N-Phosphino-amidines and -guanidines: synthesis, structure and P,N-chelate chemistry†‡

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The syntheses of the cyclic *N*-phosphino-amidines and -guanidines $Ph_2PN(Pr^i)C(NPr^i_2)N(Pr^i)$ (**1**) and $Ph_2PN(c\text{-Hex})C(R)N(c\text{-Hex})$ [R = piperazino (**2**), morpholino (**3**), Me (**4**), and Ph (**5**)] are reported. DFT studies have identified the preferred structures for compounds **1–5** with the *E*-configuration being the most stable form for the *N*-phosphino-amidines, while the *Z*-conformation is preferred for the *N*-phosphino-guanidines something that highlights the potential of such systems to act as κ^2-P,N-chelates. The differences in donor characteristics of **2–5** have been probed through the study of their corresponding P(V) selenide derivatives (**6–9**) and their complexes with the *cis*-RhCl(CO) (**10–12**) and *cis*-$PdCl_2$ (**13–17**) fragments. In line with the DFT studies both the amidines and guanidines are found to coordinate as κ^2-P,N-chelates, with the latter being moderately weaker donor ligands. The molecular structures of compounds **3** and **4**, together with those of the Rh and Pd complexes **10** and **15**, respectively, have been determined in the solid state by X-ray crystallography, the latter confirming bidentate κ^2-P,N-chelation.

Introduction

Over the last decade the study of tricoordinate phosphorus derivatives with one, two or three P–N bonds, $(R_2N)_{3-x}PR'_x$, has undergone somewhat of a renaissance. To a large extent interest in such compounds has been driven by the ease of phosphorus–nitrogen bond formation, something that facilitates the straightforward preparation of P(III) compounds with a diverse range of steric demands, as well as providing a means for the introduction of additional functionality or chirality remote from the P-centre.[1–5] Furthermore, through judicious choice of substituents at nitrogen it is possible to tune not only the Lewis basicity of the resulting amidophosphines, but also their π-acceptor character, in a simple and systematic fashion, while also opening up new reaction pathways.[6–9]

An area in which P–N bond-forming reactions have proved particularly versatile is in the synthesis of bidentate κ^2-*P*,*E* chelates (*E* = O,[10] P,[11] S,[12] Se[13]). Once coordinated, the heteroditopic nature of these types of ligand has been used to engender both control and selectivity in reactions occurring at metal centres.[14,15] In this domain, phosphorus–nitrogen chelates (*E* = N) are amongst the most widely studied of these types of scaffold and have found applications in many different transformations including olefin oligomerisation/polymerisation,[8,16–18] asymmetric hydrogenation,[19] allylic substitution,[20] hydrosilylation,[21] and C–C coupling reactions,[22] for example.

The obvious versatility of bidentate κ^2-P,N-ligands in coordination chemistry and catalysis means there is continued interest in the development of increasingly structurally diverse systems. With this in mind, it became apparent that the readily accessible H–*N*-amidines and -guanidines make attractive building blocks for the preparation of heteroditopic κ^2-P,N-ligands **I** and **II**, respectively (Fig. 1), potentially providing a ready means of tuning both their steric and electronic demands.[23] A small number of such compounds have been reported,[24–26] although their molecular structures and coordination chemistry have only briefly been explored.[27–31] Notably, though, related *C*-phosphino amidines have been reported in detail by Coles and co-workers.[32,33]

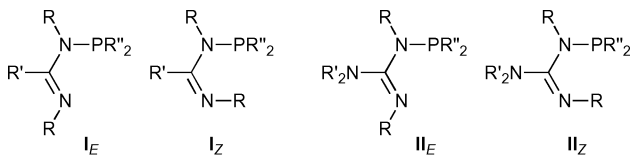

Fig. 1 Selected isomeric forms of *N*-phosphino-amidines **I** and -guanidines **II**.

Here we describe the straightforward, high-yielding syntheses of a number of variously-substituted *N*-diphenylphosphino-amidines and -guanidines. Their donor characteristics have been probed spectroscopically and a combination of computation and X-ray diffraction studies employed to assess their structures. The potential of these systems to act as κ^2-P,N-chelates with metals of relevance to catalysis, namely Rh(I) and Pd(II), has been explored.

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† Dedicated to our colleague Prof. Ken Wade on the occasion of his 75th birthday to mark his outstanding contributions to our understanding of the relationships between structure and bonding across the periodic table.

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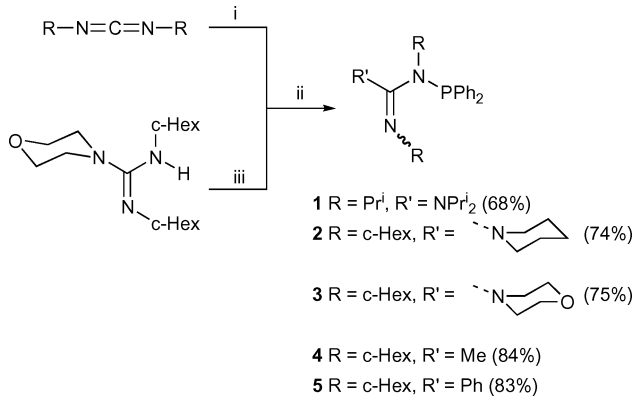
Particular emphasis is placed upon understanding the effects of the substitution pattern about the NCN skeleton.

Results and discussion

Synthesis and characterisation of *N*-phosphino-amidine and -guanidines

Exploitation of the well-established reactivity of carbodiimides towards lithium organyl and amide reagents provides ready access to a host of P,N derivatives following reaction of the resulting diazaallyl intermediates with halophosphine. In this way the *N*-phosphino-amidines **1**,**2** and -guanidines **4**,**5** were prepared in good yields (>70%) according to Scheme 1. A modification of this strategy was used to prepare the 4-morpholinecarboxamidine derivative **3** from commercially available *N,N′*-dicyclohexyl-4-morpholinecarboxamidine in a 'one-pot' procedure (Scheme 1).



Scheme 1 (i) R′Li, Et_2O, −78 °C to RT; (ii) Ph_2PCl, Et_2O, −78 °C to RT; (iii) Bu^nLi, Et_2O, −78 °C to RT.

Compounds **2–5** were isolated as moderately air stable solids, while the *N,N′*-diisopropyl derivative **1** was obtained as a viscous oil, which proved to be extremely sensitive to protonolysis, rapidly decomposing with the elimination of hydroxyphosphine-containing species *via* P–N bond cleavage. Attempts to stabilise **1** by forming the corresponding P(v) derivatives by reaction with elemental sulfur or selenium proved unsuccessful, giving intractable mixtures of products in both cases.

The $^{31}P\{^1H\}$ NMR spectra of *N*-phosphino-guanidines **1–3** and -amidine **4** each exhibit a single sharp resonance over the temperature regime 233 to 323 K, at a chemical shift consistent with an aminodiphenylphosphino moiety (Table 1).[6] Note that the ^{31}P NMR chemical shift of phosphino-amidine **4** is displaced to lower frequency compared to those observed for the functionalised guanidines **1–3**. This may be caused by the influence of the NCN *C*-substituent on the electronic properties of the P-donor moiety or as a result of differences in conformation about the imine bond between the guanidines **1–3** and the amidine **4**. In contrast, the ^{31}P NMR spectrum of the benzamidine derivative **5** (R = c-Hex; R′ = Ph) is severely broadened at ambient temperature, but partially sharpens on warming to 363 K. This presumably dynamic process could not be fully frozen out even on cooling the sample to 233 K.

The $^{13}C\{^1H\}$ NMR spectra for compounds **1–5** are consistent with acyclic structures where the Ph_2P substituent is attached to one nitrogen atom of the RNC(R′)NR moiety. The $^{13}C\{^1H\}$ NMR spectra for **1–3** exhibits two sets of *ortho*-CH resonances for the Ph_2P substituent, whereas only one set of resonances is observed for **4** and **5**.[24] Each of the compounds **1–4** displays a well-resolved doublet resonance for the N*C*N carbon atom (Table 1). However, a broad N*C*N resonance centred at 157.2 ppm is observed in the ^{13}C NMR spectrum for benzamidine **5**.

In order to try to understand the differences in the NMR data for the guanidines **1–3**, amidine **4** and benzamidine **5**, X-ray studies on **3** and **4** and a DFT investigation on these and related compounds were carried out.

X-Ray diffraction studies of *N*-phosphino-guanidine 3 and -amidine 4

The results of X-ray diffraction studies (Table 2) confirm the acyclic guanidine **3** (Fig. 2) and amidine **4** (Fig. 3) structures, with no close inter-/intra-molecular contacts of the iminic *N*-lone pair with the Ph_2P fragment. Guanidine **3** is found to adopt a formally *Z* configuration about the C–N double bond (*cf.* its parent *N,N′*-dicyclohexyl-4-morpholinecarboxamidine, which adopts an *E* arrangement).[34] Both the C(1) and N(2) centres of **3** are trigonal-planar and lie in planes that form a dihedral angle of 66.0° precluding conjugation. Contrastingly the morpholine N(3) centre is pyramidal, meaning that its lone pair is not involved in delocalisation across the CN_3 framework. The orientation of the trigonal plane centred about N(2) and the inferred position of the P-lone pair (torsion angle 7°) are consistent with overlap of the N(2) lone pair with one of the two degenerate σ*(P–R) MOs engendering some slight P–N(2) multiple bond character;[6] the P–N(2) distance is shorter than a true P–N single bond by *ca.* 0.07 Å.[35] The C(1)–N(1) bond distance is typical for a double bond (not withstanding a 6.4° twist along its axis),[35] while the N(2)–C(1) and C(1)–N(3) distances are close to the standard non-conjugated single bond distance.[35a]

In contrast to the molecular structure of guanidine **3**, amidine **4** adopts an *E* configuration (Fig. 3), which is thus ideally pre-disposed for metal κ²-P,N-chelation. The amidine core has

Table 1 Selected NMR spectroscopic data for compounds **1–9**[a]

	$\delta^{31}P\{^1H\}$[b]	$\delta^{13}C\{^1H\}$[c] *C*N_2	$^2J_{PC}$/Hz		$\delta^{31}P\{^1H\}$[b]	$\lvert{}^1J_{SeP}\rvert$/Hz
1	+49.9[d]	147.3[e]	21		—	—
2	+50.2	154.8	21	**6**	+57.6	772
3	+49.8	153.6	21	**7**	+56.3	775
4	+37.0	155.7	1	**8**	+56.3	749
5	+44.9 ($\nu_{1/2}$ 44 Hz)	157.2	9	**9**	+67.3	753

[a] $CDCl_3$, 298 K. NMR spectrometer frequencies: [b] 161.9 MHz; [c] 125.7 MHz; [d] 101.3 MHz; [e] 100.6 MHz.

