Syntheses and Structures of *exo*- and *endo*-Cyclopalladated Phenylhydrazones†

Jaume Granell,*[,a] **Rosa Moragas,**[a] **Joaquim Sales,***[,a] **Mercè Font-Bardía**[b] **and Xavier Solans**[b]
[a] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain*
[b] *Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès, s/n, 08028 Barcelona, Spain*

The reaction of substituted benzylidenephenylhydrazones with palladium(II) salts has been found to give *exo* in preference to *endo* five-membered metallacycles. The *endo* derivatives can only be obtained if the hydrazone phenyl ring contains chlorine substituents in the *ortho* or *meta* positions. The tendency of these hydrazone ligands to give *exo* derivatives, in contrast to the results found with similar *N*-benzylideneamines which favour the formation of *endo*-palladocycles, can be explained by the planarity of the hydrazone ligands, which favours the interaction of the C–H bond of the hydrazone phenyl ring with the palladium. Moreover, the aminic nitrogen atom activates this phenyl ring to electrophilic attack. The crystal structures of two of the metallacycles have been determined.

Cyclopalladation reactions have been widely studied in the past few years, and several reviews covering different aspects have been published.[1] Recent work has shown that the early rules proposed by Cope and Friedrich,[2] from cyclopalladation of *N*-benzylamines, especially the strong tendency to form five-membered metallacycles containing palladium–aromatic carbon bonds, are not strictly followed by other similar N-donor ligands. The tendency of imines to give *endo*-metallacycles (the C=N double bond is included in the metallacycle) is so strong that in mesitylimines the activation of an aliphatic C–H bond, with formation of a six-membered ring, takes place in preference to that of an aromatic C–H bond with formation of a five-membered ring.[3] Thus, it is necessary to extend the study to other N-donor ligands susceptible to metallation, in order to obtain more information about the factors that influence the ease and mode of cyclometallation reactions.

In contrast with other N-donor ligands, like amines, imines and azobenzenes, which have been extensively studied, less attention has been paid to arylhydrazones. Thus, the cyclopalladation of only a few hydrazones, derived from ketones, mainly acetophenone or benzophenone, and phenylhydrazines has been reported.[4] There is also one report on the cyclopalladation of the acetylhydrazone of acetylferrocene.[5] The compounds obtained are in all cases *endo* five-membered derivatives, except the 2,4,6-$Me_3C_6H_2C(Me)=NHC_6H_3(NO_2)_2$-2,4 derivative, which contains bulky substituents on the carbonylic carbon atom, and the *ortho* positions of the benzal ring are blocked by methyl groups; in this case the *exo*-metallacycle is obtained.[6] The number of cyclopalladated hydrazones derived from aldehydes is even lower. Thus, to the best of our knowledge, the compounds $[\{\overline{PdCl(C_6H_4NHN}=CHR)\}_2]$ (R = H or Me) are the only ones reported.[7] These cyclometallated compounds are *exo* five-membered derivatives, but is not possible to form *endo*-metallacycles with these hydrazones.

In this paper we report the results obtained in the cyclopalladation of hydrazone derivatives of benzaldehydes. They are derivatives of substituted benzaldehydes and phenylhydrazones, except two derivatives of *N*,*N*-dimethylhydrazine. These hydrazones are suitable ligands to study cyclometallation reactions because they can undergo metallation on different carbon atoms, giving metallacycles with different structures. Thus, *endo*- or *exo*-metallacycles can be obtained according to the metallated phenyl ring and the isomeric (*E* or *Z*) form adopted by the ligand. Mesitylhydrazones allow simultaneous comparison of the metallation tendency of aromatic or aliphatic carbon atoms, and the importance of the number of members of the ring formed. The electronic and steric effects of the substituents of the phenyl rings can also be estimated.

Results and Discussion

The action of $PdCl_2$ on the hydrazones **Ia**–**Ic** was examined in ethanol at room temperature for 3 d. The chloro-bridged dimeric compounds formed were treated with PPh_3 (1 : 1) in order to obtain more soluble monomeric derivatives **1**. *exo*-Metallacycles were obtained in good yields (Scheme 1). This contrasts with the strong tendency of *N*-benzylideneamines to form *endo*-metallacycles.[3b,8]

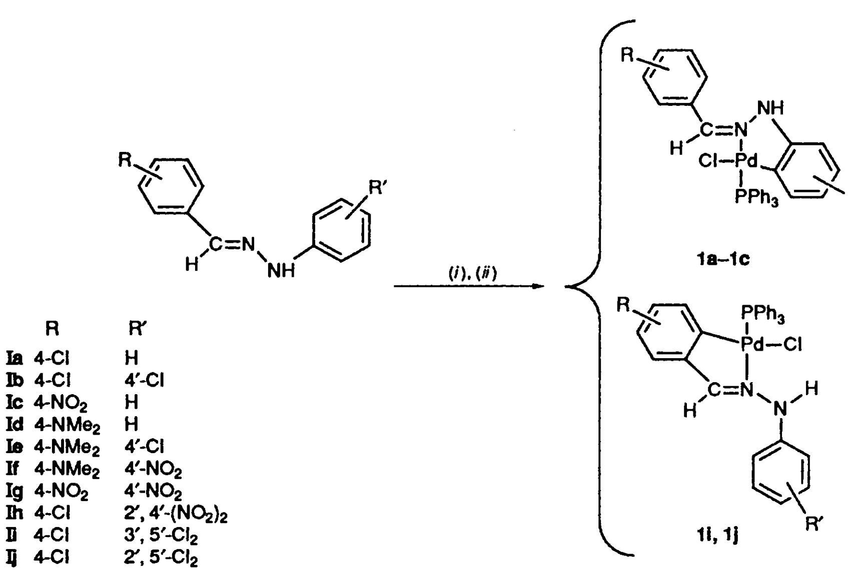
The action of $PdCl_2$ on the hydrazones **Id**–**If** was also studied. These ligands contain an electron-donating NMe_2 substituent in the benzal ring which favours the electrophilic attack of Pd^{II} and the formation of *endo*-metallacycles was expected; however, only decomposition of the ligand and formation of metallic palladium was observed. On the other hand, no reaction occurred with hydrazones **Ig** and **Ih**, containing electron-withdrawing substituents in the phenylhydrazine ring, and the unco-ordinated hydrazone was recovered in high yield.

The presence of a non-co-ordinating substituent in the carbon atom adjacent to the metallation position hinders the cyclometallation reaction.[3b,9] The action of $PdCl_2$ on the hydrazones **Ii** and **Ij**, containing chlorine substituents in the *ortho* or *meta* positions of the phenylhydrazine ring, afforded only the *endo*-metallacycles in good yields. *endo*-Metallacycles were also obtained from hydrazone **Ik**. This *N*,*N*-dimethylhydrazine derivative does not permit the formation of *exo*-metallacycles (Scheme 2).

