Synthesis of a New P_2N_2 Ligand *N,N'*-Bis[2-(diphenylphosphino)-phenyl]propane-1,3-diamine, H_2L^2, and some of its Complexes with Elements of the Nickel Triad and Rhodium: *X*-Ray Structure Analyses of the Neutral Complex [NiL^2] and the *trans*-Spanned [$Rh(CO)Cl(H_2L^2)$]†

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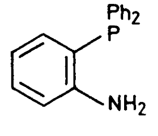
The new multidentate phosphorus–nitrogen P_2N_2 hybrid ligand *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine, H_2L^2, has been prepared by demetallation of its neutral deprotonated nickel complex [NiL^2], (**1a**), obtained from the metal-template catalysed condensation of bis(2-phenylphosphinophenylamido)nickel(II), [$Ni(HL^1)_2$], with 1,3-bis(toluene-*p*-sulphonyloxy)-propane in the presence of base. Under basic conditions, H_2L^2 forms complexes (**1b**) and (**1c**) analogous to (**1a**) with palladium(II) and platinum(II) in which the ligand is tetradentate around a square-planar metal ion. The complexes (**1**) may be protonated to form the corresponding dications [$M(H_2L^2)$]$^{2+}$, (**2a**)—(**2c**). With rhodium(I), H_2L^2 forms both the monocation [$Rh(H_2L^2)$]$^+$, (**3**), and the neutral square-planar complex [$Rh(CO)Cl(H_2L^2)$], (**4**), in which H_2L^2 behaves as a P_2 *trans*-spanning bidentate ligand. *X*-Ray crystal-structure analyses of both (**1a**) and (**4**) have been performed. Compound (**1a**) crystallises with a molecule of mesitylene as solvate in the tetragonal space group $I4_1/a$ with a = 35.246(6) and c = 13.190 (2) Å and Z = 16. Blocked full-matrix refinement of 2 837 unique reflections with $I \geqslant 3\sigma(I)$ ($3.0 < \theta < 25.0°$) gave R = 0.065 and R' = 0.062. Crystals of (**4**) have the monoclinic space group Cc with a = 12.192(2), b = 14.125(2), c = 20.474(4) Å, β = 92.85(2)°, and Z = 4. Blocked full-matrix refinement of 1 975 reflections with $I > 2.5\sigma(I)$ ($1.0 < \theta < 25.0°$) gave R = 0.041 and R' = 0.047.

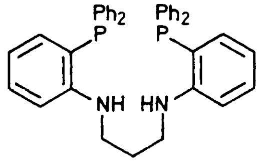
For some time we have been interested in the co-ordination chemistry of the bidentate ligand (2-aminophenyl)diphenylphosphine,[1,2] H_2L^1. The dominant feature of its chemistry with metal ions is the facile and reversible deprotonation of the co-ordinated aromatic amino group.[2] This has provided a convenient route to relatively rare examples of amido (deprotonated amino) complexes, M–NRR′, of the transition metals.[1d,2,3] Recently we have extended our studies to multidentate[4] and macrocyclic[5] ligands also containing the (2-aminophenyl)phosphino subunit.

In this paper we report the metal-template catalysed synthesis of a new multidentate phosphorus–nitrogen ligand, *N,N'*-bis[2-diphenylphosphino)phenyl]propane-1,3-diamine, H_2L^2, containing a PNNP donor sequence and its co-ordination chemistry with the metals of the nickel triad and with rhodium. The preparation of H_2L^2 takes advantage of the co-ordinated amido group as an active nucleophile.[2c,5,6]

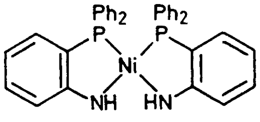
Ligands with a PNNP donor atom sequence are not yet common.[7,8] We have found that the potentially tetradentate ligand H_2L^2 can act as a P_2N_2 ligand forming both amino and amido complexes, or as a *trans*-spanning P_2 ligand[9] with only the phosphorus atoms co-ordinated.



H_2L^1



H_2L^2



[$Ni(HL^1)_2$]

Results and Discussion

The P_2N_2 ligand H_2L^2 was prepared by linking the nitrogen atoms of two molecules of the parent bidentate ligand H_2L^1. This was achieved by the reaction of 1,3-bis(toluene-*p*-sulphonyloxy)propane, $tsO(CH_2)_3Ots$, with *cis*-[$Ni(HL^1)_2$][2a] in refluxing toluene over anhydrous potassium carbonate[5,6] [equation (1)]. The mechanism involves sequential nucleophilic attack on the toluene-*p*-sulphonate substituted carbon atoms of the propane by the lone pair of each of the co-ordinated amido

$$[Ni(HL^1)_2] + tsO(CH_2)_3Ots + 2\,K_2CO_3 \longrightarrow [NiL^2] + 2\,KOts + 2\,KHCO_3 \quad (1)$$

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† {*N,N'*-Bis[2-(diphenylphosphino)phenyl]propane-1,3-diamido}-nickel(II) and {*N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine}carbonylchlororhodium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

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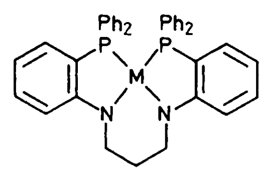
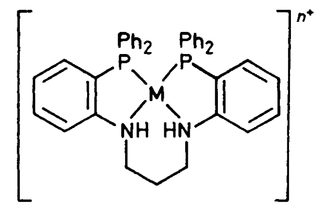




	M			M	n
(1a)	Ni^{II}		(2a)	Ni^{II}	2
(1b)	Pd^{II}		(2b)	Pd^{II}	2
(1c)	Pt^{II}		(2c)	Pt^{II}	2
			(3)	Rh^{I}	1

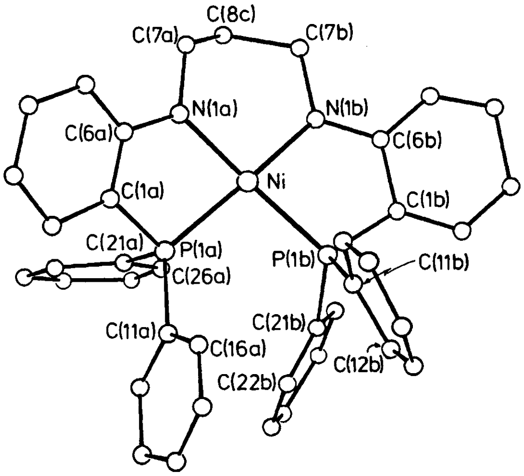


Figure 1. Molecular structure of [NiL^2], (**1a**)

