

Late Transition-Metal Complexes of 2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz: Observation of Three Distinct Ligation Modes (κ^1 -P, κ^2 -P/N and κ^3 -P/N/N')

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The one-step synthesis of the amide-functionalised tertiary phosphane 2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz (Bz = CH₂Ph), **2-HH**, by condensation of the known aminophosphane, 2-Ph₂PC₆H₄(NH₂) (**1**), with *N*-(benzyloxycarbonyl)-glycine and dicyclohexylcarbodiimide (DCC) in THF at room temperature is reported. The new ligand **2-HH** displays various coordination modes when complexed to a range of late transition-metal precursors. Hence κ^1 -P-coordination for **2-HH** is observed in the complexes ClAu(**2-HH**) (**3**), MCl₂(η^5 -Cp*)(**2-HH**) (M = Rh **4**; Ir **5**), RuCl₂(η^6 -*p*-cymene)(**2-HH**) (**6**), Pd(κ^2 -CN-C₁₂H₁₂N)Cl(**2-HH**) (**7**) and MCl₂(**2-HH**)₂ (M = Pd **8**; Pt **9**). Treatment of **8** or **9** with *t*BuOK in CH₃OH gave the bis- κ^2 -P/N-chelate complexes *cis*-M{2-Ph₂PC₆H₄NC(O)CH₂NHCO₂Bz}₂ (M = Pt **10**; Pd **11**) in which both monoanionic ligands **2-H**[−] are disposed in a *cis* geometry. The related nickel(II) complex *cis*-Ni{2-Ph₂PC₆H₄NC(O)CH₂NHCO₂Bz}₂ (**12**) was prepared from NiCl₂·6H₂O, 2 equiv. of **2-HH** and *t*BuOK in refluxing CH₃OH. Reaction of the piano-stool

complex **5** with *t*BuOK in CH₃OH gave the chiral-at-metal complex Ir(η^5 -Cp*)(2-Ph₂PC₆H₄NC(O)CH₂NCO₂Bz) (**14**), present in solution as two diastereomers. A single-crystal X-ray diffraction study of **14** confirmed the κ^3 -P/N/N'-tridentate coordination mode. Under similar conditions the chiral-at-metal ruthenium(II) complex Ru(η^6 -*p*-cymene){2-Ph₂PC₆H₄NC(O)CH₂NCO₂Bz} (**15**) was prepared in which **2**^{2−} functions efficiently as a dianionic tridentate ligand. All new compounds have been characterised by multinuclear NMR [³¹P{¹H}, ¹H], FT-IR, EI-MS, ES-MS and microanalysis. Furthermore, the X-ray structures of ten compounds have been determined and reveal, in the majority of cases, a strong propensity for the -NHC(O)CH₂NHCO₂Bz group to engage in N-H...N, N-H...O and N-H...Cl hydrogen bonding.

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Introduction

Coordination compounds of tridentate and tetradentate ligands continue to attract much interest for their variable ligating capabilities,^[1–3] stabilisation of G-quadruplex DNA,^[4] sensor,^[5] magnetic^[6] and luminescent^[7–9] properties and catalytic applications.^[10] Various donor atom combinations have been documented that contain at least one phosphorus donor atom and include for example P/N/C,^[11] P/C/N,^[12] P/N/N,^[13] P/N/O,^[14] P/N/S,^[15] P/N/P^[16] and P/N/Se.^[17] Pincer ligands based on P/C/P^[18] or P/Si/P^[19] donor sets afford interesting complexes, display unusual reactivity and find applications in catalysis. Furthermore, P/O/O and P/O/P ligands have been employed in self-assembly reactions.^[20,21] More recently the use of one or two soft selenium donor atoms in tridentate ligands of the type Se/N/O and Se/C/Se have been documented.^[22,23]

One of the most common methods for the synthesis of potentially tridentate ligand systems usually involves a Schiff base condensation reaction.^[24] This method is par-

ticularly applicable to P/N/N and P/N/O ligands. Many of these ligands bind to metals in a neutral κ^3 -tridentate fashion or ligate in a singly deprotonated form. Examples of κ^3 -tridentate ligands that utilise all three donor centres in a doubly deprotonated form are uncommon.^[15] Herein, we report the synthesis of an unsymmetrical κ^3 -P/N/N'-ligand and demonstrate the flexible ligation behaviour of this new ligand (in its neutral, monoanionic and dianionic forms) through complexation studies towards linear, pseudo-tetrahedral and square-planar transition-metal centres. All compounds have been characterized by multinuclear NMR and FT-IR spectroscopy and in ten cases by single-crystal X-ray diffraction studies.

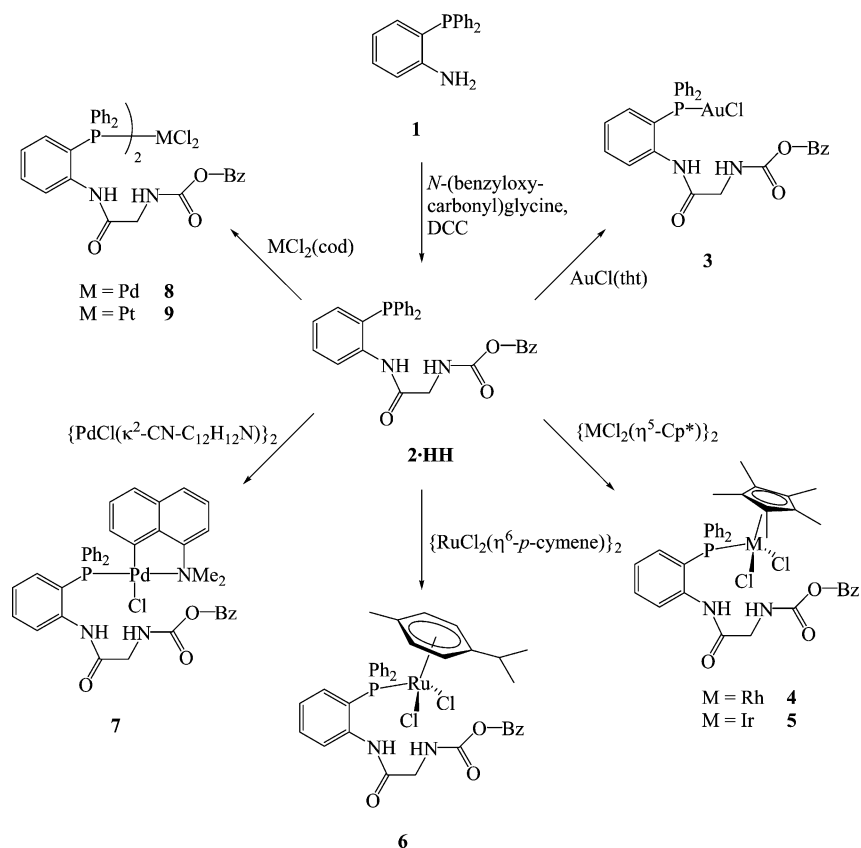
Results and Discussion

Ligand Synthesis

The new ligand 2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz (Bz = CH₂Ph) (**2-HH**) was synthesised in moderate yield (36%) by condensation of the amine-functionalised tertiary phosphane 2-Ph₂PC₆H₄(NH₂) (**1**) with *N*-(benzyloxycarbonyl)-glycine and DCC in THF (Scheme 1). Purification of the crude material comprising **2-HH** and unreacted **1** was readily accomplished by recrystallisation from CH₂Cl₂/Et₂O.

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Scheme 1.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2-HH** shows two resonances at $\delta(\text{P}) = -20.7/-21.3$ ppm [cf. $2\text{-Ph}_2\text{PC}_6\text{H}_4(\text{NH}_2)$: $\delta(\text{P}) = -20.3$ ppm, CDCl_3]. The formation of the new C–N bond was further supported by the observation of new resonances at $\delta(\text{H}) = 5.12$ (overlapping NH and OCH_2 protons) and a doublet at $\delta = 3.85$ ppm (NHCH_2) in the ^1H NMR spectrum. The FT-IR spectrum of **2-HH** clearly shows the presence of NH (3328 and 3264 cm^{-1}) and CO (1721 and 1677 cm^{-1}) functional groups. Oxidation of **2-HH** with aqueous H_2O_2 gives a smooth conversion to the tertiary phosphine oxide **2a** as inferred by two downfield ^{31}P resonances [$\delta(\text{P}) = 37.2$ and 36.9 ppm]. The observation of two similar phosphorus signals for **2a** (and **2-HH**), in the region typically expected for tertiary phosphine oxides, suggests closely related structures which we believe to be conformers due to restricted rotation about either the NH-C(O) or NH-C(O)O bonds.