As mentioned above, it is not difficult to obtain *endo* six-membered cyclometallated compounds from imines, containing palladium–aliphatic carbon bonds. In order to achieve activation of aliphatic C–H bonds of hydrazones the ligands **Il**–**Io** were studied (Schemes 2 and 3), but in no case was activation of

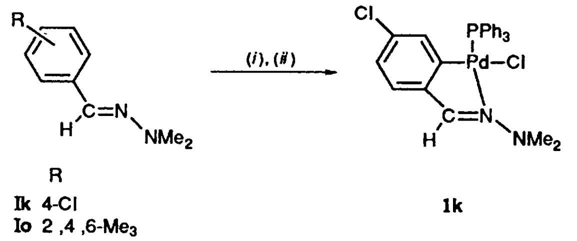
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



	R	R′
Ia	4-Cl	H
Ib	4-Cl	4′-Cl
Ic	4-NO$_2$	H
Id	4-NMe$_2$	H
Ie	4-NMe$_2$	4′-Cl
If	4-NMe$_2$	4′-NO$_2$
Ig	4-NO$_2$	4′-NO$_2$
Ih	4-Cl	2′,4′-(NO$_2$)$_2$
Ii	4-Cl	3′,5′-Cl$_2$
Ij	4-Cl	2′,5′-Cl$_2$

Scheme 1 (*i*) PdCl$_2$, EtOH, room temperature, 72 h; (*ii*) PPh$_3$, acetone, reflux, 1 h



	R
Ik	4-Cl
Io	2,4,6-Me$_3$

Scheme 2 (*i*) PdCl$_2$, EtOH, room temperature, 72 h; (*ii*) PPh$_3$, acetone, reflux, 1 h

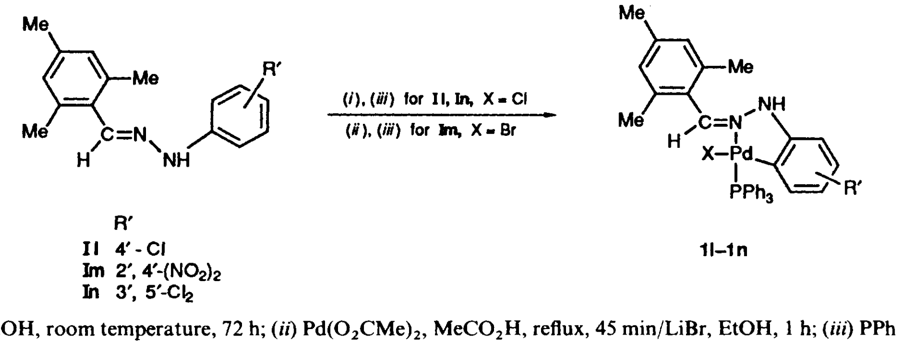
aliphatic C–H bonds detected. The *exo*-metallacycle was obtained with hydrazone **Il**, in good agreement with the strong tendency of hydrazones to afford such metallacycles. *exo*-Metallacycles were also obtained from hydrazone **Im**, which contains two electron-withdrawing substituents in the phenylhydrazine ring, and from **In**, which contains non-co-ordinating substituents in the *meta* positions of the phenylhydrazone ring. No cyclometallated compound was obtained from hydrazone **Io**, which does not permit the formation of *exo* derivatives. This different behaviour between imines and hydrazones could be explained by the higher instability of hydrazones. Only 2,4-dinitrophenylhydrazine derivatives can be treated under these energetic conditions. Hydrazone **Im** can be metallated only under these conditions. No cyclometallated compound was obtained from this ligand when it was treated with PdCl$_2$ in ethanol.

All the *exo*-metallacycles obtained have the hydrazone ligand in the *Z* form, thus, the $E \longrightarrow Z$ isomerization occurs during the cyclometallation process, in order to decrease the steric repulsion between the phenylhydrazine ring and 'PdX' moiety. If the metallation took place without isomerization of the ligand, the *exo*-cyclopalladated derivatives formed would have the phenyl ring and the PdX group on the same side of the C=N bond. Analogous results have been reported for imine derivatives.[3b]

The stability of the Pd–N bond is highly dependent on the basicity of the nitrogen atom in the imine cyclometallated compounds. Thus, while *N*-benzylideneaniline derivatives give complexes without Pd–N bonds,[10] an excess of PPh$_3$ does not break the Pd–N bond of *N*-benzylidenebenzylamine derivatives, having a more basic nitrogen atom.[8] The Pd–N bond is broken in all the hydrazone derivatives studied and compounds **2**, [PdX(C–N)(PPh$_3$)$_2$], with two PPh$_3$ are obtained if an excess of phosphine is added to the cyclometallated complexes. Compounds **2** lose one molecule of PPh$_3$, giving **1**, $[\overline{\mathrm{PdX(C{-}N})}(\mathrm{PPh_3})]$ when eluted with CHCl$_3$ over silica gel.

Characterization.—All the new compounds obtained are yellow air-stable solids. Compounds **1** and **2** are soluble in chloroform and dichloromethane and slightly soluble in ethanol and diethyl ether. Their IR spectra show the typical bands of co-ordinated hydrazones and triphenylphosphine.

Proton and ^{31}P NMR spectral data for compounds **1** and **2**, and ^{1}H NMR data for the free hydrazones, are given in Table 1. The assignment of the proton NMR signals affords conclusive evidence of the palladation position (*endo* or *exo* structure). The aromatic proton signals of the metallated ring in compounds **1**, which contains a Pd–N bond, are shifted to high field; this effect must be caused by a phosphine phenyl ring, in accordance with a *cis* arrangement of the phosphine and the metallated ring and thus a *trans* disposition of phosphorus, and nitrogen atoms. The ^{31}P chemical shifts of compounds **1** are consistent with the *trans*



	R′
Il	4′-Cl
Im	2′,4′-(NO$_2$)$_2$
In	3′,5′-Cl$_2$

Scheme 3 (*i*) PdCl$_2$, EtOH, room temperature, 72 h; (*ii*) Pd(O$_2$CMe)$_2$, MeCO$_2$H, reflux, 45 min/LiBr, EtOH, 1 h; (*iii*) PPh$_3$, acetone, reflux, 1 h

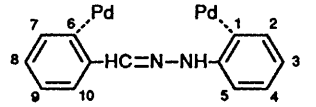
Table 1 Proton[a] and ^{31}P[b] NMR data