Table 2 Selected bond distances (Å), bond and dihedral angles (°)

	3	**10**	**4**	**15**		**10** (M = Rh)	**15** (M = Pd)
P–N(2)	1.7014(10)	1.739(2)	1.721(3)	1.7115(14)	M–P	2.1668(5)	2.1644(4)
N(2)–C(1)	1.4304(14)	1.407(2)	1.414(4)	1.383(2)	M–Cl(1)	2.4070(5)	2.3913(4)
C(1)–N(1)	1.2674(15)	1.306(2)	1.270(4)	1.301(2)	M–Cl(2)	—	2.3212(4)
C(1)–N(3)	1.4074(15)	1.370(2)	—	—	M–N(1)	2.1916(15)	2.0727(14)
N(2)–P–C(24)	107.38(5)	102.90(8)	103.7(1)	106.41(7)	M–C(30)	1.804(2)	—
N(2)–P–C(18)	102.71(5)	107.67(7)	103.9(1)	106.43(7)	P–M–Cl(1)	172.88(2)	173.93(2)
C(24)–P–C(18)	99.20(5)	101.58(8)	105.7(1)	107.13(7)	P–M–N(1)	76.25(4)	81.90(4)
Mean X–N(2)–Y	120.0	116.0	119.3	119.9	P–M–C(30)	96.19(6)	—
Mean X–C(1)–Y	120.0	120.0	120.0	120.0	P–M–Cl(2)	—	87.25(2)
Mean X–N(3)–Y	113.6	119.9	—	—	Cl(1)–M–N(1)	99.24(4)	102.54(4)
C(1)–N(1)–C(2)	120.8(1)	120.53(15)	119.8(2)	118.38(14)	Cl(1)–M–C(30)	88.74(6)	—
N(2) plane/C(1) plane	66.0	30.2	20.8	2.2	Cl(1)–M–Cl(2)	—	88.24(2)
C(1) plane/N(1) plane	6.4	23.8	1.1	10.9	N(1)–M–C(30)	171.11(7)	—
P–N(2)–C(1)–N(1)	68.3(1)	−25.4(2)	151.6(2)	2.4(2)	N(1)–M–Cl(2)	—	169.13(4)
N(2)–C(1)–N(1)–C(2)	4.6(1)	156.2(2)	179.1(2)	169.60(14)			

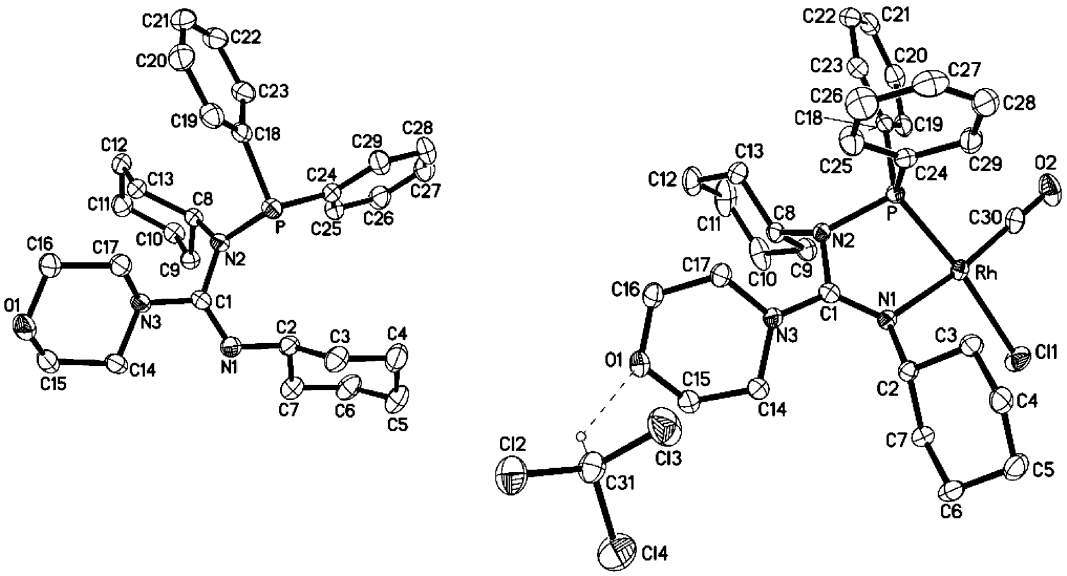


Fig. 2 Molecular structures of **3** (left) and **10**·$CDCl_3$ (right). Thermal ellipsoids are drawn at the 50% probability level.

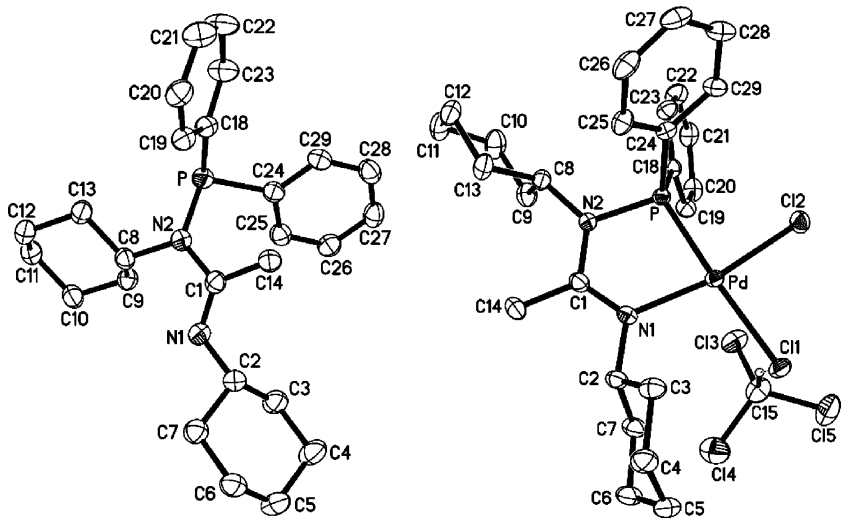


Fig. 3 Molecular structures of **4** (left) and **15**·$CDCl_3$. Thermal ellipsoids are drawn at the 50% probability level.

localised C(1)=N(1) and C(1)–N(2) bonds of 1.270(4) and 1.414(4) Å, respectively. As is the case for **3**, the N(2) and C(1) centres of **4** are trigonal-planar, but with a smaller interplanar angle of 20.8° (*cf.* **3**: 66.0°). As a result of the significant twist (19°) between the trigonal plane centred on N(2) and the inferred position of the σ*(P–R) MO, there is a weakening of the N(2)→P π-interaction and hence a slight elongation of the P–N(2) (1.721(3) Å) bond distance is observed relative to that for **3** (1.7014(10) Å).

DFT studies of *N*-phosphino-amidines and -guanidines

As discussed above, it is well-established that both amidines and guanidines may adopt a variety of different, potentially interconverting isomeric configurations (Fig. 1).[23,33] The stability of each of the various arrangements and their rates of isomerisation are intimately linked to the substitution pattern about the NCN skeleton. Here, this is clearly reflected in the different solid state molecular structures determined for the compounds **3** and **4**, which are found to adopt *Z* and *E* conformations, respectively. Since this current study seeks to assess the ability of these variously-substituted *N*-phosphino-NCN derivates to act as κ^2-P,N-chelating ligands, an understanding of the factors that influence the structure they adopt is essential and has been addressed computationally.

Initially, the structures of eight model compounds RN=CR′N(R)PPh_2 (R = Me, R′ = Me, Ph and NMe_2) were explored at the B3LYP/6-31G* level of theory, with the most stable arrangements being identified in each case (Table 3, Fig. 4). The *E*-configuration is computed to be the most stable form for the *N*-phosphino-amidines, whereas the *Z*-conformation is the preferred geometry for the *N*-phosphino-guanidines.

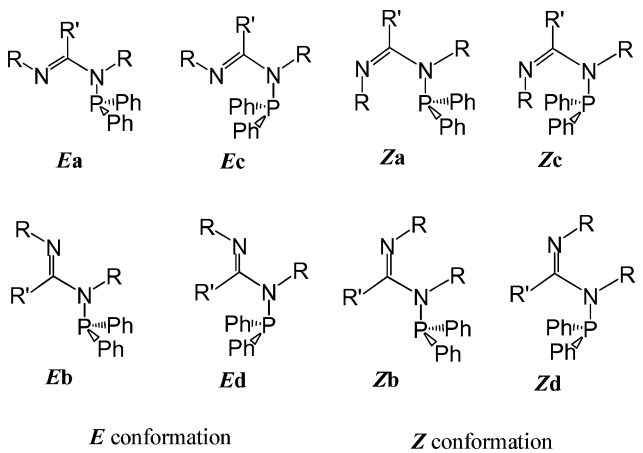


Fig. 4 Eight conformations for *N*-diphenylphosphino-amidines and -guanidines.

Table 3 Relative energies in kcal mol^{-1} for model geometries of MeN=C(R′)N(Me)PPh_2

R′	NMe_2	Me	Ph	R′	NMe_2	Me	Ph
*E*a	1.15	3.51	1.07	*Z*a	0.00	5.37	3.09
*E*b	0.54	0.00	0.00	*Z*b	1.66	6.65	4.81
*E*c	4.00	4.50	3.19	*Z*c	5.05	11.96	8.62
*E*d	4.90	3.03	4.65	*Z*d	4.27	9.84	9.19

Table 4 Relative energies for various conformations for **1**, **3**, **4** and **5** in kcal mol^{-1}

	1	**3**	**4**	**5**		**1**	**3**	**4**	**5**
*E*a	2.21	2.29	0.43	2.75	*Z*a	2.00	0.00	7.08	5.70
*E*b	0.00	0.80	0.52	0.00	*Z*b	7.46	1.85	9.39	5.70
*E*c	0.90	1.35	2.50	6.95	*Z*c	2.67	1.39	8.01	11.26
*E*d	6.26	3.00	0.00	3.96	*Z*d	2.67	2.49	7.96	9.96

The full geometries of the preferred conformers were then computed for **1**, **3**, **4** and **5** (at the B3LYP/6-31G* level of theory) and are listed in Table 4. Since both guanidines **2** and **3** are structurally very similar, it has been assumed that the relative energy trends for **3** will also apply to **2**. The variations in the relative energies between the model geometries (Table 3) and the actual geometries (Table 4) indicate that the bulky cyclohexyl and Pr^i_2N groups impart a considerable influence on the preferred conformations. The X-ray structures of **3** and **4** are in perfect accord with the most stable forms identified computationally, *i.e.* *Z*a and *E*d for **3** and **4**, respectively. Examination of the relative energy data for benzamidine **5** suggests that the *E*b form is the most stable conformation for **5**. The preferred conformation for **1** also appears to be the *E*b conformation, but here *Z*a is only 2 kcal mol^{-1} higher in energy.