To evaluate whether **2-HH** is preorganised for metal-ion coordination, an X-ray crystallographic study was performed. The molecular structure of **2-HH** (Figure 1) clearly shows that C–N coupling [$\text{C}(7)\text{--N}(1) = 1.417(2)\text{ \AA}$, Table 1] has resulted as previously indicated by the spectroscopic data. Pyramidalisation around P(1) is clearly reflected in the C–P–C bond angles which lie in the range $99.11(9)\text{--}105.14(9)^\circ$. The donor atoms P(1), N(1) and N(2) essentially all reside in the same plane and are positioned towards each other. This finding contrasts with the X-ray crystal structure of $2\text{-}\{\text{Ph}_2\text{PC}_6\text{H}_4\text{C(H)=N}\}\text{C}_6\text{H}_4\{\text{NHC(O)CH}_2\text{NHCO}_2\text{-}$

Bz}, recently reported by us, in which the -PPh_2 group points away from the N_3 core.^[25] The hydrogen H(1) forms an intramolecular hydrogen bond to N(2) [$\text{N}(1)\cdots\text{N}(2) 2.720(2)\text{ \AA}$, $\text{H}(1)\cdots\text{N}(2) 2.22(2)\text{ \AA}$, $\text{N}(1)\text{--H}(1)\cdots\text{N}(2) 116.3(17)^\circ$] and H(2) intermolecularly H-bonds to O(1B) [$\text{N}(2)\cdots\text{O}(1\text{B}) 2.927(2)\text{ \AA}$, $\text{H}(2)\cdots\text{O}(1\text{B}) 2.09(2)\text{ \AA}$, $\text{N}(2)\text{--H}(2)\cdots\text{O}(1\text{B}) 162(2)^\circ$. Symmetry operator: $B: x + 1/2, y, -z + 3/2$] leading to 1-D chains along the crystallographic a direction (Figure 2).

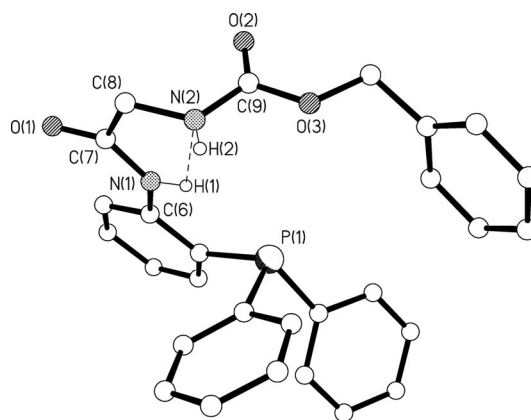


Figure 1. Molecular structure of **2-HH** showing the $\text{N}(1)\text{--H}(1)\cdots\text{N}(2)$ intramolecular H-bonding. All hydrogen atoms except H(1) and H(2) have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2·HH**, **2a**, **3**, **4·Et₂O** and **8**.

	2·HH	2a ^[a]	3 (M = Au)	4·Et₂O (M = Rh)	8 (M = Pd)
C(6)–N(1)	1.417(2)	1.408(2) [1.4110(19)]	1.428(4)	1.411(11)	1.418(4)
N(1)–C(7)	1.354(2)	1.357(2) [1.3507(19)]	1.356(5)	1.385(11)	1.344(4)
C(7)–O(1)	1.227(2)	1.2190(19) [1.2234(19)]	1.225(4)	1.221(14)	1.220(4)
N(2)–C(9)	1.355(3)	1.342(2) [1.346(2)]	1.348(5)	1.385(15)	1.326(6)
C(9)–O(2)	1.210(2)	1.216(2) [1.2143(19)]	1.208(5)	1.171(14)	1.209(5)
C(9)–O(3)	1.348(2)	1.355(2) [1.3545(19)]	1.363(5)	1.348(12)	1.367(5)
P(1)–O(7)		1.5023(11) [1.4989(11)]			
M(1)–Cl(1)			2.3111(9)	2.4180(19)	2.2999(8)
M(1)–Cl(2)				2.4086(19)	
M(1)–P(1)			2.2326(9)	2.353(2)	2.3288(8)
M(1)–M(1A)			3.0926(9)		
M(1)–C _{centroid}				1.8343(34)	
C(6)–N(1)–C(7)	130.32(17)	128.37(14) [128.59(13)]	123.9(3)	124.9(8)	126.8(3)
N(1)–C(7)–O(1)	125.76(19)	126.02(16) [125.74(15)]	123.7(4)	122.5(10)	124.5(3)
N(2)–C(9)–O(2)	125.15(19)	125.03(16) [125.46(15)]	125.8(4)	123.0(10)	126.2(4)
O(2)–C(9)–O(3)	124.79(19)	124.03(17) [125.22(15)]	124.2(4)	128.9(11)	123.3(4)
P(1)–M(1)–Cl(1)			169.99(3)	93.25(7)	86.12(3)
P(1')–M(1)–Cl(1)					93.88(3)
P(1)–M(1)–Cl(2)				89.95(7)	
Cl(1)–M(1)–Cl(2)				89.56(8)	
P(1)–M(1)–M(1A)			111.47(3)		
Cl(1)–M(1)–M(1A)			74.70(2)		

[a] Two independent molecules in the asymmetric unit. Symmetry operator: A: $x + 1/2$, y , $-z + 3/2$. Symmetry operator: ': $-x + 1$, $-y + 1$, $-z + 1$.

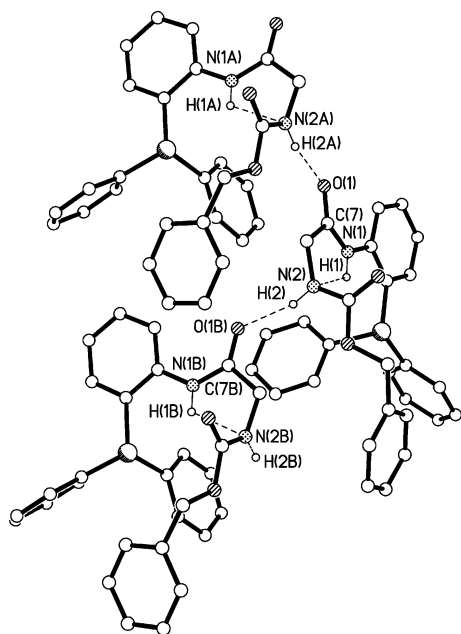


Figure 2. Intermolecular N–H...O bonding in **2·HH**. Symmetry operator: A: $x + 1/2$, y , $-z + 3/2$. Only the N–H hydrogen atoms are shown for clarity.

The structure of the phosphane oxide **2a** (Figure 3) has also been determined with selected bond lengths and angles given in Table 1. Overall the structure is similar to **2·HH** with the exception of the newly formed P=O bond [1.5023(11) Å and 1.4989(11) Å for the two independent molecules]. In contrast with **2·HH**, H(1) [and H(3)] are involved in bifurcated intramolecular H-bonding with the secondary amine nitrogen [N(2) and N(4), respectively] and

the phosphoryl oxygen [O(7) and O(8), respectively] atoms [N(1)···N(2) 2.743(2) Å, H(1)···N(2) 2.280(18) Å, N(1)–H(1)···N(2) 113.9(15)° and N(1)···O(7) 2.7394(17) Å, H(1)···O(7) 1.979(19) Å, N(1)–H(1)···O(7) 146.8(17)°]. Equivalent parameters for the second independent molecule are N(3)···N(4) 2.7580(18) Å, H(3)···N(4) 2.299(18) Å, N(3)–H(3)···N(4) 112.8(14)° and N(3)···O(8) 2.7607(17) Å, H(3)···O(8) 1.974(19) Å, N(3)–H(3)···O(8) 149.1(16)°]. An intermolecular H-bond further links molecules into chains [N(2)···O(7A) 2.8782(19) Å, H(2)···O(7A) 2.05(2) Å, N(2)–H(2)···O(7A) 161.8(18)° and N(4)···O(8B) 2.8824(17) Å, H(4)···O(8B) 2.067(19) Å, N(4)–H(4)···O(8B) 169.4(17)°]. Symmetry operators: A: $-x + 1$, $-y$, $-z + 1$, B: $-x$, $-y + 1$, $-z$].

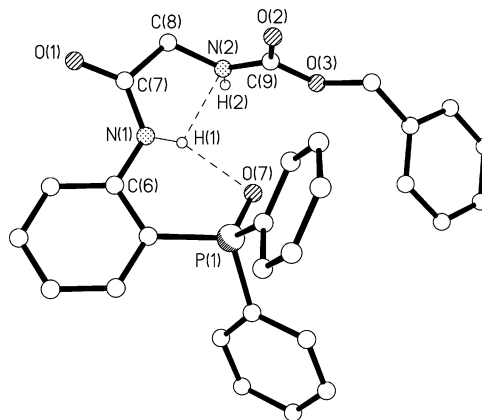


Figure 3. Molecular structure of **2a** showing the bifurcated N(1)–H(1)···N(2) and N(1)–H(1)···O(7) intramolecular H-bonding. All hydrogen atoms except H(1) and H(2) have been omitted for clarity.

