} = 12.6$, $^4J_{\text{PH}} = 1.5$, CH_2), 3.40 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, PNCH), 4.03 (sept, 4 H, $^3J_{\text{H,H}} = 6.7$, PNCH), 4.63 (sept, 1 H, $^3J_{\text{H,H}} = 6.7$, $\text{C}=\text{NCH}$). ^{13}C $\{^1\text{H}\}$ NMR (75.8 MHz, CDCl_3), major isomer **6a** only: $\delta = -15.4$ (d, $^2J_{\text{PH}} = 4.8$, $\text{Pt}-\text{CH}_3$), 22.5 [s, $\text{C}=\text{NCH}(\text{CH}_3)_2$], 24.2 [d, $^3J_{\text{PC}} = 6.0$, $\text{PNCH}(\text{CH}_3)_2$], 24.5 [d, $^3J_{\text{PC}} = 3.0$, $\text{PNCH}(\text{CH}_3)_2$], 24.7 [d, $^3J_{\text{PC}} = 7.2$, $\text{PNCH}(\text{CH}_3)_2$], 25.7 [d, $^3J_{\text{PC}} = 2.4$, $\text{PNCH}(\text{CH}_3)_2$], 38.0 (dd, $^1J_{\text{PC}} = 18.9$, $^3J_{\text{PC}} = 6.6$, exocyclic PCH_2), 47.3 (d, $^2J_{\text{PC}} = 10.8$, PNCH), 47.8 (d, $^2J_{\text{PC}} = 8.4$, PNCH), 51.0 (dd, $^1J_{\text{PC}} = 41.8$, $^3J_{\text{PC}} = 9.3$, endocyclic PCH_2), 57.2 (s, $\text{C}=\text{NCH}$), 173.6 (dd, $^2J_{\text{PC}} = 15.1$ and 3.6, $\text{C}=\text{N}$).

Synthesis of $[\text{PdMe}(\text{NCCH}_3)(\text{PNP-}\kappa^2\text{P,N})][\text{PF}_6]$ (7**):** A Schlenk tube was charged with **3** (108 mg, 0.15 mmol), NaPF_6 (28 mg, 0.17 mmol), and CH_3CN (15 mL) under nitrogen. After stirring at room temp. for 3 d, the reaction mixture was filtered and all volatile components removed in vacuo to afford **7** as a yellow solid, which

was dried under high vacuum overnight (115 mg, 91% yield), m.p. > 109–110 °C (dec.). $C_{33}H_{73}F_6N_6P_3Pd$ (867.31) calcd. C 45.70, H 8.48, N 9.69; found C 45.78, H 8.32, N 9.56. MS (FAB⁺, NBA matrix): m/z = 681 [M^+ – CH_3CN]. IR (KBr disc): $\tilde{\nu}$ = 2287 (C≡N), 2313 (C≡N). ¹H NMR (400.1 MHz, $CDCl_3$): δ = 0.50 (s, 3 H, Pd– CH_3), 1.12 [d, 12 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 1.23 [d, 12 H, $^3J_{H,H}$ = 6.8, PNCH(CH_3)₂], 1.32 [m, 30 H, PNCH(CH_3)₂ and C=NCH(CH_3)₂], 2.33 (br. s, $\nu_{1/2}$ 11 Hz, CH_3CN), 2.93 (s, 2 H, CH_2), 3.37 (d, 2 H, $^2J_{PH}$ = 11.5, CH_2), 3.43 (sept, 4 H, $^3J_{H,H}$ = 6.6, $^4J_{PH}$ = 1.6, PNCH), 3.86 (sept, 4 H, $^3J_{H,H}$ = 6.8, PNCH), 4.09 (sept, 1 H, $^3J_{H,H}$ = 6.6, C=NCH). ¹³C NMR (62.9 MHz, CD_3CN): δ = 0.3 (d, $^2J_{PC}$ = 6.6, Pd– CH_3), 23.9 [d, $^3J_{PC}$ = 3.6, C=NCH(CH_3)₂], 24.5 [d, $^3J_{PC}$ = 3.6, PNCH(CH_3)₂], 24.9 [d, $^3J_{PC}$ = 6.6, PNCH(CH_3)₂], 25.2 [d, $^3J_{PC}$ = 7.1, PNCH(CH_3)₂], 26.1 [d, $^3J_{PC}$ = 3.1, PNCH(CH_3)₂], 39.2 (dd, $^1J_{PC}$ = 20.3, $^3J_{PC}$ = 6.6, exocyclic PCH_2), 48.2 (d, $^2J_{PC}$ = 11.7, PNCH), 49.5 (d, $^2J_{PC}$ = 8.1, PNCH), 53.4 (dd, $^1J_{PC}$ = 32.0, $^3J_{PC}$ 5.1, endocyclic PCH_2), 56.1 (d, $^3J_{PC}$ = 3.0, C=NCH), 176.3 (dd, $^2J_{PC}$ = 13.5, $^2J_{PC}$ = 4.8, C=N). ¹⁹F (235.3 MHz, CD_3CN): δ = –73.3 (d, $^1J_{PF}$ = 706.5).

