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# Sterically hindered electron-withdrawing ligands: the reactions of *N*-carbazolyl phosphines with rhodium and palladium centres

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The series of *N*-carbazolyl phosphines $PPh_{3-n}(NC_{12}H_8)_n$ ($n = 1$, **L**$^1$; $n = 2$, **L**$^2$; $n = 3$, **L**$^3$) has been synthesised using BuLi to generate the *N*-carbazolyl lithium salt, followed by reaction with the appropriate chlorophosphine. The reactions between $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and four equivalents of **L**$^1$ or **L**$^2$ gave $[RhCl(CO)(\mathbf{L}^1)_2]$ **1** and $[RhCl(CO)(\mathbf{L}^2)_2]$ **2**, though attempts to synthesise the analogous complex using **L**$^3$ resulted in the formation of $[Rh(\mu\text{-}Cl)(CO)(\mathbf{L}^3)]_2$ **3** instead. The inability of **L**$^3$ to cleave the chloride bridges can be related to its considerable steric requirements. The electronic properties of **L**$^{1-3}$ were assessed by comparison of the $\nu(CO)$ values of the $[Rh(acac)(CO)(\mathbf{L}^{1-3})]$ complexes **4–6**. The increase in number of *N*-carbazolyl substituents at the phosphorus atom results in a decrease of the σ-donor and increase in the π-acceptor character in the order **L**$^1$ < **L**$^2$ < **L**$^3$. In the reactions of **L**$^{1-3}$ with $[PdCl_2(cod)]$ only **L**$^1$ was able to displace cod from the metal centre and form $[PdCl_2(\mathbf{L}^1)_2]$ **7**. The use of $[PdCl_2(NCMe)_2]$ instead of $[PdCl_2(cod)]$ resulted in the formation of the complexes $[PdCl_2(\mathbf{L}^1)_2]$ **7** from **L**$^1$, the cyclometallated complex $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ **8** from **L**$^3$, and a mixture of $[PdCl_2(\mathbf{L}^2)_2]$ **9** and $[Pd(\mu\text{-}Cl)\{PPh(NC_{12}H_8)(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ **10** from **L**$^2$. The reaction of **L**$^3$ with $[Pd(OAc)_2]$ produced the cyclometallated complex $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ **11**. The reaction of **L**$^3$ with $[Pd_2(dba)_3]\cdot CHCl_3$ produced the 14-electron complex $[Pd(\mathbf{L}^3)_2]$ **12**. The X-ray crystal structures of six complexes are reported, all of which show the presence of C–H···Pd hydrogen bonding.

## Introduction

It is widely recognised that the properties of transition metal complexes, including their catalytic activity and selectivity, can be controlled by changing the steric and electronic attributes of the ligands.[1] A recent protocol for developing stereoelectronic maps for phosphorus ligands concluded that bulky electron-poor phosphines were largely unknown, and suggested these would be useful targets.[2] Sterically demanding ligands are able to stabilise metals with low coordination numbers and/or unusual oxidation states,[3] the former being classically illustrated by low valent complexes containing Group 10 metals. Thus with small ligands, the preferred coordination number in complexes of Ni(0), Pd(0) and Pt(0) is four, giving rise to the 18-electron complexes $[M(PR_3)_4]$.[4] However complexes with lower coordination numbers can be isolated with bulky phosphines such as $PCy_3$,[5] $PBu^t{}_3$,[6] $P(o\text{-}Tol)_3$[7] and $PPh_2Np$ (Np = naphthyl).[8] The ability of bulky phosphorus ligands to stabilise coordinatively unsaturated metals in low oxidation states has great potential in catalysis, and bulky phosphorus ligands give rise to high activities in the rhodium-catalysed hydroformylation of olefins.[9]

Bearing in mind the properties of bulky phosphines and the relative dearth of sterically-demanding electron-poor ligands, we sought to prepare and study phosphorus ligands containing bulky functionalised *N*-pyrrolyl substituents. *N*-Pyrrolyl phosphines are of interest due to their strong electron-withdrawing character,[10] and we have recently reported the chemistry of such ligands functionalised with keto,[11,12] cyano,[13] aza[14] and diphenylphosphino[15] groups. An increase in the steric bulk of the *N*-pyrrolyl functionality can be achieved either by substitution at the α position or by using fused ring systems. Using the former approach, the series of (2,5-dimethyl-*N*-pyrrolyl)phenyl phosphines $PPh_{3-n}(NC_4H_2Me_2\text{-}2,5)_n$ has been prepared,[16] whereas using the fused ring strategy, tri-*N*-indolyl phosphine has been synthesised in a stepwise manner from $PF_3$ and the *N*-indolyl lithium salt.[17] *N*-Indolyl and *N*-carbazolyl phosphines have also been reported by Beller and co-workers, who used them as modifying ligands in rhodium-catalysed hydroformylation reactions.[18] However, no studies on the coordination chemistry of these ligands have been published.

In this paper we report the syntheses of the full series of *N*-carbazolyl phenyl phosphines $PPh_{3-n}(NC_{12}H_8)_n$ ($n = 1$, **L**$^1$; $n = 2$, **L**$^2$; $n = 3$, **L**$^3$) and their coordination chemistry with rhodium(I), palladium(II) and palladium(0) metal centres.

### Synthesis of *N*-carbazolyl phosphines L$^{1-3}$

Beller and co-workers have recently described the synthesis of $PPh_2(NC_{12}H_8)$ **L**$^1$ and $P(NC_{12}H_8)_3$ **L**$^3$ from the reaction of $PClPh_2$ or $PCl_3$ with carbazole in the presence of $NEt_3$.[18] In our hands it proved difficult to isolate pure samples of the ligands using this method, though on reacting two equivalents of carbazole with one equivalent of $PCl_2Ph$ it was possible to isolate and fully characterise the chlorophosphine $PClPh(NC_{12}H_8)$ which together with **L**$^2$ was the main product in the crude reaction mixture. Unexpectedly, and in contrast to most chlorophosphines, $PClPh(NC_{12}H_8)$ is a moderately air- and moisture-stable solid which readily crystallised from cold hexane (−25 °C). The $^{31}P\{^1H\}$ NMR spectrum of $PClPh(NC_{12}H_8)$ is composed of a singlet at $\delta$ 99.0, whereas the $^1H$ and $^{13}C\{^1H\}$ NMR spectra clearly indicate the presence of one carbazolyl and one phenyl substituent.

The successful syntheses of **L**$^{1-3}$ were performed using an analogous method to that reported for the syntheses of $PPh_2(NC_4H_3CN\text{-}2)$ and $P(NC_4H_4)_2(NC_4H_3CN\text{-}2)$.[13] Thus carbazole was reacted with BuLi to generate the *N*-carbazolyl lithium salt, which was subsequently reacted with $PCl_nPh_{3-n}$ ($n = 1$–3). This method enabled **L**$^{1-3}$ to be isolated as crystalline materials in good yields. The ligands **L**$^2$ and **L**$^3$ are air- and moisture-stable in the solid state and in solution, and do not react with methanol. In contrast **L**$^1$ is air- and moisture-sensitive decomposing, when not handled in inert conditions, to $Ph_2PP(O)Ph_2$ *via* hydrolysis of the P–N bond.

The compounds **L**$^{1-3}$ were fully characterised by multinuclear NMR spectroscopy and microanalysis. The $^{31}P\{^1H\}$ NMR spectra showed single resonances at $\delta$ 32.7 for **L**$^1$, $\delta$ 52.9 for **L**$^2$ and $\delta$ 77.6 for **L**$^3$, the values for **L**$^1$ and **L**$^3$ in agreement with those previously reported.[18] The observed progressive increase in chemical shift with increase in the number of carbazolyl rings is in agreement with the reduced σ-basicity

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of the phosphines as the number of *N*-carbazolyl substituents at the phosphorus atom is increased. In a similar manner to *N*-pyrrolyl substituents, *N*-carbazolyl substituents cause a broadening of the $^{31}$P NMR line widths. The line width for **L**$^3$ is *ca.* 70 Hz which is comparable with that reported for $P(NC_4H_4)_3$ (64 Hz).[10] The $^{31}$P NMR line widths of these ligands are influenced by the quadrupolar nitrogen nuclei and this serves as a useful diagnostic tool indicating the formation of P–N bonded products.

The $^1$H and $^{13}C\{^1H\}$ NMR spectra of **L**$^{1-3}$ were assigned on the basis of $^1$H–$^1$H and $^{13}$C–$^1$H NMR correlation experiments using the numbering scheme shown in Fig. 1. All the signals were sharp at ambient temperature suggesting that the carbazolyl rings are free to rotate. In the $^1$H NMR spectra small $^5J_{HP}$ couplings were observed between the phosphorus atom and the chemically equivalent $H_4$ and $H_5$ protons and confirmed by $^1$H–$^{31}$P NMR correlation experiments. Similar $^5J_{HP}$ couplings were seen in the spectra of 7-aza-*N*-indolyl phosphines.[14]

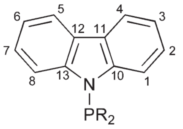

**Fig. 1** Numbering scheme for the carbazolyl ring.

### The reactions of L$^{1-3}$ with $[Rh(\mu\text{-}Cl)(CO)_2]_2$

The reactions of four equivalents of **L**$^1$ or **L**$^2$ with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ gave the complexes *trans*-[RhCl(CO)(**L**$^1$)$_2$] **1** and *trans*-[RhCl(CO)(**L**$^2$)$_2$] **2**. The products precipitated out of solution on the addition of hexane, and were purified by recrystallisation from dichloromethane–hexane. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** both contain doublets, confirming the expected *trans* geometry. The carbonyl stretching frequencies were observed in the IR spectrum at 1992 cm$^{-1}$ for **1** and at 2000 cm$^{-1}$ for **2** and are similar to those reported for the related *N*-pyrrolyl phosphine complexes *trans*-[RhCl(CO)$\{PPh_n(NC_4H_4)_{3-n}\}_2$] ($n = 2$, 1992 cm$^{-1}$; $n = 1$, 2007 cm$^{-1}$).[10] Thus the replacement of *N*-pyrrolyl with *N*-carbazolyl seems to have little effect on the electronic properties of the ligand.

The reaction between four equivalents of **L**$^3$ and $[Rh(\mu\text{-}Cl)(CO)_2]_2$ proceeded differently from the analogous reactions using **L**$^1$ and **L**$^2$, and after a few minutes the formation of a yellow precipitate **3** was observed. The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of a doublet at $\delta$ 90.0 with $^1J_{PRh}$ 257 Hz. The $^1$H NMR spectrum showed distinctive signals for all the protons of the carbazolyl ring with the signal assigned to the chemically equivalent $H_1$ and $H_8$ protons shifted to low field ($\delta$ 7.75) compared with those in the free ligand ($\delta$ 7.11–7.19). In the IR spectrum the $\nu$(CO) absorption was observed at 2015 cm$^{-1}$. Compound **3** is only sparingly soluble, which prevented the carbonyl carbon from being observed in the $^{13}C\{^1H\}$ NMR spectrum.