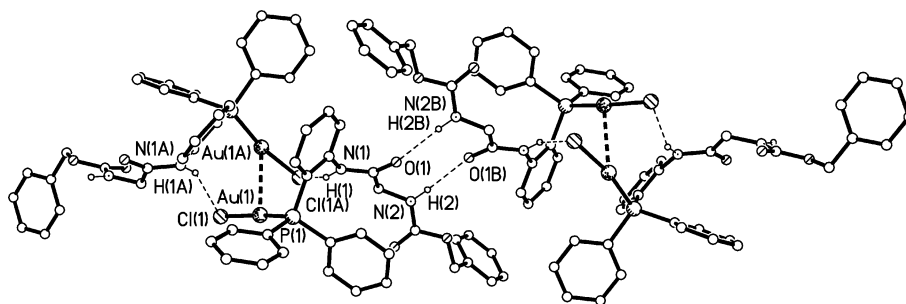


Figure 4. Packing plot of **3** showing those H-atoms involved in H-bonding and the aurophilic interaction. Symmetry operators: A $-x + 1, y, -z + 3/2$, B $-x + 1/2, -y + 1/2, -z + 1$.

Complexation Studies

κ^1 -P-Coordination

A range of late transition-metal complexes with **2·HH** were prepared (Scheme 1) either by substitution of a labile ligand (tht for **3**, cod for **8** and **9**) or chloride-bridge cleavage of an organometallic dimer (as in the case of **4–7**). All the mononuclear complexes were isolated in good to excellent yields (68–98%) and have been fully characterised by NMR, FT-IR and microanalysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data for complexes **3–9** show the expected down-field shifts upon P-coordination of **2·HH** (see Exp. Sect.).

The X-ray structure of **3** (Figure 4, Table 1) clearly reveals coordination at P of an AuCl unit. The Au–Cl and Au–P bond lengths are normal although the Cl–Au–P bond angle [$169.99(3)^\circ$] deviates some 10° from the ideal angle expected for a linear geometry.^[26,27] This “bending back” can presumably be attributed to the strong aurophilic interaction [$3.0926(9) \text{ \AA}$] between two molecules of **3** leading to a dimer pair.^[27–29] Intermolecular hydrogen bonding between pendant $\text{NHC(O)CH}_2\text{NHCO}_2\text{Bz}$ groups leads to a classic head-to-tail arrangement [$\text{N}(2)\cdots\text{O}(1\text{B})$ $3.034(4) \text{ \AA}$, $\text{H}(2)\cdots\text{O}(1\text{B})$ $2.17(2) \text{ \AA}$, $\text{N}(2)\cdots\text{H}(2)\cdots\text{O}(1\text{B})$ $168(4)^\circ$]. The remaining N(H) group within each aurophilic linked dimer is involved in intramolecular N–H $\cdots$ Cl hydrogen bonding [$\text{N}(1)\cdots\text{Cl}(1\text{A})$ $3.347(3) \text{ \AA}$, $\text{H}(1)\cdots\text{Cl}(1\text{A})$ $2.52(2) \text{ \AA}$, $\text{N}(1)\cdots\text{H}(1)\cdots\text{Cl}(1\text{A})$ $152(3)^\circ$].

Compound **4·Et₂O** (Figure 5, Table 1) shows a classic piano-stool arrangement about the central Rh^{III} centre comprising a pentahapto coordinated Cp*, two chlorides and a monodentate bound phosphane **2·HH**. Although no unusual structural features were observed there was an intramolecular N–H $\cdots$ Cl hydrogen bond [$\text{N}(1)\cdots\text{Cl}(2)$ $3.188(8) \text{ \AA}$, $\text{H}(1)\cdots\text{Cl}(2)$ $2.35 \text{ \AA}$, $\text{N}(1)\cdots\text{H}(1)\cdots\text{Cl}(2)$ 159°]. This H-bond motif is similar to that found in **3**.

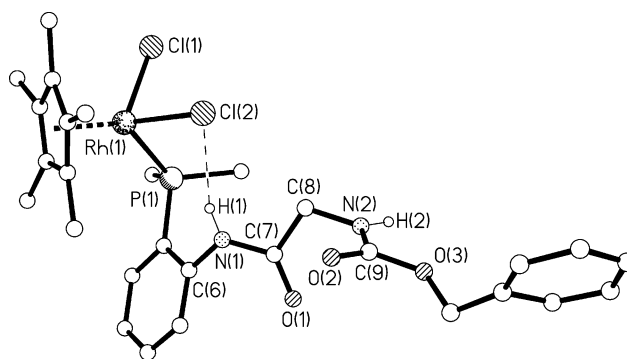


Figure 5. Molecular structure of **4·Et₂O**. The intermolecular H-bonded diethyl ether solvent has been omitted for clarity. Only the phenyl ipso carbons on P(1) are shown.

The X-ray structure of **8** (Figure 6, Table 1) reveals a *trans* stereochemistry of the two phosphane (**2·HH**) ligands. The Pd–Cl [$2.2999(8) \text{ \AA}$] and Pd–P [$2.3288(8) \text{ \AA}$] bond

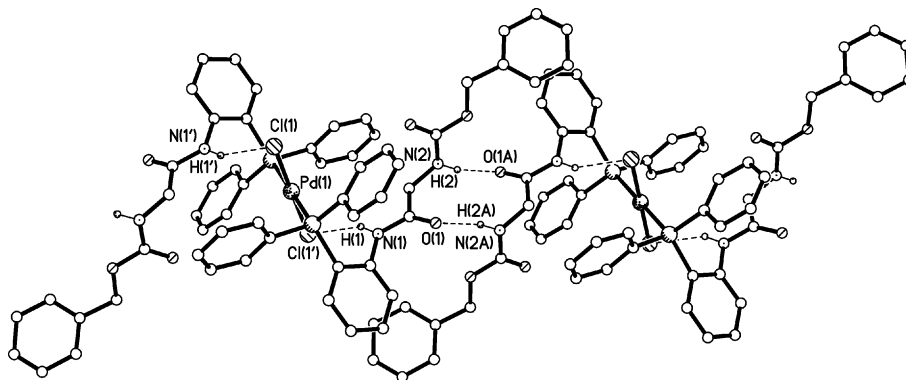
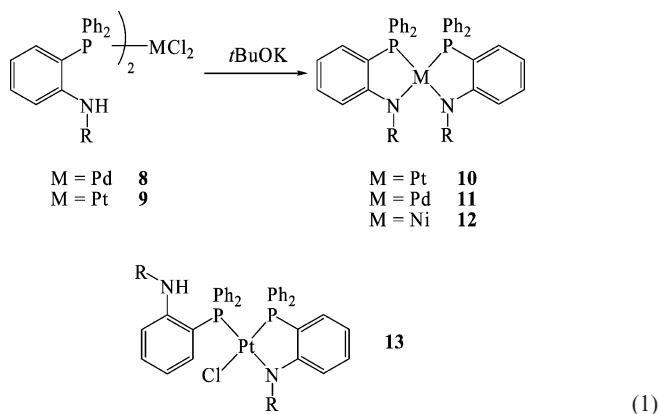


Figure 6. Packing plot of **8** showing the two H-bonding motifs. Symmetry operators: ' $-x + 1, -y + 1, -z + 1$; A: $-x + 1, -y + 1, -z$.

lengths are normal and compare favourably with other $\text{PdCl}_2(\text{PR}_3)_2$ complexes with a *trans* disposition.^[30] The $-\text{NHC}(\text{O})\text{CH}_2\text{N}(\text{H})\text{CO}_2\text{Bz}$ dangling groups are clearly positioned above and below the PdCl_2P_2 coordination plane. The hydrogen-bonding motif in **8** resembles that previously observed for the Au^{I} complex **3**. Hence H(1) forms an intramolecular $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bond [$\text{N}(1)\cdots\text{Cl}(1')$ 3.102(3) Å, $\text{H}(1)\cdots\text{Cl}(1')$ 2.30(2) Å, $\text{N}(1)-\text{H}(1)\cdots\text{Cl}(1')$ 152(3)°]. Furthermore, the N(2)–H(2) and an adjacent carbonyl O(1) are involved in hydrogen bonding affording an $\text{R}^2_2(10)$ ten-membered ring [$\text{N}(2)\cdots\text{O}(1\text{A})$ 2.866(4) Å, $\text{H}(2)\cdots\text{O}(1\text{A})$ 2.01(3) Å, $\text{N}(2)-\text{H}(2)\cdots\text{O}(1\text{A})$ 167(4)°]. Both these H-bonds are stronger than those found in **3**.