Synthesis of [PdMe(NCCH₃)(PNP- κ^2P,N)]{B[3,5-(CF₃)₂C₆H₃]}₄ (8): To a mixture of **3** (125 mg, 0.14 mmol) and Na[B[3,5-(CF₃)₂C₆H₃]}₄ (100 mg, 0.14 mmol) was added acetonitrile (20 mL) at room temp. After 3 d at room temp., the solution was filtered to eliminate NaCl and the solvent subsequently removed under reduced pressure to afford a yellow solid of **8**, which was dried under high vacuum overnight (194 mg, 91% yield), m.p. 57–60 °C. $C_{65}H_{85}BF_{24}N_6P_2Pd$ (1585.35): calcd. C 49.24, H 5.42, N 5.30; found C 49.16, H 5.50, N 5.26. MS (FAB⁺, NBA matrix): m/z = 681 (M^+ – CH_3CN). IR (KBr disc): $\tilde{\nu}$ = 2288 (C≡N), 2316 (C≡N). ¹H NMR (400.1 MHz, $CDCl_3$): δ = 0.50 (s, 3 H, Pd CH_3), 1.11 [d, 12 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 1.23 [d, 12 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 1.30–1.37 [m, 30 H, C=NCH(CH_3)₂ and PNCH(CH_3)₂], 2.23 (s, 3 H, CH_3CN), 2.90 (s, 2 H, CH_2), 3.39–3.48 [m, 6 H, PNCH(CH_3)₂ and CH_2], 3.82 [sept, 4 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 4.08 [sept, 1 H, $^3J_{H,H}$ = 6.6, C=NCH(CH_3)₂], 7.54 (s, 4 H, *p*-C₆H₃), 7.71 (8 H, *o*-C₆H₃). ¹³C NMR (62.9 MHz, CD_3CN): δ = 0.3 (d, $^2J_{PC}$ = 6.2, Pd CH_3), 23.8 [d, $^4J_{PC}$ = 3.5, C=NCH(CH_3)₂], 24.5 [d, $^3J_{PC}$ = 3.5, PNCH(CH_3)₂], 24.8 [d, $^3J_{PC}$ = 6.9, PNCH(CH_3)₂], 25.2 [d, $^3J_{PC}$ = 7.6, PNCH(CH_3)₂], 26.1 [d, $^3J_{PC}$ = 2.8, PNCH(CH_3)₂], 39.1 (dd, $^1J_{PC}$ = 20.5, $^3J_{PC}$ = 6.6 exocyclic PCH_2), 48.2 [d, $^2J_{PC}$ = 11.8, PNCH(CH_3)₂], 49.4 [d, $^2J_{PC}$ = 8.3, PNCH(CH_3)₂], 53.3 (dd, $^1J_{PC}$ = 32.5, $^3J_{PC}$ = 4.8, endocyclic PCH_2), 56.0 [d, $^3J_{PC}$ = 2.8, C=NCH(CH_3)₂], 124.0 (s, *p*-C₆H₃), 127.6 (s, *m*-C₆H₃), 130.3 (m, CF₃), 136.0 (s, *o*-C₆H₃), 163.0 (q, $^1J_{BC}$ = 49.8, *ipso*-C₆H₃), 176.2 (dd, $^2J_{PC}$ = 12.9, $^2J_{PC}$ = 3.8, C=N). ¹⁹F NMR (235.3 MHz, CD_3CN): δ = –63.8 (s, CF₃).