The calculated HOMOs in the lowest energy minima of **1**, **3**, **4** and **5** all possess considerable lone-pair character at the P-atom. Natural population analyses on each of these geometries afford N–P Wiberg bond orders and charges at P that are all similar with values of 0.8 and 1.1, respectively, consistent with the molecular structures of **3** and **4** determined crystallograpically. The HOMO-1 and HOMO-2 of each of these systems have substantial contributions located at the nitrogen atoms of the C=N bonds. Together these data confirm the potential of these compounds to act as κ^2-P,N-chelating ligands.

Elucidation of the origins of the differences in solution-state dynamic behaviour of benzamidine **5** compared to that observed for either amidine **4** or guanidines **1–3** is complex. Not only are all the compounds subject to *E*/*Z* isomerisation of the C–N multiple bond,[23,32,33] but *N*-phosphino-amidines are also known to be susceptible to intramolecular phosphatropic rearrangement.[25] This latter process involves migration of the R_2P moiety between the two amidine *N*-atoms *via* a heterocyclic intermediate (Fig. 5), with the magnitude of the free energy of activation ($\Delta G^{\dagger}$) having been shown to be directly linked to the nature of the amidine substituents R and R′. Since identification of the processes giving rise to the differences in fluxional behaviour between **4** and **5** by variable temperature NMR spectroscopic studies proved inconclusive, differences between these two compounds were explored computationally.

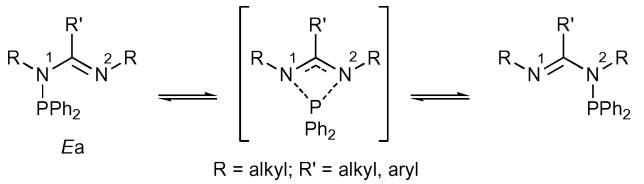


Fig. 5 Intramolecular phosphatropic rearrangement of *N*-phosphino-amidines.[24]

Initially, a comparison of the energy barriers for isomerisation between the *Z*and *E* forms of both **4** and **5** were determined. Values of 27.5 (**4**) and 24.2 (**5**) kcal mol^{-1} were obtained, which rule out interconversion between these isomers for both compounds.

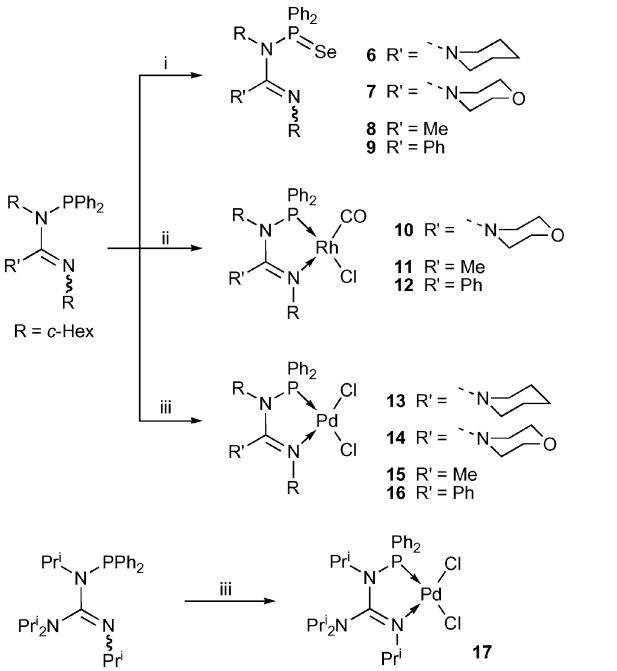
Next, it was of interest to explore the ease with which intramolecular phosphatropic rearrangement may occur for **4** *versus* **5**. The energy barriers for this process were computed for **4** and **5** and found to be 14.8 and 19.1 kcal mol^{-1}, respectively, assuming an *E*a-conformation, Fig. 5, (something confirmed crystallographically for **4**) as the starting geometry, as this is the most likely precursor to the phosphatropic rearrangement. For comparison, an identical procedure was used to compute the energy barrier for the rearrangement of the known benzamidine MeN=C(Ph)N(Me)PPh$_2$, which gave a value of $\Delta G^{\ddagger} = 24.0$ kcal mol^{-1} that is in excellent agreement with the experimentally determined value of 25 kcal mol^{-1}.[24] Since the structure of this latter compound differs from that of **5** only in that it bears methyl rather than cyclohexyl groups, it is likely that the lower barrier to rearrangement of **5** is steric in origin. However, it is clear that the small difference in energy for the phosphatropic rearrangement of **4** compared with that for **5** ($\Delta\Delta G^{\ddagger} = 4.3$ kcal mol^{-1}) cannot explain the differences observed in the solution-state NMR spectra of **4** and **5**.

Both the crystallographically- and computationally-determined molecular structures of compounds **4** and **5** highlight the significant steric bulk about the NCN skeleton. This is likely to limit free rotation in solution, particularly about the N–P bond, which could give rise to the observed differences in the ^{31}P NMR spectra of **4** and **5**. Thus, the barriers to rotation about the N–P axis for both compounds **4** and **5** were estimated computationally, assuming the *E*a-conformation shown in Fig. 5 for both structures. In each case, the barrier was found to be 7 kcal mol^{-1}, a value that is in broad agreement with those computed for the parent aminophosphine H_2NPH_2 (5.78–9.38 kcal mol^{-1}), obtained at different levels of theory, and consistent with only slight P–N multiple bond character.[36] Clearly, since the rotational barrier is identical for both **4** and **5**, this again does not explain the differences in their observed NMR spectra.

Donor characteristics of *N*-phosphino-amidines and -guanidines

Two complementary methods have been used to assess the potential ligand characteristics of compounds **2–5**. An estimate of the Lewis basicity of the *P*-donor component of each compound can be made from the magnitude of the $^1J_{SeP}$ coupling constant obtained from the corresponding selenides, **6–9**, each of which presents a single sharp resonance by ^{31}P NMR spectroscopy (Scheme 2, Table 1).¶[37] The guanidinyl phosphine selenide derivatives **6** and **7** display values of $|^1J_{SeP}|$ of *ca.* 770 Hz, while those from the Ph$_2$P-functionalised amidines **8** and **9** are significantly smaller, *ca.* 750 Hz, and comparable to Ph$_2$P(Se)NEt$_2$ ($|^1J_{SeP}| =$ 746 Hz).[6]

The significant divergence in the magnitudes of the $^1J_{SeP}$ coupling constants between those for the guanidines (**6**,**7**) and those for the amidines (**8**,**9**) is most readily explained in terms of differences in geometry about P. For both **6** and **7** competition for a vacant σ*(P–R) MO of appropriate symmetry for back-bonding



Scheme 2 (i) Se, $CDCl_3$, RT, 1 h; (ii) 1/2 $[RhCl(CO)_2]_2$, CO, $CDCl_3$, RT, 1 h; (iii) $[PdCl_2(MeCN)_2]$, CH_2Cl_2, RT, 18 h.

from N or Se will induce a flattening about the P-centre and hence augment it's degree of s-character. In turn, this will give rise to the larger magnitudes of $^1J_{SeP}$ observed.¶ Consequently, it is clear from this study that varying the nature of the substituent on the *C*-atom of the NCN skeleton (alkyl, aryl or amino) provides a ready means of tuning the donor characteristics of this type of P,N-chelating metal scaffold in a straightforward fashion.

In order to probe the donor characteristics of compounds **3–5** when acting as chelating κ^2-P,N-ligands, their corresponding [RhCl(CO)(κ^2-*P,N*)] (**10–12**) complexes were prepared through reaction with half an equivalent of $[RhCl(CO)_2]_2$ under an atmosphere of CO (Scheme 2). Each complex was isolated in near-quantitative yield as an air-stable solid and as a single regioisomer, according to ^{13}C and ^{31}P NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum of complexes **10–12** features a sharp doublet resonance to high frequency of that for the free ligands, with a $^1J_{RhP}$ coupling constant of *ca.* 175 Hz (Table 5). Geometries in which P lies *trans* to Cl are suggested by ^{13}C{^{1}H} NMR spectroscopy, which presents a single carbonyl resonance for each complex at *ca.* δ 185 ppm (d, $^1J_{RhC}$ *ca.* 75 Hz).[8] Notably, no tractable product could be obtained from the reaction of **1** with $[RhCl(CO)_2]_2$.

Phosphino-guanidine **3** adopts a *Z* configuration about the imine bond in the solid-state (*vide supra*). As a result, in order for **3** to coordinate in a bidentate κ^2-P,N-fashion, a prior formal *E*/*Z* isomerisation is required (Scheme 3). Thus, although spectroscopic analysis of **10** was suggestive of a *cis*-[RhCl(CO)(**3**)] coordination, it was of interest to probe the structure of the complex by X-ray diffraction.

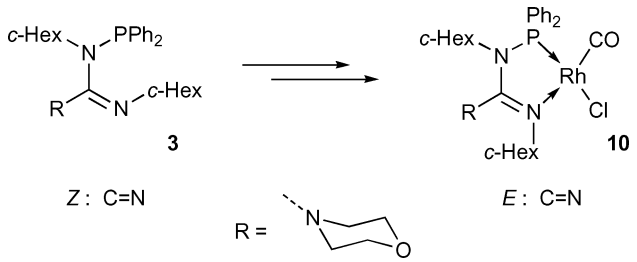
The molecular structure of the rhodium(I) complex **10**·$CDCl_3$ (Fig. 2, Table 2) confirms that **3** does indeed act as a κ^2-P,N-chelate, consistent with the low barrier to *Z*/*E* isomerism of the imine bond determined (*vide supra*) for these *N*-phosphino-guanidines.[32,38] The rhodium centre of **10** is near-square planar,

¶ The greater the magnitude of $^1J_{SeP}$, the greater the s-character of the *P*-lone pair and hence the poorer its donating ability.