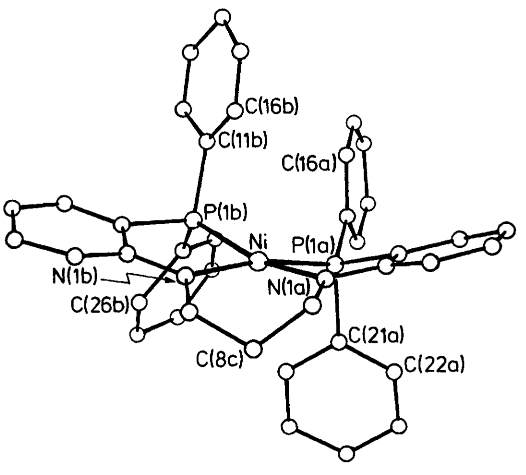


Figure 2. A view of complex (**1a**) showing the tetrahedral distortion and staggered phenyl rings

nitrogen atoms. Whereas 1,3-dichloro- and 1,3-dibromo-propane do not react with [Ni(HL^1)$_2$] under similar conditions, the mixed disubstituted alkane 1-chloro-3-(toluene-*p*-sulphonyl-oxy)propane reacts to give only [NiL^2], (**1a**). Thus, initial attack occurs at the tosylated carbon, followed by substitution at the chloro-substituted carbon. The latter step is facilitated by closure of the six-membered chelate ring. Protons liberated in the course of the reaction (1) are removed by the excess of base. Green needles of the deprotonated complex (**1a**) were obtained from toluene–methanol in 76% yield. Treatment of a benzene solution of (**1a**) with aqueous sodium cyanide gave, after work up, free H_2L^2 as a white air-stable solid in 63% yield.

The palladium and platinum complexes [ML^2][M = Pd (**1b**) or Pt (**1c**)] were readily isolated after the addition of triethylamine to solutions containing [M(H$_2$L^2)]$^{2+}$ (**2b**) or (**2c**). These dications were prepared by the reaction of the free ligand with palladium(II) or platinum(II) chloride in warm *N*,*N*-dimethylformamide (dmf). The analogous nickel species, [Ni(H$_2$L^2)]$^{2+}$, (**2a**), was isolated as the dinitrate after protonation of (**1a**) with dilute nitric acid.

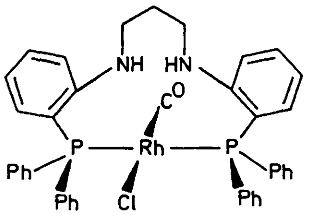
The ^{31}P n.m.r. spectra of complexes (**1a**), (**1b**), (**2a**), and (**2b**) each consisted of a single peak. For the platinum(II) complexes (**1c**) and (**2c**) the expected patterns due to their A_2X spin systems were observed with coupling constants similar to those for *cis*-[Pt(HL^1)$_2$][1a,2b] and *cis*-[Pt(H$_2$L^1)$_2$]$^{2+}$.[1a,b] The increase in *J*(PtP) from 3 056 to 3 292 Hz on protonation of (**1c**) is characteristic of the change from an amido to amino nitrogen donor *trans* to a phosphorus atom.[6,10] A similar change in *J*(PtP) from 3 032 to 3 370 Hz on conversion of *cis*-[Pt(HL^1)$_2$] into *cis*-[Pt(H$_2$L^1)$_2$]$^{2+}$ has been attributed to the increased *trans* influence of the amido group relative to that of the amino ligand.[1a,6] Square-planar tetradentate co-ordination of the P_2N_2 ligand H_2L^2 and its conjugate base $(L^2)^{2-}$ was thus confirmed.

The mass spectra of the neutral complexes (**1**) each exhibited a base peak corresponding to the molecular ion [ML^2]$^+$ at *m*/*e* 650, 698, and 787 for M = Ni, Pd, and Pt respectively, with intense signals due to the double charged ions [ML^2]$^{2+}$ at *m*/*e* 325, 349, and 393.5 also present, indicating a high degree of thermal stability of these complexes.

The structure (Figure 1) of the neutral nickel complex (**1a**), as its mesitylene solvate, has been determined by *X*-ray crystal-structure analysis. Selected bond lengths and angles are given in Table 1. The ligand $(L^2)^{2-}$ was found to behave as a P_2N_2 tetradentate ligand giving approximately square-planar geometry around the metal ion. The chemically equivalent bonds in the two halves of the molecule are of equal length (within experimental error) but there is a marked tetrahedral distortion shown by the donor atoms from ideal square-planar geometry (Figure 2). This is seen as a displacement of the metal and its donors from their least-squares plane of best fit by about 0.02 and 0.2 Å respectively[Ni 0.02, P(1a) 0.20, P(1b) −0.21, N(1a) −0.24, and N(1b) 0.22 Å]. The origin of this distortion appears to be the sterically constrained six-membered chelate ring containing the two amido nitrogen donor atoms. Both the intramolecular N(1a) ··· N(1b) distance of 2.89 Å and the N(1a)–Ni–N(1b) angle of 97.5(3)° are significantly larger than the corresponding values [2.61 Å and 88.7(6)°] in the unconstrained and rigorously square-planar structure of *cis*-[Ni(HL^1)$_2$],[2a] indicating that the trimethylene bridge between the two nitrogen donors prevents the amido groups from assuming optimal (closer) positions. Part of this effect is due to the large angles [totalling 360° for both N(1a) and N(1b)] required around each amido nitrogen for *sp*^{2} hybridisation. As a consequence of this large N(1a) ··· N(1b) separation the two phosphorus donors have been pushed toward each other with a P(1a) ··· P(1b) distance of 3.23 Å and P(1a)–Ni–P(1b) angle of 97.1(1)°, compared to the corresponding values of 3.39 Å and 101.5(2)° in the less sterically constrained [Ni(HL^1)$_2$].[2a] The tetrahedral distortion allows the two phosphorus donor atoms to be further apart than they would be if the geometry around the nickel atom was rigorously square planar. The five-membered Ni–P–C–C–N chelate rings, which each contain a rigid *o*-phenylene backbone, show little of the effects of the overall distortion. Thus, the N ··· P distances of 2.71 (1a) and 2.76 Å (1b) and the N–Ni–P angles of 82.9(2), (1a), and 85.2(2)°, (1b), are close to the values of 2.75 Å and 84.9(3)° in *cis*-[Ni(HL^1)$_2$].[2a]