Compound	Aromatic	HC=N, NH	Aliphatic	^{31}P
Ia	7.60 [d, ^3J(HH) = 8.7, H^6, H^{10}] 7.37–7.27 (br m, H^2, H^4, H^7, H^9) 7.13 [d, ^3J(HH) = 7.6, H^1, H^5] 6.91 [t, ^3J(HH) = 7.6, H^3]	7.63 (s, HC=N) NH[c]		
1a	7.85–7.34 (br m, H^6, H^7, H^9, H^{10}, PPh_3) 6.84 [t, ^3J(HH) = 7.9, H^4] 6.55 [d, ^3J(HH) = 8.1, H^5] 6.34 [t, ^3J(HH) = 8.0, H^3] 6.13 [t, ^4J(HP) = ^3J(HH) = 8.0, H^2]	8.69 [d, ^4J(HP) = 4.41, HC=N] 8.13 [d, ^4J(HP) = 3.61, NH]		43.4
2a	7.80–6.60 (br m, H^{2-10}, PPh_3)	8.62 (s, HC=N) 8.08 (s, NH)		23.6
Ib	7.57 [d, ^3J(HH) = 8.3, H^6, H^{10}] 7.36–7.21 (br m, H^2, H^4, H^7, H^9) 7.02 [d, ^3J(HH) = 7.6, H^1, H^5]	7.63 (s, HC=N) NH[c]		
1b	7.82–7.35 (br m, H^6, H^7, H^9, H^{10}, PPh_3) 6.76 [dd, ^3J(HH) = 8.3, ^4J(HH) = 2.1, H^4] 6.45 [d, ^3J(HH) = 8.3, H^5] 6.15 [dd, ^4J(HH) = 2.1, ^4J(HP) = 6.8, H^2]	8.61 [d, ^4J(HP) = 3.8, HC=N] 8.10 [d, ^4J(HH) = 3.1, NH]		42.3
2b	7.90–6.80 (br m, H^{2-10}, PPh_3)	8.30 (s, HC=N) NH[c]		24.0
Ic	8.23 [d, ^3J(HH) = 8.11, H^7, H^9] 7.78 [d, ^3J(HH) = 8.11, H^6, H^{10}] 7.32 [t, ^3J(HH) = 7.37, H^2, H^4] 7.16 [d, ^3J(HH) = 8.11, H^1, H^5] 6.96 [t, ^{3}J(HH) = 7.37, H^3]	7.71 (s, HC=N) 7.27 (s, NH)		
1c	8.40 [d, ^3J(HH) = 8.23, H^7, H^9] 8.26–7.38 (br m, H^6, H^{10}, PPh_3) 6.84 [t, ^3J(HH) = 8.23, H^4] 6.58 [d, ^3J(HH) = 8.23, H^5] 6.36 [t, ^3J(HH) = 8.23, H^3] 6.16 [t, ^3J(HH) = 8.23, ^4J(HP) = 8.3, H^2]	8.78 [d, ^4J(HP) = 4.43, HC=N] NH[c]		42.2
2c	8.2–7.1 (br m, H^6, H^7, H^9, H^{10}, PPh_3) 7.0–6.0 (br m, H^{2-5})	8.53 (s, HC=N) NH[c]		23.7
Ii	7.60 [d, ^3J(HH) = 7.8, H^6, H^{10}] 7.33 [d, ^3J(HH) = 7.8, H^7, H^9] 6.97 [d, ^4J(HH) = 2.7, H^1, H^5] 6.87 [t, ^4J(HH) = 2.7, H^3]	7.64 (s, HC=N) 7.26 (s, NH)		
1i	8.80–6.90 (br m, H^1, H^3, H^5, H^9, H^{10}, PPh_3) 6.23 [dd, d, ^4J(HP) = 7.9, ^4J(HH) = 2.5, H^7]	8.10 [d, ^4J(HP) = 5.0, HC=N] 9.31 [d, ^4J(HP) = 3.2, NH]		40.3
2i	7.80–7.20 (br m, H^1, H^3, H^5, H^9, H^{10}, PPh_3) 6.80 [d, ^4J(HH) = 2.5, H^7]	HC=N[c] NH[c]		23.2
Ij	7.61 [d, ^3J(HH) = 7.6, H^6, H^{10}] 7.58 [d, ^4J(HH) = 2.7, H^5] 7.35 [d, ^3J(HH) = 7.6, H^7, H^9] 7.20 [d, ^3J(HH) = 7.8, H^2] 6.78 [dd, ^3J(HH) = 7.8, ^4J(HH) = 2.3, H^3]	8.05 (s, NH) 7.80 (s, HC=N)		
1j	7.75–6.90 (br m, H^2, H^4, H^5, H^9, H^{10}, PPh_3) 6.25 [dd, ^3J(HP) = 8.0, ^4J(HH) = 2.3, H^7]	9.30 (br s, NH) 7.90 [d, ^4J(HP) = 5.0, HC=N]		40.6
2j	7.75–6.90 (br m, H^2, H^4, H^5, H^7, H^9, H^{10}, PPh_3)	8.00 (s, HC=N) NH[c]		22.6
Ik	7.53 [d, ^3J(HH) = 7.5, H^6, H^{10}] 7.28 [d, ^3J(HH) = 7.5, H^7, H^9]	7.17 (s, HC=N)	2.97 (s, NMe_2)	
1k	8–6.8 (br m, H^9, H^{10}, PPh_3) 6.25 [d, ^4J(HP) = 5.0, H^7]	HC=N[c]	3.2 (m, NMe_2)	42.6
2k	7.60–7.22 (br m, PPh_3) 6.8–6.4 (br m, H^7, H^9, H^{10})	HC=N[c]	2.84 (s, NMe_2)	17.7
Il	7.40–6.90 (br m, H^1, H^2, H^4, H^5, H^7, H^9)	8.08 (s, HC=N) NH[c]	2.48 (s, Me^6, Me^{10}) 2.33 (s, Me^8)	
1l	7.8–7.4 (br m, PPh_3) 6.97 (s, H^7, H^9) 6.73 [dd, ^3J(HH) = 8.6, ^4J(HH) = 2.1, H^4] 6.30 [d, ^3J(HH) = 8.6, H^5] 6.16 [dd, ^4J(HP) = 7.22, ^4J(HH) = 2.16, H^2]	8.73 [d, ^4J(HP) = 4.33, HC=N] NH[c]	2.34 (s, Me^8) 2.29 (s, Me^6, Me^{10})	42.6
2l	7.8–7.3 (br m, PPh_3) 6.98 (s, H^7, H^9) 6.74 [dd, ^3J(HH) = 8.59, ^4J(HH) = 2.15, H^4] 6.32 [d, ^3J(HH) = 8.59, H^5] 6.19 [d, ^4J(HH) = 2.15, H^2]	8.7 (s, HC=N) NH[c]	2.35 (s, Me^8) 2.27 (s, Me^6, Me^{10})	28.8
Im	9.22 [d, ^4J(HH) = 2.5, H^4] 8.4 [dd, ^3J(HH) = 9.6, ^4J(HH) = 2.5, H^2] 7.96 [d, ^3J(HH) = 9.6, H^1] 6.97 (s, H^7, H^9)	11.34 (s, NH) 8.49 (s, HC=N)	2.55 (s, Me^6, Me^{10}) 2.33 (s, Me^8)	

Table 1 (*continued*)

Compound	Aromatic	HC=N, NH	Aliphatic	^{31}P
1m	8.68 [d, ^4J(HH) = 3.5, H^4] 7.85–7.75 (br m, H^2, PPh$_3$) 7.05 (s, H^7, H^9)	11.22 [br d, ^4J(HP) = 4.0, NH] 9.14 [d, ^4J(HP) = 3.5, HC=N]	2.37 (s, Me^8) 2.32 (s, Me^6, Me^{10})	41.8
2m	8.72 [d, ^4J(HH) = 2.5, H^4] 7.80–7.30 (br m, H^2, PPh$_3$) 6.97 (s, H^7, H^9)	11.26 (s, NH) HC=N^c	2.38 (s, Me^8) 2.24 (s, Me^6, Me^{10})	23.8
In	7.43 (s, H^3) 7.10–6.80 (br m, H^1, H^5, H^7, H^9)	8.05 (s, HC=N) 7.37 (br s, NH)	2.41 (2, Me^6, Me^{10}) 2.33 (s, Me^8)	
1n	7.9–7.0 (br m, H^7, H^9, PPh$_3$) 6.98 (br s, H^5) 6.37 (br s, H^3)	8.5 (br s, HC=N) NH^c	2.35 (s, Me^8) 2.27 (s, Me^6, Me^{10})	32.3
2n	8.05–6.70 (br m, H^3, H^5, H^7, H^9, PPh$_3$)	HC=N^c NH^c	2.33 (s, Me^6, Me^{10}) 2.20 (s, Me^8)	21.9

[a] In CDCl$_3$; chemical shifts (δ) in ppm with respect to internal SiMe$_4$; coupling constants in Hz; numbering as below.



[b] In CHCl$_3$; chemical shifts (δ) in ppm with respect 85% H$_3$PO$_4$. [c] Not visible: resonance obscured by those of aromatic protons.

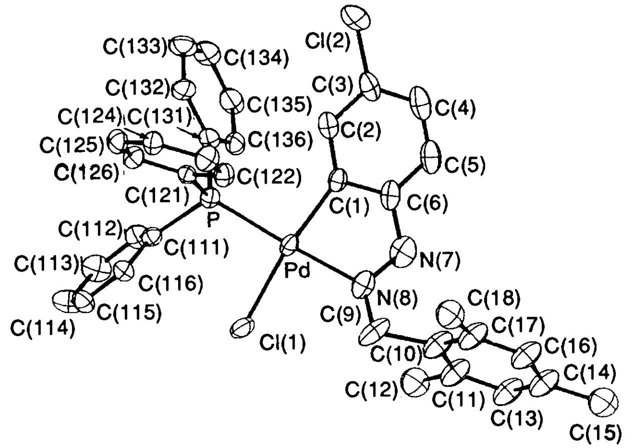


Fig. 1 Molecular structure of compound **1l**. The mesityl ring is disordered (see Experimental section)