When the filtrate solvent was removed under reduced pressure, a white powder was observed which was revealed by NMR spectroscopy to be unreacted **L**$^3$, suggesting **3** contains a phosphine : rhodium ratio of less than 2 : 1. The identity of **3** was subsequently revealed by X-ray crystallographic studies to be the chloro-bridged dimer [Rh($\mu$-Cl)(CO)(**L**$^3$)]$_2$. Repetition of the reaction using only two equivalents of **L**$^3$ led to **3** as the only solid product. Attempts to obtain *trans*-[RhCl(CO)(**L**$^3$)$_2$] using a significant excess of ligand, higher temperature and/or prolonged reaction time were unsuccessful. Since $P(NC_4H_4)_3$ readily reacts with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ to form *trans*-[RhCl(CO)$\{P(NC_4H_4)_3\}_2$], the inability of **L**$^3$ to form the analogous complex *trans*-[RhCl(CO)(**L**$^3$)$_2$] is likely to be a consequence of its steric bulk.

### The X-ray crystal structures of *trans*-[RhCl(CO)(L$^2$)$_2$]·1.6CH$_2$Cl$_2$ (2·1.6CH$_2$Cl$_2$) and [Rh($\mu$-Cl)(CO)(L$^3$)]$_2$·2CH$_2$Cl$_2$ (3·2CH$_2$Cl$_2$)

Single crystals of *trans*-[RhCl(CO)(**L**$^2$)$_2$]·1.6CH$_2$Cl$_2$ (**2**·1.6CH$_2$Cl$_2$) were grown from the slow diffusion of hexane into a dichloromethane solution. The molecular structure of *trans*-[RhCl(CO)(**L**$^2$)$_2$] is shown in Fig. 2 and selected bond distances and angles are given in Table 1. The asymmetric unit contains half of a molecule of the metal complex and two partial occupancy molecules of dichloromethane. The metal centre is located on an inversion centre and consequently the chloride and the carbonyl ligands are disordered in a 50 : 50 ratio across this symmetry element. The tendency for rhodium complexes to crystallise in forms that involve disorder of chloride and carbonyl ligands across inversion centres has been previously reported for both mononuclear[19] and binuclear[12] complexes. The metal adopts a distorted square planar geometry with *cis* angles between 88.4(3) and 91.6(3)°. The **L**$^2$ ligands in **2**·1.6CH$_2$Cl$_2$ adopt crystallographic cone angles[20] of 171°, and the sums of the angles around N(1) and N(2) are consistent with the presence of small pyramidal distortions. The supramolecular structure of **2**·1.6CH$_2$Cl$_2$ is dominated by C–H$\cdots\pi$ interactions.

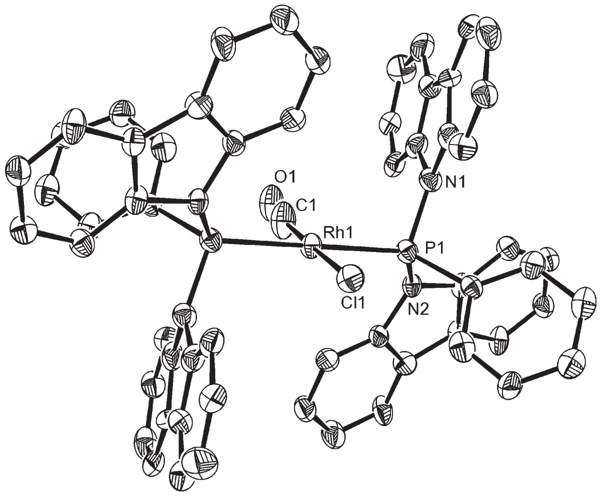

**Fig. 2** Molecular structure of *trans*-[RhCl(CO)(**L**$^2$)$_2$]·1.6CH$_2$Cl$_2$ (**2**·1.6CH$_2$Cl$_2$) with thermal ellipsoids shown at the 30% probability level and solvent molecules removed for clarity.

Single crystals of [Rh($\mu$-Cl)(CO)(**L**$^3$)]$_2$·2CH$_2$Cl$_2$ (**3**·2CH$_2$Cl$_2$) were grown from the slow diffusion of hexane into a dichloromethane solution. The molecular structure is shown in Fig. 3 and selected bond distances and angles are given in Table 1. The asymmetric unit contains half a molecule of the dimer and a molecule of dichloromethane. The complex lies about an inversion centre and the remainder is generated by symmetry. The complex consists of two rhodium centres in distorted square planar coordination geometries linked together by two bridging chlorides and with the phosphorus ligands mutually *trans* along the Rh$\cdots$Rh axis. The *cis* angles around each rhodium atom lie between 83.995(19) and 93.39(2)°. The Rh(1)$\cdots$Rh(1)′ distance of 3.590 Å indicates the absence of a metal–metal bond.

The planar conformation adopted by **3** contrasts with those reported for a number of other chloro-bridged rhodium(I) dimers, which have structures bent along the Cl$\cdots$Cl axis

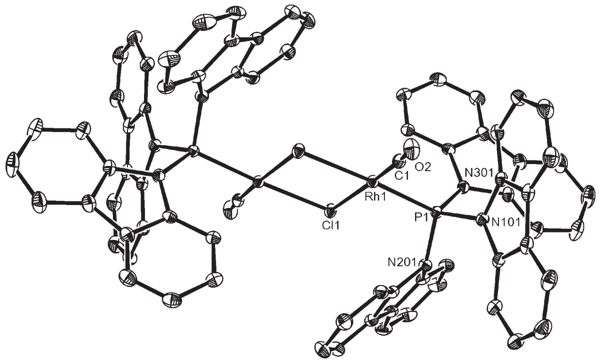

**Fig. 3** Molecular structure of [Rh($\mu$-Cl)(CO)(**L**$^3$)]$_2$·2CH$_2$Cl$_2$ (**3**·2CH$_2$Cl$_2$) with thermal ellipsoids shown at the 30% probability level and solvent molecules removed for clarity.

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**Table 1** Selected bond lengths and angles for **2**·$1.6CH_2Cl_2$[a] and **3**·$2CH_2Cl_2$[b]

| **2**·$1.6CH_2Cl_2$[a] | | **3**·$2CH_2Cl_2$[b] | |
|---|---|---|---|
| Rh(1)–P(1) | 2.311(3) | Rh(1)–P(1) | 2.2030(6) |
| Rh(1)–Cl(1) | 2.384(15) | Rh(1)–Cl(1) | 2.4142(5) |
| | | Rh(1)–Cl(1)′ | 2.4167(5) |
| Rh(1)–C(1) | 1.75(4) | Rh(1)–C(1) | 1.819(2) |
| C(1)–O(1) | 1.11(7) | C(1)–O(2) | 1.146(3) |
| P(1)–N(1) | 1.708(10) | P(1)–N(101) | 1.7039(19) |
| P(1)–N(2) | 1.696(9) | P(1)–N(201) | 1.7081(19) |
| | | P(1)–N(301) | 1.6894(19) |
| C(1)–Rh(1)–P(1) | 89.6(15) | C(1)–Rh(1)–P(1) | 93.04(7) |
| C(1)–Rh(1)–P(1)′ | 90.4(15) | C(1)–Rh(1)–Cl(1) | 89.35(7) |
| P(1)–Rh(1)–Cl(1) | 88.4(3) | P(1)–Rh(1)–Cl(1)′ | 93.39(2) |
| P(1)–Rh(1)–Cl(1)′ | 91.6(3) | Cl(1)–Rh(1)–Cl(1)′ | 83.995(19) |
| C(1)–Rh(1)–Cl(1) | 177.3(17) | P(1)–Rh(1)–Cl(1) | 176.74(2) |
| | | C(1)–Rh(1)–Cl(1)′ | 170.83(7) |
| | | Rh(1)–Cl(1)–Rh(1)′ | 96.004(19) |

[a] Primed atoms generated by the symmetry operation $-x + 1/2, -y + 3/2, -z$. [b] Primed atoms generated by the symmetry operation $-x, -y + 1, -z + 1$.

and shorter metal–metal distances. For example the complex $[Rh(\mu\text{-}Cl)(CO)(PPhMe_2)]_2$ has a Rh···Rh distance of 3.167 Å.[21] Recently the nature of such interactions and their significance in determining non-planar geometries has been addressed by means of structural analysis and MO calculations on a series of complexes of the general formula $[L_2M(\mu\text{-}X)_2ML_2]$.[22] This analysis suggested that bending is energetically favourable for rhodium(I) complexes, but since the stabilisation is small (2–3 kJ mol$^{-1}$) steric repulsion between bulky terminal substituents could lead to the formation of planar structures. This is not always the case, however, and the complex $[Rh(\mu\text{-}Cl)(Bu^t{}_2PCH_2PBu^t{}_2)]_2$ adopts a bent structure with a short metal–metal distance of 3.26 Å, despite the presence of very bulky phosphorus ligands.[23] In this case it has been suggested that the conformation adopted is influenced by packing effects. Folding along the Cl···Cl axis increases the gap between the bulky *tert*-butyl groups on one side of the molecule thus creating space for 'embedding' of the *tert*-butyl groups of a neighbouring molecule of the complex.

Geometrical calculations give a crystallographic cone angle of 191° for **L**$^3$ in **3**. Small pyramidal distortions were observed at the nitrogen atoms N(101) and N(201) in **3**, with the values for the sums of the angles around these nitrogen atoms 356.3° and 351.3° respectively, whilst that for N(301) is 358.6°. This is consistent with the P–N bonds to N(101) and N(201) being significantly longer than those to N(301). Deviations of the sum of the angles around nitrogen atoms from the ideal value of 360° are related to the presence of C–H···π and π···π stacking interactions which dominate the packing in the crystal structure. The carbazolyl rings containing N(101) and N(301) are both involved in π···π stacking interactions with the shortest C···C distances of 3.41 and 3.48 Å respectively.

## The reactions of L$^{1-3}$ with [Rh(acac)(CO)$_2$]

In order to compare IR data, it was desirable to have mononuclear carbonyl rhodium complexes for the complete series of *N*-carbazolyl phosphines. Complexes of the type [Rh(acac)(CO)(L)] were expected to be less sterically crowded than [RhCl(CO)(L)$_2$] since only one phosphine ligand is present in each complex. Moreover such complexes have previously been prepared for the entire series of *N*-pyrrolyl phenyl phosphines[24] and for the bulky phosphatri(3-methyl-*N*-indolyl)methane $P(NC_8H_4Me)_3CH$ and tri(3-methyl-*N*-indolyl)phosphine $P(NC_8H_5Me)_3$ ligands,[25,26] so a good amount of data are available for comparison.

The reaction of one equivalent of **L**$^1$, **L**$^2$ or **L**$^3$ with [Rh(acac)(CO)$_2$] in dichloromethane produced the complexes [Rh(acac)(CO)(**L**$^1$)] **4**, [Rh(acac)(CO)(**L**$^2$)] **5** and [Rh(acac)(CO)(**L**$^3$)] **6** in good yields. All the complexes were fully characterised on the basis of IR and NMR spectroscopy and microanalysis. In addition the crystal structure of **5** was determined by X-ray crystallography. The reactions were monitored by IR spectroscopy, which demonstrated increased reaction times on going from **L**$^1$ to **L**$^3$. The synthesis of **6** was particularly problematic because complete conversion in dichloromethane could only be obtained after more than 48 h under reflux using an excess of ligand. This excess proved to be difficult to separate from the desired product preventing analytically pure sample of **6** from being obtained *via* this route. Optimum reaction conditions were established using refluxing acetone as solvent, as the excess ligand crystallises on cooling to room temperature, leaving the product in solution.