Table 1. Bond lengths (Å) and angles (°) for [NiL^2] (**1a**)

Ni–P(1a)	2.160(3)	Ni–P(1b)	2.148(3)	C(7a)–C(8c)	1.512(12)	C(7b)–C(8c)	1.502(12)
Ni–N(1a)	1.923(7)	Ni–N(1b)	1.923(7)	C(1a)–C(2a)	1.395(11)	C(1b)–C(2b)	1.392(11)
P(1a)–C(1a)	1.779(9)	P(1b)–C(1b)	1.788(9)	C(2a)–C(3a)	1.396(12)	C(2b)–C(3b)	1.403(12)
P(1a)–C(11a)	1.810(9)	P(1b)–C(11b)	1.815(8)	C(3a)–C(4a)	1.378(12)	C(3b)–C(4b)	1.364(12)
P(1a)–C(21a)	1.830(8)	P(1b)–C(21b)	1.821(8)	C(4a)–C(5a)	1.368(11)	C(4b)–C(5b)	1.368(12)
N(1a)–C(6a)	1.377(10)	N(1b)–C(6b)	1.352(10)	C(5a)–C(6a)	1.426(11)	C(5b)–C(6b)	1.450(11)
N(1a)–C(7a)	1.457(11)	N(1b)–C(7b)	1.475(10)	C(1a)–C(6a)	1.396(11)	C(1b)–C(6b)	1.401(11)
P(1b)–Ni–P(1a)	97.1(1)	N(1a)–Ni–P(1a)	82.9(2)	C(2a)–C(1a)–P(1a)	126.9(7)	C(6a)–C(1a)–P(1a)	111.0(7)
N(1a)–Ni–P(1b)	166.1(2)	N(1b)–Ni–P(1a)	169.1(2)	C(6a)–C(1a)–C(2a)	122.0(9)	C(3a)–C(2a)–C(1a)	120.4(9)
N(1b)–Ni–P(1b)	85.2(2)	N(1b)–Ni–N(1a)	97.5(3)	C(4a)–C(3a)–C(2a)	116(1)	C(5a)–C(4a)–C(3a)	126(1)
C(1a)–P(1a)–Ni	102.0(3)	C(11a)–P(1a)–Ni	129.1(3)	C(6a)–C(5a)–C(4a)	117.9(9)	C(1a)–C(6a)–N(1a)	117.5(8)
C(11a)–P(1a)–C(1a)	105.1(4)	C(21a)–P(1a)–Ni	108.5(3)	C(5a)–C(6a)–N(1a)	124.9(8)	C(5a)–C(6a)–C(1a)	117.6(9)
C(21a)–P(1a)–C(1a)	106.3(4)	C(21a)–P(1a)–C(11a)	104.1(4)	C(8c)–C(7a)–N(1a)	111.5(8)	C(7b)–C(8c)–C(7a)	113.6(9)
C(1b)–P(1b)–Ni	102.5(3)	C(11b)–P(1b)–Ni	112.2(3)	C(8c)–C(7b)–N(1b)	114.2(9)	C(5b)–C(6b)–N(1b)	124.9(8)
C(11b)–P(1b)–C(1b)	104.5(4)	C(21b)–P(1b)–Ni	120.5(3)	C(1b)–C(6b)–N(1b)	119.8(8)	C(1b)–C(6b)–C(5b)	115.3(8)
C(21b)–P(1b)–C(1b)	106.9(4)	C(21b)–P(1b)–C(11b)	108.7(4)	C(4b)–C(5b)–C(6b)	119.0(9)	C(3b)–C(4b)–C(5b)	125(1)
C(6a)–N(1a)–Ni	121.3(6)	C(7a)–N(1a)–Ni	123.0(6)	C(2b)–C(3b)–C(4b)	117(1)	C(1b)–C(2b)–C(3b)	119.7(9)
C(7a)–N(1a)–C(6a)	115.7(8)	C(7b)–N(1b)–Ni	123.2(6)	C(6b)–C(1b)–P(1b)	111.1(7)	C(2b)–C(1b)–P(1b)	125.3(7)
C(6b)–N(1b)–Ni	121.3(6)	C(6b)–N(1b)–C(7b)	115.5(7)	C(2b)–C(1b)–C(6b)	123.6(8)		



(4)

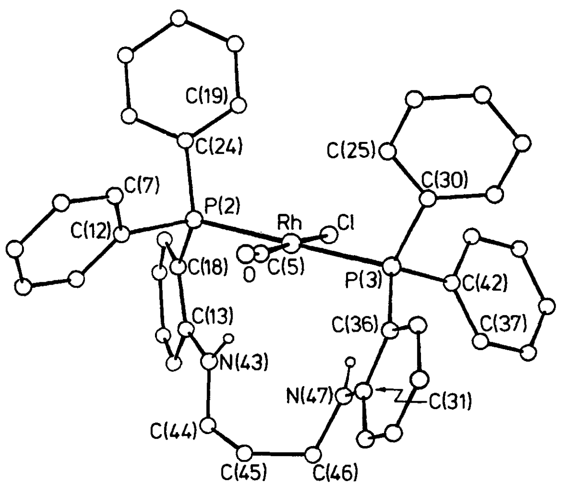


Figure 3. Molecular structure of *trans*-[Rh(CO)Cl(H$_2$L^2)] (4)

The six-membered Ni–N(1a)–C(7a)–C(8c)–C(7b)–N(1b) chelate ring has a flattened boat configuration with both Ni (0.21 Å) and C(8c) (0.70 Å) on the same side of the plane formed by N(1a) (0.05 Å), N(1b) (−0.05 Å), C(7a) (−0.06 Å), and C(7b) (0.06 Å). The phenyl rings on P(1a) have adopted a staggered configuration relative to those on P(1b), Figure 2, whereas in the similar unconstrained complexes *cis*-[Pt(HL^1)$_2$][2b] and *cis*-[Ni(HL^1)$_2$][2a] similar rings lie parallel and roughly eclipsed. There are no close contacts between the mesitylene solvate molecule and the metal complex (**1a**).