Table 5 Selected NMR spectroscopic data for complexes **10–17**[a]

	$\delta^{31}P\{^1H\}$[b]	$^1J_{RhP}$/Hz	$\delta^{13}C\{^1H\}$[c] CN_2	$^2J_{PC}$/Hz	ν_{CO}[d]/cm^{-1}
10	+112.1	176	165.7	24	1994
11	+124.9	175	170	br	1995
12	+124.7	177	170.0	br	2000
13	+84.3 ($\nu_{1/2}$ 144 Hz)	—	167.8	25	—
14	+85.5 ($\nu_{1/2}$ 131 Hz)[g]	—	166.5	25	—
15	+108.0	—	168.9	br	—
16	+106.3 ($\nu_{1/2}$ 170 Hz)[e]	—	[f]	[f]	—
	+95.1 ($\nu_{1/2}$ 254 Hz)	—	[f]	[f]	—
17	+81.2[h]	—	—	—	—

[a] $CDCl_3$, 298 K. [b] 161.9 MHz. [c] 125.7 MHz. [d] KBr, $CDCl_3$. [e] +106.3 : +95.1 = 8 : 1 at 298 K. [f] Not observed. [g] 75.8 MHz. [h] 101.3 MHz.



Scheme 3

with a slight tetrahedral distortion (7.7° twist); the P-donor moiety occupies a position *trans* to Cl, as predicted on the basis of relative *trans*-influences. The metallacycle assumes a puckered envelope conformation, with the P atom being displaced by 0.81 Å from the RhN(1)C(1)N(2) plane. This non-planarity of the metallacycle is responsible for the narrow P,N-bite angle of 76.25(4)° (*cf.* typically 83.0–87.7° in other [RhCl(CO)(P,N)]-type complexes with five-membered κ^2-P,N-chelates[39]) and the slightly longer than usual Rh–N(1) distance (2.1916(5) Å), which is typically in the range 2.10–2.15 Å for Rh←N(sp^2) bonds.[35]

There is a clear change in the bonding pattern and conformation of **3** following its coordination with Rh(I). Partial bond delocalisation about the guanidine CN_3 core ensues, which is reflected by the pyramidalisation of the N(2) and the planarization of the N(3) centres. The C(1)=N(1) bond is lengthened by 0.04 Å accompanied by an increase in twist to 23.8° (from 6.4° in **3**), while both the N(2)–C(1) and C(1)–N(3) bonds are shortened. The P–N(2) bond is also weakened, as a result of the reduction in the N → P π-interaction [**3**: 1.7014(10), **10**: 1.739(2) Å]. The cyclohexyl and morpholine substituents are in *cis* positions with respect to the C(1)=N(1) bond (Z_{anti}), compared to the *trans* (E_{anti}) configuration observed in unbound **3**.

From the IR spectra of the rhodium carbonyl complexes **10–12** CO stretching frequencies of *ca.* 1996 cm^{-1} are obtained. These values are indicative of ligands **2–5** being comparatively weak Lewis bases,[6,17] in agreement with the magnitudes of $^1J_{SeP}$ from their corresponding selenides (*vide supra*). Only small differences (*ca.* 5 cm^{-1}) are observed between the values of νCO for the guanidine- (**10**,**11**) and amidine-based (**12**) complexes. This indicates that in these *cis*-chelated complexes the *N*-donor moiety (=N–*c*Hex in each case) that lies *trans* to the reporter carbonyl ligand has the dominant influence on the C–O bonding, as may be expected.

The similarity in the spectroscopic data between complexes **10–12** is strongly suggestive of κ^2-P,N-chelation in each case.

Synthesis and characterisation of $PdCl_2$ complexes 13–17

To further explore the coordination chemistry of compounds **1–5** a study of their $PdCl_2$ complexes was undertaken. Here the isoelectronic relationship between Rh(I) and Pd(II) facilitates a direct comparison between the two different metal systems. Reaction of compounds **1–5** with [$PdCl_2$(MeCN)$_2$] leads to the formation of the corresponding [$PdCl_2$(P,N)] complexes **13–17**, which are isolated as air-/moisture-stable yellow or orange solids in excellent yields of typically >75% (Scheme 2). The exception is [$PdCl_2$(**1**)] (**17**), which forms cleanly according to ^{31}P NMR spectroscopy, but starts to decompose with the formation of 'palladium black' after *ca.* 1 h in solution.

In solution the phosphino-guanidine derivatives [$PdCl_2$(κ^2-P,N-**2**,**3**)] (**13**,**14**) each display a single broad resonance at *ca.* δ +85 ppm by $^{31}P\{^1H\}$ NMR (298 K) spectroscopy, with the magnitude of $\Delta\delta$ (*ca.* +35 ppm) being consistent with the coordination of the P-donor moiety to palladium (Table 2). On cooling to 233 K, two resonances became apparent in each case at *ca.* δ +90 and +80 ppm in an approximately 1 : 8 ratio, respectively, which clearly correspond to two Pd-bound P-species. On warming to 353 K the ^{31}P NMR spectra of **13** and **14** both collapsed to a single sharp resonance.

The behaviour of the two amidine-derived palladium(II) complexes **15** and **16** is quite different, again highlighting the influence of the substituent on the N*C*N carbon atom. The methyl-substituted phosphino amidine complex [$PdCl_2$(κ^2-P,N-**4**)] (**15**) has a static structure in solution ($^{31}P\{^1H\}$ NMR δ +108.0 ppm) between 233 and 363 K (Table 3). In contrast, its phenyl-substituted counterpart [$PdCl_2$(κ^2-P,N-**5**)] (**16**) behaves in a manner analogous to that for complexes **13** and **14**, exhibiting two broad resonances (δ +106, +95.1 ppm) at ambient temperature, with the two chemical shifts being consistent with two Pd-bound phosphine species. On cooling a sample of **16** to 233 K both resonances sharpen significantly, while heating to 363 K causes these two peaks to collapse to a broad single signal (δ +103.0 ppm, $\nu_{1/2}$ 500 Hz).

In order to probe the origins of this dynamic behaviour, the molecular masses of complexes **14** and **16** were determined cryoscopically[40] in solution. In both cases masses consistent with monomeric structures [$PdCl_2$(P,N)] were obtained. This rules out any monomer–dimer interconversion in solution. Equally, although the morpholine-substituted derivative **3** clearly acts as

a P,N-chelate with Rh(I) in complex **10**, it is possible that this may not be the case with Pd in complex **14**, chelation through either of the hard iminic *N*- or *O*-donor centres of the morpholine unit also being possible. However, since identical dynamic behaviour is observed with the piperazino derivative **13** that has no *O*-donor functionality, this is clearly not the explanation. Furthermore, since fluxionality is observed for both guanidine (**13**, **14**) and amidine complexes (**16**), exchange of *N*-imine and *N*-amine donation can be eliminated.

Consequently, despite the comparatively large chemical shift difference between the two species being observed for complexes **13**, **14** and **16**, this temperature-dependent behaviour is largely ascribed to conformational changes of the cyclohexyl substituents at the ligand periphery combined with hindered rotation of the phenyl substituent. This is consistent with the all-isopropyl-substituted complex **17** presenting a static structure, with a single sharp resonance being observed δ +81.2 ppm in its $^{31}P\{^{1}H\}$ NMR spectrum.

Since methyl-substituted amidine complex **15** does not exhibit any dynamic behaviour in solution within the temperature range 233–363 K it was of interest to verify its structure. Thus, an X-ray diffraction study was undertaken (**15**·$CDCl_3$, Fig. 3, Table 2), which confirms the expected P,N-chelation about a distorted square planar Pd centre. The Pd, P, Cl(2) and N(1) atoms are coplanar, while Cl(1) lies out of their plane by 0.15 Å. Both the N(2) and C(1) centres retain their planarity upon complexation, the interplanar angle dropping to 2.2° (*cf.* 20.8° (**5**)), while the twist around the C(1) = N(1) bond increases only moderately, from 1.1° in **5** to 10.9° in **15**. Thus the P,N-containing metallacycle of **15** is much less puckered than in **10**, adopting an envelope conformation with the Pd atom deviating by 0.27 Å from the PN(2)C(1)N(1) plane. Consequently, the P,N-bite angle of **15** (81.90(4)°) is much wider than that in **10**, 76.25(4)°.

Summary

These studies have shown the utility of readily available amidines and guanidines as building blocks for the straightforward preparation of structurally diverse *N*-phosphino-amidines and -guanidines. A combination of computational and spectroscopic investigations has highlighted the impact of the substitution pattern about the NCN backbone upon both their structure and donor properties, with the guanidine series of compounds being weaker donors. Irrespective of the conformation of the various substituted *N*-phosphino-amidines and -guanidines, low calculated barriers to *E*/*Z* isomerism permit their coordination as strongly bound κ^2-P,N-chelates, despite comparatively weak Lewis basicities. The application of P,N-ligands **1–5** in a number of metal-catalysed transformations is on-going.

Experimental

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a Saffron Scientific nitrogen-filled glove box. All NMR-scale reactions were conducted using Young's tap valve NMR tubes. Bulk solvents were freshly obtained from an Innovative Technologies SPS facility and deoxygenated prior to use. $CDCl_3$, d_2-tetrachloroethane (TCE-d_2) and d_8-toluene were distilled from P_2O_5 and subsequently handled under nitrogen.

Palladium and rhodium salts were used on loan from Johnson Matthey. All solid reagents were used as received. Where appropriate liquid reagents were dried, distilled and deoxygenated, while gases were passed through a drying column (silica/$CaCO_3$/P_4O_{10}) prior to use.[41] The complexes $[PdCl_2(MeCN)_2]$[42] and $\{RhCl(CO)_2\}_2$[43] were prepared according to slight modifications of the literature procedures. Elemental grey selenium (Aldrich), *N,N′*-diisopropylcarbodiimide (Aldrich), *N,N′*-dicyclohexylcarbodiimide (Aldrich), *N,N′*-dicyclohexyl-4-morpholinecarboxamide (Aldrich), Ph_2PCl (Aldrich), PhLi {solution in hexanes} (Aldrich), MeLi {solution in hexanes} (Aldrich), were all used as received.