κ^2 -PIN-Coordination

Having established the classic κ^1 -P coordination mode that would be expected for the tertiary phosphine **2·HH**, the ease by which this ligand could chelate transition metals forming five-membered $\text{M}-\text{P}-\text{C}-\text{C}-\text{N}$ metallacycles was explored.^[31] Accordingly when compounds **8** or **9** were treated with *t*BuOK in CH_3OH the solids **10** or **11** were isolated in high yields [Equation (1), $\text{R} = \text{C}(\text{O})\text{CH}_2\text{NHCO}_2\text{Bz}$]. The Ni^{II} complex **12** was obtained directly from $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, 2 equiv. of **2·HH** and *t*BuOK in refluxing CH_3OH . In all cases the $^{31}\text{P}\{\text{H}\}$ NMR spectra of **10–12** showed new downfield phosphorus resonances at $\delta(\text{P})$ 19.7 (**10**), 42.2 (**11**) and 21.2 (**12**) ppm. Furthermore, the $J(\text{PtP})$ coupling constant for **10** was ca. 400 Hz less than found for **9** in accord with P *trans* to N. Whilst attempts to prepare a clean sample of the single deprotonated chelate complex **13** failed, a few X-ray quality crystals of **13** were obtained and the X-ray structure determined (vide infra).



The X-ray structures of **10–12** have each been determined (Figure 7 for compound **10**, Supporting Information for compounds **11** and **12**). All three compounds are isostructural and comprise a central metal chelated by two, *cis*-disposed, κ^2 -P/N-ligands. The M–P and M–N bond lengths (Table 2) are normal and are similar to previous documented cases.^[31] Furthermore, the central metal is displaced by 0.0347 Å (**10**), 0.0341 Å (**11**) and 0.0259 Å (**12**) out of the basal plane of the four donor atoms [P(1), P(2), N(1) and N(3)]. In addition, both five-membered chelate rings in **10–**

12 adopt a conformation best described as envelope with the metal atom at the tip of the flap and with hinge angles [$\text{M}(1)/\text{P}(1)/\text{N}(1)$ vs. $\text{N}(1)/\text{C}(6)/\text{C}(1)/\text{P}(1)$ and $\text{M}(1)/\text{P}(2)/\text{N}(3)$ vs. $\text{N}(2)/\text{C}(34)/\text{C}(29)/\text{P}(2)$] in the range 29.4–33.9°. The pendant groups on N(1) and N(3) point away from each other and are involved in different hydrogen bonding arrangements (Supporting Information). Hence H(4) is intramolecular H-bound to O(4) [$\text{N}\cdots\text{O}$ 2.614(4) Å, 2.23(3) Å, 109(3)° for **10**; $\text{N}\cdots\text{O}$ 2.619(3) Å, 2.24(3) Å, 110(2)° for **11**; $\text{N}\cdots\text{O}$ 2.591(3) Å, 2.19(3) Å, 109(2)° for **12**]. In contrast, the C(O) and NH groups of the second chain are involved in intermolecular H-bonding affording dimer pairs [$\text{N}\cdots\text{O}$ 2.791(4) Å, 2.02(4) Å, 172(4)° for **10**; $\text{N}\cdots\text{O}$ 2.786(3) Å, 2.00(3) Å, 173(3)° for **11**; $\text{N}\cdots\text{O}$ 2.800(3) Å, 1.987(18) Å, 173(3)° for **12**].

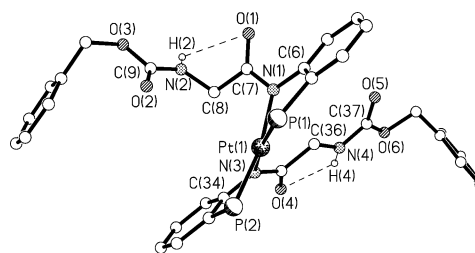


Figure 7. Molecular structure of **10** (compounds **11** and **12** are isostructural and not shown). The phenyl rings on P(1) and P(2) have been removed for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **10–12**.

	10 (M = Pt)	11 (M = Pd)	12 (M = Ni)
M(1)–N(1)	2.089(2)	2.0916(17)	1.933(2)
M(1)–N(3)	2.103(2)	2.1127(17)	1.963(2)
M(1)–P(1)	2.2315(8)	2.2420(6)	2.1635(7)
M(1)–P(2)	2.2273(8)	2.2408(6)	2.1602(7)
C(6)–N(1)	1.425(4)	1.421(3)	1.427(3)
N(1)–C(7)	1.355(4)	1.351(3)	1.347(3)
C(7)–O(1)	1.233(3)	1.237(3)	1.232(3)
N(2)–C(9)	1.331(4)	1.334(3)	1.334(4)
C(9)–O(2)	1.218(4)	1.214(3)	1.213(3)
C(9)–O(3)	1.366(4)	1.367(3)	1.360(3)
C(34)–N(3)	1.415(4)	1.415(3)	1.420(3)
N(3)–C(35)	1.367(4)	1.353(3)	1.349(3)
C(35)–O(4)	1.222(4)	1.233(3)	1.232(3)
N(4)–C(37)	1.339(4)	1.340(3)	1.339(3)
C(37)–O(5)	1.209(4)	1.205(3)	1.209(3)
C(37)–O(6)	1.350(4)	1.356(3)	1.352(3)
N(1)–M(1)–N(3)	96.89(9)	98.47(7)	97.05(9)
N(1)–M(1)–P(1)	81.28(7)	81.04(5)	83.21(6)
N(1)–M(1)–P(2)	168.31(7)	167.73(5)	165.77(7)
P(1)–M(1)–P(2)	101.26(3)	100.31(2)	97.93(3)
P(2)–M(1)–N(3)	82.16(7)	82.04(5)	84.59(6)
P(1)–M(1)–N(3)	171.74(7)	171.30(5)	168.74(6)

The X-ray structure of **13·Et}_2\text{O}** has also been determined (Figure 8, Table 3). The asymmetric unit comprises two molecules of the platinum complex and two molecules of Et_2O (one independent molecule shown in Figure 8). Both molecules display the expected square-planar geometry comprising one κ^1 -P-monodentate, a κ^2 -P/N-didentate and

a chlorido ligand. The Pt lies 0.1197 Å (0.1084 Å for the second independent molecule) out of the basal plane. Both Pt–P distances are similar despite the different *trans* ligands [Pt–P 2.2450(10) and 2.2421(10) Å for P *trans* to Cl; Pt–P 2.2666(11) and 2.2703(11) Å for P *trans* to NR₂]. The Pt–P–C–N chelate ring is markedly distorted with hinge angles of 34.0° and 35.5° for the two independent molecules. The NHC(O) hydrogen on the κ¹-P-monodentate bound ligand is intramolecularly H-bonded to the terminal chloride [N...Cl 3.177(4), 3.165(4) Å, H...Cl 2.43(4), 2.38(4) Å, N–H...Cl 155(4), 169(4)°]. Furthermore, within the same group, the NH hydrogen in the NHCO₂Bz group is involved in H-bonding to the Et₂O solvate [N...O 2.972(5), 3.000(5) Å, H...O 2.21(4), 2.18(4) Å, N–H...O 165(5), 169(4)°]. The other chain on the κ²-P/N-chelate ligand forms a head-to-tail R₂²(10) H-bonded ring [N...O 2.903(5), 2.973(4) Å, H...O 2.18(4), 2.16(4) Å, N–H...O 166(5), 160(4)°] (Supporting Information).

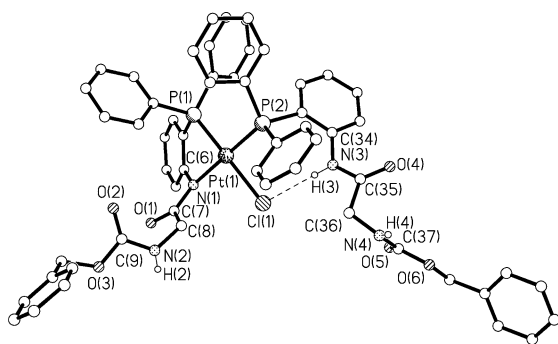


Figure 8. Molecular structure of **13**·Et₂O showing one independent molecule only. The diethyl ether solvent and all hydrogen atoms except those on nitrogen have been omitted for clarity.

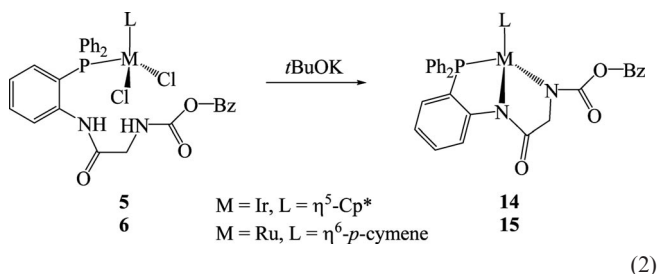
Table 3. Selected bond lengths [Å] and angles [°] for compound **13**·Et₂O.