Rhodium(I) complexes of H$_2$L^2 were also prepared. For example, the very air-sensitive square-planar cation [Rh(H$_2$L^2)]$^+$ (**3**) was obtained as the hexafluorophosphate from the reaction of the ligand with [{Rh(cod)Cl}$_2$] (cod = 1,5-cyclo-octadiene). The stereochemistry of this ion was indicated by a single doublet [δ 59.1 p.p.m. (dmf)] in its ^{31}P n.m.r. spectrum with a coupling constant [*J*(RhP) 173 Hz] typical of square-planar rhodium(I) complexes.[8b,c,11] Unlike the dications (**2a**)—(**2c**) the monocation (**3**) does not produce an analogue of the neutral complexes (**1a**)—(**1c**) when treated with triethylamine. Moreover the *in situ* ^{31}P n.m.r. spectrum of a reaction mixture containing (**3**) and triethylamine failed to show significant changes in either the phosphorus chemical shift or the rhodium–phosphorus coupling constant, indicating that deprotonation of the co-ordinated amino groups had not taken place. A similar lack of reactivity has been observed[11] with other rhodium(I) complexes of H$_2$L^1. However deprotonation of both rhodium(I) complexes containing a carbonyl ligand *trans* to the amino group of a co-ordinated 2-aminophenylphosphino moiety and rhodium(III) complexes of H$_2$L^1 has been reported.[1d,4,11] Thus the acidity of the co-ordinated anilino group appears to be critically dependent on the charge density on the metal centre.

In contrast to the tetradentate behaviour of H$_2$L^2 discussed above, the pale yellow compound, *trans*-[Rh(CO)Cl(H$_2$L^2)], (**4**), in which the ligand is bidentate and *trans*-spanning, was formed as a crystalline precipitate from equimolar amounts of [NBu$^n_4$][Rh(CO)$_2$Cl$_2$] and H$_2$L^2. The insolubility of this complex in common organic solvents prevented the observation of its ^{31}P n.m.r. spectrum. A single carbonyl stretch (1 960 cm^{-1}) and a rhodium–chloride stretch (315 cm^{-1}) were seen in the solid-sate i.r. spectrum.

The structure of complex (**4**) was determined by *X*-ray crystal-structure analysis and is shown in Figure 3. Bond lengths and angles are given in Table 2. The geometry about rhodium approximates square planar: no atom deviates from the least-squares plane through rhodium and the four donor atoms by more than 0.033 Å. There is a systematic movement of the chloro and carbonyl ligands away from the phenyl groups which lie closest to the co-ordination plane and this is reflected in distortions of 2.5° in the angles about rhodium. The P$_2$N$_2$ ligand H$_2$L^2 co-ordinates, through the phosphorus atoms only, to *trans* sites of the rhodium atom and the overall geometry of the complex closely approaches two-fold symmetry. The view in Figure 4 shows that the pseudo-symmetry axis, passing through the rhodium atom and perpendicular to the co-ordination plane, is violated only by the central propylene linkage of the ligand and by the carbonyl and chloride ligands. The rhodium

Table 2. Bond lengths(Å) and angles(°) for [Rh(CO)Cl(H_2L^2)], (**4**)

P(2)–Rh	2.317(5)	P(3)–Rh	2.341(5)	C(45)–C(44)	1.322(32)	C(46)–C(45)	1.476(26)
Cl–Rh	2.382(5)	C(5)–Rh	1.785(14)	C(18)–C(13)	1.390(15)	C(36)–C(31)	1.459(14)
O–C(5)	1.000(16)			C(13)–C(14)	1.506(19)	C(31)–C(32)	1.355(18)
C(18)–P(2)	1.857(12)	C(36)–P(3)	1.784(12)	C(15)–C(14)	1.326(23)	C(32)–C(33)	1.374(21)
C(12)–P(2)	1.858(8)	C(30)–P(3)	1.830(9)	C(16)–C(15)	1.436(25)	C(33)–C(34)	1.289(18)
C(24)–P(2)	1.819(8)	C(42)–P(3)	1.796(9)	C(17)–C(16)	1.396(22)	C(34)–C(35)	1.418(17)
N(43)–C(13)	1.354(23)	N(47)–C(31)	1.369(23)	C(18)–C(17)	1.364(17)	C(36)–C(35)	1.393(16)
N(43)–C(44)	1.403(29)	N(47)–C(46)	1.501(27)				
P(3)–Rh–P(2)	179.5(2)	Cl–Rh–P(2)	87.1(2)	C(13)–C(18)–P(2)	117.6(9)	C(17)–C(18)–P(2)	120.3(8)
Cl–Rh–P(3)	92.6(1)	C(5)–Rh–P(2)	92.7(4)	C(17)–C(18)–C(13)	121.9(11)	C(24)–C(19)–C(20)	120.0(5)
C(5)–Rh–P(3)	87.6(4)	C(5)–Rh–Cl	177.6(4)	C(19)–C(24)–P(2)	117.3(4)	C(23)–C(24)–P(2)	122.7(5)
C(12)–P(2)–Rh	119.8(3)	C(18)–P(2)–Rh	111.5(4)	C(25)–C(30)–P(3)	119.3(4)	C(29)–C(30)–P(3)	120.7(5)
C(18)–P(2)–C(12)	101.1(4)	C(24)–P(2)–Rh	113.3(3)	C(29)–C(30)–C(25)	120.0(6)	C(36)–C(31)–C(32)	115.9(11)
C(24)–P(2)–C(12)	102.6(4)	C(24)–P(2)–C(18)	107.2(4)	N(47)–C(31)–C(32)	126.1(12)	N(47)–C(31)–C(36)	117.8(12)
C(30)–P(3)–Rh	111.7(3)	C(36)–P(3)–Rh	111.3(4)	C(33)–C(32)–C(31)	122.7(10)	C(34)–C(33)–C(32)	123.3(13)
C(36)–P(3)–C(30)	106.2(5)	C(42)–P(3)–Rh	117.3(3)	C(35)–C(34)–C(33)	118.8(12)	C(36)–C(35)–C(34)	120.1(11)
C(42)–P(3)–C(30)	100.3(4)	C(42)–P(3)–C(36)	109.1(5)	C(31)–C(36)–P(3)	119.1(9)	C(35)–C(36)–P(3)	121.5(8)
O–C(5)–Rh	172.8(13)	C(12)–C(7)–C(8)	120.0(6)	C(35)–C(36)–C(31)	119.2(10)	C(37)–C(42)–P(3)	119.1(5)
C(7)–C(12)–P(2)	114.7(5)	C(11)–C(12)–P(2)	125.3(5)	C(41)–C(42)–P(3)	120.8(5)	C(41)–C(42)–C(37)	120.0(6)
C(11)–C(12)–C(7)	120.0(6)	C(18)–C(13)–C(14)	116.1(12)	C(44)–N(43)–C(13)	124.6(19)	C(45)–C(44)–N(43)	118.5(20)
N(43)–C(13)–C(14)	116.8(12)	N(43)–C(13)–C(18)	126.8(14)	C(46)–C(45)–C(44)	132.6(20)	N(47)–C(46)–C(45)	116.5(16)
C(15)–C(14)–C(13)	121.4(12)	C(16)–C(15)–C(14)	119.6(15)	C(46)–N(47)–C(31)	118.4(19)		
C(17)–C(16)–C(15)	119.5(15)	C(18)–C(17)–C(16)	121.1(12)				