Synthesis of [PdMe(PNP- κ^2P,N)]{BPh₄} (9): A Schlenk tube was charged with **3** (0.60 g, 0.84 mmol), NaBPh₄ (0.32 g, 0.93 mmol), and CH_3CN (80 mL) under nitrogen. The resulting suspension was stirred at room temp. for 3 d and subsequently filtered under nitrogen to give a clear yellow solution. Removal of solvent in vacuo afforded **9** as a brown/orange solid that was dried under high vacuum overnight (0.77 g, 92%), m.p. 100–102 °C. $C_{55}H_{90}BN_5P_2Pd$ (1000.52): calcd. C 66.02, H 9.07, N 7.00; found C 66.84, H 9.06, N 6.75. MS (FAB⁺, NBA matrix): m/z = 681 [M^+]. ¹H NMR (400.1 MHz, $CDCl_3$): δ = 0.51 (s, 3 H, Pd CH_3), 1.14 [d, 12 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 1.25 [d, 12 H, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 1.33 [m, 30 H, PNCH(CH_3)₂ and C=NCH(CH_3)₂], 2.90 (s, 2 H, CH_2), 3.36 (d, 2 H, $^2J_{PH}$ = 11.7, CH_2), 3.42 [sept, 4 H, $^3J_{H,H}$ = 6.6, $^4J_{PH}$ = 1.8, PNCH(CH_3)₂], 3.85 [4 H, sept, $^3J_{H,H}$ = 6.6, PNCH(CH_3)₂], 4.07 [sept, 1 H, $^3J_{H,H}$ = 6.7, C=NCH(CH_3)₂];

6.91 (4 H, pseudo-t, $^3J_{H,H}$ = 7.3, *p*-C₆H₅), 7.07 (8 H, pseudo-t, $^3J_{H,H}$ = 7.3, *m*-C₆H₅), 7.48 (8 H, br. s, *o*-C₆H₅). ¹³C NMR (62.9 MHz, CD_3CN): δ = 0.4 (s, Pd CH_3), 23.9 [d, $^4J_{PC}$ = 4.1, C=NCH(CH_3)₂], 24.6 [d, $^3J_{PC}$ = 3.6, PNCH(CH_3)₂], 24.9 [d, $^3J_{PC}$ = 6.6, PNCH(CH_3)₂], 25.3 [d, $^3J_{PC}$ = 6.6, PNCH(CH_3)₂], 26.1 [d, $^3J_{PC}$ = 3.1, PNCH(CH_3)₂], 38.4 (dd, $^1J_{PC}$ = 20.7, $^3J_{PC}$ = 6.3, exocyclic PCH_2), 48.2 [d, $^2J_{PC}$ = 11.7, PNCH(CH_3)₂], 49.5 [d, $^2J_{PC}$ = 8.6, PNCH(CH_3)₂], 52.6 (d, $^1J_{PC}$ = 32.4, $^3J_{PC}$ = 4.7, endocyclic PCH_2), 123.2 (s, *p*-C₆H₅), 127.0 (m, *m*-C₆H₅), 137.1 (s, *o*-C₆H₅), 165.2 (q, $^1J_{BC}$ = 49.4, *ipso*-C₆H₅).