$^{31}P\{^1H\}$ NMR and IR spectroscopic data for complexes **4–6** are given in Table 2 together with those for related complexes. The phosphorus chemical shift is in all cases shifted downfield from the free ligands, and the $^1J_{PRh}$ coupling constant increases with the number of *N*-carbazolyl substituents at the phosphorus atom. A similar trend has been observed for the series of phenyl *N*-pyrrolyl phosphines.[24] Trends in the IR data for **4–6** are also similar to those observed for the *N*-pyrrolyl phosphines, with *ν*(CO) increasing with the number of *N*-carbazolyl substituents. Together the NMR and IR data support the assertion that the order of decreasing π-accepting and increasing σ-donating ability is **L**$^3$ > **L**$^2$ > **L**$^1$. The $^1J_{PRh}$ data for *N*-pyrrolyl and *N*-carbazolyl phosphines suggest very similar electronic characters, though the IR data suggest $PPh_2(NC_4H_4)$ and $PPh(NC_4H_4)_2$ are more electron-withdrawing than **L**$^1$ and **L**$^2$.

## The X-ray crystal structure of [Rh(acac)(CO)(L$^2$)] 5

The X-ray crystal structure of complex [Rh(acac)(CO)(**L**$^2$)] **5** is shown in Fig. 4 and selected bond angles and distances are given in Table 3. The rhodium centre adopts a distorted square planar coordination geometry with *cis* angles ranging from 89.08(9)° to 91.02(10)°. The Rh(1)–P(1) bond distance of 2.2108(8) Å is longer than that found in the structures of [Rh(acac)(CO){$P(NC_4H_4)_3$}] [2.166(1) Å][24] and [Rh(acac)(CO){$P(NC_8H_4Me)_3CH$}] [2.1783(12)][26] but shorter than that in the structure of [Rh(acac)(CO)(PPh$_3$)] [2.244(2) Å].[27] This is in agreement with the spectroscopic data in Table 4 which indicates **L**$^2$ is a weaker σ-donor/stronger π-acceptor than PPh$_3$, but a stronger σ-donor/weaker π-acceptor than $P(NC_4H_4)_3$ or $P(NC_8H_4Me)_3CH$. This is consistent with the number of *N*-carbazolyl groups present on **L**$^2$. The Rh–O bond distances in **5** differ due to the different *trans* influences of the phosphine and carbonyl ligands. The Rh(1)–O(2) bond distance in **5** can be compared to those reported for [Rh(acac)(CO)(PPh$_3$)] [2.087(4) Å], [Rh(acac)(CO){$P(NC_4H_4)_3$}] [2.054(2) Å] and [Rh(acac)(CO){$P(NC_8H_4Me)_3CH$}] [2.043(3) Å]. The observed trend leads to the same order of phosphine electronic properties as that based on Rh–P distances.

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**Table 2** Spectroscopic data for complexes **4**–**6** and related compounds

| | $\delta(^{31}P)$ | $^1J_{PRh}$/Hz | $\nu$(CO)/cm$^{-1}$ | Ref. |
|---|---|---|---|---|
| $[Rh(acac)(CO)\{PPh_2(NC_{12}H_8)\}]$ **4** | 71.1 | 190 | 1990$^a$ | This work |
| $[Rh(acac)(CO)\{PPh(NC_{12}H_8)_2\}]$ **5** | 98.1 | 216 | 1997$^a$ | This work |
| $[Rh(acac)(CO)\{P(NC_{12}H_8)_3\}]$ **6** | 101.1 | 255 | 2012$^a$ | This work |
| $[Rh(acac)(CO)\{PPh_2(NC_4H_4)\}]$ | 90.0 | 194 | 2000$^b$ | 24 |
| $[Rh(acac)(CO)\{PPh(NC_4H_4)_2\}]$ | 104.7 | 218 | 2009$^b$ | 24 |
| $[Rh(acac)(CO)\{P(NC_4H_4)_3\}]$ | 102.5 | 251 | 2012$^b$ | 24 |
| $[Rh(acac)(CO)\{P(NC_8H_5Me)_3\}]$ | 97.4 | 248 | 2005$^a$ | 26 |
| $[Rh(acac)(CO)\{P(NC_8H_4Me)_3CH\}]$ | 65.9 | 243 | 2024$^a$ | 26 |
| $[Rh(acac)(CO)\{P(OPh)_3\}]$ | 212.1 | 293 | 2006$^b$ | 53 |
| $[Rh(acac)(CO)(PPh_3)]$ | 48.6 | 180 | 1975$^b$ | 52 |

$^a$ $CH_2Cl_2$. $^b$ KBr.

**Table 3** Selected bond lengths and angles for **5** and **8**·½$CH_2Cl_2$$^a$

| **5** | | **8**·½$CH_2Cl_2$$^a$ | |
|---|---|---|---|
| Rh(1)–P(1) | 2.2108(8) | Pd(1)–P(2) | 2.2159(18) |
| Rh(1)–C(36) | 1.792(3) | Pd(1)–C(23) | 1.991(8) |
| Rh(1)–O(1) | 2.036(2) | Pd(1)–Cl(1) | 2.3875(17) |
| Rh(1)–O(2) | 2.071(2) | Pd(1)–Cl(1)′ | 2.433(2) |
| C(36)–O(3) | 1.166(4) | P(2)–N(1) | 1.694(6) |
| P(1)–N(1) | 1.712(3) | P(2)–N(2) | 1.679(6) |
| P(1)–N(2) | 1.705(3) | P(2)–N(3) | 1.701(6) |
| C(36)–Rh(1)–P(1) | 91.02(10) | C(23)–Pd(1)–P(2) | 84.36(19) |
| C(36)–Rh(1)–O(2) | 89.82(12) | C(23)–Pd(1)–Cl(1) | 93.0(2) |
| O(1)–Rh(1)–O(2) | 89.08(9) | P(2)–Pd(1)–Cl(1) | 170.60(7) |
| O(1)–Rh(1)–P(1) | 90.01(7) | C(23)–Pd(1)–Cl(1)′ | 178.87(19) |
| C(36)–Rh(1)–O(1) | 176.97(12) | P(2)–Pd(1)–Cl(1)′ | 96.37(7) |
| O(2)–Rh(1)–P(1) | 178.26(7) | Cl(1)–Pd(1)–Cl(1)′ | 86.41(7) |
| | | Pd(1)–Cl(1)–Pd(1)′ | 93.59(7) |

$^a$ Primed atoms generated by the symmetry operation $-x + 1, -y + 1, -z + 2$.

**Table 4** Selected bond lengths and angles for **11**·2¼$CH_2Cl_2$

| | | | |
|---|---|---|---|
| Pd(1)–P(1) | 2.2199(11) | Pd(3)–P(3) | 2.2051(11) |
| Pd(1)–C(2) | 1.996(4) | Pd(3)–C(78) | 1.986(5) |
| Pd(1)–O(1) | 2.078(3) | Pd(3)–O(5) | 2.072(3) |
| Pd(1)–O(3) | 2.137(3) | Pd(3)–O(7) | 2.124(3) |
| Pd(2)–P(2) | 2.1943(10) | Pd(4)–P(4) | 2.1938(10) |
| Pd(2)–C(38) | 1.987(4) | Pd(4)–C(114) | 1.989(5) |
| Pd(2)–O(4) | 2.075(3) | Pd(4)–O(8) | 2.076(3) |
| Pd(2)–O(2) | 2.126(3) | Pd(4)–O(6) | 2.133(3) |
| P(1)–N(1) | 1.681(3) | P(3)–N(7) | 1.691(4) |
| P(1)–N(2) | 1.707(4) | P(3)–N(8) | 1.685(3) |
| P(1)–N(3) | 1.684(3) | P(3)–N(9) | 1.688(3) |
| P(2)–N(4) | 1.683(4) | P(4)–N(10) | 1.681(4) |
| P(2)–N(5) | 1.694(4) | P(4)–N(11) | 1.692(3) |
| P(2)–N(6) | 1.688(3) | P(4)–N(12) | 1.689(4) |
| C(2)–Pd(1)–O(1) | 90.15(17) | C(78)–Pd(3)–O(5) | 89.46(17) |
| O(1)–Pd(1)–O(3) | 87.13(13) | O(5)–Pd(3)–O(7) | 91.28(14) |
| C(2)–Pd(1)–P(1) | 82.76(15) | C(78)–Pd(3)–P(3) | 83.97(14) |
| O(3)–Pd(1)–P(1) | 99.34(10) | O(7)–Pd(3)–P(3) | 94.46(9) |
| O(1)–Pd(1)–P(1) | 169.21(9) | O(5)–Pd(3)–P(3) | 169.02(9) |
| C(2)–Pd(1)–O(3) | 175.14(15) | C(78)–Pd(3)–O(7) | 174.61(13) |
| C(38)–Pd(2)–O(4) | 91.42(15) | C(114)–Pd(4)–O(8) | 91.46(17) |
| O(4)–Pd(2)–O(2) | 89.80(13) | O(8)–Pd(4)–O(6) | 91.03(14) |
| C(38)–Pd(2)–P(2) | 84.13(12) | C(114)–Pd(4)–P(4) | 82.95(13) |
| O(2)–Pd(2)–P(2) | 92.98(10) | O(6)–Pd(4)–P(4) | 93.25(9) |
| O(4)–Pd(2)–P(2) | 164.48(9) | O(8)–Pd(4)–P(4) | 169.17(9) |
| C(38)–Pd(2)–O(2) | 173.35(15) | C(114)–Pd(4)–O(6) | 171.64(14) |

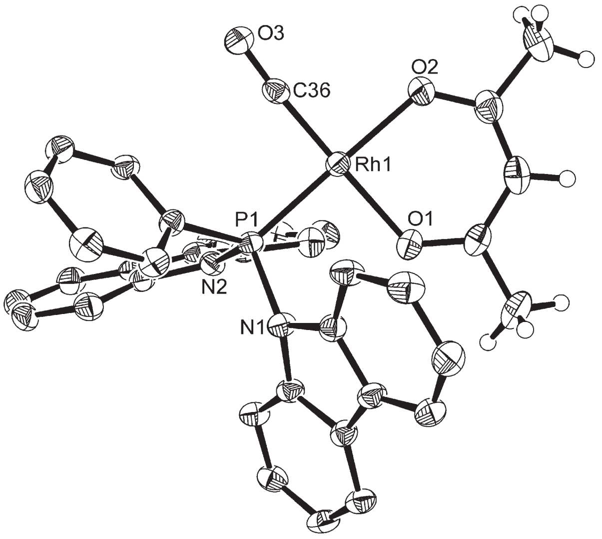

**Fig. 4** Molecular structure of $[Rh(acac)(CO)(L^2)]$ (**5**) with thermal ellipsoids shown at the 30% probability level.