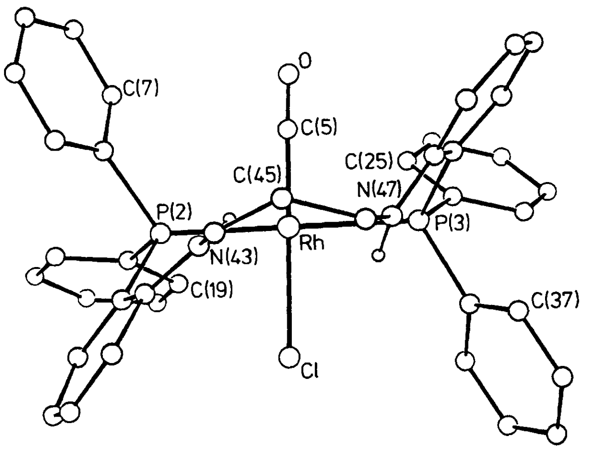


Figure 4. A view of complex (**4**) along the pseudo-symmetry axis

to nitrogen distances, 3.37(2) and 3.46(2) Å, clearly indicate that there is no bonding between these atoms. Likewise, the distances from rhodium to the calculated amine hydrogen-atom site,* 2.53 and 2.86 Å, indicate no significant interactions, and these hydrogen atoms are not hydrogen bonded to any other atoms within the complex. The rhodium to donor atom distances are of limited accuracy because of correlation problems experienced in the refinement. However, all distances are within the observed ranges for such bonds.[12] The structure of (**4**) consists of discrete neutral molecules, packed with no intermolecular contacts shorter than the van der Waals radii sum. The dichloromethane solvate molecule could not be located.

Experimental

Materials and techniques used were as described previously.[1a,d] Samples were dried at 50 °C (20 mmHg *ca.* 266 Pa) for 5 h. Carbon-13 n.m.r. spectra were recorded on a Bruker HFX 90 spectrometer operating at 22.63 MHz, using 8- and 10-mm concentric tubes with $SiMe_4$ as internal standard and D_2O as external lock. Mass spectra were obtained by the Mass Spectroscopy Unit, University of Sydney. The salt [NBu^n_4][$Rh(CO)_2Cl_2$] was prepared by a literature method.[13]

*1,3-Bis(toluene-*p*-sulphonyloxy)propane.*[14,15]—Propane-1,3-diol (20 g, 0.26 mol) was dissolved in pyridine (170 cm^3, 2.11 mol) and toluene-*p*-sulphonyl chloride (110 g, 0.58 mol) was added in small portions keeping the temperature below 10 °C. The mixture was stirred for 3 h then poured into a slurry of ice (1 kg) and 10 mol dm^{-3} HCl (300 cm^3) with vigorous stirring. The crude product settled out as an oil which quickly solidified. Recrystallisation from ethanol (200 cm^3) gave white crystals (41 g, 41%): ^1H n.m.r. δ 2.0 [2 H, q, $^3J(OCH_2–CH_2)$ 6, OCH_2CH_2], 2.5 (6 H, s, Me), 4.1 [4 H, t, $^3J(OCH_2–CH_2)$ 6 Hz, OCH_2], and 7.2—8.0 (8 H, m, aromatic).

*1-Chloro-3-(toluene-*p*-sulphonyloxy)propane.*[16]—3-Chloro-1-propanol (18.9 g, 0.2 mol) and toluene-*p*-sulphonyl chloride (37.9 g, 0.2 mol) were dissolved in dry diethyl ether (140 cm^3) and powdered sodium hydroxide (22.4 g, 0.56 mol) added in small portions while cooling the mixture to below 10 °C. After the addition was complete the mixture was stirred for 3 h at room temperature. Ice–water (200 cm^3) was added and the two-phase mixture separated. The organic phase was evaporated to give the crude product which was used without purification: ^1H n.m.r. δ 2.1 (2 H, q, OCH_2CH_2), 2.4 (3 H, s, Me), 3.6 [2 H, t, $^3J(OCH_2–CH_2)$ 6, $ClCH_2$], 4.2 [2 H, t, $^3J(OCH_2–CH_2)$ 6 Hz, OCH_2], and 7.3–7.8 (4 H, m, aromatic).

[$Ni(H_2L^1)_2$][NO_3]$_2$·H_2O.[1a,17]—The ligand H_2L^1 (27.7 g, 0.1 mol) was dissolved in boiling 90% aqueous ethanol (50 cm^3) and then treated with a solution of $Ni(NO_3)_2·6H_2O$ (14.5 g, 0.05 mol) in boiling aqueous ethanol (50 cm^3). The solution was cooled (5 °C) overnight and the resultant crystalline mass filtered off and washed with ethanol. The orange crystals were dried to yield the complex (34.0 g, 90%).

cis-[$Ni(HL^1)_2$]·Me_2CO.[2a,17]—The complex [$Ni(H_2L^1)_2$][NO_3]$_2$·H_2O (10.0 g, 13.2 mmol) was suspended in acetone (50 cm^3) and triethylamine (20 cm^3, 27.3 mmol) added. Brown

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* The positions of the hydrogen atoms bonded to the nitrogens were calculated assuming sp^2 hybridisation and a bond length of 0.97 Å.

crystals soon formed and were filtered off, washed with acetone, and dried (8.3 g, 95%), m.p. 206—207 °C, $\nu_{max.}$(NH) 3 676(br) and 3 670(br) cm^{-1}. N.m.r.: ^{1}H, δ 2.1 (6 H, s, acetone), 3.7 (2 H, br s, NH), and 5.9—8.1 (28 H, m, aromatic); ^{31}P (CHCl$_3$), δ 42.3 (85%, *cis* isomer) and 30.9 p.p.m. (15%, *trans* isomer). *m/e* 610 (M^+) and 305 (M^{2+}).