	13 ·Et ₂ O ^[a]
Pt(1)–Cl(1)	2.3761(10) [2.3743(10)]
Pt(1)–P(1)	2.2450(10) [2.2421(10)]
Pt(1)–P(2)	2.2666(11) [2.2702(11)]
Pt(1)–N(1)	2.097(3) [2.088(3)]
C(6)–N(1)	1.423(5) [1.419(5)]
N(1)–C(7)	1.358(5) [1.362(5)]
C(7)–O(1)	1.242(5) [1.234(5)]
N(2)–C(9)	1.335(6) [1.346(6)]
C(9)–O(2)	1.219(6) [1.216(5)]
C(9)–O(3)	1.360(6) [1.361(5)]
C(34)–N(3)	1.411(5) [1.414(5)]
N(3)–C(35)	1.362(5) [1.358(5)]
C(35)–O(4)	1.213(5) [1.214(5)]
N(4)–C(37)	1.346(6) [1.345(5)]
C(37)–O(5)	1.210(5) [1.210(5)]
C(37)–O(6)	1.361(5) [1.360(5)]
Cl(1)–Pt(1)–N(1)	90.21(9) [89.58(9)]
Cl(1)–Pt(1)–P(1)	163.75(4) [164.42(4)]
Cl(1)–Pt(1)–P(2)	89.22(4) [90.16(4)]
P(1)–Pt(1)–P(2)	100.29(4) [100.18(4)]
P(1)–Pt(1)–N(1)	80.60(9) [80.27(9)]
P(2)–Pt(1)–N(1)	178.45(9) [179.02(9)]

[a] Two independent molecules in the asymmetric unit.

κ³-P/N/N'-Coordination

To evaluate whether **2**·HH could function effectively as a tridentate system, the Ir^{III} complex **5** was treated with *t*BuOK in refluxing CH₃OH [Equation (2)]. The ³¹P{¹H} NMR spectrum of the crude material revealed two new phosphorus signals at δ(P) 16.0 and 8.0 ppm in a 1.0:3.2 ratio. Both phosphorus resonances are assigned to the two diastereomers of the chiral-at-metal complex Ir(η⁵-Cp*)(2-Ph₂PC₆H₄NC(O)CH₂NCO₂Bz) (**14**) containing a κ³-dianionic P/N/N' ligand. Similarly the Ru^{II} complex **6** gave, under similar conditions, the chiral-at-metal complex Ru(η⁶-*p*-cymene){2-Ph₂PC₆H₄NC(O)CH₂NCO₂Bz} (**15**) in 80% isolated yield. The ³¹P{¹H} NMR spectrum of **15** showed two new signals at δ(P) 50.2 and 46.6 ppm, in an approximate 1.0:1.0 ratio, consistent with the presence of two diastereomers. Other characterising data are given in the Exp. Sect.



(2)

In order to establish unambiguously the coordination mode of **2** we were fortunate to obtain a few crystals of **14** which indeed confirmed κ³-P/N/N'-coordination. The X-ray structure of **14** (Figure 9, Table 4) confirms this tridentate coordination mode for **2**. The ligand chelates forming two five-membered rings, Ir(1)–P(1)–C(1)–C(6)–N(1) and Ir(1)–N(2)–C(8)–C(7)–N(1), that display hinge angles of 30.4° [Ir(1)/P(1)/N(1) vs. P(1)/C(1)/C(6)/N(1)] and 25.3° [Ir(1)/N(1)/N(2) vs. N(1)/C(7)/C(8)/N(2)]. The Ir(1)–P(1) length is in the range typically expected^[32] and the Ir(1)–N(1)/N(2) distances are very similar. There are significant differences between the P(1)–Ir(1)–N(1) [76.4(2)°] and P(1)–

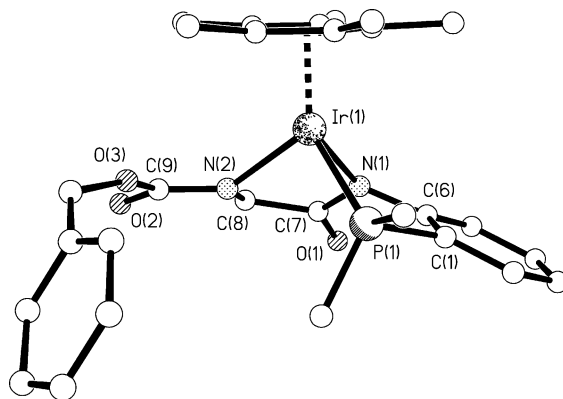


Figure 9. Molecular structure of **14** showing the major disorder component only. All hydrogen atoms removed for clarity. Only the phenyl *ipso* carbon atoms on P(1) are shown.

Ir(1)–N(2) [97.5(3)°] bond angles presumably as a consequence of the differing phenyl vs. alkyl backbones separating the P/N donor atoms. Within the Ir(1)–N(2)–C(8)–C(7)–N(1) ring the Ir(1), N(1), C(7), C(8) atoms are co-planar to within ± 0.03 Å whilst N(2) is the flap of an envelope lying 0.58 Å out of this plane. For the other five-membered ring, N(1), C(6), C(1) and P(1) are co-planar to within ± 0.02 Å whilst Ir(1) lies 0.98 Å out of this plane.

Table 4. Selected bond lengths [Å] and angles [°] for compound **14**.

	14 ^[a]
Ir(1)–P(1)	2.271(2)
Ir(1)–N(1)	2.085(8)
Ir(1)–N(2)	2.082(9)
Ir(1)–C _{centroid}	1.8459(42)
C(6)–N(1)	1.409(11)
N(1)–C(7)	1.368(13)
C(7)–O(1)	1.232(12)
N(2)–C(9)	1.29(2)
C(9)–O(2)	1.37(2)
C(9)–O(3)	1.22(2)
P(1)–Ir(1)–N(1)	76.4(2)
P(1)–Ir(1)–N(2)	97.5(3)
N(1)–Ir(1)–N(2)	77.0(4)
C(6)–N(1)–C(7)	120.0(8)
N(1)–C(7)–O(1)	125.2(10)
N(2)–C(9)–O(2)	120.7(15)
O(2)–C(9)–O(3)	120.0(16)

[a] Major component.

Conclusions

In summary, we have shown that a new P/N/N'-functionalised ligand **2-HH** can display various coordination modes dependant on the geometry of the transition-metal centre (linear, square-planar or pseudo-tetrahedral). This flexibility in ligand geometry mirrors our previous studies with a P/N/N'/N''-tetradentate system which likewise can adopt numerous coordination motifs.^[25] The amide functional groups adopt various secondary hydrogen-bonding interactions and in solution, we believe some of these compounds exist as conformers due to hindered amide-bond rotation. Further studies are in progress and will be reported in due course.

Experimental Section

Materials: All reactions were carried out in air with the exception of **2-HH** whose synthesis was conducted under dry, oxygen-free nitrogen. All solvents were distilled prior to use. The compound 2-Ph₂PC₆H₄(NH₂) (**1**) was a kind donation from Dr S. M. Aucott whereas AuCl(tht) (tht = tetrahydrothiophene),^[33] MCl₂(cod) (M = Pt, Pd; cod = cycloocta-1,5-diene),^[34] {RuCl₂(η⁶-p-cymene)}₂,^[35] {MCl₂(η⁵-Cp*)}₂ (M = Rh, Ir)^[36] and {PdCl(κ²-CN-C₁₂H₁₂N)}₂^[37] were prepared according to published procedures. All other reagents were purchased from commercial suppliers and used directly without further purification.

Instrumentation: FT-IR spectra were recorded as KBr pellets over the range 4000–200 cm^{−1} using a Perkin–Elmer system 2000 FT spectrometer. ¹H NMR and ³¹P{¹H} NMR spectra (298 ± 2 K)

were recorded either with Bruker AC250 or DPX-400 FT spectrometers with chemical shifts (δ) reported relative to external TMS or H₃PO₄. All NMR spectra (250 or 400 MHz) were recorded in CDCl₃ solutions unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Preparation of 2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz, (2-HH): A solution of **1** (2.003 g, 7.222 mmol), *N*-(benzyloxycarbonyl)glycine (1.511 g, 7.222 mmol) and 1,3-dicyclohexylcarbodiimide, DCC, (1.594 g, 7.725 mmol) in THF (60 mL) was stirred at ambient temperature, under nitrogen for 4 d. The solid was removed by filtration, washed with some THF and the combined filtrate evaporated to dryness. The residue was taken up in CH₂Cl₂ (25 mL), passed through a small plug and Et₂O (80 mL) added. The solid **2-HH** was collected by suction filtration, washed with a small portion of Et₂O and dried. Yield 1.217 g, 36%. Selected data: ³¹P NMR (CDCl₃): δ = −20.7, −21.3 (ratio 8.0:1.0) ppm. ¹H NMR (CDCl₃): δ = 8.45 (s, 1 H, arom. H), 8.14 (m, 1 H, arom. H), 7.37–7.26 (m, 15 H, arom. H), 7.08 (t, 1 H, arom. H), 6.92 (dt, 1 H, arom. H), 5.12 (s, 3 H, overlapping OCH₂ and NH), 3.79 (d, ³J = 4 Hz, 2 H, NCH₂) ppm. FT-IR (KBr): ν̄ = 3328, 3264 (NH), 1721 (CO), 1677 (amide I), 1522 (amide II) cm^{−1}. EI-MS: *m/z* = 468 [M⁺]. C₂₈H₂₅N₂O₃P (468.5): calcd. C 71.78, H 5.39, N 5.98; found C 71.67, H 5.18, N 5.77.