Synthesis of [Mo(CO)₄(PNP- κ^2P,N)] (10): To a cold (–30 °C) solution of [Mo(CO)₄(pip)₂] (0.15 g, 0.41 mmol) in CH_2Cl_2 (10 mL) was added dropwise a CH_2Cl_2 solution (10 mL) of **1** (0.23 g, 0.41 mmol). The solution became brown on warming to room temp. After stirring for 18 h, the volatile components were removed under reduced pressure. The resulting solid was dissolved in a minimum of CH_2Cl_2 (ca. 2 mL) and pentane added dropwise until the solution became turbid. Subsequent recrystallisation at –30 °C afforded **10** as yellow-orange single crystals (0.20 g, 64% yield) that were isolated by filtration, m.p. 172–174 °C. $C_{34}H_{67}N_5O_4P_2Mo$ (767.81): calcd. C 53.18, H 8.81, N 9.12; found C 53.23, H 8.53, N 9.12. MS (EI): m/z = 740 [M^+ – CO], 712 [M^+ – 2 CO]. IR (Nujol): $\tilde{\nu}$ = 2009 (CO), 1897 (CO), 1882 (CO), 1822 (CO). ¹H NMR (270.1 MHz, C_6D_6): δ = 1.01 [d, 12 H, $^3J_{H,H}$ = 6.4, PNCH(CH_3)₂], 1.08 [d, 12 H, $^3J_{H,H}$ = 6.4, PNCH(CH_3)₂], 1.27 (24 H, overlapping d, measurable coupling constants $^3J_{H,H}$ = 8.2 and 7.9 Hz), 1.48 [d, 6 H, $^3J_{H,H}$ = 6.2, C=NCH(CH_3)₂], 2.94 (s, 2 H, br, CH_2), 3.14 (m, 4 H, PNCH), 3.59 (s, 2 H, br, CH_2), 4.07 (m, 4 H, PNCH), 4.13 (sept, 1 H, $^3J_{H,H}$ = 6.4, C=NCH). ¹³C NMR (100.6 MHz, C_6D_6): δ = 24.0 [d, $^3J_{PC}$ = 6.2, PNCH(CH_3)₂], 24.4 [d, $^3J_{PC}$ = 7.0, PNCH(CH_3)₂], 24.6 (br), 26.1 (s, br), 39.9 (dd, $^3J_{PC}$ = 3.2, $^1J_{PC}$ = 18.8, exocyclic CH_2), 47.3 (d, $^2J_{PC}$ = 11.1, PNCH), 50.3 (d, $^2J_{PC}$ = 10.7, PNCH), 51.5 (dd, $^3J_{PC}$ = 12.0, $^1J_{PC}$ 21.6, endocyclic CH_2), 56.2 (s, C=NCH), 176.1 (overlapping dd, measurable coupling constants $^2J_{CP}$ = 10.9 and 11.7 Hz, C=N), 210.1 (d, $^2J_{PC}$ = 8.4, CO), 218.5 (d, $^2J_{PC}$ = 42.9, CO), 221.8 (d, $^2J_{PC}$ = 9.1, CO).

Preparation of 10 from [Mo(cht)(CO)₃]: Toluene (10 mL) was added to a mixture of **1** (0.20 g, 0.36 mmol) and [Mo(cht)(CO)₃] (0.08 g, 0.36 mmol) at room temp. After stirring at room temp. for 2 d, the reaction mixture was heated to 70 °C for a further 3 d. Complex **10** was observed as the only phosphorus-containing product by ³¹P NMR spectroscopy. Subsequent removal of all volatile components under reduced pressure afforded a brown waxy solid. Washing with ether (3 × 10 mL) afforded **10** as an orange-brown solid (0.08 g, 28% yield).

Synthesis of *fac*-[Cr(CO)₃(NCMe)(PNP- κ^2P,N)] (11): To a solution of *fac*-[Cr(CO)₃(NCMe)₃] (0.2 g, 0.8 mmol) in toluene (10 mL) was added a toluene (10 mL) solution of **1** (0.44 g, 0.8 mmol) at –30 °C. The solution slowly darkened from yellow to orange/brown upon stirring at room temp. for 2 d. Removal of solvent in vacuo afforded a dark brown waxy solid. The product was extracted into toluene (3 mL) and pentane (ca. 2 mL) added. After cooling at –30 °C for 12 h, yellow-orange microcrystals of **11** were isolated by filtration and dried in vacuo for 4 d, at room temp. (0.12 g, 23% yield). No reliable analyses could be obtained presumably due to subsequent decomposition. MS (FAB⁺, NBA matrix): m/z = 639 [M^+ – CH_3CN – 2 CO], 611 [M^+ – CH_3CN – 3 CO]. IR (Nujol): $\tilde{\nu}$ = 1941 (w, CO), 1885 (s, CO), 1821 (s, CO). ¹H NMR (270.1 MHz, $CDCl_3$): δ = 1.25 (54H br. m), 2.28 (3 H, br. s, CH_3CN), 2.90 (2 H, br. s, CH_2), 3.39 (9 H, br. m, PNCH, CH_2 , and CH_3CN), 3.97 (4 H, br. m, PNCH), 4.22 (1 H, br. m, C=