[NiL^2].—The complex [Ni(HL^1)$_2$]·Me$_2$CO (12.3 g, 18.4 mmol), 1,3-bis(toluene-*p*-sulphonyloxy)propane (7.1 g, 18.5 mmol), and anhydrous potassium carbonate (10.2 g, 73.8 mmol) were refluxed in toluene (100 cm^3) overnight. The resultant green solution was filtered and evaporated to approximately 20 cm^3. This concentrated solution was warmed (steam-bath) and hot methanol (approximately 100 cm^3) added. Green crystals soon formed and were filtered off, washed with methanol containing a little triethylamine, then dried (8.35 g, 76%), m.p. 213—6 °C (Found: C, 71.75; H, 5.30; N, 4.20. $C_{39}H_{34}N_2NiP_2$ requires C, 71.90; H, 5.25; N, 4.30%). N.m.r.: ^{1}H, δ 1.8 (2 H, br m, CH$_2$C*H*$_2$CH$_2$), 2.9 (4 H, br t, NCH$_2$), and 5.9—7.8 (18 H, m, aromatic); ^{31}P (CHCl$_3$), δ 41.6 p.p.m. *m/e* 650 (M^+) and 325 (M^{2+}).

H$_2$L^2.—The complex [NiL^2] (2.45 g, 3.76 mmol) was dissolved in benzene (20 cm^3) and the green solution stirred with 10% sodium cyanide solution (20 cm^3) until the colour had been discharged (approximately 20 min). The organic layer was separated, washed with brine (20 cm^3), dried (sodium sulphate), and passed down a short alumina column (2.5 × 10 cm) eluting with benzene. The now colourless solution was evaporated and the residue taken up in hot ethanol (20 cm^3) with sufficient benzene to complete dissolution. After 3 d at −18 °C a white solid had formed and was filtered off (1.41 g, 63%), m.p. 132—134 °C (Found: C, 77.75; H, 6.10; N, 4.60; P, 9.75. $C_{39}H_{36}N_2P_2$ requires C, 78.75; H, 6.10; N, 4.70; P, 10.40%); $\nu_{max.}$(NH) 3 397 and 3 360 cm^{-1} (Nujol) N.m.r.: ^{13}C*, δ 28.8 (s, NCH$_2$*C*H$_2$) 41.3 (s, NCH$_2$), 110.6 [s, C(3a)], 117.3 [s, C(5a)], 119.1 [d, ^nJ(PC) 9, C(1a)], 128.0—134.3 [m, C(4a), C(6a), C(2b)—C(4b)], 135.9 [d, ^nJ(PC) 8, C(1b)], and 151.2 [d, ^nJ(PC) 17 Hz, C(2a)]; ^{1}H, δ 1.6 [2 H, q, ^3J(NCH$_2$–CH$_2$) 6, CH$_2$C*H*$_2$CH$_2$], 3.0 [4 H, t, ^3J(NCH$_2$–CH$_2$) 6 Hz, NCH$_2$], and 6.3—7.6 (18 H, m, aromatic); ^{31}P (CH$_2$Cl$_2$), δ −21.5 p.p.m. *m/e* 594 (M^+).

[Ni(H$_2$L^2)][NO$_3$]$_2$·H$_2$O.—Dilute nitric acid (2 mol dm^{-3}) was added dropwise to a stirred suspension of [NiL^2] (1.00 g, 1.54 mmol) in methanol (10 cm^3) until the green crystals had completely dissolved. The resulting orange solution was cooled (5 °C) overnight whereupon large orange-red crystals formed. These were filtered off, and rapidly lost solvent of crystallisation. The resulting brown powder was dried to give the product (0.65 g, 54%), m.p. 160 °C (decomp.) (Found: C, 58.40; H, 4.70; N, 7.05. $C_{39}H_{38}N_4NiO_7P_2$ requires C, 58.90; H, 4.80; N, 7.05%); ^{31}P n.m.r. (CHCl$_3$) δ 39.0 p.p.m. (br) (as the trifluoroacetate, prepared *in situ* from [NiL^2] and trifluoroacetic acid).

[PdL^2].—Palladium(II) chloride (0.50 g, 2.8 mmol) and H$_2$L^2 (1.68 g, 2.8 mmol) were stirred in dmf (5 cm^3) at 60 °C overnight. The orange solution was diluted with methanol (30 cm^3) and triethylamine added. An orange-red precipitate quickly formed (1.89 g, 87%), m.p. 248—250 °C; ^{31}P n.m.r. (CHCl$_3$) δ 45.7 p.p.m. *m/e* 698 (M^+) and 349 (M^{2+}).

[Pd(H$_2$L^2)]$^{2+}$.—A sample for ^{31}P n.m.r. spectroscopy was prepared *in situ* by addition of hydrogen chloride [vapour from hydrochloric acid (10 mol dm^{-3})] to a solution of [PdL^2]: ^{31}P n.m.r. (CHCl$_3$) δ 47.4 p.p.m.

[PtL^2].—Platinum(II) chloride (0.50 g, 1.9 mmol) and H$_2$L^2 (1.12 g, 1.9 mmol) were stirred together at 120 °C for 5 min in dmf (5 cm^3), to which a few drops of hydrochloric acid (10 mol dm^{-3}) had been added. The solution was cooled and triethylamine added to produce a dark yellow solution. The addition of water (20 cm^3) gave a heavy yellow precipitate which was filtered off, dried, and redissolved in chloroform. Yellow crystals formed on the addition of methanol (1.18 g, 79%), m.p. ≈ 270 °C (turns red with melting); ^{31}P n.m.r. (CHCl$_3$) δ 27.0 p.p.m. [*J*(PtP) 3 056 Hz]; *m/e* 787 (M^+) and 393.5 (M^{2+}).

[Pt(H$_2$L^2)]$^{2+}$.—A sample for ^{31}P n.m.r. spectroscopy was prepared as for the analogous palladium species: ^{31}P n.m.r. (CHCl$_3$) δ 25.5 p.p.m. [*J*(PtP) 3 292 Hz].

[Rh(H$_2$L^2)]PF$_6$.—The complex [{Rh(cod)Cl}$_2$] (150 mg, 0.30 mmol) and H$_2$L^2 (360 mg, 0.61 mmol) were stirred in methanol (10 cm^3) for 15 min under a nitrogen atmosphere. Ammonium hexafluorophosphate (200 mg, 1.12 mmol) was added and stirring continued for 20 min. Water (5 cm^3) was slowly added to complete precipitation of the yellow product which was isolated by filtration, washed with water, and dried (215 mg, 90%); $\nu_{max.}$(NH) 3 270 cm^{-1} (Nujol); ^{31}P n.m.r. (dmf) δ 59.1 p.p.m. [*J*(RhP) 173 Hz].