2-Ph₂P(O)C₆H₄NHC(O)CH₂NHCO₂Bz (2a): The tertiary phosphane oxide was prepared by oxidation of **2-HH** (0.040 g, 0.085 mmol) with aq. H₂O₂ (27.5% w/w, 6 drops) in CDCl₃. Yield 0.027 g, 66%. Selected data: ³¹P NMR (CDCl₃): δ = 37.2, 36.9 (ratio 1:5.4) ppm. ¹H NMR (CDCl₃): δ = 11.30 (s, 1 H, NH), 8.47 (m, 1 H, arom. H), 7.61–6.90 (m, 18 H, arom. H), 5.40 (t, 1 H, NH), 5.06 (s, 2 H, OCH₂), 3.92 (d, ³J = 4 Hz, 2 H, NCH₂) ppm. FT-IR (KBr): ν̄ = 3255 (NH), 1720 (CO), 1712, 1694 (amide I), 1536 (amide II) 1153 (PO) cm^{−1}. ES-MS: *m/z* = 485 [M + H⁺]. C₂₈H₂₅N₂O₄P (484.5): calcd. C 69.41, H 5.21, N 5.78; found C 69.40, H 5.21, N 5.70.

Preparation of AuCl{2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz} (3): **2-HH** (0.103 g, 0.220 mmol) was added to a CH₂Cl₂ (10 mL) solution of AuCl(tht) (0.071 g, 0.22 mmol). The colourless solution was stirred for 20 min, concentrated under reduced pressure to ca. 1–2 mL and Et₂O (20 mL) and hexanes (20 mL) added. The solid **3** was collected by suction filtration and dried. Yield 0.147 g, 95%. Selected data: ³¹P NMR (CDCl₃): δ = 20.9 ppm. ¹H NMR (CDCl₃): δ = 8.30 (s, 1 H, NH), 7.96 (m, 1 H, arom. H), 7.56–6.80 (m, 18 H, arom. H), 5.42 (br., 1 H, NH), 5.08 (s, 2 H, OCH₂), 3.81 (d, ³J = 6 Hz, 2 H, NCH₂) ppm. FT-IR (KBr): ν̄ = 3362, 3274 (NH), 1724 (CO), 1691 (amide I), 1506 (amide II), 318 (AuCl) cm^{−1}. ES-MS: *m/z* = 665 [M – Cl]. C₂₈H₂₅AuClN₂O₃P (700.9): calcd. C 47.98, H 3.60, N 4.00; found C 48.12, H 3.36, N 3.88.

Preparation of Ir(η⁵-Cp*)Cl₂{2-Ph₂PC₆H₄NHC(O)CH₂NHCO₂Bz} (5): **2-HH** (0.072 g, 0.154 mmol) was added to a CH₂Cl₂ (10 mL) solution of {IrCl₂(η⁵-Cp*)}₂ (0.061 g, 0.077 mmol). The orange solution was stirred for 20 min, passed through a small plug, concentrated under reduced pressure to ca. 1–2 mL and Et₂O (10 mL) added. The solid **5** was collected by suction filtration and dried. Yield 0.130 g, 98%. Selected data: ³¹P NMR (CDCl₃): δ = 0.0, −0.2 (ratio 4.0:1) ppm. ¹H NMR (CDCl₃): δ = 8.80 (s, 1 H, arom. H), 7.85–6.81 (m, 17 H, arom. H), 5.07 (br., 1 H, NH), 4.95, 4.91 (both s, 2 H, OCH₂), 3.83, 2.99 (both br., 2 H, NCH₂), 1.22 (d, ⁴J = 2 Hz, 15 H, Cp*) ppm. FT-IR (KBr): ν̄ = 3282, 3242, 3226, 3211 (NH), 1729 (CO), 1710 (amide I), 1514 (amide II) cm^{−1}. ES-MS:

$m/z = 795$ [$M - 2 \text{ Cl} - \text{H}$]. $\text{C}_{38}\text{H}_{40}\text{Cl}_2\text{IrN}_2\text{O}_3\text{P}$ (867.6): calcd. C 52.65, H 4.66, N 3.23; found C 52.82, H 4.85, N 2.88.

Rh($\eta^5\text{-Cp}^*$)Cl $_2$ {2-Ph $_2$ PC $_6$ H $_4$ NHC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (4): The rhodium(III) complex was prepared from **2-HH** and {RhCl $_2$ ($\eta^5\text{-Cp}^*$)} $_2$ (89%). Selected data: ^{31}P NMR (CDCl_3): $\delta = 27.4$ [$J(\text{RhP}) = 143 \text{ Hz}$], 27.2 [$J(\text{RhP}) = 143 \text{ Hz}$] (ratio 3.0:1.0) ppm. ^1H NMR (CDCl_3): $\delta = 9.24$ (s, 1 H, arom. H), 8.07–6.99 (m, 17 H, arom. H), 5.22 (br., 1 H, NH), 5.10, 5.06 (both s, 2 H, OCH $_2$), 3.88, 3.05 (both br., 2 H, NCH $_2$), 1.40 (d, $^4J = 3.6 \text{ Hz}$, 15 H, Cp*) ppm. FT-IR (KBr): $\tilde{\nu} = 3237, 3194$, (NH), 1726 (CO), 1706 (amide I), 1509 (amide II) cm^{-1} . ES-MS: $m/z = 705$ [$M - 2 \text{ Cl} - \text{H}$]. $\text{C}_{38}\text{H}_{40}\text{Cl}_2\text{N}_2\text{O}_3\text{PRh} \cdot 0.5\text{CH}_2\text{Cl}_2$ (820.0): calcd. C 56.39, H 5.05, N 3.42; found C 56.18, H 5.08, N 3.34.

Preparation of Ru($\eta^6\text{-p-cymene}$)Cl $_2$ {2-Ph $_2$ PC $_6$ H $_4$ NHC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (6): **2-HH** (0.098 g, 0.21 mmol) was added to a CH_2Cl_2 (10 mL) solution of {RuCl $_2$ ($\eta^6\text{-p-cymene}$)} $_2$ (0.064 g, 0.10 mmol). The orange solution was stirred for 15 min and concentrated under reduced pressure to ca. 1–2 mL. Addition of Et $_2$ O (10 mL) gave **6** which was collected by suction filtration and dried. Yield 0.146 g, 90%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 24.3, 23.7$ (ratio 5.5:1.0) ppm. ^1H NMR (CDCl_3): $\delta = 8.89$ (s, 1 H, arom. H), 8.01 (m), 7.88–7.08 (m), 5.30–4.89 (m, *p*-cymene, OCH $_2$, NCH $_2$), 2.89 (sept., 1 H, CH), 1.87 (s, 3 H, CH $_3$), 1.24 [br, 6 H, CH(CH $_3$) $_2$] ppm. FT-IR (KBr): $\tilde{\nu} = 3365, 3237, 3208$ (NH), 1730 (CO), 1704 (amide I), 1522 (amide II) cm^{-1} . ES-MS: $m/z = 775$ [M]. $\text{C}_{38}\text{H}_{39}\text{Cl}_2\text{N}_2\text{O}_3\text{-PRu}$ (774.7): calcd. C 58.91, H 5.08, N 3.62; found C 58.76, H 4.94, N 3.51.

Preparation of Pd($\kappa^2\text{-CN-C}_{12}\text{H}_{12}\text{N}$)Cl{2-Ph $_2$ PC $_6$ H $_4$ NHC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (7): **2-HH** (0.121 g, 0.258 mmol) was added to a CH_2Cl_2 (20 mL) solution of {PdCl($\kappa^2\text{-CN-C}_{12}\text{H}_{12}\text{N}$)} $_2$ (0.079 g, 0.13 mmol). The yellow solution was stirred for 30 min and concentrated under reduced pressure to ca. 1–2 mL. Addition of Et $_2$ O (10 mL) and petroleum ether (b.p. 60–80 °C, 20 mL) gave **7** which was collected by suction filtration and dried. Yield 0.134 g, 68%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 38.8$ ppm. ^1H NMR (CDCl_3): $\delta = 9.17$ (s, 1 H, arom. H), 7.83–6.81 (m, 23 H, arom. H), 6.61 (t, 1 H, arom. H), 6.45 (t, 1 H, arom. H), 5.21 (br., 1 H, NH), 4.94 (s, 2 H, OCH $_2$), 3.54 (d, $J = 2.8 \text{ Hz}$, 2 H, NCH $_2$), 3.42 (s, 6 H, CH $_3$) ppm. FT-IR (KBr): $\tilde{\nu} = 3420, 3297$ (NH), 1725 (CO), 1691 (amide I), 1498 (amide II) cm^{-1} . ES-MS: $m/z = 745$ [$M - \text{Cl}$]. $\text{C}_{40}\text{H}_{37}\text{ClN}_3\text{O}_3\text{PPd}$ (780.6): calcd. C 61.54, H 4.79, N 5.38; found C 61.64, H 4.38, N 5.05.