The sums of the angles at the nitrogen atoms in **5** are 355.4° and 358.4°, thus indicating the presence of small pyramidal distortions. Geometric calculations give a crystallographic cone angle for **L²** in this structure of 181°, slightly larger than that observed in **2**·1.6$CH_2Cl_2$. The extended structure is dominated by the presence of C–H···π interactions.

## Palladium(II) complexes of $L^{1-3}$

The reaction of two equivalents of **L¹** with one equivalent of $[PdCl_2(cod)]$ in dichloromethane produced complex $[PdCl_2(L^1)_2]$ **7** in good yield. The $^{31}P\{^1H\}$ NMR spectrum of **7** showed a singlet at $\delta$ 51.3 which is shifted downfield compared to that of the free ligand. In contrast with **L¹**, neither **L²** nor **L³** were observed to react with $[PdCl_2(cod)]$, even on reflux. However, **L³** reacts with $[PdCl_2(NCMe)_2]$ to give the cyclometalled complex $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ **8**, which was isolated in good yield (77%) as a crystalline material.

The formation of the cyclometallated complex **8** is likely to be a consequence of the high steric requirement of **L³**, which places the carbazolyl hydrogen atom $H_1$ close enough to the metal centre so that the C–H bond is activated towards the metal insertion reaction. Cyclometallated complexes have been reported for a number of other bulky phosphorus ligands including P(*o*-Tol)₃[28] and PNp₃.[29] Such compounds have attracted attention recently as catalysts for various transition metal catalysed C–C bond formation reactions. Pre-formed or *in situ*-generated cyclometallated palladium complexes of the phosphine ligands P(*o*-Tol)₃[30] and PNp₃[31] have been reported to be excellent catalysts for Heck-type coupling reactions, and cyclometallated ligands based on phosphites[32,33] and phosphinites[34] have very high activities in Suzuki and Heck reactions.

In order to investigate the generality of cyclometallation reactions with carbazolyl phosphines, the reactions between **L¹** or **L²** and $[PdCl_2(NCMe)_2]$ were also investigated. The reaction of **L¹** with $[PdCl_2(NCMe)_2]$ proceeded similarly to the reaction of this ligand with $[PdCl_2(cod)]$, and complex **7** was isolated as a yellow powder. In contrast, the reaction between two equivalents of **L²** and $[PdCl_2(NCMe)_2]$ produced more than one compound. After crystallisation, both orange crystals and a yellow powder were obtained, and these were separated manually. The orange and yellow products were identified as $[PdCl_2(L^2)_2]$ **9** and $[PdCl\{PPh(NC_{12}H_8)(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ **10** respectively on the basis of NMR spectroscopy

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and microanalysis. The $^{31}$P{$^{1}$H} NMR spectrum of **9** showed a single resonance at $\delta$ 70.0, whereas the $^{1}$H NMR spectrum showed distinctive signals for the protons of the carbazolyl and phenyl rings of **L²**. Compound **10** was not very soluble, but the $^{31}$P{$^{1}$H} NMR spectrum showed a singlet at $\delta$ 86.8, whereas the $^{1}$H NMR showed an overlapping group of signals in the aromatic region that were consistent with the reduced symmetry engendered by the cyclometallation. The ligand **L²** therefore shows a coordination behaviour towards $[PdCl_2(NCMe)_2]$ that is midway between those observed for **L¹** and **L³**. The lower steric requirement of **L²** compared with **L³** means that the former is still able to coordinate at the metal centre but at the same time the higher steric requirement with respect to **L¹** renders formation of a cyclometallated complex possible under the mild reaction conditions used.

Since cyclometallated complexes of palladium are an important group of complexes[35] it was decided to develop a more rational method towards obtaining a cyclometalled palladium complex of **L³**. It was also desirable that such a complex would present a higher solubility than **8** to facilitate potential use in catalysis. One possible way of increasing the solubility of **8** is to replace the bridging chlorides with bridging acetate ligands, so $Pd(OAc)_2$ was used instead of $[PdCl_2(NCMe)_2]$. The reaction of one equivalent of **L³** with $Pd(OAc)_2$ in warm toluene produced the complex $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2$ **11** in good yield (90%). The complex was isolated as a yellow powder, which exhibited a good solubility in various organic solvents. Recrystallisation from dichloromethane–hexane produced crystals suitable for X-ray crystallographic studies. The $^{31}$P{$^{1}$H} NMR spectrum of **11** showed a sharp single resonance at $\delta$ 85.5. The $^{1}$H NMR spectrum showed complex signals for the aromatic protons, which integrated well with the signal for the protons of the bridging acetates to give a ratio of 46 : 6.

### The X-ray crystal structures of $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2\cdot\frac{1}{2}CH_2Cl_2$ (8·½CH₂Cl₂) and $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2\cdot 2\frac{1}{4}CH_2Cl_2$ (11·2¼CH₂Cl₂)

Crystals of $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2\cdot\frac{1}{2}CH_2Cl_2$ **8** suitable for X-ray crystallographic studies were obtained by slow diffusion of hexane into a dichloromethane solution. The asymmetric unit consisted of half a molecule of the complex and a partial occupancy dichloromethane molecule. The complex lies about an inversion centre and the remaining portion was generated by symmetry. The molecular structure is shown in Fig. 5 and selected bond distances and angles are given in Table 3. The coordination geometry at each metal centre is distorted square planar with the *cis* angles between 84.36(19) and 96.37(7)°.

The Pd···Pd distance of 3.514 Å rules out the presence of a metal–metal interaction in agreement with formal electron counting. The Pd(1)–P(1) distance of 2.2159(18) Å falls towards the lower end of the wide range of Pd–PR$_3$ bond lengths.[36] Similar short Pd–P distances have been reported for the structures of the related cyclometallated complexes such as $[Pd(\mu\text{-}OAc)\{o\text{-}CH_2C_6H_4P(o\text{-}Tol)_2\text{-}\kappa^2 P,C\}]_2$ [2.216(1) Å].[28] The Pd(1)–C(23) bond distance of 1.991(8) Å is long for a palladium–carbon bond[36] and can be compared with the value in the structure of $[Pd(\mu\text{-}Cl)\{P(OC_6H_3Bu^t_2\text{-}2,4)_2(OC_6H_2Bu^t_2\text{-}2,4)\text{-}\kappa^2 P,C\}]_2$ [2.1668(17) Å].[32]

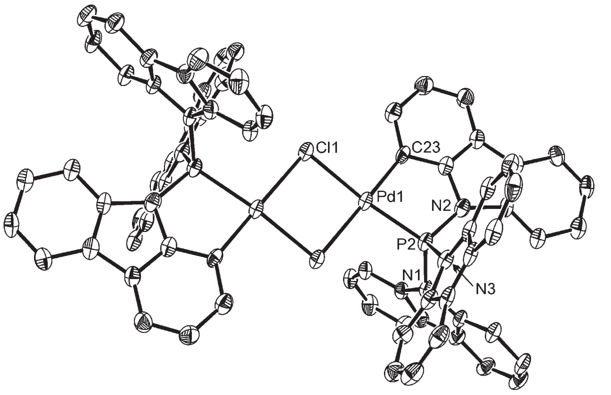

**Fig. 5** Molecular structure of $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2\cdot\frac{1}{2}CH_2Cl_2$ (**8**·½CH₂Cl₂) with thermal ellipsoids shown at the 30% probability level and solvent molecules removed for clarity.

The angles around P(1) and N(2) are of interest in evaluating the distortions concomitant with cyclometallation. The large value of C(13)–N(2)–P(1) [140.9(5)°] compared with C(24)–N(2)–P(1) [112.9(5)°] suggests that formation of the cyclometallated ring can be obtained by bending the carbazolyl ring in the direction of the metal centre. N(2) does not have a significant pyramidal distortion, as reflected by the sum of angles around this atom being 359.9°. Small pyramidal distortions are observed for the other nitrogen atoms N(1) and N(3), and these have their origins in interactions observed in the extended structure. Indeed, all of the carbazolyl rings present in **8** are involved in π···π stacking interactions.

Crystals of $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2\cdot 2\frac{1}{4}CH_2Cl_2$ (**11**·2¼CH₂Cl₂) were obtained by slow diffusion of hexane into a dichloromethane solution. The asymmetric unit contains two crystallographically independent molecules of the complex and 4½ molecules of dichloromethane. The structure of one of the complex molecules is reported in Fig. 6 and selected bond distances and angles for both molecules are reported in Table 4. The two complex molecules in **11** show minor differences in the bond lengths and angles, of which the most significant are the Pd···Pd distances, Pd(1)···Pd(2) 3.0245(4) Å and Pd(3)···Pd(4) 3.1681(4) Å. These are shorter than the Pd···Pd distance in the structure of **8** due to the geometry imposed by the bridging acetate ligands. Pyramidal distortions on the nitrogen atoms are largely absent.

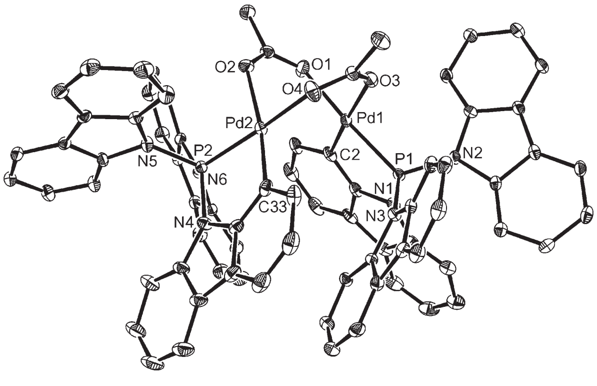

**Fig. 6** Molecular structure of one of the independent molecules present in the crystal structure of $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7\text{-}\kappa^2 P,C\}]_2\cdot 2\frac{1}{4}CH_2Cl_2$ (**11**·2¼CH₂Cl₂) with thermal ellipsoids shown at the 30% probability level and solvent molecules removed for clarity.

The angles between the two coordination planes are 43° and 50° in the two independent molecules, based on Pd(1) and Pd(3) respectively. This allows intramolecular π···π interactions to occur, with the closest inter-plane C···C distance at 3.27 Å. The Pd···Pd distances and inter-coordination plane angles are similar to those in the analogous compound based on $P(o\text{-}Tol)_3$[28] whereas the coordination planes in the $PBu^t(o\text{-}Tol)_2$ analogue are further apart [Pd···Pd 3.41 Å, angle 60°].[37] The supramolecular structure of **11**·2¼CH₂Cl₂ shows the presence of π···π stacking and C–H···π interactions.

### The synthesis and characterisation of $[Pd(L^3)_2]$ 12

Since bulky phosphorus ligands have been extensively used for the formation of coordinatively unsaturated complexes of transition metals in low oxidation states it was of interest to extend our studies on the coordination chemistry of **L³** to palladium(0)

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centres. Thus $\mathbf{L}^3$ was reacted with $[Pd_2(dba)_3]\cdot CHCl_3$ with the aim of isolating either the 14-electron complex $[Pd(\mathbf{L}^3)_2]$ or the 16-electron complex $[Pd(dba)(\mathbf{L}^3)_2]$. The stabilities of these Pd(0) complexes of $\mathbf{L}^3$ are expected to benefit not only from the steric bulk of the ligand but also from its strong π-accepting character.