Table 2 Summary of crystallographic data

	1l	**1m**
Formula	$C_{34}H_{31}Cl_2N_2PPd$	$C_{34}H_{30}BrN_4O_4PPd{\cdot}CCl_2H_2$
M	675.61	858.51
Symmetry	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a/Å	40.108(4)	9.429(2)
b/Å	7.805(1)	10.420(2)
c/Å	21.045(3)	18.334(3)
α/°		92.23(3)
β/°	100.66(3)	90.26(3)
γ/°		96.11(2)
U/Å^3	6474(2)	1790(1)
D_c/g cm^{-3}	1.384	1.597
Z	8	2
F(000)	2744.0	864.0
Crystal size/mm	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
μ(Mo-Kα)/cm^{-1}	8.02	19.30

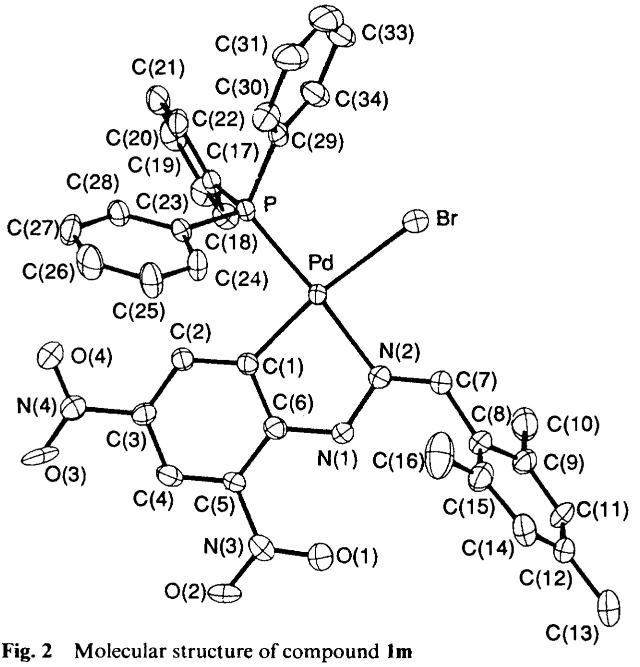


Fig. 2 Molecular structure of compound **1m**

arrangement between phosphorus and nitrogen, and those of compounds **2** indicate a *trans* arrangement of the two PPh$_3$ ligands. The signal assigned to the methinic protons in exocyclic cyclometallated compounds is shifted to low field in relation to the free ligand. This shift can be explained by the paramagnetic anisotropy of the palladium atom and indicates a close arrangement between the metal and the methinic group, suggesting a *Z* form for the ligand, as has been reported for similar exocyclic derivatives from imines.[3b] The low-field shift of the signal assigned to the NH proton is stronger for the endocyclic than the exocyclic cyclometallated derivatives, showing that the ligand adopts a conformation in which the NH group is close to palladium in the endocyclic compounds in order to minimize steric repulsion. Analogous results have been reported for cyclometallated compounds of hydrazones derived from ketones.[6]

The signal assigned to the NH group in compounds derived from 2,4-dinitrophenylhydrazine, **1m** and **2m**, appears strongly shifted to low fields (δ 11.2–11.5) suggesting the existence of an intramolecular hydrogen bond between the *o*-nitro substituent and the NH group.[11] The crystal structure of compound **1m** confirms this interaction (see below).

Molecular Structures of Compounds **1l** *and* **1m**.—The crystal structures of compounds **1l** and **1m** are shown in Figs. 1 and 2, bond lengths and angles are listed in Tables 3 and 4, and atomic coordinates in Tables 5 and 6. The molecular structures of both compounds consist of discrete molecules separated by van der Waals distances. The palladium atom is in a slightly distorted square-planar environment co-ordinated to phosphorus, carbon, halide and the iminic nitrogen atom in both complexes.

Table 3 Bond distances (Å) and angles (°) for compound **1l**

Cl–Pd	2.369(2)	C(3)–C(2)	1.406(8)	C(116)–C(111)	1.397(7)	C(125)–C(124)	1.366(9)
N(8)–Pd	2.077(5)	C(4)–C(3)	1.364(9)	C(113)–C(112)	1.387(9)	C(126)–C(125)	1.381(8)
C(1)–Pd	2.005(6)	C(5)–C(4)	1.353(11)	C(114)–C(113)	1.408(11)	C(132)–C(131)	1.384(8)
P(1)–Pd	2.254(1)	C(6)–C(5)	1.385(10)	C(115)–C(114)	1.360(9)	C(136)–C(131)	1.406(8)
N(7)–N(8)	1.391(8)	N(7)–C(6)	1.423(9)	C(116)–C(115)	1.353(8)	C(133)–C(132)	1.416(7)
C(9)–N(8)	1.278(9)	C(111)–P	1.828(5)	C(122)–C(121)	1.367(6)	C(134)–C(133)	1.383(10)
C(3)–Cl(2)	1.739(7)	C(121)–P	1.823(5)	C(126)–C(121)	1.399(7)	C(135)–C(134)	1.356(10)
C(2)–C(1)	1.370(8)	C(131)–P	1.818(4)	C(123)–C(122)	1.400(8)	C(136)–C(135)	1.393(7)
C(6)–C(1)	1.394(7)	C(112)–C(111)	1.379(8)	C(124)–C(123)	1.381(8)		

N(8)–Pd–Cl(1)	91.3(2)	C(2)–C(3)–Cl(2)	119.0(5)	C(131)–P–C(121)	107.3(2)	C(124)–C(123)–C(122)	119.7(5)
C(1)–Pd–Cl(1)	171.3(1)	C(4)–C(3)–Cl(2)	120.2(5)	C(112)–C(111)–P	122.0(4)	C(125)–C(124)–C(123)	120.8(5)
C(1)–Pd–N(8)	80.9(2)	C(4)–C(3)–C(2)	120.9(6)	C(116)–C(111)–P	119.3(4)	C(126)–C(125)–C(124)	119.6(5)
P–Pd–Cl(1)	92.0(1)	C(5)–C(4)–C(3)	118.8(6)	C(116)–C(111)–C(112)	118.5(5)	C(125)–C(126)–C(121)	120.3(5)
P–Pd–N(8)	176.2(2)	C(6)–C(5)–C(4)	120.5(6)	C(113)–C(112)–C(111)	120.7(6)	C(132)–C(131)–P	122.4(4)
P–Pd–C(1)	96.0(1)	C(5)–C(6)–C(1)	122.3(6)	C(114)–C(113)–C(112)	119.4(6)	C(136)–C(131)–P	117.7(4)
N(7)–N(8)–Pd	111.1(4)	N(7)–C(6)–C(1)	118.2(5)	C(115)–C(114)–C(113)	119.0(6)	C(136)–C(131)–C(132)	119.8(4)
C(9)–N(8)–Pd	128.9(5)	N(7)–C(6)–C(5)	119.5(5)	C(116)–C(115)–C(114)	121.6(6)	C(133)–C(132)–C(131)	119.1(5)
C(9)–N(8)–N(7)	120.1(6)	C(111)–P–Pd	114.7(1)	C(115)–C(116)–C(111)	120.8(5)	C(134)–C(133)–C(132)	119.8(6)
C(2)–C(1)–Pd	131.7(4)	C(121)–P–Pd	110.4(1)	C(122)–C(121)–P	119.0(4)	C(135)–C(134)–C(133)	121.1(5)
C(6)–C(1)–Pd	112.1(4)	C(121)–P–C(111)	104.3(2)	C(126)–C(121)–P	121.3(4)	C(136)–C(135)–C(134)	120.2(6)
C(6)–C(1)–C(2)	116.0(5)	C(131)–P–Pd	116.8(2)	C(126)–C(121)–C(122)	119.7(5)	C(135)–C(136)–C(131)	119.8(6)
C(3)–C(2)–C(1)	121.3(5)	C(131)–P–C(111)	102.2(2)	C(123)–C(122)–C(121)	119.8(5)	C(6)–N(7)–N(8)	112.8(5)