Preparation of PdCl $_2$ {2-Ph $_2$ PC $_6$ H $_4$ NHC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (8): **2-HH** (0.226 g, 0.482 mmol) was added to a CH_2Cl_2 (20 mL) solution of PdCl $_2$ (cod) (0.069 g, 0.24 mmol). The yellow solution was stirred for ca. 1 h and concentrated under reduced pressure to ca. 1–2 mL. Addition of Et $_2$ O (10 mL) and hexanes (10 mL) gave **8** which was collected by suction filtration and dried. Yield 0.260 g, 97%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 19.9, 19.1$ ppm. ^1H NMR (CDCl_3): $\delta = 8.43$ (s, 2 H, arom. H), 7.75–7.06 (m, 38 H, arom. H), 5.24 (br., 2 H, NH), 5.03 (s, 4 H, OCH $_2$), 3.35 (br., 4 H, NCH $_2$) ppm. FT-IR (KBr): $\tilde{\nu} = 3312$ (NH), 1724 (CO), 1700 (amide I), 1506 (amide II) cm^{-1} . ES-MS: $m/z = 1041$ [$M - 2 \text{ Cl} - \text{H}$]. $\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{N}_4\text{O}_6\text{P}_2\text{Pd}$ (1114.3): calcd. C 60.36, H 4.53, N 5.03; found C 60.25, H 4.17, N 4.77.

PtCl $_2$ {2-Ph $_2$ PC $_6$ H $_4$ NHC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (9): This compound was prepared from PtCl $_2$ (cod) and two equiv. of **2-HH** (91%). Selected data: ^{31}P NMR (CDCl_3): $\delta = 6.7$ [$J(\text{PtP}) = 3657 \text{ Hz}$] (major species) ppm. ^1H NMR (CDCl_3): $\delta = 9.23$ (s, 2 H, arom. H), 7.78–6.77 (m, 38 H, arom. H), 5.60 (br., 2 H, NH), 5.10 (s, 4 H, OCH $_2$), 3.79 (br., 4 H, NCH $_2$) ppm. FT-IR (KBr): $\tilde{\nu} = 3377$ (NH), 1718 (CO and amide I), 1498 (amide II) cm^{-1} . ES-MS: $m/z = 1131$ [$M -$

$2 \text{ Cl} - \text{H}$]. $\text{C}_{56}\text{H}_{50}\text{Cl}_2\text{N}_4\text{O}_6\text{P}_2\text{Pt}$ (1203.0): calcd. C 55.91, H 4.20, N 4.66; found C 55.84, H 3.82, N 4.48.

Preparation of *cis*-Pd{2-Ph $_2$ PC $_6$ H $_4$ NC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (11): *t*BuOK (0.035 g, 0.31 mmol) was added to a CH $_3$ OH (5 mL) suspension of **8** (0.125 g, 0.112 mmol) to give a yellow solution followed by the immediate formation of a yellow solid. The mixture was refluxed for 3 h and left to cool overnight. The solid **11** was collected by suction filtration, washed with a small portion of CH $_3$ OH and dried. Yield 0.103 g, 88%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 42.2$ ppm. ^1H NMR (CDCl_3): $\delta = 8.04$ (m, 2 H, arom. H), 7.43–6.91 (m, 36 H, arom. H), 5.73 (br., 2 H, NH), 5.08 (s, 4 H, OCH $_2$), 4.33 (m, 4 H, NCH $_2$) ppm. FT-IR (KBr): $\tilde{\nu} = 3377$ (NH), 1718 (CO and amide I), 1498 (amide II) cm^{-1} . ES-MS: $m/z = 1131$ [$M - 2 \text{ Cl} - \text{H}$]. $\text{C}_{56}\text{H}_{48}\text{N}_4\text{O}_6\text{P}_2\text{Pd}$ (1041.4): calcd. C 64.59, H 4.66, N 5.38; found C 63.78, H 4.68, N 5.24.

***cis*-Pt{2-Ph $_2$ PC $_6$ H $_4$ NC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (10):** This complex was likewise prepared from **9** (88%). Selected data: ^{31}P NMR (CDCl_3): $\delta = 19.7$ [$J(\text{PtP}) = 3217 \text{ Hz}$] ppm. FT-IR (KBr): $\tilde{\nu} = 3377$ (NH), 1718 (CO and amide I), 1498 (amide II) cm^{-1} . ES-MS: $m/z = 1130$ [M^+]. $\text{C}_{56}\text{H}_{48}\text{N}_4\text{O}_6\text{P}_2\text{Pt}$ (1130.1): calcd. C 59.52, H 4.29, N 4.96; found C 59.08, H 3.96, N 4.77.

Preparation of *cis*-Ni{2-Ph $_2$ PC $_6$ H $_4$ NC(O)CH $_2$ NHCO $_2$ Bz} $_2$ (12): A mixture of NiCl $_2$ ·6H $_2$ O (0.025 g, 0.11 mmol), **2-HH** (0.103 g, 0.220 mmol) and *t*BuOK (0.035 g, 0.32 mmol) in CH $_3$ OH (10 mL) was refluxed for 3 h. The mixture was left to stand to deposit an orange crystalline material that was collected by filtration under suction and dried. Yield 0.022 g, 21%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 21.2$ ppm. FT-IR (KBr): $\tilde{\nu} = 3377, 3245$ (NH), 1714 (CO and amide I) cm^{-1} . ES-MS: $m/z = 993$ [M]. $\text{C}_{56}\text{H}_{48}\text{N}_4\text{NiO}_6\text{P}_2$ (993.7): calcd. C 67.70, H 4.88, N 5.64; found C 67.74, H 4.84, N 5.37.

Preparation of Ir($\eta^5\text{-Cp}^*$){2-Ph $_2$ PC $_6$ H $_4$ NC(O)CH $_2$ NCO $_2$ Bz} $_2$ (14): A mixture of **5** (0.029 g, 0.033 mmol) and *t*BuOK in CH $_3$ OH (5 mL) was refluxed, under nitrogen for 3 h. The solution was cooled and the solvents evaporated to dryness under reduced pressure. Examination of the crude mixture revealed two new major species at $\delta(\text{P}) = 16.0$ and 8.0 ppm in a 1:3.2 ratio. Crystallisation was achieved using CDCl_3 /petroleum ether (b.p. 60–80 °C) to give a small quantity of crystalline material identified as **14**. Selected data: ^{31}P NMR (C_6D_6): $\delta = 17.7, 8.8$ (ratio 1.4:1.0) ppm. ^1H NMR (C_6D_6): $\delta = 8.66$ (dd, 1 H, arom. H), 8.60 (dd, 1 H, arom. H), 8.03 (m, 1 H, arom. H), 7.80 (m, 1 H, arom. H), 7.63–6.72 (m, 34 H, arom. H), 5.64 (d, $J = 17.6 \text{ Hz}$, 1 H, CH $_2$), 5.44 (dd, 2 H, CH $_2$), 5.09 (d, $J = 11.6 \text{ Hz}$, 1 H, CH $_2$), 4.96 (d, $J = 17.6 \text{ Hz}$, 1 H, CH $_2$), 4.87 (d, $J = 11.2 \text{ Hz}$, 1 H, CH $_2$), 4.44 (d, $J = 17.6 \text{ Hz}$, 1 H, CH $_2$), 4.28 (d, $J = 17.2 \text{ Hz}$, 1 H, CH $_2$), 1.30 (d, $J = 2.4 \text{ Hz}$, 15 H, Cp*), 1.08 (d, $J = 2.0 \text{ Hz}$, 15 H, Cp*) ppm. FT-IR (KBr): $\tilde{\nu} = 1658, 1626$ (CO and amide I) cm^{-1} . ES-MS: $m/z = 795$ [$M + \text{H}$] $^+$. $\text{C}_{37}\text{H}_{38}\text{Ir-N}_2\text{O}_3\text{P}$ (781.9): calcd. C 56.83, H 4.91, N 3.58; found C 56.69, H 4.71, N 3.45.