When a dichloromethane solution of $[Pd_2(dba)_3]\cdot CHCl_3$ was added to a dichloromethane solution containing four equivalents of $\mathbf{L}^3$, a change in colour from dark red to yellow occurred after 2 h stirring. The addition of diethyl ether afforded precipitation of a yellow powder, which was formulated on the basis of $^{31}P\{^1H\}$ NMR, $^1H$ NMR and IR spectroscopy and microanalysis as $[Pd(\mathbf{L}^3)_2]$ **12**. The $^{31}P\{^1H\}$ NMR spectrum of **12** is composed of a single resonance at $\delta$ 75.1 slightly upfield of the free ligand. The $^1H$ NMR spectrum showed the expected signals for the carbazolyl substituents and the absence of signals for dba.

Crystals of **12** suitable for X-ray diffraction studies were obtained by reacting $[Pd_2(dba)_3]\cdot CHCl_3$ with $\mathbf{L}^3$ in toluene instead of dichloromethane. These crystals are much more stable than those obtained from dichloromethane and can be stored for weeks without significant decomposition. Moreover toluene solutions of **12** are considerably more stable than those in dichloromethane and on standing at ambient temperature under inert atmosphere do not result in the formation of palladium black. However they are not thermally stable as evidenced by the rapid formation of palladium black as soon as the temperature is increased to *ca.* 80 °C.

No intermediates of the type $[Pd(dba)(\mathbf{L}^3)_2]$ were observed in the $^{31}P\{^1H\}$ NMR spectra. This contrasts with observations made on the bulky polyaromatic phosphines $PPh_2Np$, $PPhNp_2$ and $PPh_2An$ (An = anthracenyl).[8] Under similar reaction conditions these ligands are unable to completely displace dba from $[Pd_2(dba)_3]\cdot CHCl_3$ leading to complexes of the type $[Pd(dba)(L)_2]$, even with excess phosphine. The ligand $PNp_3$ does not displace any dba from $[Pd_2(dba)_3]\cdot CHCl_3$ even using forcing conditions. The inability of the polyaromatic phosphines to form 14-electron complexes similar to **12** was attributed to their large steric demands. If this is the case, the ability of $\mathbf{L}^3$ to form **12** despite its even greater steric demand must be attributed to its increased π-acceptor character.

### The X-ray crystal structure of $[Pd(\mathbf{L}^3)_2]\cdot 2C_7H_8$ ($\mathbf{12}\cdot 2C_7H_8$)

Yellow single crystals of $[Pd(\mathbf{L}^3)_2]\cdot 2C_7H_8$ ($\mathbf{12}\cdot 2C_7H_8$) suitable for X-ray analysis were grown from a toluene solution. The crystallographic study revealed that the asymmetric unit contains two crystallographic independent halves of the complex and two molecules of toluene. Both palladium atoms lie on inversion centres, and the remaining portions of each molecule are generated by symmetry. The structure of one of the independent complex molecules is shown in Fig. 7 and selected bond distances and angles for both molecules are reported in Table 5. There are no chemically important differences in the bond distances and angles of two molecules. The presence of the inversion centres ensures linear coordination geometries with the carbazolyl substituents of the two phosphorus atoms assuming a staggered conformation. The ligands assume rotor conformations and intramolecular C–H···π interactions are present between the two phosphine ligands on each complex. The ligands adopt crystallographic cone angles of 209° in both independent molecules, which is considerably larger than the value observed in $\mathbf{3}\cdot 2CH_2Cl_2$, reflecting the greater steric demands of the rotor conformation.

The sums of the angles around the nitrogen atoms are in the range 352.7–358.3° suggesting the presence of small pyramidal distortions for some of the carbazolyl groups. The Pd–P distances of 2.2341(6) Å and 2.2408(6) Å are shorter than those in the structures of the other complexes of the type $[PdL_2]$ that have been structurally characterised—$[Pd\{P(o\text{-}Tol)_3\}_2]$ [2.276(1) Å],[7] $[Pd(PBu^t_2Ph)_2]$ [2.285(2) Å],[6] $[Pd(PBu^t_3)_2]$ [2.285(3) Å],[38] $[Pd(PCy_3)_2]$ [2.26 Å],[39] $[Pd\{PBu^t_2(C_5H_4FeCp)\}_2]$ [2.2764(7) Å],[40] $[Pd\{PCy_2(C_6H_4\{Ph\text{-}2\})\}_2]$ [2.2744(11), 2.2778(11) Å][41] and $[Pd\{P(C_6H_3Mes_2\text{-}3,5\}_2]$ [2.2838(9) Å][42]—reflecting the greater π-acceptance of $\mathbf{L}^3$. The metal centre in **12** is completely enclosed by the carbazolyl substituents such that coordination of another ligand to the metal centre without drastic rearrangements would seem not possible. This may be taken as indirect evidence to explain the inability to synthesise *trans*-$[RhCl(CO)(\mathbf{L}^3)_2]$ and $[PdCl_2(\mathbf{L}^3)_2]$ on steric grounds. The supramolecular structure of $\mathbf{12}\cdot 2C_7H_8$ is dominated by C–H···π interactions.

**Table 5** Selected bond lengths and angles for $\mathbf{12}\cdot 2C_7H_8$[a]

| | | | |
|---|---|---|---|
| Pd(1)–P(1) | 2.2341(6) | Pd(2)–P(2) | 2.2408(6) |
| P(1)–N(1) | 1.712(2) | P(2)–N(4) | 1.707(2) |
| P(1)–N(2) | 1.707(2) | P(2)–N(5) | 1.717(2) |
| P(1)–N(3) | 1.699(2) | P(2)–N(6) | 1.700(2) |
| P(1)–Pd(1)–P(1)′ | 180.0 | P(2)–Pd(2)–P(2)″ | 180.0 |

[a] Primed atoms generated by the symmetry operation −*x*, −*y*, −*z*. Double primed atoms generated by the symmetry operation −*x*, −*y*, −*z* + 1.

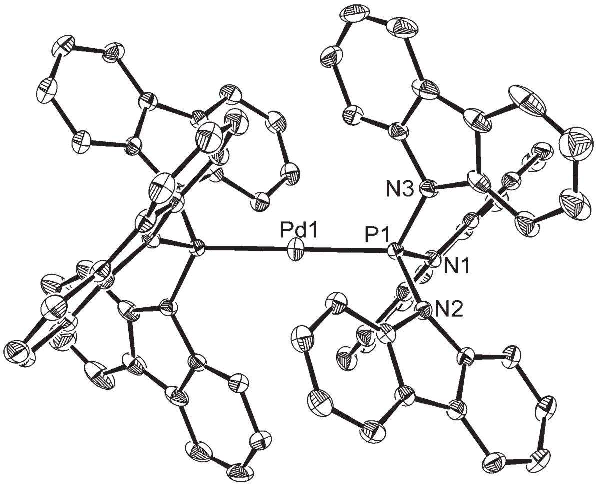

**Fig. 7** Molecular structure of one of the independent molecules present in the crystal structure of $[Pd(\mathbf{L}^3)_2]\cdot 2C_7H_8$ ($\mathbf{12}\cdot 2C_7H_8$) with thermal ellipsoids shown at the 30% probability level and solvent molecules removed for clarity.

### Intramolecular C–H···M interactions

All of the crystal structures reported in this paper show evidence of intramolecular C–H···M interactions, details of which are given in Table 6. These interactions are all best described as C–H···M hydrogen bonds as opposed to agostic[43] or pseudo-agostic[44] interactions. The description as hydrogen bonds is based partly on the geometric parameters and partly on the nature of the $d^8$ and $d^{10}$ metal centres, both of which present filled orbitals for interaction with the C–H bonds. The C–H···M interactions herein generally exhibit angles at hydrogen between 134 and 144°, typical of this type of hydrogen bond, the exceptions being compounds **5** and $\mathbf{12}\cdot 2C_7H_8$. In the structure of **5**, one of the acac oxygen atoms also acts as a hydrogen bond acceptor, and the interaction is best described as an intramolecular multi-centre hetero-acceptor hydrogen bond.[44] In $\mathbf{12}\cdot 2C_7H_8$ the C–H···Pd interactions are notably less directional and involve all of the carbazolyl rings. Short metal–hydrogen distances were also observed in the structures of $[Pd\{P(o\text{-}Tol)_3\}_2]$[7] and $[Pd\{P^tBu_3\}_2]$[7] and are likely to be a feature of all such coordinatively unsaturated molecules with bulky ligands. The observations of C–H···M hydrogen bonding parallel the ease of cyclometallation in the palladium complexes of $\mathbf{L}^2$ and $\mathbf{L}^3$, where these interactions can be regarded as intermediates on the pathway to C–H activation. It is notable that there is no evidence for any of the C–H···M interactions observed in the

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**Table 6** Intramolecular C–H···M and C–H···O hydrogen bonds present in the crystal structures of **2**·1.6$CH_2Cl_2$, **3**·2$CH_2Cl_2$, **5**, **8**·½$CH_2Cl_2$, **11**·2¼$CH_2Cl_2$ and **12**·2$C_7H_8$

| | Hydrogen bond | C···X/Å | H···X/Å | C–H···X/° |
|---|---|---|---|---|
| **2**·1.6$CH_2Cl_2$ | C(15)–H(15)···Rh(1) | 3.458 | 2.65 | 144 |
| **3**·2$CH_2Cl_2$ | C(312)–H(312)···Rh(1) | 3.402 | 2.68 | 134 |
| **5** | C(14)–H(14)···Rh(1) | 3.378 | 2.77 | 122 |
| | C(14)–H(14)···O(1) | 3.322 | 2.40 | 162 |
| **8**·½$CH_2Cl_2$ | C(11)–H(11)···Pd(1) | 3.436 | 2.65 | 140 |
| **11**·2¼$CH_2Cl_2$ | C(14)–H(14)···Pd(1) | 3.199 | 2.43 | 138 |
| | C(59)–H(59)···Pd(2) | 3.150 | 2.40 | 136 |
| | C(99)–H(99)···Pd(3) | 3.259 | 2.51 | 136 |
| | C(135)–H(135)···Pd(4) | 3.168 | 2.37 | 141 |
| **12**·2$C_7H_8$ | C(11)–H(11)···Pd(1) | 3.385 | 2.96 | 108 |
| | C(14)–H(14)···Pd(1) | 3.181 | 2.70 | 112 |
| | C(26)–H(26)···Pd(1) | 3.260 | 2.71 | 118 |
| | C(38)–H(38)···Pd(2) | 3.190 | 2.73 | 111 |
| | C(50)–H(50)···Pd(2) | 3.366 | 2.99 | 105 |
| | C(62)–H(62)···Pd(2) | 3.266 | 2.70 | 119 |

solid state being retained in solution. In all of the complexes the $^1H$ NMR spectra showed $H_1$ and $H_8$ to be equivalent.