Table 4 Bond distances (Å) and angles (°) for compound **1m**

Br–Pd	2.471(1)	O(4)–N(4)	1.180(7)	C(11)–C(9)	1.390(8)	C(28)–C(23)	1.388(6)
P–Pd	2.256(1)	C(5)–C(4)	1.374(7)	C(12)–C(11)	1.344(9)	C(25)–C(24)	1.381(8)
C(1)–Pd	2.005(4)	N(3)–C(5)	1.449(7)	C(13)–C(12)	1.511(10)	C(26)–C(25)	1.336(8)
N(2)–Pd	2.087(4)	C(6)–C(5)	1.397(7)	C(14)–C(12)	1.418(9)	C(27)–C(26)	1.388(9)
C(17)–P	1.820(4)	O(1)–N(3)	1.203(7)	C(15)–C(14)	1.339(8)	C(28)–C(27)	1.383(7)
C(23)–P	1.814(4)	O(2)–N(3)	1.217(8)	C(16)–C(15)	1.523(9)	C(30)–C(29)	1.390(7)
C(29)–P	1.822(4)	N(1)–C(6)	1.352(6)	C(18)–C(17)	1.379(7)	C(34)–C(29)	1.347(7)
C(2)–C(1)	1.371(6)	N(2)–N(1)	1.361(6)	C(22)–C(17)	1.369(6)	C(31)–C(30)	1.392(8)
C(6)–C(1)	1.420(6)	C(7)–N(2)	1.250(6)	C(19)–C(18)	1.380(7)	C(32)–C(31)	1.303(12)
C(3)–C(2)	1.385(7)	C(8)–C(7)	1.458(7)	C(20)–C(19)	1.328(8)	C(33)–C(32)	1.425(10)
N(4)–C(3)	1.463(6)	C(9)–C(8)	1.374(8)	C(21)–C(20)	1.398(8)	C(34)–C(33)	1.380(9)
C(4)–C(3)	1.361(7)	C(15)–C(8)	1.407(7)	C(22)–C(21)	1.401(7)	C(35)–Cl(1)	1.670(10)
O(3)–N(4)	1.202(7)	C(10)–C(9)	1.515(10)	C(24)–C(23)	1.386(6)	C(35)–Cl(2)	1.773(9)

P–Pd–Br	92.9(1)	O(3)–N(4)–C(3)	118.5(5)	C(15)–C(8)–C(7)	120.0(5)	C(22)–C(21)–C(20)	118.8(5)
C(1)–Pd–Br	171.9(1)	O(4)–N(4)–C(3)	118.2(5)	C(15)–C(8)–C(9)	119.5(5)	C(21)–C(22)–C(17)	119.8(4)
C(1)–Pd–P	95.1(1)	O(4)–N(4)–O(3)	123.3(5)	C(10)–C(9)–C(8)	122.3(5)	C(24)–C(23)–P	119.4(3)
N(2)–Pd–Br	90.9(1)	C(5)–C(4)–C(3)	117.9(5)	C(11)–C(9)–C(8)	118.3(5)	C(28)–C(23)–P	120.9(4)
N(2)–Pd–P	175.9(1)	N(3)–C(5)–C(4)	117.8(4)	C(11)–C(9)–C(10)	119.2(6)	C(28)–C(23)–C(24)	119.5(4)
N(2)–Pd–C(1)	81.0(2)	C(6)–C(5)–C(4)	121.7(4)	C(12)–C(11)–C(9)	123.5(6)	C(25)–C(24)–C(23)	119.4(4)
C(17)–P–Pd	113.7(1)	C(6)–C(5)–N(3)	120.4(4)	C(13)–C(12)–C(11)	121.0(7)	C(26)–C(25)–C(24)	121.5(5)
C(23)–P–Pd	110.8(1)	O(1)–N(3)–C(5)	120.4(5)	C(14)–C(12)–C(11)	117.1(5)	C(27)–C(26)–C(25)	120.1(5)
C(23)–P–C(17)	109.1(2)	O(2)–N(3)–C(5)	117.4(5)	C(14)–C(12)–C(13)	121.9(6)	C(28)–C(27)–C(26)	119.8(5)
C(29)–P–Pd	117.3(1)	O(2)–N(3)–O(1)	122.1(6)	C(15)–C(14)–C(12)	121.3(5)	C(27)–C(28)–C(23)	119.6(5)
C(29)–P–C(17)	102.6(2)	C(5)–C(6)–C(1)	119.9(4)	C(14)–C(15)–C(8)	120.1(5)	C(30)–C(29)–P	121.0(3)
C(29)–P–C(23)	102.4(2)	N(1)–C(6)–C(1)	117.3(4)	C(16)–C(15)–C(8)	120.3(5)	C(34)–C(29)–P	118.9(4)
C(2)–C(1)–Pd	131.4(3)	N(1)–C(6)–C(5)	122.8(4)	C(16)–C(15)–C(14)	119.5(5)	C(34)–C(29)–C(30)	120.1(4)
C(6)–C(1)–Pd	111.8(3)	N(2)–N(1)–C(6)	118.5(4)	C(18)–C(17)–P	116.7(3)	C(31)–C(30)–C(29)	118.3(5)
C(6)–C(1)–C(2)	116.8(4)	N(1)–N(2)–Pd	110.4(3)	C(22)–C(17)–P	123.6(3)	C(32)–C(31)–C(30)	121.0(6)
C(3)–C(2)–C(1)	121.8(4)	C(7)–N(2)–Pd	131.0(4)	C(22)–C(17)–C(18)	119.7(4)	C(33)–C(32)–C(31)	122.5(6)
N(4)–C(3)–C(2)	120.5(4)	C(7)–N(2)–N(1)	117.9(4)	C(19)–C(18)–C(17)	119.9(4)	C(34)–C(33)–C(32)	115.6(6)
C(4)–C(3)–C(2)	121.9(4)	C(8)–C(7)–N(2)	127.4(5)	C(20)–C(19)–C(18)	121.2(5)	C(33)–C(34)–C(29)	122.5(5)
C(4)–C(3)–N(4)	117.5(4)	C(9)–C(8)–C(7)	120.0(5)	C(21)–C(20)–C(19)	120.4(5)	Cl(2)–C(35)–Cl(1)	110.3(5)

The largest deviations from the mean plane determined by the five atoms are +0.059 for C(1) and +0.017 Å for N(2) in **1l** and **1m** respectively. The phosphine adopts a *trans* arrangement in relation to iminic nitrogen in both compounds. The angles between adjacent atoms in the co-ordination sphere lie in the range 96.0(1) (P–Pd–C) to 80.9(2)° (N–Pd–C) for **1l** and 95.1(1) (P–Pd–C) to 81.0(2)° (N–Pd–C) for **1m**. The smallest of these angles are those between the co-ordinating nitrogen and carbon atoms of the chelated ligand. The palladium–ligand distances are similar to those reported for other cyclometallated compounds derived from hydrazones.[6,12] Both metallacycles present an *exo* structure, because the C=N bond is not contained in the metallacycle, and the hydrazone moiety adopts the *Z* form, in accord with NMR data. The N–N=C–C moiety is nearly planar, the torsion angles being 2.2(6) and 5.24(4)° respectively for **1l** and **1m**.