[Rh(CO)Cl(H$_2$L^2)]·0.125CH$_2$Cl$_2$.—This complex was obtained by layering an acetone (20 cm^3) solution of [NBu^n$_4$][Rh(CO)$_2$Cl$_2$] (600 mg, 1.28 mmol) on top of a dichloromethane (20 cm^3) solution of H$_2$L^2 (1.26 g, 1.28 mmol) and allowing diffusion/reaction to proceed over 2 d. The yellow crystals were filtered off, washed with methanol, and dried (920 mg, 95%), m.p. 220 °C decomp. (Found: C, 62.05; H, 4.65; Cl, 5.85; N, 3.60. $C_{40.125}H_{36.25}Cl_{1.25}N_2OP_2Rh$ requires C, 62.45; H, 4.75; Cl, 5.75; N, 3.60%); $\nu_{max.}$(NH) 3 320 and 3 280, (CO) 1 960, and (RhCl) 315 cm^{-1} (Nujol); *m/e* 718 (0.5), 692 (9), and 346 (1%).

Crystallography.—Crystal data. (**1a**).C$_6$H$_3$Me$_3$-1,3,5, $C_{48}H_{46}N_2NiP_2$, $M = 771.6$, tetragonal, $a = 35.246(6)$, $c = 13.190(2)$ Å, $U = 16\,385.7$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $I4_1/a$, $Z = 16$, $D_c = 1.25$ g cm^{-3}, $F(000) = 6\,496$.

A dark green crystal of dimensions 0.36 × 0.12 × 0.09 mm, μ(Mo-K_α) = 5.38 cm^{-1}, was used in the data collection which was carried out using a Philips PW 1 100 four-circle single-crystal diffractometer in the θ range 3.0—25.0° with a scan width of 0.6° using the technique previously described[18] to obtain 2 837 unique data with $I \geqslant 3\sigma(I)$. No absorption corrections were applied.

(**4**), $C_{40}H_{36}ClN_2OP_2Rh$, $M = 761.0$, monoclinic, $a = 12.192(2)$, $b = 14.125(2)$, $c = 20.474(4)$ Å, $\beta = 92.85(2)°$, $U = 3\,521.7$ Å^3 (by least-squares refinement of diffractometer setting angles for 25 automically centred reflections $\lambda = 0.71069$ Å), space group Cc, $Z = 4$, $D_c = 1.435$ g cm^{-3}.

The crystal was a yellow prism of dimensions 0.21 × 0.12 × 0.08 mm, μ(Mo-K_α) = 6.02 cm^{-1}. Data collection was carried out using a CAD4 diffractometer in 3ω—4θ mode with ω scan width (1.10 + 0.35 tan θ)°, aperture width (2.40 × 0.50 tan θ) mm, and graphite-monochromated Mo-K_α radiation to obtain 1 975 unique reflections with $I \geqslant 2.5\sigma(I)$. Lorentz, polarisation, crystal decay (less than 2%), and absorption (min. 1.04 to max. 1.08)[19] effects were corrected for.

Structure analysis and refinement. The structures were solved

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* The 2-aminophenyl ring is labelled 'a' and the unsubstituted phenyl ring 'b'. Within each ring, carbon atoms are labelled 1,2, *etc.* starting from the substituent atom of highest atomic weight and so that the numbering of ring substitution is lowest.

Table 3. Fractional atomic co-ordinates for [NiL^2] (**1a**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.184 12(3)	0.139 65(3)	0.007 81(9)	C(13a)	0.050 5(3)	0.094 8(3)	0.246 7(8)
P(1a)	0.143 29(6)	0.149 90(6)	0.126 83(20)	C(14a)	0.066 5(3)	0.062 5(3)	0.285 7(8)
P(1b)	0.157 68(6)	0.089 81(6)	−0.053 84(19)	C(15a)	0.105 6(3)	0.056 3(3)	0.277 5(7)
N(1a)	0.214 0(2)	0.175 4(2)	0.083 7(6)	C(16a)	0.128 6(2)	0.083 9(2)	0.232 6(7)
N(1b)	0.215 4(2)	0.138 1(2)	−0.111 5(5)	C(21a)	0.111 1(2)	0.187 6(2)	0.085 5(6)
C(1a)	0.172 1(2)	0.169 9(2)	0.223 7(6)	C(22a)	0.098 6(2)	0.215 3(2)	0.152 3(7)
C(2a)	0.163 0(3)	0.173 6(2)	0.326 1(7)	C(23a)	0.073 6(2)	0.243 4(3)	0.117 7(7)
C(3a)	0.188 8(3)	0.190 1(3)	0.393 5(8)	C(24a)	0.062 3(3)	0.244 0(3)	0.020 6(7)
C(4a)	0.222 1(3)	0.203 5(3)	0.352 2(8)	C(25a)	0.074 9(3)	0.217 2(3)	−0.048 7(8)
C(5a)	0.232 1(2)	0.201 2(2)	0.252 1(7)	C(26a)	0.100 0(2)	0.188 3(3)	−0.014 8(7)
C(6a)	0.206 8(2)	0.182 4(2)	0.184 5(7)	C(11b)	0.166 8(2)	0.047 9(2)	0.022 4(6)
C(7a)	0.246 5(3)	0.195 2(3)	0.041 0(8)	C(12b)	0.144 1(2)	0.015 8(2)	0.021 0(6)
C(8c)	0.241 6(3)	0.202 3(3)	−0.071 3(8)	C(13b)	0.153 8(3)	−0.015 6(3)	0.080 6(7)
C(7b)	0.244 4(3)	0.167 0(3)	−0.134 6(8)	C(14b)	0.186 0(3)	−0.014 9(3)	0.139 2(7)
C(6b)	0.212 5(2)	0.109 6(2)	−0.179 5(7)	C(15b)	0.209 3(3)	0.016 7(2)	0.138 0(7)
C(5b)	0.237 2(3)	0.104 3(3)	−0.266 2(7)	C(16b)	0.199 8(2)	0.048 4(3)	0.081 2(7)
C(4b)	0.230 9(3)	0.074 2(3)	−0.329 6(8)	C(21b)	0.107 7(2)	0.090 4(2)	−0.088 9(6)
C(3b)	0.202 7(3)	0.048 0(3)	−0.318 8(8)	C(22b)	0.078 5(2)	0.080 9(2)	−0.022 6(7)
C(2b)	0.178 6(3)	0.052 1(3)	−0.234 8(7)	C(23b)	0.040 9(3)	0.087 4(2)	−0.050 5(7)
C(1b)	0.184 1(2)	0.082 1(2)	−0.167 8(7)	C(24b)	0.032 8(3)	0.103 5(3)	−0.142 5(8)
C(11a)	0.112 7(2)	0.116 5(2)	0.191 4(7)	C(25b)	0.061 3(3)	0.112 8(3)	−0.209 5(8)
C(12a)	0.073 7(3)	0.122 0(3)	0.198 2(7)	C(26b)	0.099 2(2)	0.106 3(2)	−0.182 8(7)