Routine solution phase NMR spectra were collected on a Bruker AM250, Varian Unity 300, or a Varian Inova 500 at ambient probe temperatures (~290 K). Variable temperature spectra were collected on a Varian Inova 500. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^{1}H), ^{13}C shift of the solvent (^{13}C), or external aqueous 85% H_3PO_4 (^{31}P). For ^{1}H NMR spectra, ^{31}P-coupled resonances were verified by running $^{1}H\{^{31}P\}$ experiments. ^{13}C NMR spectra were assigned with the aid of DEPT-90, DEPT-135 and ^{1}H–^{13}C correlation experiments. Chemical shifts are reported in ppm and coupling constants in Hz.

FAB (3-nitrobenzyl alcohol matrix) and EI mass spectra were recorded on a Kratos Concept 1H instrument and are reported in (*m*/*z*). Mass spectra were recorded either in Durham (ES: Micromass Autospec; MALDI ToF: Applied Biosystems Voyager-DE STR) or by the EPSRC National Mass Spectrometry Service at the University of Wales, Swansea, (ES: Waters ZQ-4000) and are reported in (*m*/*z*). The isotope distributions for all parent ion peaks for metal complexes were verified *via* comparison with a theoretical isotope pattern.

Elemental analyses were performed by Mrs. J. Dostal, Chemistry Analytical Services Department, Durham University or Mr S. Boyer, London Metropolitan University. Infrared spectra were collected on Perkin Elmer 1600 or Spectrum1 spectrophotometers using KBr discs or a solution cell fitted with KBr windows.

N,*N*,*N′*,*N″*-Tetraisopropyl-*N*-diphenylphosphino-guanidine 1

To a stirred, cooled (−78 °C) solution of *N,N′*-diisopropylcarbodiimide (2.5 mL, 16.14×10^{-3} mol) in diethyl ether (200 mL) was added dropwise $Bu^{n}Li$ (2.0 M, pentane, 8.1 mL, 16.14×10^{-3} mol), and the vessel left to warm to RT over 1 h, to give an opaque white solution. After re-cooling (−78 °C), an ethereal solution (80 mL) of Ph_2PCl (2.9 mL, 16.14×10^{-3} mol) was added dropwise *via* cannula. The mixture was allowed to stir at −78 °C for 1 h before being left to warm to RT, then stirred for 18 h, resulting in a yellow solution and white precipitate. Removal of solvent under reduced pressure left a yellow oil. Addition of CH_2Cl_2 (20 mL) followed by filtration and removal of all volatile components *in vacuo* left **1** as a viscous yellow oil (4.52 g, 68%). Attempts to purify **1** by distillation and column chromatography lead to its decomposition; hence it was used without further purification. ^{1}H (250.1 MHz, $CDCl_3$) δ: 7.44 (4H, br pseudo-t, $^{3}J_{HH}$ = 7.0, *o*-C_6H_5), 7.30 (6H, m, *m*- + *p*-C_6H_5), 3.82 (1H, m, NC*H*), 3.60 (2H, m, NC*H*), 3.44 (1H, sept, $^{3}J_{HH}$ = 6.7, NC*H*), 1.10 (12H, br s, CH_3), 1.05 (6H, br s, CH_3), 0.90 (6H, br s, CH_3);

$^{13}C\{^1H\}$ (100.6 MHz, $CDCl_3$) δ: 147.3 (d, $^2J_{PC}$ = 20.7, *C*=N), 139.6 (br d, $^2J_{PC}$ = 18, *o*-C_6H_5), 136.4 (br d, $^2J_{PC}$ = 18, *o*-C_6H_5), 131.9 (s, *p*-C_6H_5), 131.5 (d, $^1J_{PC}$ = 51, *i*-C_6H_5), 127.2 (br, *m*-C_6H_5), 50.4 (d, $^4J_{PC}$ = 5.5, =N*C*H), 47.5 (s, N*C*H), 45.9 (s, N*C*H), 24.2 (s, *C*H$_3$), 22.0 (s, *C*H$_3$), 21.2 (s, *C*H$_3$); $^{31}P\{^1H\}$ (101.3 MHz, $CDCl_3$) δ: + 49.9; MS (FAB$^+$): 412 (MH)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-piperidine-1-carboxamidine 2

To a stirred, cooled (−78 °C) solution of piperidine (0.42 mL, 4.85 × 10^{-3} mol) in diethyl ether (15 mL) was added dropwise Bu^{n}Li (2.55 M, pentane, 1.9 mL, 4.85 × 10^{-3} mol), and the vessel left to warm to RT over 2 h. After re-cooling (−78 °C), an ethereal (25 mL), cooled solution of *N,N*′-dicyclohexylcarbodiimide (1.0 g, 4.85 × 10^{-3} mol) was added dropwise *via* cannula. The mixture was allowed to warm to RT, then stirred for 2 h. Volatile components were removed *in vacuo*. The resulting solid was dissolved in Et_2O (20 mL), cooled at −78 °C and Ph_2PCl (0.87 mL, 4.85 × 10^{-3} mol) was added dropwise, to give an opaque white solution. The mixture was allowed to warm slowly to RT, then stirred for 18 h. The solvents were removed under vacuum, hexane added and the mixture filtered. Concentration and recrystallisation from hexane afforded **2** as a white solid (1.70 g, 74%). Anal. Calc. for $C_{30}H_{42}N_3P$ requires: C, 75.75; H, 8.90; N, 8.83. Found: C, 75.81; H, 8.99; N, 8.87. ^1H (499.9 MHz, $CDCl_3$) δ: 7.50 (4H, br s, *o*-C_6H_5), 7.35 (6H, m, *m*- + *p*-C_6H_5), 3.49 (1H, m, C^1H C_6H_{11}), 3.40 (1H, m, C$^{1\prime}H$ C_6H_{11}), 3.03 (4H, m, C$^1H_2$ pip); 1.87–0.80 (26H, 4 overlapping m, C_6H_{11} + pip); $^{13}C\{^1H\}$ (125.6 MHz, $CDCl_3$) δ: 154.8 (d, $^2J_{PC}$ = 21, *C*=N), 139.9 (d, $^1J_{PC}$ = 102, *i*-C_6H_5), 135.0 (d, $^2J_{PC}$ = 20, *o*-C_6H_5), 131.3 (d, $^2J_{PC}$ = 16, *o*-C_6H_5), 129.8 (s, *p*-C_6H_5), 128.3 (br s, *m*-C_6H_5), 59.8 (d, $^2J_{PC}$ = 5, C^{1}H-C_6H_{11}), 56.6 (s, C^{1}H-C_6H_{11}), 49.5 (s, C^{1}H$_2$ pip), 35.3 (br s, $C^{2/2\prime}H_2$ C_6H_{11}), 33.2 (br s, $C^{2/2\prime}H_2$–C_6H_{11}), 26.7 (br s, $C^{3/3\prime}H_2$–C_6H_{11}), 26.1 (s, $C^{4/4\prime}H_2$–C_6H_{11}), 26.0 (s, $C^{4/4\prime}H_2$–C_6H_{11}), 25.7 (s, C^2H_2–$C_5H_{10}N$), 25.2 (br s, $C^{3/3\prime}H_2$–C_6H_{11}), 24.9 (s, C^3H_2–$C_5H_{10}N$); $^{31}P\{^1H\}$ (161.90 MHz, $CDCl_3$) δ: +50.2; MS (ES$^+$): 292.4 (M-PPh$_2$)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-4-morpholinecarboxamidine 3

To a stirred, cooled (−78 °C) solution of *N,N*′-dicyclohexyl-4-morpholinecarboxamide (9.43 g, 3.21 × 10^{-2} mol) in diethyl ether (200 mL) was added dropwise Bu^{n}Li (2.0 M, pentane, 16.1 mL, 3.21 × 10^{-2} mol), and the vessel left to warm to RT over 1 h, to give an opaque white solution. After re-cooling (−78 °C), an ethereal solution (80 mL) of Ph_2PCl (5.8 mL, 3.21 × 10^{-2} mol) was added dropwise *via* cannula. The mixture was allowed to stir at −78 °C for 1 h before being left to warm to RT, then stirred for 18 h, resulting in a colourless solution with a thick white precipitate. Removal of solvent under reduced pressure left a yellow oil. Addition, and subsequent removal, of CH_2Cl_2 (50 mL) gave a yellow oily solid. Dissolution of the oil in toluene and filtration through a glass frit to remove the white solid, gave an orange solution. Concentration and crystallisation at −30 °C gave colourless crystals of **3** suitable for an X-ray structure determination (11.34 g, 74%). Anal. Calc. for $C_{29}H_{40}N_3OP$: C, 72.93; H, 8.44; N, 8.80%. Found: C, 72.99; H, 8.48; N, 8.86%. ^1H (499.9 MHz, C_6D_6) δ: 7.59 (4H, br pseudo-t, $^3J_{HH}$ = 7.0, *o*-C_6H_5), 7.09 (6H, m, *m*- + *p*-C_6H_5), 3.80–3.49 (6H, m, C$^{1,1\prime}H$ C_6H_{11} + OCH_2CH_2N), 3.19 (4H, m, OCH$_2$CH_2N), 1.83–0.90 (20H, *m*, C_6H_{11}); $^{13}C\{^1H\}$ (125.7 MHz, C_6D_6) δ: 153.6 (d, $^2J_{PC}$ = 20.5, *C*=N), 140.7 (br s, *i*-C_6H_5), 135.3 (br s, *o*-C_6H_5), 131.8 (br s, *o*-C_6H_5), 128.4 (br s, *m*- + *p*-C_6H_5), 67.0 (s, OCH_2CH_2N), 60.2 (d, $^2J_{PC}$ = 5.5, C^{1}H-C_6H_{11}), 57.0 (s, C^{1}H-C_6H_{11}), 50.1 (s, OCH$_2$$CH_2$N), 36.0 (br s, $C^{2/2\prime}H_2$–C_6H_{11}), 33.9 (br s, $C^{2/2}H_2$–C_6H_{11}), 27.5 (br s, $C^{3/3}H_2$–C_6H_{11}), 26.9 (br s, $C^{4/4\prime}H_2$–C_6H_{11}), 26.4 (br s, $C^{4/4\prime}H_2$–C_6H_{11}), 25.7 (br s, $C^{3/3\prime}H_2$–C_6H_{11}); $^{31}P\{^1H\}$ (125.7 MHz, C_6D_6) δ: +49.8 (s); MS (FAB$^+$): 478 (MH)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-acetamidine 4