Preparation of Ru($\eta^6\text{-p-cymene}$){2-Ph $_2$ PC $_6$ H $_4$ NC(O)CH $_2$ NCO $_2$ Bz} $_2$ (15): A mixture of **6** (0.071 g, 0.092 mmol) and *t*BuOK (0.027 g, 0.24 mmol) in CH $_3$ OH (10 mL) was stirred at room temperature for ca. 4 h then refluxed, under nitrogen for 2 h. The solution was cooled and the solvents evaporated to dryness under reduced pressure. The crude material was taken up in CH $_2$ Cl $_2$ (10 mL) and passed through a Celite plug. The volume was concentrated under reduced pressure to 1–2 mL and diethyl ether (10 mL)/hexanes (10 mL) added. The precipitate was left to stand overnight, filtered and dried in vacuo to give **15**. Yield 0.051 g, 80%. Selected data: ^{31}P NMR (CDCl_3): $\delta = 50.2, 46.6$ (ratio 1.0:1.0) ppm. ^1H NMR (CDCl_3): $\delta = 7.73$ (dd, 1 H, arom. H), 7.65 (dd, 1 H, arom. H),

7.44–6.97 (m, 34 H, arom. H), 6.85 (t, 1 H, arom. H), 6.78 (t, 1 H, arom. H), 5.16–4.66 (m, 12 H, *p*-cymene, CH₂), 3.97 (d, 1 H, CH₂), 3.80 (d, 1 H, CH₂), 3.72 (dd, 2 H, CH₂), 2.38 (sept., 1 H, CH), 2.06 (sept., 1 H, CH), 1.79 (s, 3 H, CH₃), 1.47 (s, 3 H, CH₃), 0.98 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)₂], 0.91 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)₂], 0.77 [dd, *J* = 6.8 Hz, 6 H, CH(CH₃)₂] ppm. FT-IR (KBr): $\tilde{\nu}$ = 1647, 1619 (CO and amide I) cm⁻¹. EI-MS: *m/z* = 702 [M]⁺. C₃₈H₃₇N₂O₃PRu·H₂O (720.7): calcd. C 63.32, H 5.47, N 3.89; found C 62.97, H 4.96, N 3.71.

X-ray Crystallography: Suitable crystals were grown by vapour diffusion of diethyl ether into either a CH₂Cl₂ (for **4**·Et₂O, **10**, **11**) or CDCl₃ (for **2a**, **3**, **8**) solution. Crystals of **14** were obtained by layering petroleum ether (b.p. 60–80 °C) over a CDCl₃ solution. Slow

evaporation to dryness of a CH₂Cl₂/Et₂O filtrate from the reaction of [PtCl₂(cod)]/1 equiv. **2**·HH (for **13**·Et₂O) or CDCl₃/Et₂O solution (for **2**·HH) afforded suitable X-ray quality crystals. A warm solution of NiCl₂·6H₂O, **2**·HH and *t*BuOK in CH₃OH was cooled over 2 d to give suitable crystals of **12**. Measurements were made with either a Bruker AXS SMART 1000 CCD area-detector diffractometer^[38] for **2**·HH, **2a**, **4**·Et₂O, **10**–**12**, **13**·Et₂O and **14** using sealed-tube graphite-monochromated Mo-*K*_α radiation and narrow frame exposures (0.3°) in ω or a Bruker-Nonius 95-mm CCD kappa diffractometer^[39,40] equipped with a rotating-anode generator for **3** and **8**. Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by

Table 5. Crystallographic data for **2**·HH, **2a**, **3**, **4**·Et₂O and **8**.

Compound	2 ·HH	2a	3	4 ·Et ₂ O	8
Empirical formula	C ₂₈ H ₂₅ N ₂ O ₃ P	C ₂₈ H ₂₅ N ₂ O ₄ P	C ₂₈ H ₂₅ AuClN ₂ O ₃ P	C ₄₂ H ₅₀ Cl ₂ N ₂ O ₄ PRh	C ₅₆ H ₅₀ Cl ₂ N ₄ O ₆ P ₂ Pd
Formula weight	468.47	484.47	700.89	851.62	1114.24
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2₁2₁2₁</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.7453(6)	10.0621(5)	22.952(5)	8.4053(3)	9.8211(2)
<i>b</i> [Å]	17.9907(11)	13.8305(6)	12.739(3)	17.2229(7)	12.3556(3)
<i>c</i> [Å]	26.6542(17)	18.7642(9)	17.885(4)	28.0623(12)	13.4933(3)
α [°]		95.1715(8)			73.3569(15)
β [°]		93.9950(8)	94.44(3)		69.6192(15)
γ [°]		110.7979(8)			68.1251(11)
Volume [Å ³]	4673.1(5)	2416.7(2)	5213.6(18)	4062.4(3)	1401.06(5)
<i>Z</i>	8	4	8	4	1
<i>T</i> [K]	150(2)	150(2)	120(2)	150(2)	120(2)
Density (calcd.) [Mg/m ³]	1.332	1.332	1.786	1.392	1.321
Absorption coeff. [mm ⁻¹]	0.151	0.152	5.840	0.634	0.534
Crystal	plate, colourless	block, colourless	block, colourless	block, orange	plate, yellow
Crystal size [mm ³]	0.71 × 0.10 × 0.06	0.52 × 0.32 × 0.14	0.28 × 0.14 × 0.06	0.56 × 0.32 × 0.13	0.28 × 0.10 × 0.04
θ Range [°]	2.26–29.05	1.59–29.16	2.98–27.49	1.45–28.99	3.18–27.50
Reflections collected	38962	21740	26325	35012	29162
Independent reflections	5816	11284	5958	9701	6423
	[<i>R</i> _{int} = 0.0578]	[<i>R</i> _{int} = 0.0172]	[<i>R</i> _{int} = 0.0566]	[<i>R</i> _{int} = 0.0404]	[<i>R</i> _{int} = 0.1545]
Final <i>R</i> , <i>R</i> _w	0.0452, 0.1049	0.0392, 0.0992	0.0281, 0.0637	0.0775, 0.1800	0.0589, 0.1593

Table 6. Crystallographic data for **10**–**12**, **13**·Et₂O and **14**.

Compound	10	11	12	13 ·Et ₂ O	14
Empirical formula	C ₅₆ H ₄₈ N ₄ O ₆ P ₂ Pt	C ₅₆ H ₄₈ N ₄ O ₆ P ₂ Pd	C ₅₆ H ₄₈ N ₄ NiO ₆ P ₂	C ₆₀ H ₅₉ ClN ₄ O ₇ P ₂ Pt	C ₃₈ H ₃₈ IrN ₂ O ₃ P
Formula weight	1130.01	1041.32	993.63	1240.59	793.87
Crystal system	triclinic	triclinic	triclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	10.9838(5)	10.9942(6)	10.8720(6)	13.0842(5)	14.5434(6)
<i>b</i> [Å]	12.0189(6)	12.0245(6)	12.0122(6)	18.0484(7)	19.0261(9)
<i>c</i> [Å]	18.9373(9)	18.9440(10)	18.9051(10)	25.0130(9)	24.0410(11)
α [°]	86.5717(8)	86.3778(9)	84.0006(10)	109.3285(6)	
β [°]	75.4249(7)	75.5354(9)	75.6778(9)	91.6609(6)	
γ [°]	89.6824(8)	89.6384(9)	89.4411(9)	98.6980(6)	
Volume [Å ³]	2415.1(2)	2420.0(2)	2378.8(2)	5489.9(4)	6652.2(5)
<i>Z</i>	2	2	2	4	8
<i>T</i> [K]	150(2)	150(2)	150(2)	150(2)	150(2)
Density (calcd.) [Mg/m ³]	1.554	1.429	1.387	1.501	1.585
Absorption coeff. [mm ⁻¹]	3.028	0.506	0.533	2.720	4.102
Crystal	block, colourless	block, yellow	block, orange	block, colourless	block, yellow
Crystal size [mm ³]	0.35 × 0.16 × 0.13	0.43 × 0.34 × 0.16	0.28 × 0.16 × 0.07	0.42 × 0.34 × 0.11	0.23 × 0.22 × 0.15
θ Range [°]	1.70–29.02	1.70–29.00	1.70–29.08	1.23–25.00	1.69–25.00
Reflections collected	21653	21527	21340	40463	45915
Independent reflections	11226	11181	11032	19293	5877
	[<i>R</i> _{int} = 0.0255]	[<i>R</i> _{int} = 0.0216]	[<i>R</i> _{int} = 0.0324]	[<i>R</i> _{int} = 0.0269]	[<i>R</i> _{int} = 0.0470]
Final <i>R</i> , <i>R</i> _w ^[a]	0.0300, 0.0585	0.0338, 0.0783	0.0457, 0.1083	0.0302, 0.0677	0.0471, 0.1307

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for “observed” reflections having $F^2 > 2\sigma(F^2)$. $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ for all data.

direct methods (Patterson synthesis for **10** and **11**) and refined on F^2 values for all unique data by full-matrix least-squares.^[41] Table 5 and Table 6 give further details. All non-hydrogen atoms were refined anisotropically. For **14** the C(11) > C(16) ring is common to both disorder components and there are two possible conformations of the linkage between this ring and N(2): 56.0(11)% of the time via C(9), O(3), C(10) and 44.0(11)% of the time via C(9X), O(3X), C(10X). For compound **4**·Et₂O a molecule of badly disordered Et₂O was modelled by the Platon Squeeze procedure.^[42] The X-ray structures of **11** (Figure S1) and **12** (Figure S2), with full atom numbering schemes, are given in the Supporting Information.

CCDC-706564 (for **2**·HH), -706565 (for **2a**), -706566 (for **3**), -706567 (for **4**·Et₂O), -706568 (for **8**), -706569 (for **10**), -706570 (for **11**), -706571 (for **12**), -706572 (for **13**·Et₂O) and -706573 (for **14**) contain the complete set of X-ray crystallographic structural data. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Four figures showing additional crystal structures, packing plots, and full atom numbering.

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