## Conclusions

The series of *N*-carbazolyl phosphines $PPh_{3-n}(NC_{12}H_8)_n$ ($n = 1$, **L**$^1$; $n = 2$, **L**$^2$; $n = 3$, **L**$^3$) has been synthesised *via* formation of the *N*-carbazolyl lithium salt, which was subsequently reacted with the chlorophosphines $PCl_nPh_{3-n}$ ($n = 1$–3). The *N*-carbazolyl group has similar electronic properties to the *N*-pyrrolyl group, while being more sterically demanding. Thus these ligands form a series of bulky electron-withdrawing phosphines, which are an under-represented class of ligand.[2] The variation in stereoelectronic properties on increasing the number of *N*-carbazolyl groups is manifested in differences in reactivity to water, and also in the products observed from reaction with rhodium(I) and palladium(II) centres. Differences in the products of the reaction with $[Pd_2(dba)_3]\cdot CHCl_3$ and an excess of phosphine between **L**$^3$ and polyaromatic phosphines reflects the importance of both steric and electronic factors in determining the reaction products. The observation of C–H···M hydrogen bonds is observed with rhodium(I), palladium(II) and palladium(0). These hydrogen atoms can be readily activated with palladium(II) as reflected by the facile synthesis of cyclometallated products.

## Experimental

### General experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen or argon, using dry dioxgen-free solvents unless noted otherwise. Microanalyses (C, H and N) were carried out by Mr Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet 510P spectrometer as KBr pellets, Nujol mulls on KBr discs or in solutions using KBr cells. NMR spectra were recorded on JEOL EX-270, Varian Mercury 400 and Bruker Avance 300 spectrometers referenced to TMS or 85% $H_3PO_4$. The complexes $[Rh(\mu\text{-}Cl)(CO)_2]_2$,[45] $[Rh(acac)(CO)_2]$,[46] $[PdCl_2(cod)]$,[47] $[PdCl_2(NCMe)_2]$[48] and $[Pd_2(dba)_3]\cdot CHCl_3$[49] were prepared by standard literature methods. Carbazole was recrystallised from boiling acetone before use, whereas triethylamine was distilled over potassium.

### Synthesis of *N*-carbazolyldiphenylphosphine L$^1$

A 2.5 M hexane solution of BuLi (5.0 cm$^3$, 12.5 mmol) was added dropwise to a stirred THF–hexane solution (50 cm$^3$) of carbazole (2.10 g, 12.6 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Hexane was added to precipitate a white powder, which was isolated by filtration, washed with hexane and then redissolved in THF (50 cm$^3$). $PClPh_2$ (2.76 g, 12.5 mmol) was added dropwise and the reaction mixture was stirred for 3 h. The solution was filtered and the solvent was evaporated under reduced pressure. The resulting white solid was washed with hexane and dried under reduced pressure. Recrystallisation from THF–hexane at −25 °C gave colourless crystals of **L**$^1$. Yield: 4.17 g (95%). Calc. for $C_{24}H_{18}NP$: C, 82.0; H, 5.16; N, 3.99. Found: C, 81.8; H, 5.27; N, 3.90%. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): $\delta$ 32.7 (s). $^1H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 8.21 (m, 2H, $H_{4,5}$), 7.71 (m, 2H, $H_{1,8}$), 7.61 (m, 4H, $H_o$), 7.44–7.39 (m, 10H, $H_m$, $H_p$, $H_{2,7}$, $H_{3,6}$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 143.5 (d, $^2J_{CP}$ 7 Hz, $C_{10,13}$), 134.1 (d, $^1J_{CP}$ 13 Hz, $C_i$), 131.0 (d, $^2J_{CP}$ 20 Hz, $C_o$), 129.0 (s, $C_p$), 128.4 (d, $^3J_{CP}$ 6 Hz, $C_m$), 125.8 (s, $C_{11,12}$), 125.4 (s, $C_{2,7}$), 120.5 (s, $C_{4,5}$), 119.9 (s, $C_{3,6}$), 113.6 (d, $^3J_{CP}$ 12 Hz, $C_{1,8}$).

### Synthesis of di-*N*-carbazolylphenylphosphine L$^2$

As for **L**$^1$ using carbazole (3.00 g, 17.9 mmol), BuLi (7.2 cm$^3$ of 2.5 M hexane solution, 18.0 mmol) and $PCl_2Ph$ (1.61 g, 9.0 mmol). Recrystallisation from boiling acetone gave colourless crystals of **L**$^2$. Yield: 3.16 g (80%). Calc. for $C_{30}H_{21}N_2P$: C, 81.8; H, 4.81; N, 6.36. Found: C, 81.6; H, 4.80; N, 6.30%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta$ 52.9 (s). $^1H$ NMR (300.2 MHz, $CDCl_3$): $\delta$ 8.05–8.01 (m, 4H, $H_{4,5}$), 7.62–7.55 (m, 4H, $H_{1,8}$), 7.54–7.48 (m, 3H, $H_m$, $H_p$), 7.46–7.43 (m, 2H, $H_o$), 7.43–7.24 (m, 8H, $H_{2,7}$, $H_{3,6}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta$ 143.2 (d, $^2J_{CP}$ 7 Hz, $C_{10,13}$), 132.4 (d, $^1J_{CP}$ 6 Hz, $C_i$), 131.3 (d, $^3J_{CP}$ 22 Hz, $C_m$), 130.6 (s, $C_p$), 129.5 (d, $^2J_{CP}$ 6 Hz, $C_o$), 126.4 (s, $C_{11,12}$), 126.2 (s, $C_{2,7}$), 121.4 (s, $C_{3,6}$), 120.3 (s, $C_{4,5}$), 113.8 (d, $^3J_{CP}$ 14 Hz, $C_{1,8}$).

### Synthesis of tri-*N*-carbazolylphosphine L$^3$

As for **L**$^1$ using carbazole (3.00 g, 17.9 mmol), BuLi (7.2 cm$^3$ of 2.5 M hexane solution, 18.0 mmol), $PCl_3$ (3.0 cm$^3$ of 2.0 M dichloromethane solution, 6.0 mmol). Recrystallisation from boiling acetone gave colourless crystals. Yield: 2.98 g (94%). Calc. for $C_{36}H_{24}N_3P$: C, 81.6; H, 4.57; N, 7.93. Found: C, 81.2; H, 4.49; N, 7.93%. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): $\delta$ 77.6 (s). $^1H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 8.07 (d *ps* quin, 6H, $^3J_{HH}$ 8.0 Hz, $^4J_{HH}$ 1.6 Hz, $^5J_{HH}$ 0.8 Hz, $^5J_{HP}$ 0.8 Hz, $H_{4,5}$), 7.28–7.24 (m, 6H, $H_{3,6}$), 7.19–7.11 (m, 12H, $H_{1,8}$, $H_{2,7}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta$ 142.1 (d, $^2J_{CP}$ 10 Hz, $C_{10,13}$), 127.2 (s, $C_{2,7}$), 126.9 (s, $C_{11,12}$), 122.3 (s, $C_{4,5}$), 120.7 (s, $C_{3,6}$), 113.4 (d, $^3J_{CP}$ 13 Hz, $C_{1,8}$).

### Isolation of *N*-carbazolylchlorophenylphosphine

A THF solution (40 cm$^3$) of triethylamine (1.02 g, 10.1 mmol), carbazole (1.50 g, 9.0 mmol) and $PCl_2Ph$ (0.6 cm$^3$, 4.4 mmol) was stirred for 24 h. The solution was separated by filtration and the solvent eliminated under reduced pressure. The resulting white powder was extracted with hexane from which

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the compound crystallised at −25 °C. Yield: 0.410 g (30%). Calc. for $C_{18}H_{13}ClNP$: C, 69.8; H, 4.23; N, 4.52. Found: C, 70.0; H, 4.41; N, 4.45%. $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $CDCl_3$): $\delta$ 99.0 (s). $^{1}H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 8.05–8.03 (m, 2H, $H_{4,5}$), 7.67–7.64 (m, 2H, $H_o$), 7.55–7.54 (m, 2H, $H_{1,8}$), 7.46–7.42 (m, 3H, $H_m$, $H_p$), 7.37–7.30 (m, 4H, $H_{2,7}$, $H_{3,6}$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta$ 141.2 (d, $^{2}J_{CP}$ 9 Hz, $C_{10,13}$), 135.9 (d, $^{3}J_{CP}$ 27 Hz, $C_{11,12}$), 129.9 (d, $^{1}J_{CP}$ 6 Hz, $C_i$), 129.3 (d, $^{2}J_{CP}$ 2 Hz $C_o$), 128.7 (d, $^{3}J_{CP}$ 20 Hz $C_m$), 128.0 (d, $^{4}J_{CP}$ 3 Hz $C_p$), 125.1 (s, $C_{2,7}$), 121.1 (s, $C_{3,6}$), 119.3 (s, $C_{4,5}$), 113.1 (d, $^{3}J_{CP}$ 14 Hz, $C_{1,8}$).

### Synthesis of *trans*-$[RhCl(CO)(L^1)_2]$ 1

$[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.077 g, 0.20 mmol) was added with stirring to a dichloromethane solution (20 cm$^3$) of **L$^1$** (0.280 g, 0.80 mmol). After 2 h stirring the solvent was removed under reduced pressure and the resulting yellow powder washed with diethyl ether and dried under reduced pressure. Yield: 0.313 g (90%). Calc. for $C_{49}H_{36}ClN_2OP_2Rh$: C, 67.7; H, 4.17; N, 3.22. Found: C, 67.7; H, 4.21; N, 3.29%. $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 59.4 (d, $^{1}J_{PRh}$ 137 Hz). $^{1}H$ NMR (399.8 MHz, $CD_2Cl_2$): $\delta$ 8.02 (d, 4H, $^{3}J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.84–7.79 (m, 8H, $H_o$), 7.75 (d, 4H, $^{3}J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.50–7.39 (m, 12H, $H_m$, $H_p$), 7.26–7.22 (m, 4H, $H_{3,6}$), 7.13–7.09 (m, 4H, $H_{2,7}$). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 185.9 (dt, $^{1}J_{CRh}$ 75 Hz, $^{2}J_{CP}$ 16 Hz, CO), 142.8 (s, $C_{10,13}$), 133.3 (s, $C_p$), 131.4 (m, $C_o$, $C_i$), 128.7 (m, $C_m$), 126.8 (s, $C_{11,12}$), 125.5 (s, $C_{2,7}$), 121.7 (s, $C_{3,6}$), 120.1 (s, $C_{4,5}$), 116.2 (s, $C_{1,8}$). IR ($CH_2Cl_2$, cm$^{-1}$): 1992s [$\nu$(CO)].