To a stirred, cooled (−78 °C) solution of *N,N*′-dicyclohexyl-carbodiimide (1.0 g, 4.85 × 10^{-3} mol) in diethyl ether (25 mL) was added dropwise MeLi (1.6 M, hexane, 3.0 mL, 4.85 × 10^{-3} mol), and the vessel left to warm to RT over 1 h. After re-cooling (−78 °C), Ph_2PCl (0.87 mL, 4.85 × 10^{-3} mol) was added dropwise. The mixture was allowed to warm to RT, then stirred for 18 h. The solvents were removed under vacuum, pentane added and the solution filtered. Prolonged standing in pentane gave rise to colourless crystals of **4** suitable for an X-ray structure determination (1.65 g, 84%). Anal. Calc. for $C_{26}H_{35}N_2P$ requires: C, 76.81; H, 8.68; N, 6.89. Found: C, 76.71; H, 8.64; N, 6.80. ^1H (499.8 MHz, $CDCl_3$) δ: 7.53–7.27 (10H, m, C_6H_5), 4.02 (m, 1H, C$^{1/1}H$-C_6H_{11}), 3.03 (1H, m, C$^{1/1}H$-C_6H_{11}), 1.58 (3H, s, CH_3), 2.02–1.21 (20H, m, CH_2–C_6H_{11}); $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$) δ: 155.7 (d, $^2J_{PC}$ 1, *C*=N), 139.1 (d, $^1J_{PC}$ = 17, *i*-C_6H_5), 131.4 (d, J_{PC} = 20.23, *o*- or *m*-C_6H_5), 128.2 (d, J_{PC} = 5, *o*- or *m*-C_6H_5), 128.1 (s, *p*-C_6H_5), 58.5 (d, $^2J_{PC}$ = 17.5, C$^{1\prime}$H-C_6H_{11}), 57.4 (s, C^{1}H-C_6H_{11}), 34.6 (s, C^2H_2–C_6H_{11}), 33.3 (d, $^3J_{PC}$ = 11.5, $C^{2\prime}H_2$–C_6H_{11}), 26.8 (s, $C^{3/3\prime}H_2$–C_6H_{11}), 26.3 (s, $C^{4/4\prime}H_2$–C_6H_{11}), 26.1 (s, $C^{4/4\prime}H_2$–C_6H_{11}), 24.8 (s, $C^{3/3\prime}H_2$–C_6H_{11}), 17.0 (d, $^3J_{PC}$ = 7 Hz, *C*H$_3$); $^{31}P\{^1H\}$ (161.90 MHz, $CDCl_3$) δ: +37.0; MS (EI): 406 (M), 329 (M-Ph), 221 (M-PPh$_2$).

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-benzamidine 5

To a stirred, cooled (−78 °C) solution of *N,N*′-dicyclohexyl-carbodiimide (1.0 g, 4.85 × 10^{-3} mol) in diethyl ether (25 mL) was added dropwise PhLi (2.0 M, Bu_2O, 2.4 mL, 4.85 × 10^{-3} mol), and the vessel left to warm to RT over 2 h. After re-cooling (−78 °C), an ethereal, cooled solution (10 mL) of Ph_2PCl (0.87 mL, 4.85 × 10^{-3} mol) was added dropwise *via* cannula. The mixture was allowed to warm to RT, then stirred for 18 h. The volatile components were removed under vacuum, hexane added and the mixture filtered. Removal of the solvent *in vacuo* afforded **5** as a white solid (1.74 g, 83%) that was used without further purification. Anal. Calc. for $C_{31}H_{37}N_2P$ requires: C, 79.45; H, 7.96; N, 5.98. Found: C, 79.51; H, 8.00; N, 6.01. ^1H (499.8 MHz, $CDCl_3$) δ: 7.57 (4H, pseudo-t, $^3J_{HH}$ = 16.0, *o*-*(P)*C_6H_5), 7.60–7.10 (9H, m, C_6H_5), 7.08 (2H, d,$^3J_{HH}$ = 8.0, *o*-C_6H_5), 3.15 (1H, m, C$^{1,1\prime}H$-C_6H_{11}), 2.54 (1H, m, C$^{1,1\prime}H$-C_6H_{11}), 2.27 (2H, m, C_6H_{11}), 1.66–0.80 (18H, m, C_6H_{11}); $^{13}C\{^1H\}$ (125.6 MHz, $CDCl_3$) δ: 157.2 (d, $^2J_{PC}$ = 9, *C*=N), 138.9 (d, $^1J_{PC}$ = 15, *i*-*(P)*C_6H_5), 136.4 (d, $^3J_{PC}$ = 2, *i*-C_6H_5), 132.6 (d, $^2J_{PC}$ = 21.5, *o*-*(P)*C_6H_5), 128.4 and 128.1 (s, *o*- + *m*-C_6H_5), 127.9 (s, *p*-C_6H_5), 127.8 (d, $^3J_{PC}$ = 6.5, *m*-*(P)*C_6H_5), 127.4 (d, $^4J_{PC}$ = 2, *p*-*(P)*C_6H_5), 59.9 (d, $^2J_{PC}$ = 10, C$^{1\prime}$H-C_6H_{11}), 58.8 (s, C^{1}H-C_6H_{11}), 33.3 (d, $^3J_{PC}$ = 8.2, $C^{2\prime}H_2$–C_6H_{11}), 34.7 (s, C^2H_2–C_6H_{11}), 26.8 (s, *C*H$_2$), 26.1 (s, *C*H$_2$), 25.8 (s, *C*H$_2$), 24.6 (s,

CH_2); $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: +44.9 (br s, $\nu_{1/2}$ = 44 Hz); MS (ES^+): 283.5 $(M–PPh_2)^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-selenide-piperidine-1-carboxamidine 6

A Young's tap NMR tube was charged with Se (8 mg, 1.03 × 10^{-4} mol), **2** (40 mg, 8.41 × 10^{-5} mol) and $CDCl_3$ (0.75 mL). Compound **6** was obtained quantitatively (by ^{31}P NMR spectroscopy) after 12 h at RT. $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: +57.6 (s + satellites, $^1J_{SeP}$ = 772).

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-selenide-4-morpholinecarboxamidine 7

A Young's tap NMR tube was charged with Se (8 mg, 1.03 × 10^{-4} mol), **3** (41 mg, 8.58 × 10^{-5} mol) and $CDCl_3$ (0.75 mL). The tube was then sonicated for 18 h, affording **7** quantitatively (by ^{31}P NMR spectroscopy). $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: + 56.3 (s + satellites, $^1J_{SeP}$ = 775).

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-selenide-acetamidine 8

A Young's tap NMR tube was charged with Se (8 mg, 1.03 × 10^{-4} mol), **4** (50 mg, 0.1 × 10^{-3} mol) and $CDCl_3$ (0.70 mL). Compound **8** was obtained quantitatively (by ^{31}P NMR spectroscopy) after 12 h at RT. $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: + 63.2 (s + satellites, $^1J_{SeP}$ = 749).

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-selenide-benzamidine 9

A Young's tap NMR tube was charged with Se (8 mg, 1.03 × 10^{-4} mol), **5** (50 mg, 9.0 × 10^{-5} mol) and $CDCl_3$ (0.80 mL). Compound **9** was obtained quantitatively (by ^{31}P NMR spectroscopy) after 12 h at RT. $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: + 67.3 (s + satellites, $^1J_{SeP}$ = 753).

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-4-morpholinecarboxamidine rhodium carbonyl chloride 10

A Young's tap NMR tube was charged with **3** (59 mg, 1.23 × 10^{-4} mol), $\{Rh(CO)_2Cl\}_2$ (24 mg, 6.17 × 10^{-5} mol) and sealed. $CDCl_3$ (0.75 mL) was added and the tube freeze/thaw degassed, back-filled with N_2 and sealed. After 30 min, when gas evolution had finished, the solution was freeze/thaw degassed, back-filled with an atmosphere of CO, sealed and left to stand at RT for 1 h, resulting in a yellow solution. Layering hexane on top of the $CDCl_3$ solution, yielded crystals of **10** suitable for an X-ray structure determination, after standing for 1 week (12 mg, 30%). Anal. Calc. for $C_{30}H_{40}N_3O_2PClRh.CDCl_3$: C, 48.71; H, 5.54; N, 5.50. Found: C, 48.82; H, 5.59; N, 5.45%. ^1H (499.9 MHz, $CDCl_3$) δ: 7.86 (4H, m, *o*-C_6H_5), 7.51 (6H, m, *m*- + *p*-C_6H_5), 3.73 (4H, m, OCH_2CH_2N), 3.25 (6H, m, OCH_2CH_2N + $C^{1/1'}H$-C_6H_{11}), 2.74 (2H, m, C_6H_{11}), 1.77–0.61 (18H, 4 overlapping m, C_6H_{11}); $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$) δ: 188.1 (d, $^1J_{RhC}$ = 74, Rh-*C*O), 165.7 (dd, $^2J_{PC}$ = 24, $^2J_{RhC}$ = 3.5, *C*=N), 134.3 (d, $^2J_{PC}$ = 14.5, *o*-C_6H_5), 132.2 (d, $^4J_{PC}$ = 2, *p*-C_6H_5), 132.0 (dd, $^1J_{PC}$ = 52.5, $^2J_{RhC}$ = 1.7, *i*-C_6H_5), 128.7 (d, $^3J_{PC}$ = 12, *m*-C_6H_5), 66.4 (s, OCH_2CH_2N), 64.1 (s, $C^{1'}H$-C_6H_{11}), 62.0 (s, C^1H-C_6H_{11}), 49.8 (s, OCH_2CH_2N), 33.7 (s, $C^{2/2'}H_2$–C_6H_{11}), 32.7 (s, $C^{2/2'}H_2$–C_6H_{11}), 26.9 (s, $C^{3/3'}H_2$–C_6H_{11}), 26.3 (s, $C^{3/3'}H_2$–C_6H_{11}), 25.3 (s, $C^{4/4'}H_2$–C_6H_{11}), 25.0 (s, $C^{4/4'}H_2$–C_6H_{11}); $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: +112.1 (d, $^1J_{RhP}$ = 176); MS (FAB^+): 608 $(M - Cl)^+$; IR (KBr, $CDCl_3$ solution): ν(CO) = 1994 cm^{-1}.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-acetamidine rhodium carbonyl chloride 11