NCH). ^{13}C NMR (75.8 MHz, CDCl_3): δ = 22.6 (br. s, CH_3CN), 24.0 [br. C=NCH(CH_3) $_2$], 24.2 [br. d, $^3J_{\text{PC}}$ = 6.6, PNCH(CH_3) $_2$], 24.6 [br. d, $^3J_{\text{PC}}$ = 6.6, PNCH(CH_3) $_2$], 24.9 (br. s), 25.9 (br. s), 39.6 (br. d, $^1J_{\text{PC}}$ = 21.1, exocyclic CH_2), 47.3 (br. d, $^2J_{\text{PC}}$ = 10.8, PNCH), 49.4 (br. d, $^2J_{\text{PC}}$ = 9.0, PNCH), 52.8 (br. m, endocyclic PCH_2), 57.3 (br. s, C=NCH), 127.8 (br. s, CH_3CN), 176.3 (br. m, C=NiPr), 219.5 (br. d, $^2J_{\text{PC}}$ = 14.5, CO), 227.9 (br. s, CO), 229.0 (br. d, $^2J_{\text{PC}}$ = 18.1, CO).

Reaction of $[\text{PdMe}_2(\text{PNP}-\kappa^2\text{P},\text{N})]$ (5**) with dppe:** An NMR tube was charged under nitrogen with **5** (0.01 g, 0.01 mmol), dppe (0.005 g, 0.01 mmol), and dry CDCl_3 (0.5 mL). The reaction mixture was shaken and left to stand at room temp. for 30 min. ^{31}P NMR (101.3 MHz, CDCl_3): δ = +55.7 ($\text{PdMe}_2\{\text{dppe}\}$), +53.1 (d, $^4J_{\text{PP}}$ = 14.5 Hz, [PNP]), +46.2 (d, $^4J_{\text{PP}}$ = 14.5 Hz, [PNP]).

X-ray Crystallographic Study: Crystal Data for **1**: $\text{C}_{30}\text{H}_{67}\text{N}_5\text{P}_2$, M = 559.8, orthorhombic, $Pbca$ (no. 61), a = 17.888(1), b = 18.586(2), c = 21.924(2) Å, V = 7289(1) Å 3 , Z = 8, D_c = 1.020 g·cm $^{-3}$, $\mu(\text{Mo}-K_\alpha)$ = 1.40 cm $^{-1}$, T = 293 K, yellow/white blocks; 6404 independent measured reflections, F refinement, R_1 = 0.028, R_w = 0.029, 2743 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $20 \leq 50^\circ$], 334 parameters. Crystal Data for **2**: $\text{C}_{30}\text{H}_{67}\text{Cl}_2\text{N}_5\text{P}_2\text{Pd}$, M = 737.1, monoclinic, $P2_1/c$ (no. 14), a = 14.617(1), b = 15.998(3), c = 18.323(3) Å, β = 109.44(1)°, V = 4040(1) Å 3 , Z = 4, D_c = 1.212 g·cm $^{-3}$, $\mu(\text{Cu}-K_\alpha)$ = 58.5 cm $^{-1}$, T = 293 K, yellow platy needles; 5989 independent reflections, F^2 refinement, R_1 = 0.066, wR_2 = 0.164, 4241 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $20 \leq 120^\circ$], 362 parameters. Crystal Data for **10**: $\text{C}_{34}\text{H}_{67}\text{MoN}_5\text{O}_4\text{P}_2$, M = 767.8, monoclinic, $P2_1/n$ (no. 14), a = 13.722(1), b = 17.284(1), c = 19.098(2) Å, β = 109.19(1)°, V = 4278.0(6) Å 3 , Z = 4, D_c = 1.192 g·cm $^{-3}$, $\mu(\text{Mo}-K_\alpha)$ = 4.19 cm $^{-1}$, T = 293 K, yellow blocks; 7494 independent reflections, F^2 refinement, R_1 = 0.050, wR_2 = 0.106, 5006 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $20 \leq 50^\circ$], 415 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165966 to -165968. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Electronic Supporting Information: Variable-temperature ^1H NMR spectra for complexes **7–9** together with ORTEP views of the molecular structures of ligand **1** and complexes **2** and **10** have been deposited (see also footnote on the first page of this article).

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