### Synthesis of *trans*-$[RhCl(CO)(L^2)_2]$ 2

As for **1** using $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.088 g, 0.23 mmol) and **L$^2$** (0.400 g, 0.91 mmol). Yield: 0.460 g (97%). Calc. for $C_{61}H_{42}ClN_4OP_2Rh\cdot\frac{1}{2}CH_2Cl_2$: C, 67.8; H, 3.98; N, 5.14. Found: C, 67.8; H, 4.01; N, 5.24%. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta$ 86.4 (d, $^{1}J_{PRh}$ 159 Hz). $^{1}H$ NMR (300.2 MHz, $CDCl_3$): $\delta$ 8.01 (d, 8H, $^{2}J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.85–7.78 (m, 4H, $H_o$), 7.61 (dm, 8H, $^{2}J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.46–7.41 (m, 2H, $H_p$), 7.32–7.21 (m, 12H, $H_{3,6}$, $H_m$), 7.04–6.91 (m, 8H, $H_{2,7}$). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 186.1 (dt, $^{1}J_{CRh}$ 75 Hz, $^{2}J_{CP}$ 15 Hz, CO), 142.5 (m, $C_{10,13}$), 134.0 (m, $C_p$), 131.9 (m, $C_o$, $C_i$), 128.5 (m, $C_m$), 127.2 (m, $C_{11,12}$), 126.3 (s, $C_{2,7}$), 122.4 (s, $C_{3,6}$), 120.2 (s, $C_{4,5}$), 116.4 (s, $C_{1,8}$). IR ($CH_2Cl_2$, cm$^{-1}$): 2000s [$\nu$(CO)].

### Synthesis of *trans*-$[Rh(\mu\text{-}Cl)(CO)(L^3)]_2$ 3

$[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.031 g, 0.08 mmol) was added with stirring to a dichloromethane solution (20 cm$^3$) of **L$^3$** (0.085 g, 0.16 mmol). After *ca.* 15 min a yellow precipitate started to form. The reaction mixture was stirred overnight and the precipitate isolated by filtration, washed with small portions of dichloromethane and dried under reduced pressure. Yield: 0.095 g (85%). Calc. for $C_{74}H_{48}Cl_2N_6O_2P_2Rh_2\cdot\frac{1}{4}CH_2Cl_2$: C, 63.1; H, 3.46; N, 5.95. Found: C, 63.0; H, 3.48; N, 5.91%. $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 90.0 (d, $^{1}J_{PRh}$ 257 Hz). $^{1}H$ NMR (399.8 MHz, $CD_2Cl_2$): $\delta$ 8.00 (d, 12H, $^{3}J_{HH}$ 8.0 Hz, $H_{4,5}$), 7.75 (d, 12H, $^{3}J_{HH}$ 8.0 Hz, $H_{1,8}$), 7.25 (ps t, 12H, $^{3}J_{HH}$ 8.0 Hz, $H_{3,6}$), 7.03 (ps t, 12H, $^{3}J_{HH}$ 8.0 Hz, $H_{2,7}$). IR ($CH_2Cl_2$, cm$^{-1}$): 2015s [$\nu$(CO)].

### Synthesis of $[Rh(acac)(CO)(L^1)]$ 4

A dichloromethane solution (20 cm$^3$) of $[Rh(acac)(CO)_2]$ (0.100 g, 0.39 mmol) and **L$^1$** (0.141 g, 0.40 mmol) was stirred for 4 h after which the solvent was removed under reduced pressure. The resulting yellow powder was crystallised from hexane at −25 °C. Yield: 0.200 g (89%). Calc. for $C_{30}H_{25}NO_3PRh$: C, 62.0; H, 4.33; N, 2.41. Found: C, 61.4; H, 4.99; N, 2.20%. $^{1}H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 8.10 (d, 2H, $^{3}J_{HH}$ 8.4 Hz, $H_{4,5}$), 8.06 (dm, 2H, $^{3}J_{HH}$ 7.6 Hz, $H_{1,8}$), 7.74–7.68 (m, 4H, $H_o$), 7.44–7.40 (m, 2H, $H_p$), 7.38–7.33 (m, 4H, $H_m$), 7.28–7.24 (m, 2H, $H_{2,6}$), 7.20–7.15 (m, 2H, $H_{3,7}$), 5.38 (s, 1H, CH), 2.09 (s, 3H, $CH_3$), 1.39 (s, 3H, $CH_3$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta$ 189.4 (dd, $^{1}J_{CRh}$ 76 Hz, $^{2}J_{CP}$ 26 Hz, CO), 187.7 (s, C=O), 186.1 (s, C=O), 143.2 (d, *J* 2 Hz), 132.7 (d, *J* 12 Hz), 131.9 (s), 131.1 (s), 128.6 (d *J* 11 Hz), 126.7 (d, *J* 4 Hz), 125.8 (s), 121.6 (s), 120.0 (s), 116.7 (d, *J* 4 Hz), 101.1 (d, *J* 2 Hz, CH), 27.9 (d, *J* 6 Hz, $CH_3$), 26.7 (s, $CH_3$).

### Synthesis of $[Rh(acac)(CO)(L^2)]$ 5

A dichloromethane solution (30 cm$^3$) of $[Rh(acac)(CO)_2]$ (0.166 g, 0.64 mmol) and **L$^2$** (0.284 g, 0.64 mmol) was heated at reflux for 6 h after which half of the solvent was removed under reduced pressure, resulting in the formation of a yellow precipitate. Hexane was added, resulting in the formation of more precipitate, which was isolated by filtration and washed with hexane. Yield: 0.380 g (88%). Calc. for $C_{36}H_{28}N_2O_3PRh$: C, 64.5; H, 4.21; N, 4.18. Found: C, 64.2; H, 4.19; N, 4.12%. $^{1}H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 8.04 (d, 4H, $^{3}J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.89 (d, 4H, $^{3}J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.81–7.76 (m, 2H, $H_o$), 7.43–7.39 (m, 1H, $H_p$), 7.33–7.28 (m, 2H, $H_m$), 7.28–7.24 (m, 4H, $H_{3,6}$), 7.16–7.11 (m, 4H, $H_{2,7}$), 5.27 (s, 1H, CH), 2.04 (s, 3H, $CH_3$), 1.04 (s, 3H, $CH_3$). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$): $\delta$ 187.8 (dd, $^{1}J_{CRh}$ 76 Hz, $^{2}J_{CP}$ 26 Hz, CO), 187.0 (s, C=O), 185.7 (s, C=O), 142.3 (d, $^{2}J_{CP}$ 4 Hz, $C_{10,13}$), 133.7 (dd, $^{2}J_{CRh}$ 63 Hz, $^{1}J_{CP}$ 4 Hz, $C_i$), 132.1 (d, $^{2}J_{CP}$ 15 Hz, $C_o$), 131.3 (d, $^{3}J_{CP}$ 2 Hz, $C_{11,12}$), 127.9 (d, $^{3}J_{CP}$ 12 Hz, $C_m$), 126.6 (d, $^{4}J_{CP}$ 4 Hz, $C_p$), 125.9 (s, $C_{2,7}$), 121.8 (s, $C_{3,6}$), 119.5 (s, $C_{4,5}$), 116.0 (d, $^{3}J_{CP}$ 4 Hz, $C_{1,8}$), 100.6 (d, $^{3}J_{CRh}$ 2 Hz, CH), 27.4 (d, $^{3}J_{CRh}$ 5 Hz, $CH_3$), 25.4 (s, $CH_3$).

### Synthesis of $[Rh(acac)(CO)(L^3)]$ 6

An acetone solution (20 cm$^3$) of $[Rh(acac)(CO)_2]$ (0.040 g, 0.16 mmol) and **L$^3$** (0.106 g, 0.20 mmol) was heated at reflux for 8 h. On cooling the excess of **L$^3$** slowly precipitated. The solution was separated by filtration and the solvent eliminated under reduced pressure. The resulting yellow powder was washed with hexane and dried under reduced pressure. Yield: 0.100 g (85%). Calc. for $C_{42}H_{31}N_3O_3PRh$: C, 66.4; H, 4.11; N, 5.53. Found: C, 66.2; H, 4.10; N, 5.43%. $^{1}H$ NMR (399.8 MHz, $CDCl_3$): $\delta$ 7.98 (d, 6H, $^{3}J_{HH}$ 8.0 Hz, $H_{4,5}$), 7.74 (d, 6H, $^{3}J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.27–7.21 (m, 6H, $H_{3,6}$), 7.07–7.03 (m, 6H, $H_{2,7}$), 5.17 (s, 1H, CH), 1.96 (s, 3H, $CH_3$), 0.81 (s, 3H, $CH_3$).

### Synthesis of $[PdCl_2(L^1)_2]$ 7

$[PdCl_2(cod)]$ (0.230 g, 0.81 mmol) was added to a dichloromethane solution (30 cm$^3$) of **L$^1$** (0.605 g, 1.72 mmol) with stirring. After a few minutes a yellow precipitate started to form. Stirring was continued for a further 2 h and the precipitate isolated by filtration, washed with hexane and dichloromethane, then dried under reduced pressure. Yield: 0.423 g (60%). Calc. for $C_{48}H_{36}Cl_2N_2P_2Pd\cdot CH_2Cl_2$: C, 61.0; H, 3.97; N, 2.90. Found: C, 61.4; H, 3.97; N, 3.10%. $^{31}P\{^{1}H\}$ NMR (109.3 MHz, $CD_2Cl_2$): $\delta$ 51.3 (s). $^{1}H$ NMR (270.2 MHz, $CD_2Cl_2$): $\delta$ 8.02 (d, 4H, $^{2}J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.84–7.79 (m, 8H, $H_o$), 7.75 (d, 4H, $^{2}J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.50–7.39 (m, 12H, $H_p$, $H_m$), 7.26–7.22 (m, 4H, $H_{3,6}$), 7.13–7.09 (m, 4H, $H_{2,7}$).

### Formation of $[Pd(\mu\text{-}Cl)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2$ 8

A dichloromethane solution (20 cm$^3$) of **L$^3$** (0.100 g, 0.19 mmol) and $[PdCl_2(NCMe)_2]$ (0.048 g, 0.19 mmol) was stirred for 4 h at room temperature. The solution was layered with hexane and left at ambient temperature. After 2 days small orange crystals were present which were separated by filtration. Yield 0.096 g (77%). Calc. for $C_{72}H_{46}Cl_2N_6P_2Pd_2\cdot CH_2Cl_2$: C, 61.5; H, 3.39; N, 5.89. Found: C, 61.3; H, 3.44; N, 5.85%.

### Formation of $[PdCl_2(L^2)_2]$ 9 and $[Pd(\mu\text{-}Cl)\{PPh(NC_{12}H_8)\text{-}(NC_{12}H_7)\text{-}\kappa^2 P,C\}]_2$ 10

$[PdCl_2(NCMe)_2]$ (0.059 g, 0.23 mmol) was added to a dichloromethane solution (20 cm$^3$) of **L$^2$** (0.200 g, 0.45 mmol) with stirring. The mixture was stirred for 8 h and the solvent removed under reduced pressure. The resulting yellow powder was washed

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with diethyl ether, dissolved in dichloromethane and layered with hexane. On standing orange crystals and a yellow powder separated out of solution. The crystals and the powder were separated manually. **9**: Calc. for $C_{60}H_{42}Cl_2N_4P_2Pd\cdot\tfrac{1}{4}CH_2Cl_2$: C, 67.0; H, 3.97; N, 5.19. Found: C, 66.9; H, 3.94; N, 5.26%. $^{31}P\{^1H\}$ NMR (109.3 MHz, $CD_2Cl_2$): $\delta$ 70.0 (s). $^1H$ NMR (300.2 MHz, $CD_2Cl_2$): $\delta$ 8.03 (d, 8H, $^2J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.67–7.43 (m, 6H, $H_o$, $H_p$), 7.50 (d, 8H, $^2J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.28–7.21 (m, 12H, $H_m$, $H_{3,6}$), 7.02–6.96 (m, 8H, $H_{2,7}$). **10**: Calc. for $C_{60}H_{40}Cl_2N_4P_2Pd_2\cdot CH_2Cl_2$: C, 58.7; H, 3.39; N, 4.49. Found: C, 58.5; H, 3.42; N, 4.38%. $^{31}P\{^1H\}$ NMR (109.3 MHz, $CD_2Cl_2$): $\delta$ 86.8 (s).