In compound **1m** the NH group is involved in an intramolecular hydrogen bond to the *o*-nitro group. The distance N(1)···O(1) is 2.559 Å, similar to those found for free *o*-nitrohydrazones.[11]. The dihedral angles between the hydrazone moiety and both the metallacycle and the co-ordination plane are smaller in **1m** (8.94 and 12.77° respectively) than in **1l** (24.0 and 16.7° respectively), which does not contain such an intramolecular hydrogen bond. It seems that the intramolecular

Table 5 Final atomic coordinates (× 10^4; Pd, Cl and P, × 10^5) of compound **Il***

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pd	88 271(1)	42 511(5)	14 310(2)	C(133)	7 768(2)	−180(9)	83(3)
Cl(1)	89 994(5)	42 992(28)	25 698(9)	C(134)	8 010(2)	−1 177(8)	−129(3)
N(8)	9 257(1)	5 607(6)	1 310(3)	C(135)	8 344(2)	−998(8)	127(3)
Cl(2)	80 325(6)	44 340(22)	−11 679(8)	C(136)	8 451(2)	249(7)	594(3)
C(1)	8 724(1)	4 535(6)	468(3)	N(7)	9 306(2)	5 514(7)	674(3)
C(2)	8 429(2)	4 331(6)	26(3)	C(9)	9 462(2)	6 467(9)	1 727(5)
C(3)	8 416(2)	4 670(7)	−635(3)	C(10)	9 751(2)	7 402(13)	1 403(7)
C(4)	8 699(2)	5 188(8)	−857(3)	C(11)	10 055(2)	6 506(13)	1 440(7)
C(5)	8 990(2)	5 438(8)	−426(4)	C(12)	10 072(6)	4 687(29)	1 701(12)
C(6)	9 000(2)	5 172(7)	228(3)	C(13)	10 334(2)	7 295(13)	1 253(7)
P	83 611(3)	26 979(14)	14 984(5)	C(14)	10 309(2)	8 981(13)	1 029(7)
C(111)	8 406(1)	1 277(6)	2 200(2)	C(15)	10 595(7)	9 950(40)	810(13)
C(112)	8 496(2)	−421(7)	2 167(3)	C(16)	10 005(2)	9 878(13)	993(7)
C(113)	8 541(2)	−1 449(8)	2 714(3)	C(17)	9 726(2)	9 089(13)	1 180(7)
C(114)	8 496(2)	−740(9)	3 307(4)	C(18)	9 410(7)	10 127(35)	1 255(12)
C(115)	8 412(2)	944(9)	3 331(3)	C(10′)	9 766(2)	7 421(8)	1 770(6)
C(116)	8 369(1)	1 948(8)	2 798(2)	C(11′)	10 058(2)	6 762(8)	1 591(6)
C(121)	8 009(1)	4 104(6)	1 585(2)	C(12′)	9 420(5)	9 967(27)	2 156(9)
C(122)	8 029(2)	5 804(6)	1 441(3)	C(13′)	10 342(2)	7 810(8)	1 605(6)
C(123)	7 765(2)	6 911(8)	1 518(3)	C(14′)	10 332(2)	9 516(8)	1 799(6)
C(124)	7 489(2)	6 283(9)	1 752(3)	C(15′)	10 623(7)	10 695(27)	1 679(14)
C(125)	7 466(2)	4 581(8)	1 888(3)	C(16′)	10 040(2)	10 174(8)	1 978(6)
C(126)	7 725(1)	3 483(7)	1 808(3)	C(17′)	9 757(2)	9 127(8)	1 964(6)
C(131)	8 209(1)	1 244(6)	833(2)	C(18′)	10 093(3)	4 797(19)	1 434(8)
C(132)	7 868(2)	1 048(7)	577(3)				

* Primed atoms refer to atoms corresponding to the alternative position of the triphenylmethyl moiety.

Table 6 Final atomic coordinates (× 10^4; Pd, Br and P, × 10^5) of compound **Im**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pd	11 487(3)	42 502(3)	20 860(2)	C(14)	3 040(7)	9 363(5)	4 354(3)
Br	29 401(6)	54 680(6)	13 262(3)	C(15)	3 130(5)	8 315(5)	3 917(3)
P	7 400(10)	26 243(10)	12 376(6)	C(16)	4 421(7)	7 561(7)	3 978(5)
C(1)	−256(4)	3 471(4)	2 805(3)	C(17)	−1 143(4)	2 085(4)	1 090(2)
C(2)	−1 058(5)	2 294(4)	2 801(3)	C(18)	−2 052(5)	3 035(5)	1 055(3)
C(3)	−2 017(5)	1 967(4)	3 351(3)	C(19)	−3 488(5)	2 700(5)	921(4)
N(4)	−2 980(5)	769(4)	3 287(3)	C(20)	−4 022(5)	1 473(6)	831(4)
O(3)	−3 752(7)	490(5)	3 789(3)	C(21)	−3 146(6)	483(5)	905(4)
O(4)	−2 943(5)	117(4)	2 748(3)	C(22)	−1 682(4)	813(4)	1 027(3)
C(4)	−2 174(5)	2 776(5)	3 939(3)	C(23)	1 664(4)	1 255(4)	1 474(3)
C(5)	−1 357(5)	3 950(5)	3 971(3)	C(24)	2 363(5)	1 276(5)	2 141(3)
N(3)	−1 568(6)	4 832(5)	4 582(3)	C(25)	3 185(6)	297(6)	2 292(3)
O(1)	−961(6)	5 909(4)	4 607(3)	C(26)	3 319(6)	−675(5)	1 810(4)
O(2)	−2 370(7)	4 437(6)	5 061(3)	C(27)	2 610(6)	−729(5)	1 142(4)
C(6)	−404(5)	4 321(4)	3 418(3)	C(28)	1 797(5)	248(4)	969(3)
N(1)	385(5)	5 484(4)	3 428(2)	C(29)	1 367(4)	2 933(4)	315(2)
N(2)	1 385(4)	5 712(4)	2 902(2)	C(30)	419(6)	3 128(5)	−242(3)
C(7)	2 136(6)	6 776(5)	2 931(3)	C(31)	957(8)	3 304(7)	−941(3)
C(8)	2 000(6)	7 870(5)	3 436(3)	C(32)	2 319(10)	3 332(6)	−1 066(3)
C(9)	842(6)	8 560(5)	3 389(3)	C(33)	3 330(7)	3 161(6)	−507(4)
C(10)	−351(8)	8 202(7)	2 838(5)	C(34)	2 772(6)	2 961(5)	179(3)
C(11)	825(7)	9 676(6)	3 827(4)	Cl(1)	4 248(3)	3 684(3)	3 542(2)
C(12)	1 870(7)	10 105(5)	4 305(3)	Cl(2)	6 357(3)	5 265(3)	2 807(2)
C(13)	1 794(10)	11 333(7)	4 763(5)	C(35)	5 087(9)	3 881(9)	2 748(5)

hydrogen bond reinforces the planarity of the cyclometallated compound derived from the *o*-nitrohydrazone. This suggests that the aminic nitrogen atom has more sp^2 character in **Im**, with the lone pair of electrons in the p_z orbital, as has been proposed for free hydrazones.[13] The N–C(metallated ring) bond is shorter, 1.352(6) *vs.* 1.423(9) Å, and the C–N(aminic)–N(iminic) angle is larger, 118.5(4) *vs.* 112.8(5)°, in **Im** than in **Il**, suggesting that there is some conjugation of this lone pair of electrons with the metallated ring. The five-membered metallacycle is nearly planar in compound **Im**, the largest deviation being that for the iminic nitrogen atom N(2), −0.061 Å, in agreement with this sp^2 hybridization of aminic nitrogen. However, in compound **Il** the metallacycle adopts an envelope conformation with the nitrogen atom N(8) out of the plane (0.362 Å) defined by the other four atoms, in agreement with more sp^3 character of the aminic nitrogen.

Conclusion

The results described in this work show the tendency of hydrazones derived from aldehydes to form exocyclic cyclometallated compounds. *endo*-Metallacycles are only obtained from the *N*,*N*-dimethylhydrazone derivative **Ik**, where the *exo*-metallacycle cannot be formed, or from hydrazones **Ii** and **Ij** where the presence of chloro substituents in the *ortho* and *meta* positions of the phenylhydrazine ring hinders the palladium attack. Nevertheless, the formation of the *endo*-metallacycle with the hydrazone **Ii** shows that the difference in stability between *exo*-

and *endo*-metallacycles derived from hydrazones is not very large, because a minor change, like the presence of a non-coordinating substituent in the position adjacent to that of metallation, gives *endo*-metallacycles in high yields.