Table 4. Fractional atomic co-ordinates for [Rh(CO)Cl(H$_2$L^2)] (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.5000	0.246 3(1)	0.7500	C(25)	0.326 7(6)	0.067 3(5)	0.677 4(2)
P(2)	0.596 3(4)	0.243 6(4)	0.850 5(2)	C(26)	0.279 1(6)	−0.020 4(5)	0.662 6(2)
P(3)	0.403 5(3)	0.247 9(4)	0.648 3(2)	C(27)	0.250 3(6)	−0.043 8(5)	0.597 8(2)
Cl	0.673 5(4)	0.246 8(3)	0.701 4(2)	C(28)	0.269 1(6)	0.020 5(5)	0.547 8(2)
C(5)	0.370 3(11)	0.251 3(9)	0.786 7(6)	C(29)	0.316 7(6)	0.108 2(5)	0.562 7(2)
O	0.296 6(7)	0.245 6(7)	0.805 7(4)	C(30)	0.345 5(6)	0.131 6(5)	0.627 5(2)
C(7)	0.444 5(6)	0.205 3(4)	0.941 8(3)	C(31)	0.311 0(10)	0.427 8(7)	0.662 7(4)
C(8)	0.382 9(6)	0.219 6(4)	0.996 5(3)	C(32)	0.222 0(14)	0.485 3(7)	0.658 5(6)
C(9)	0.401 1(6)	0.299 6(4)	1.035 5(3)	C(33)	0.118 7(12)	0.453 3(9)	0.639 7(7)
C(10)	0.480 9(6)	0.365 3(4)	1.019 8(3)	C(34)	0.097 5(10)	0.366 2(9)	0.625 1(7)
C(11)	0.542 5(6)	0.351 1(4)	0.965 0(3)	C(35)	0.184 3(9)	0.299 3(9)	0.629 0(6)
C(12)	0.524 4(6)	0.271 1(4)	0.926 0(3)	C(36)	0.290 4(10)	0.328 1(7)	0.647 9(5)
C(13)	0.680 2(13)	0.425 8(8)	0.836 9(6)	C(37)	0.457 7(6)	0.349 8(4)	0.539 6(3)
C(14)	0.772 9(11)	0.496 3(9)	0.840 1(6)	C(38)	0.513 0(6)	0.365 3(4)	0.482 5(3)
C(15)	0.876 0(15)	0.469 4(12)	0.852 6(8)	C(39)	0.591 6(6)	0.300 6(4)	0.463 3(3)
C(16)	0.899 8(14)	0.371 7(14)	0.866 4(8)	C(40)	0.615 1(6)	0.220 4(4)	0.501 2(3)
C(17)	0.813 6(12)	0.307 1(8)	0.869 6(6)	C(41)	0.559 8(6)	0.204 9(4)	0.558 3(3)
C(18)	0.707 7(9)	0.333 5(7)	0.854 6(4)	C(42)	0.481 1(6)	0.269 6(4)	0.577 5(3)
C(19)	0.658 0(6)	0.062 1(4)	0.819 8(2)	N(43)	0.581 9(14)	0.456 7(14)	0.811 7(9)
C(20)	0.703 4(6)	−0.027 3(4)	0.831 8(2)	C(44)	0.553 1(27)	0.552 3(14)	0.803 2(12)
C(21)	0.750 1(6)	−0.049 2(4)	0.893 5(2)	C(45)	0.466 4(12)	0.573 3(8)	0.764 6(7)
C(22)	0.751 5(6)	0.018 3(4)	0.943 3(2)	C(46)	0.439 5(27)	0.556 5(14)	0.694 5(10)
C(23)	0.706 1(6)	0.107 7(4)	0.931 3(2)	N(47)	0.417 7(17)	0.455 7(12)	0.674 5(8)
C(24)	0.659 4(6)	0.129 6(4)	0.869 6(2)				

by heavy-atom (Patterson) methods.[20,21] All other non-hydrogen atoms were located from subsequent Fourier difference syntheses.

For complex (**4**) the space group of higher symmetry *C*2/*c* in which the rhodium atom lies on a C_2 symmetry element was considered. The additional symmetry is adhered to by most but not all of the structure. As a result the chloro and carbonyl ligands atoms could not be refined anisotropically in the non-centrosymmetric space group *Cc* because of correlation problems in the refinement due to near-matrix singularities. The terminal phenyl groups of (**4**) were included as rigid planar groups (C–C 1.40 Å) with isotropic thermal parameters for the carbon atoms. The chloro and carbonyl group atoms in (**4**) were also assigned isotropic thermal parameters but all other non-hydrogen atoms were refined anisotropically. For complex (**1a**) only the nickel, phosphorus, and nitrogen atoms were assigned anisotopic thermal parameters.

Hydrogen atoms were included at calculated sites [C–H 1.08 Å for (**1a**) and 0.97 Å for (**4**)], except for the methyl group hydrogens of the mesitylene solvate molecules in (**1a**), and were given fixed thermal factors (0.1 Å^2).

Blocked full-matrix least-squares refinement[21] converged for (**1a**). $C_6H_3Me_3$-1,3,5 with $R = 0.065$ and $R' = 0.062$ $\{w = 1/[\sigma^2(F_o)]\}$, and for (**4**) with $R = 0.041$ and $R' = 0.047$ $\{w = 2.44/[\sigma^2(F_o) + 0.000\,55\ F_o{}^2]\}$. For both structures final Fourier difference maps showed no regions of significant electron density. The final atomic co-ordinates for (**1a**) and (**4**) are given in Tables 3 and 4 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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