### Synthesis of $[Pd(\mu\text{-}O_2CCH_3)\{P(NC_{12}H_8)_2(NC_{12}H_7)\text{-}\kappa^2P,C\}]_2$ 11

**L³** (0.172 g, 0.32 mmol) was added to a toluene solution (20 cm³) of $Pd(OAc)_2$ (0.071 g, 0.32 mmol) with stirring. The solution which had rapidly changed colour form dark red to yellow was heated at 50 °C for 10 min and then allowed to cool to ambient temperature. Stirring was continued for 1 h, after which half of the solvent was evaporated under reduced pressure and hexane added to precipitate a yellow powder. The precipitate was isolated by filtration, washed with hexane and dried under reduced pressure. Yield: 0.198 g (90%). Calc. for $C_{76}H_{52}N_6O_4P_2Pd_2\cdot\tfrac{1}{2}CH_2Cl_2$: C, 64.2; H, 3.73; N, 5.87. Found: C, 64.4; H, 4.05; N, 5.42%. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 85.5 (s). $^1H$ NMR (399.8 MHz, $CD_2Cl_2$): $\delta$ 7.87 (br, 8H), 7.60 (d, 4H, $J$ 8.0 Hz), 7.14–7.06 (m, 12H), 7.00–6.97 (m, 4H), 6.83 (br, 8H), 6.71–6.66 (m, 6H), 6.27–6.24 (m, 2H), 5.87–5.82 (m, 2H), 2.01 (s, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 180.4 (s, $CO_2$), 140.3 (m), 136.5 (m), 133.5 (m), 133.5 (s), 128.7 (s), 127.2 (s), 126.1 (s), 124.7 (s), 122.8(s), 122.6(s), 121.8 (s), 121.0 (s), 120.4 (m), 118.1 (m), 116.8 (s), 115.8 (s), 115.5 (s), 25.3 (s, $CH_3$). IR (Nujol, cm⁻¹): 1577s, 1560s [$\nu(CO_2)$].

### Synthesis of $[Pd(L^3)_2]$ 12

A toluene solution (20 cm³) containing $[Pd_2(dba)_3]\cdot CHCl_3$ (0.130 g, 0.13 mmol) and **L³** (0.266 g, 0.50 mmol) was stirred for 4 h with the formation of a pale yellow powder. This was separated by filtration, washed with small amounts of toluene and dried under reduced pressure. Yield: 0.278 g (95%). Calc. for $C_{72}H_{48}N_6P_2Pd\cdot 2C_7H_8$: C, 76.5; H, 4.78; N, 6.23. Found: C, 76.5; H, 4.82; N, 6.36%. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 75.1 (s). $^1H$ NMR (399.8 MHz, $CD_2Cl_2$): $\delta$ 8.01 (d, 12H, $^2J_{HH}$ 7.6 Hz, $H_{4,5}$), 7.16 (d, 12H, $^2J_{HH}$ 8.4 Hz, $H_{1,8}$), 7.13–7.09 (m, 12H, $H_{3,5}$), 6.50–6.46 (m, 12H, $H_{2,6}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ 138.7 (m), 129.7 (s), 128.9 (s), 126.0 (s), 123.1 (s), 120.6 (s).

### Crystallography

Single crystals of compounds **2**·1.6$CH_2Cl_2$, **3**·2$CH_2Cl_2$, **5**, **8**·½$CH_2Cl_2$, **11**·2¼$CH_2Cl_2$ and **12**·2$C_7H_8$ were analysed using a Nonius Kappa CCD diffractometer and molybdenum radiation throughout. Details of the data collections, solutions and refinements are given in Table 7. The structures were solved using SHELXS-97[50] and refined using SHELXL-97.[51] Absorption corrections (semi-empirical from equivalent reflections) were applied to data for **2**·1.6$CH_2Cl_2$, **3**·2$CH_2Cl_2$, **11**·2¼$CH_2Cl_2$ and **12**·2$C_7H_8$. [Max./min. transmission factors 0.94 0.83, 0.92 0.87, 0.94 0.83 and 0.97 0.84 respectively]. Convergence was routine throughout with the exception of the observations below.

Despite valiant recrystallisation efforts, the optimum quality crystal for **2**·1.6$CH_2Cl_2$ was of mediocre quality, and very thin. Early fall-off in diffracting power is reflected in $R$(sigma), $R$(int), final residuals for these data and the anomalously large residual electron density maximum in the Difference Fourier map within 1.505 Å of H(11). Structural solution revealed that the asymmetric in this structure unit contains one half of a molecule of the metal complex, with the metal located at an inversion centre. Consequently, the chloride and carbonyl ligands

**Table 7** Crystallographic information for compounds **2**·1.6$CH_2Cl_2$, **3**·2$CH_2Cl_2$, **5**, **8**·½$CH_2Cl_2$, **11**·2¼$CH_2Cl_2$ and **12**·2$C_7H_8$

| | **2**·1.6$CH_2Cl_2$ | **3**·2$CH_2Cl_2$ | **5** | **8**·½$CH_2Cl_2$ | **11**·2¼$CH_2Cl_2$ | **12**·2$C_7H_8$ |
|---|---|---|---|---|---|---|
| Formula | $C_{62.6}H_{45.2}Cl_{4.2}N_4OP_2Rh$ | $C_{76}H_{52}Cl_6N_6O_2P_2Rh_2$ | $C_{36}H_{28}N_2O_3PRh$ | $C_{72.5}H_{47}Cl_3N_6P_2Pd_2$ | $C_{78.25}H_{56.5}Cl_{4.5}N_6O_4P_2Pd_2$ | $C_{86}H_{64}N_6P_2Pd$ |
| $M$ | 1183.17 | 1561.70 | 670.48 | 1383.25 | 1579.06 | 1349.77 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $C2/c$ | $P$-1 | $P2_1$ | $C2/c$ | $P$-1 | $P2_1/a$ |
| $a$/Å | 23.578(3) | 9.6961(1) | 9.5970(2) | 24.1570(6) | 14.1030(2) | 17.3830(1) |
| $b$/Å | 10.7760(15) | 10.4176(2) | 9.6070(3) | 13.6460(4) | 20.2240(2) | 17.6020(1) |
| $c$/Å | 22.130(3) | 16.6691(2) | 16.4220(3) | 19.1730(5) | 26.1330(2) | 23.0830(2) |
| $\alpha$/° | 90 | 100.410(1) | 90 | 90 | 82.938(1) | 90 |
| $\beta$/° | 102.729(10) | 93.018(1) | 101.828(2) | 96.119(1) | 76.081(1) | 110.840(1) |
| $\gamma$/° | 90 | 96.993(1) | 90 | 90 | 75.331(1) | 90 |
| $U$/Å³ | 5484.5(13) | 1638.90(4) | 1481.93(6) | 6284.3(3) | 6983.67(13) | 6600.76(8) |
| $Z$ | 4 | 1 | 2 | 4 | 4 | 4 |
| $\mu$/mm⁻¹ | 0.621 | 0.852 | 0.670 | 0.799 | 0.790 | 0.383 |
| Reflections collected | 17517 | 45302 | 28158 | 51606 | 84972 | 134895 |
| Independent reflections | 4739 | 7542 | 6747 | 5516 | 29695 | 15090 |
| $R$(int) | 0.1594 | 0.0534 | 0.0807 | 0.1403 | 0.0683 | 0.0842 |
| $R$1, w$R$2 | 0.1231, 0.2980 | 0.0331, 0.0778 | 0.0353, 0.0727 | 0.0671, 0.1453 | 0.0543, 0.1184 | 0.0484, 0.1218 |
| $R$ indices (all data) | 0.2164, 0.3661 | 0.0445, 0.0824 | 0.0466, 0.0772 | 0.1205, 0.1706 | 0.0864, 0.1310 | 0.0741, 0.1383 |

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are disordered in a 1 : 1 ratio about this symmetry element. The asymmetric unit was also found to contain two dichloromethane fragments, each at 0.4 occupancy. These solvent fragments are proximate to crystallographic symmetry elements and hence are disordered. Partial solvent atoms were refined isotropically, and hydrogen atoms were omitted therein.

In $\mathbf{3}\cdot 2CH_2Cl_2$ the asymmetric unit was also seen to consist of one half of a molecule of **3** plus one molecule of dichloromethane. The solvent chlorine atoms were disordered but readily modelled. Nonetheless, analysis of the least squares output indicated that the largest shifts were associated with the partial solvent carbons [C(40), C(40B)]. Consequently, the positional coordinates of these partial occupancy atoms were fixed in the final convergence run.

The asymmetric unit in $\mathbf{11}\cdot 2\frac{1}{4}CH_2Cl_2$ was seen to comprise two molecules of **11** in addition to four and a half molecules of dichloromethane. Three of the solvent molecules [*i.e.* those based on C(153), C(154) and C(155)] were seen to exhibit full site occupancy with no disorder. However, the solvent molecule based in C(156) exhibited 50% occupancy and the chlorines therein were best modelled as being evenly distributed over 3 sites each at 0.33 occupancy. The remaining solvent molecule was also disordered. Optimum refinement was achieved by treating this dichloromethane as being shared between 3 sites based on C(157) (50%), C(158) (25%) and C(159) (25%). Carbon chlorine bond distances were restrained to being the same within individual disordered fragments, as were the ADPs in the individual fragments of the molecule based on C(157)–(159). However, analysis of the least squares output indicated that the most diffuse region of the electron density map surrounded the partial solvent carbons [C(157), C(158), C(159)], which also registered the largest shifts. Consequently, the positional coordinates of these partial occupancy atoms were not refined in the final convergence run.

The asymmetric unit in $\mathbf{12}\cdot 2C_7H_8$ was seen to be equivalent to two independent halves of the palladium complex, in addition to two full molecules of toluene. One of the toluene molecules is slightly disordered, but attempts to model this disorder did not afford any significant improvement in convergence.

Crystallographic data for compounds $\mathbf{2}\cdot 1.6CH_2Cl_2$, $\mathbf{3}\cdot 2CH_2Cl_2$, **5**, $\mathbf{8}\cdot \frac{1}{2}CH_2Cl_2$, $\mathbf{11}\cdot 2\frac{1}{4}CH_2Cl_2$ and $\mathbf{12}\cdot 2C_7H_8$ have been deposited as CCDC 241491–241496.

See http://www.rsc.org/suppdata/dt/b4/b408841g/ for crystallographic data in .CIF or other electronic format.

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