A Young's tap NMR tube was charged with **4** (50 mg, 1.23 × 10^{-4} mol), $\{Rh(CO)_2Cl\}_2$ (24 mg, 6.17 × 10^{-5} mol) and $CDCl_3$ (0.75 mL). After 30 min, the solution was freeze/thaw degassed, back-filled with an atmosphere of CO, sealed and left to stand at RT for 1 h, resulting in a yellow solution. Complex **11** was obtained quantitatively (by ^{31}P NMR spectroscopy) as a single product and subsequently isolated as a yellow–orange solid on removal of solvent *in vacuo* (64 mg, 91%). Anal. Calc. for $C_{27}H_{35}N_2OPRhCl$: C, 56.60; H, 6.16; N, 4.89. Found: C, 56.68; H, 6.23; N, 4.99. ^1H (499.9 MHz, $CDCl_3$) δ: 7.91–7.86 (4H, m, C_6H_5), 7.62–7.56 (6H, m, C_6H_5), 3.64 (1H, m, $C^{1/1'}H$-C_6H_{11}), 3.24 (1H, br s, $C^{1/1'}H$-C_6H_{11}), 2.48 (3H, s, CH_3), 2.27–0.81 (20H, m, C_6H_{11}); $^{13}C\{^1H\}$ (125.6 MHz, $CDCl_3$) δ: 181.3 (d, $^1J_{RhC}$ = 78.5, Rh-*C*O), 133.1 (d, J_{PC} = 14, *o*- or *m*-C_6H_5), 132.9 (bs, *p*-C_6H_5), 129.6 (d, J_{PC} = 11, *o*- or *m*-C_6H_5), 62.7 (s, $C^{1/1'}H$-C_6H_{11}), 62.1 (br s, $C^{1/1'}H$-C_6H_{11}), 32.9 (s, CH_2), 26.9 (s, CH_2), 25.8 (s, CH_2), 25.2 (s, CH_2), 25.1 (s, CH_2), 19.5 (br s, CH_3); $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: + 124.9 (br d, $^1J_{RhP}$ = 175.1); IR (KBr, $CDCl_3$ solution): ν(CO) = 1995 cm^{-1}. Note, despite acquisition of spectra with long relaxation delay times, the C=N carbon and *ipso*-C_6H_5 resonances could not be observed.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-benzamidine rhodium carbonyl chloride 12

A Young's tap NMR tube was charged with **5** (50 mg, 1.07 × 10^{-4} mol), $\{Rh(CO)_2Cl\}_2$ (21 mg, 5.35 × 10^{-5} mol) and $CDCl_3$ (0.75 mL). The tube was freeze/thaw degassed, back-filled with N_2 and sealed. After 1 day, compound **12** was obtained quantitatively (by ^{31}P NMR spectroscopy) as a single product, which was isolated as a brown waxy solid following removal of solvent under reduced pressure (65 mg, 95%). Anal. Calc. for $C_{32}H_{37}N_2OPRhCl$: C, 60.53; H, 5.87; N, 4.41. Found: C, 60.80; H, 6.02; N, 4.55. ^1H (499.9 MHz, $CDCl_3$) δ: 7.94 (4H, m, C_6H_5), 7.60–7.46 (9H, m, C_6H_5), 7.22 (2H, m, C_6H_5), 3.11 (1H, br s, $C^{1/1'}H$-C_6H_{11}), 2.88 (3H, br s, C_6H_{11}), 1.74–0.56 (18H, m, C_6H_{11}); $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$) δ: 187.3 (br, Rh-*C*O), 170.0 (br s, C=N), 133.2 (d, J_{PC} = 13.5, *o*- or *m*-(P)C_6H_5), 132.1 (dd, $^1J_{PC}$ = 56, $^2J_{RhC}$ = 2, *i*-(P)C_6H_5), 132.0 (s, C_6H_5), 130.5 (s, C_6H_5), 129.0 (d, J_{PC} = 10.5, *o*- or *m*-(P)C_6H_5), 128.5 (br s, C_6H_5 +*p*-(P)C_6H_5), 64.2 (br s, $C^{1/1'}H$-C_6H_{11}), 62.1 (br s, $C^{1/1'}H$-C_6H_{11}), 34.5 (br s, CH_2), 31.6 (s, CH_2), 27.0 (br s, CH_2), 25.8 (s, CH_2), 24.9 (br s, CH_2), 24.5 (s, CH_2); $^{31}P\{^1H\}$ (161.9 MHz, $CDCl_3$) δ: +124.7 (d, $^1J_{RhP}$ = 181.5); IR (KBr, $CDCl_3$ solution): ν(CO) = 2000 cm^{-1}.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-piperidine-1-carboxamidine palladium dichloride 13

To a solution of **2** (460 mg, 0.98 × 10^{-5} mol) in CH_2Cl_2 (20 mL) was added dropwise a solution of $PdCl_2(MeCN)_2$ (250 mg, 0.98 × 10^{-5} mol) was dissolved in CH_2Cl_2 (20 mL) to give a very dark orange solution. The mixture was stirred for 1 h. All volatile components were removed *in vacuo* to afford **13** as a dark yellow–brown solid, which was washed with diethyl ether (3 × 5 mL) and

dried *in vacuo* (489 mg, 77%). Anal. Calc. for $C_{31}H_{37}N_2PPdCl_2$ requires: C, 57.64; H, 5.77; N, 4.34. Found: C, 57.59; H, 5.60; N, 4.21. ^{1}H (499.9 MHz, $CDCl_3$) δ: 7.97 (4H, m, *o*-C_6H_5), 7.61 (2H, m, *p*-C_6H_5), 7.49 (4H, m, *m*-C_6H_5); 3.47–2.98 (6H, 3 overlapping m, $C^{1,1'}H$-C_6H_{11} + C^1H_2–$C_5H_{10}N$), 1.77–0.95 (26H, 4 overlapping m, C_6H_{11} + $C_5H_{10}N$); ^{13}C{^{1}H} (125.7 MHz, C_6D_6) δ: 167.8 (d, $^2J_{PC}$ = 25, *C*=N), 134.6 (d, J_{PC} = 13, *o*- or *m*-C_6H_5), 133.4 (d, $^4J_{PC}$ = 3, *p*-C_6H_5), 129.0 (d, J_{PC} = 13, *o*- or *m*-C_6H_5), 127.22 (d, $^1J_{PC}$ = 62, *i*-C_6H_5), 66.0 (s, $C^{1/1'}$H-C_6H_{11}), 63.0 (s, $C^{1/1'}$H-C_6H_{11}), 51.5 (s, C^1H-$C_5H_{10}N$), 33.6 (s, $C^{2/2'}H_2$–C_6H_{11}), 32.6 (s, $C^{2/2'}H_2$–C_6H_{11}), 26.9 (s, $C^{3/3'}H_2$–C_6H_{11}), 26.5 (s, $C^{3/3'}H_2$–C_6H_{11}), 25.8 (s, C^2H_2–$C_5H_{10}N$), 25.1 (br s, $C^{4/4'}H_2$–C_6H_{11}), 24.9 (s, $C^{4/4'}H_2$–$C_5H_{10}N$), 23.7 (s, C^3H_2–$C_5H_{10}N$); ^{31}P{^{1}H} (161.90 MHz, $CDCl_3$) δ: +84.4 (br s, $\nu_{1/2}$ = 131 Hz); MS (MALDI): 617.5 (M–Cl)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-4-morpholinecarboxamidine palladium dichloride 14

To a mixture of **3** (424 mg, 1.16 × 10^{-3} mol) and $PdCl_2$(COD) (321 mg, 1.12 × 10^{-3} mol) was added cold (−78 °C) CH_2Cl_2 (30 mL), the mixture then being left to stir and warm to RT over 18 h. Volatile components were removed under reduced pressure to leave **14** as a yellow powder, which was washed with diethyl ether (3 × 30 mL) and dried *in vacuo* (578 mg, 95%). Anal. Calc. for $C_{29}H_{40}N_3OPCl_2Pd$: C, 53.18; H, 6.16; N, 6.42%. Found: C, 53.25; H, 6.22; N, 6.34%. ^{1}H (301.2 MHz, $CDCl_3$) δ: 7.98 (4H, dd, $^3J_{HH}$ = 7.6, $^3J_{PH}$ = 6.4, *o*-C_6H_5), 7.64 (2H, dd, $^3J_{HH}$ = 7.5, $^5J_{PH}$ = 2.3, *p*-C_6H_5), 7.52 (4H, dd, $^3J_{HH}$ = 7.6, $^4J_{PH}$ = 2.9, *m*-C_6H_5), 3.87–3.71 (4H, m, OCH_2CH_2N), 3.51–3.03 (8H, m, OCH_2CH_2N + C_6H_{11}), 1.69 (8H, m, C_6H_{11}), 1.48 (2H, m, C_6H_{11}), 1.39–0.90 (8H, m, C_6H_{11}); ^{13}C{^{1}H} (75.8 MHz, $CDCl_3$) δ: 166.5 (d, $^2J_{PC}$ = 24.5, *C*=N), 134.5 (d, $^2J_{PC}$ = 13, *o*-C_6H_5), 133.6 (d, $^4J_{PC}$ = 3, *p*-C_6H_5), 129.1 (d, $^3J_{PC}$ = 12.5, *m*-C_6H_5), 126.9 (d, $^1J_{PC}$ = 62, *i*-C_6H_5), 66.5 (s, OCH_2CH_2N), 66.0 (s, $C^{1'}$H-C_6H_{11}), 63.2 (s, C^1H-C_6H_{11}), 50.2 (s, OCH_2CH_2N), 33.5 (s, CH_2–C_6H_{11}), 32.6 (s, CH_2–C_6H_{11}), 26.9 (s, CH_2–C_6H_{11}), 26.4 (s, CH_2–C_6H_{11}), 25.1 (s, CH_2–C_6H_{11}), 24.7 (s, CH_2–C_6H_{11}); ^{31}P{^{1}H} (121.94 MHz, $CDCl_3$) δ: +84.6 (br s, $\nu_{1/2}$ = 131 Hz); MS (FAB$^+$): 618 (M − Cl)$^+$, 583 (M-2Cl)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-acetamidine palladium dichloride 15