These results are very different from those obtained with imines. *N*-Benzylideneamines show a strong tendency to form endocyclic cyclometallated compounds. This tendency is so strong that it permits the activation of aliphatic C–H bonds, with formation of a six-membered metallacycle, in preference to the activation of an aromatic C–H bond, with formation of a five-membered metallacycle.[3]

The factors that influence the ease and mode of cyclopalladation of N-donor ligands are not thoroughly understood, but the following mechanism is widely accepted: (*i*) initial co-ordination of the ligand to the metal, and (*ii*) electrophilic attack of Pd^{II} on the aromatic C–H bonds. It is conceivable that the direction of the C–H vector, with respect to the metal, has a crucial role in the cyclometallation processes. It seems that an approach of the C–H bond to the co-ordination plane of the metal favours the reaction, in good agreement with an electrophilic attack of Pd^{II} using its empty $d_{x^2-y^2}$ orbital. Recently, mechanistic studies on the cyclometallation of *o*-arylphenoxide ligands at Group 5 metal centres suggest that rotation of the aryl ring to be metallated into a coplanar conformation, in which the C–H bond about to be activated is brought close to the metal centre, is a contributing factor to cyclometallation reactions.[14] Moreover, extended-Huckel calculations, carried out on cyclometallated carbyne compounds, indicate a strong interaction between the occupied π orbital of the metallacarbyne and the empty $d_{x^2-y^2}$ orbital of Pd^{II}, showing the acidic character of this palladium orbital.[15]

The molecular structures of free imines, like PhCH=NPh, show that the dihedral angle between the methinic phenyl ring and the HC=N plane is smaller (*ca.* 8–15°) than that between the amine phenyl ring and the methinic group (*ca.* 40–50°).[16] This may explain the great tendency of imines to form endocyclic compounds. The crystal structures of hydrazones show, in contrast, that the dihedral angles between the hydrazone phenyl ring and the methinic group are small, and the ligands adopt more planar conformations.[13,17] This small dihedral angle between the hydrazone phenyl ring and the methinic group permits the C–H bond of the ring to be near the co-ordination plane of Pd^{II}, in the co-ordination compound formed previous to the metallation,* and consequently the metallation of such an aromatic ring is favoured. Moreover, the nitrogen lone pair activates the hydrazine phenyl ring to electrophilic attack. The formation of *exo*-metallacycles with hydrazone **Im**, which contains two strongly electron-withdrawing substituents in the *ortho* and *para* positions of the phenylhydrazine ring, can also be explained by this mechanism. The intramolecular hydrogen bond between the *o*-NO_2 substituent and the NH group, confirmed by the crystal structure determination of compound **1m**, reinforces the planarity of the phenylhydrazone ring and the iminic moiety and consequently the approach of the C–H bond to the co-ordination plane of the metal.

Hydrazones derived from ketones, PhRC=NNHPh, usually afford endocyclic cyclometallated compounds.[4,6] The formation of *exo*-metallacycles with these ligands would give cyclometallated compounds with more steric congestion caused by the proximity between the palladium and the ketonic R groups. This factor does not apply to hydrazones derived from aldehydes PhHC=NNHPh, because in both cases (*endo-* or *exo-* metallacycles) there is a hydrogen atom in the proximity of the metal.

It is possible to conclude that the difference in stability between *endo-* and *exo*-metallacycles derived from hydrazones is not very large and minor changes, like the presence of substituents in specific positions, can induce the formation of one or the other metallacycle.

Experimental

Routine NMR spectra were obtained on a Bruker WP 80SY spectrometer (^1H, 80.13 MHz; $^{31}P-\{^1H\}$, 32.8 MHz); 200 MHz ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Infrared spectra were recorded as KBr disks on a Perkin Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

Materials and Synthesis.—Solvents were dried and distilled before use. The hydrazones were obtained from the corresponding benzaldehydes and the appropriate hydrazines under standard conditions (refluxing ethanol).[18]

Compounds **1**. A stirred suspension of $PdCl_2$ (2 mmol, 0.35 g) in EtOH (30 cm^3) was treated with the corresponding hydrazone (2.2 mmol) for 3 d at room temperature. The precipitate formed was washed with ethanol and diethyl ether and used without further purification in the preparation of **1**. This precipitate was treated with PPh_3 (2 mmol, 0.52 g) in refluxing acetone (30 cm^3) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100:1) as eluent: **1a**, yield 760 mg (60%), m.p. 134–136 °C (decomp.) (Found: C, 57.8; H, 3.7; N, 4.2. $C_{31}H_{25}Cl_2N_2PPd$ requires C, 58.75; H, 3.95; N, 4.40%); **1b**, yield 670 mg (50%), m.p. 135–140 °C (decomp.) (Found: C, 55.7; H, 4.0; N, 4.2. $C_{31}H_{24}Cl_3N_2PPd$ requires C, 55.70; H, 3.60; N, 4.20%); **1c**, yield 710 mg (55%), m.p. 148–150 °C (decomp.) (Found: C, 57.9, H, 4.0; N, 6.3. $C_{31}H_{25}ClN_3O_2PPd$ requires C, 57.75; H, 3.90; N, 6.50%); **1i**, yield 770 mg (55%), m.p. 180–185 °C (decomp.) (Found: C, 53.0; H, 3.3; N, 3.8. $C_{31}H_{23}Cl_4N_2PPd$ requires C, 52.95; H, 3.25; N, 4.00%); **1j**, yield 840 mg (60%), m.p. 188–192 °C (decomp.) (Found: C, 52.3; H, 3.3; N, 3.7. $C_{31}H_{23}Cl_4N_2PPd$ requires C, 52.95; H, 3.25; N, 4.00%); **1k**, yield 460 mg (40%), m.p. 170–172 °C (decomp.) (Found: C, 54.2; H, 4.2; N, 4.4. $C_{27}H_{25}Cl_2N_2PPd$ requires C, 55.35; H, 4.25; N, 4.80%); **1l**, yield 610 mg (45%), m.p. 194–198 °C (decomp.) (Found: C, 60.2; H, 4.6; N, 4.1. $C_{34}H_{31}Cl_2N_2PPd$ requires C, 60.40; H, 4.60; N, 4.15%); **1n**, yield 640 mg (45%), m.p. 186–188 °C (decomp.) (Found: C, 57.4; H, 4.2; N, 3.8. $C_{34}H_{30}Cl_3N_2PPd$ requires C, 57.45; H, 4.20; N, 3.95%).

Compound **1m** was prepared as follows. A stirred suspension of $Pd(O_2CMe)_2$ (2 mmol, 0.45 g) in acetic acid (30 cm^3) was treated with hydrazone **Im** (0.75 g, 2.2 mmol) and refluxed for 45 min. The precipitate formed was washed with ethanol and ether and used, without further purification, in the preparation of **1m**. It was treated with PPh_3 (2 mmol, 0.52 g) and LiBr (2 mmol, 0.174 g) in refluxing acetone (30 cm^3) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was purified by column chromatography over SiO_2, with $CHCl_3$–MeOH (100:1) as eluent, to give compound **1m**, 930 mg (60% yield), m.p. 224–228 °C (decomp.) (Found: C, 53.2; H, 4.0; N, 7.1. $C_{34}H_{30}BrN_4O_4PPd$ requires C, 52.60; H, 3.85; N, 7.20%).