A solution of **4** (0.52 g, 1.28 × 10^{-3} mol) in CH_2Cl_2 (15 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (0.33 g, 1.28 × 10^{-3} mol) in CH_2Cl_2 (10 mL). The mixture was allowed to stir for 18 h, the orange suspension turning to a yellow solution. Removal of volatile components under reduced pressure afforded an orange–yellow solid, which was washed with Et_2O. Layering hexane on top of a $CDCl_3$ solution of **15** yielded suitable crystals for an X-ray structure determination, after standing for 1 week. (0.63 g, 84%). Anal. Calc. for $C_{26}H_{35}Cl_2N_2PPdCDCl_3$: C, 46.05; H, 5.30; N, 3.98. Found: C, 45.88; H, 5.01; N, 3.76. ^{1}H (499.9 MHz, $CDCl_3$) δ: 8.00–7.97 (4H, m, *o*-C_6H_5), 7.67–7.64 (2H, m, *p*-C_6H_5), 7.57–7.53 (4H, m, *m*-C_6H_5), 3.82 (1H, br s, $C^{1/1'}H$-C_6H_{11}), 3.06 (1H, br s, $C^{1/1'}H$-C_6H_{11}), 2.83 (2H, br s, C_6H_{11}), 2.45 (3H, s, CH_3), 1.82–0.81 (18H, m, C_6H_{11}); ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$) δ: 168.9 (br s, *C*=N), 133.9 (d, J_{PC} = 12, *o*- or *m*-C_6H_5), 133.5 (d, $^4J_{PC}$ = 3, *p*-C_6H_5), 129.3 (d, J_{PC} = 12.5, *o*- or *m*-C_6H_5), 126.5 (d, $^1J_{PC}$ = 64, *i*-C_6H_5), 62.2 (d, $^2J_{PC}$ = 3, $C^{1'}$H-C_6H_{11}), 53.7 (s, C^1H-C_6H_{11}), 32.6 (s, $C^{2/2'}H_2$–C_6H_{11}), 31.5 (s, $C^{2/2'}H_2$–C_6H_{11}), 26.8 (s, CH_2), 26.0 (s, CH_2), 25.1 (s, CH_2), 24.8 (s, CH_2), 19.4 (d, $^3J_{PC}$ = 9.5, CH_3); ^{31}P{^{1}H} (161.9 MHz, $CDCl_3$) δ: +108.0; MS (MALDI): 549 (M − Cl)$^+$.

N,*N*′-Dicyclohexyl-*N*-diphenylphosphino-benzamidine palladium dichloride 16

To a solution of **5** (111 mg, 0.24 × 10^{-3} mol) in CH_2Cl_2 (10 mL) was added a solution of $PdCl_2(MeCN)_2$ (61.50 mg, 0.24 × 10^{-3} mol) in CH_2Cl_2 (10 mL), giving rise to a dark orange solution. The mixture was stirred for 4 h. Volatile components were removed *in vacuo* and the residue was washed with both hexane and Et_2O, affording **16** as an orange solid (0.14 g, 92%). Anal. Calc. for $C_{31}H_{37}N_2PPdCl_2$: C, 57.64; H, 5.77; N, 4.34. Found: C, 57.77; H, 5.89; N, 4.45. ^{1}H (499.9 MHz, $CDCl_3$) δ: 8.10 (2H, m, C_6H_5), 7.67–7.29 (13H, m, C_6H_5), 3.01 (2H, br s, C_6H_{11}), 1.81–0.48 (20H, 4 overlapping m, C_6H_{11}); ^{13}C{^{1}H} (125.7 MHz, $CDCl_3$) δ: 134.1 (d, J_{PC} = 12.5, *o*- or *m*-(P)C_6H_5), 133.6 (s, *p*-(P)C_6H_5), 131.3 (s, C_6H_5), 130.1 (s, C_6H_5), 129.3 (d, J_{PC} = 12, *o*- or *m*-(P)C_6H_5), 127.0 (d, $^1J_{PC}$ = 67 HZ, *i*-C_6H_5), 126.9 (s, C_6H_5), 66.1 (s, $C^{1/1'}$H-C_6H_{11}), 63.1 (s, $C^{1/1'}$H-C_6H_{11}), 33.4 (s, CH_2), 31.6 (s, CH_2), 25.8 (s, CH_2), 26.5 (s, CH_2), 24.8 (s, CH_2), 24.2 (s, CH_2); only 1 *ipso*-C_6H_5 resonance could be observed; ^{31}P{^{1}H} (161.9 MHz, $CDCl_3$) δ: +106.7; MS (MALDI): 610.5 (M − Cl)$^+$.

N,*N*,*N*′,*N*″-Tetraisopropyl-*N*-diphenylphosphino-guanidine palladium dichloride 17

A Schlenk flask was charged with **1** (200 mg, 0.49 × 10^{-3} mol) and $PdCl_2$(COD) (139 mg, 0.49 × 10^{-3} mol). The vessel was cooled to −78 °C and CH_2Cl_2 (30 mL) added. The mixture was allowed to warm to RT over 6 h, whereupon the CH_2Cl_2 was removed under reduced pressure to leave **17** as a yellow powder, which was washed with diethyl ether (3 × 10 mL) and dried *in vacuo* (229 mg, 80%). Anal. Calc. for $C_{25}H_{38}N_3PPdCl_2$ requires: C, 50.98; H, 6.52; N, 7.14%. Found: C, 51.01; H, 6.66; N, 7.12%. ^{1}H (250.1 MHz, $CDCl_3$) δ: 7.98 (4H, m, *o*-C_6H_5), 7.57 (2H, m, *p*-C_6H_5), 7.40 (4H, m, *m*-C_6H_5), 4.01 (m, 1H, NC*H*), 3.73 (3H, sept., $^3J_{HH}$ 7.6, NC*H*), 1.47 (6H, d, $^3J_{HH}$ 7.6, CH_3), 1.30 (12H, m, CH_3), 0.95 (6H, d, $^3J_{HH}$ 7.6, CH_3); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$) δ: 169.6 (d, $^2J_{PC}$ 24.5, =N*C*), 135.1 (d, $^2J_{PC}$ = 13.5, *o*-C_6H_5), 133.6 (d, $^4J_{PC}$ = 3, *p*-C_6H_5), 129.0 (d, $^3J_{PC}$ = 12.5, *m*-C_6H_5), 127.4 (d, $^1J_{PC}$ = 61, *i*-C_6H_5), 57.6 (s, N*C*H), 54.5 (s, N*C*H), 53.5 (s, N*C*H), 24.3 (s, *C*H_3), 23.6 (d, $^5J_{PC}$ = 12, *C*H_3), 23.0 (s, *C*H_3); ^{31}P{^{1}H} (101.3 MHz, $CDCl_3$) δ: +81.2; MS (FAB$^+$): 554 (M − Cl)$^+$.

X-Ray crystallography

The single crystal X-ray diffraction experiments (Table 6) were carried out for **3** and **10** on a Bruker APEX 2000 CCD diffractometer, for **4** on a Rigaku R-Axis SPIDER IP diffractometer, and for **15** on a Bruker SMART 6000 CCD diffractometer, using Oxford Cryrostream N_2 cooling devices and graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The diffraction of **4** was extremely weak (mean $I/\sigma(I)$ < 2.8). The data were corrected for absorption by semi-empirical method (on Laue equivalents) for **3** and **10**,[44] by numerical integration (on crystal face-indexing) for **15**. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using

Table 6 Crystal data and X-ray experimental details

	3	**4**	**10**	**15**
CCDC deposition no.	293165	663533	293166	663534
Formula	$C_{29}H_{40}N_3OP$	$C_{26}H_{35}N_2P$	$C_{30}H_{40}ClN_3O_2PRh{\cdot}CDCl_3$	$C_{26}H_{35}Cl_2N_2PPd{\cdot}CDCl_3$
Formula weight	477.61	406.53	764.35	704.20
T/K	150	120	150	120
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$ (#14)	*Pbca* (#61)	$P2_1/c$ (#14)	$P2_1/n$ (#14, non-standard)
a/Å	10.1116(5)	19.450(2)	21.4996(9)	8.0573(5)
b/Å	9.8929(4)	10.630(1)	9.3920(4)	22.988(2)
c/Å	26.4573(12)	22.218(2)	16.7107(7)	16.876(1)
β/°	90.047(1)	90	103.496(1)	98.13(1)
V/Å^3	2646.6(2)	4593.6(8)	3281.1(2)	3094.3(4)
Z and ρ_{calc}/g cm^{-3}	4, 1.199	8, 1.176	4, 1.547	4, 1.512
μ(Mo-Kα)/mm^{-1}	0.13	0.13	0.93	1.10
Reflections collected, unique (R_{int})	21815, 5768 (0.025)	36129, 4043 (0.136)	16859, 7141 (0.028)	53693, 13064 (0.055)
R_1 [$I > 2\sigma(I)$] and wR_2 (all data)[a]	0.039, 0.114	0.078, 0.153	0.027, 0.067	0.034, 0.084

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

the SHELXTL programs.[45] All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' at idealised positions.

CCDC reference numbers 293165, 663533, 293166 and 663534 for **3**, **4**, **10** and **15**, respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715736c

Computations

All *ab initio* computations were carried out with the Gaussian 03 package.[46] The model and full geometries discussed here were optimised using the B3LYP/6-31G* level of theory[47,48] with no symmetry constraints. Frequency calculations on these optimised geometries have no imaginary frequencies. The electronic structures were also computed at the same level of theory. The energy barriers to phosphatropic rearrangement were estimated by optimisation of the geometries with both N–P distances being equivalent. The rotational barriers along the N–P bond were calculated by fixing the C1–N2–P–C24 torsional angle at 30° angle intervals and optimised. The *Z*- and *E*-imine rearrangement barriers were determined by fixing the N2–C1–N1–C2 dihedral angle to 90° and the geometries otherwise fully optimised.

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