Compounds **2**. Stirred suspensions of compounds **1** (0.5 mmol) were treated with PPh_3 (0.75 mmol, 0.19 g) in refluxing acetone (30 cm^3) for 1 h and then filtered. The filtrate was concentrated *in vacuo* and the solid obtained after addition of ether was washed with ether and recrystallized from $CHCl_3$: **2a**, yield 380 mg (85%), m.p. 124–127 °C (decomp.) (Found: C, 65.3; H, 4.6; N, 3.0. $C_{49}H_{40}Cl_2N_2P_2Pd$ requires C, 65.65; H, 4.45; N, 3.10%); **2b**, yield 325 mg (70%), m.p. 188–190 °C (decomp.) (Found: C, 62.6; H, 3.9; N, 2.9. $C_{49}H_{39}Cl_3N_2P_2Pd$ requires C, 63.25; H, 4.20; N, 3.00%); **2c**, yield 271 mg (60%), m.p. 174–176 °C (decomp.) (Found: C, 64.4; H, 4.4; N, 4.6. $C_{49}H_{40}ClN_3O_2P_2Pd$ requires C, 64.90; H, 4.40; N, 4.65%); **2i**, yield 144 mg (30%), m.p. 188–191 °C (decomp.) (Found: C, 60.8; H, 3.9; N, 2.4. $C_{49}H_{38}Cl_4N_2P_2Pd$ requires C, 60.95; H, 3.95; N, 2.90%); **2j**, yield 241

---

* Palladium(II) is usually bonded to the iminic nitrogen of hydrazones. Co-ordination of the aminic nitrogen occurs only if there is a large steric congestion around the iminic nitrogen.

mg (50%), m.p. 200–202 °C (decomp.) (Found: C, 59.4; H, 3.9; N, 2.6. $C_{49}H_{38}Cl_4N_2P_2Pd$ requires C, 60.95; H, 3.95; N, 2.90%); **2k**, yield 148 mg (35%), m.p. 185–187 °C (decomp.) (Found: C, 63.6; H, 4.7; N, 3.3. $C_{45}H_{40}Cl_2N_2P_2Pd$ requires C, 63.80; H, 4.70; N, 3.30%); **2l**, yield 211 mg (45%), m.p. 192–196 °C (decomp.) (Found: C, 65.4; H, 4.8; N, 2.9. $C_{52}H_{46}Cl_2N_2P_2Pd$ requires C, 66.55; H, 4.90; N, 3.00%); **2m**, yield 210 mg (40%), m.p. 200–204 °C (decomp.) (Found: C, 60.5; H, 4.4; N, 5.2. $C_{52}H_{45}BrN_4O_4P_2Pd$ requires C, 60.15; H, 4.35; N, 5.40%); **2n**, yield 192 mg (40%), m.p. 198–200 °C (decomp.) (Found: C, 63.9; H, 4.6; N, 2.9. $C_{52}H_{45}Cl_3N_2P_2Pd$ requires C, 64.20; H, 4.65; N, 2.90%).

X-Ray Structure Analysis.—Data collection. Prismatic crystals (0.1 × 0.1 × 0.2 mm) were selected and mounted on a Phillips PW-1100 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 \leqslant \theta \leqslant 16°$) and refined by the least-squares method. Intensities were collected at 25 °C with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), using the ω–2θ scan technique. For compound **1l** 5509 reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 4790 of which were assumed as observed [$I \geqslant 2.5\sigma(I)$]. For compound **1m** 6399 reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 5669 of which were assumed as observed [$I \geqslant 2.5\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity control, but significant intensity decay was not observed. Lorentz-polarization but no absorption corrections were made.

Structure solution and refinement. The structures were solved by Patterson synthesis, using the SHELXS computer program,[19] and refined by full-matrix least squares with the SHELX 76 program.[20] The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = \sigma^2(F_o) + 0.012|F_o|)^{-1}$; f, f' and f'' were taken from ref. 21. For compound **1l** the trimethylphenyl moiety was disordered, an occupancy factor of 0.5 being assigned to each atom according to the peak heights in the difference synthesis. The position of 18 H atoms were computed and refined with overall isotropic thermal parameters, using a riding model. The final R factor was 0.064 (R' = 0.073) for all observed reflections. The number of refined parameters was 329. Maximum shift/e.s.d. = 0.1, maximum and minimum peaks in final difference synthesis 0.4 and −0.4 e Å^{-3}. For compound **1m** the positions of 32 H atoms were computed and refined with overall isotropic thermal parameters, using a riding model. The final R factor was 0.062 (R' = 0.070) for all observed reflections. The number of refined parameters was 436. Maximum shift/e.s.d. = 0.1, maximum and minimum peaks in final difference synthesis 0.4 and −0.4 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (DGICYT) (Grant No. PB 86-575) for financial support and Johnson Matthey for a loan of palladium chloride.

References

1 M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **10**, 73; I. Omae, *Chem. Rev.*, 1979, **79**, 287; G. R. Newkome, W. E. Peuckett, V. K. Gupta and G. E. Kiefer. *Chem. Rev.*, 1986, **86**, 451; I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137; V. V. Dunina, O. A. Zalevskaya and V. M. Potatov, *Russ. Chem. Rev.*, 1988, **57**, 250.

2 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.

3 (*a*) J. Albert, J. Granell, J. Sales, X. Solans and M. Font, *Organometallics*, 1986, **5**, 2567; (*b*) J. Albert, R. M. Ceder, M. Gómez, J. Granell and J. Sales, *Organometallics*, 1992, **11**, 1536.

4 B. N. Cockburn, D. W. Howe, T. Keating, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1973, 404; J. Dehand, M. Pfeffer, and M. Zinsius, *Inorg. Chim. Acta*, 1975, **13**, 229; J. Dehand, J. Jordanov and M. Pfeffer, *J. Chem. Soc., Dalton Trans.*, 1976, 1553; P. Espinet, G. García, F. J. Herrero, Y. Jeanin and Philoche-Levisalles, *Inorg. Chem.*, 1989, **28**, 4207.

5 N. Nonoyama and M. Sugimoto, *Inorg. Chim. Acta*, 1979, **35**, 131.

6 J. Granell, R. Moragas, J. Sales, M. Font-Bardia and X. Solans, *J. Organomet. Chem.*, 1992, **431**, 359.

7 J. M. Thompson and R. F. Heck, *J. Org. Chem.*, 1975, **40**, 2667.

8 J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, 1984, **273**, 393.

9 J. M. Vila, M. T. Periera, E. Gayoso and M. Gayoso, *Transition Met. Chem.*, 1986, **11**, 342.

10 H. Onoue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431; J. Granell, D. Sainz, J. Sales, X. Solans and M. Font. *J. Chem. Soc., Dalton Trans.*, 1986, 1785.

11 M. G. B. Drew and G. R. Willey, *J. Chem. Soc., Perkin Trans. 2*, 1986, 215.

12 J. Dehand, J. Fischer, M. Pfeffer, A. Mitschler and M. Zinsius, *Inorg. Chem.*, 1975, **15**, 2675; G. Le Borgne, S. E. Bouaoud, D. Granjean, P. Braunstein, J. Dehand and M. Pfeffer, *J. Organomet. Chem.*, 1977, **136**, 375.

13 B. Vickery, G. R. Willey and M. G. B. Drew, *J. Chem. Soc., Perkin Trans. 2*, 1981, 155.

14 R. W. Chesnut, G. G. Jacob, J. S. Yu, P. E. Famwick and I. P. Rothwell, *Organometallics*, 1991, **10**, 321.

15 P. F. Engel, M. Pfeffer, J. Fischer and A. Dedieu, *J. Chem. Soc., Chem. Commun.*, 1991, 1274.

16 H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1970, **53**, 1747; H. Nakai, M. Shiro, K. Ezumi, S. Sakata and T. Kubota, *Acta Crystallogr., Sect. B*, 1976, **32**, 1827; H. Nakai, K. Ezumi and M. Shiro, *Acta Crystallogr., Sect. B*, 1981, **37**, 193.

17 G. Tosi, L. Cardellini and G. Bocelli, *Acta Crystallogr., Sect. B*, 1988, **44**, 55; G. R. Willey and M. G. B. Drew, *Acta Crystallogr., Sect. C*, 1985, **41**, 589.

18 S. Patai, *The Chemistry of the Carbon–Nitrogen Double Bond*, Wiley, New York, 1976; Beilstein, *Handbuch der Organische Chemie*, 1935, **15**, 137, series H.

19 G. M. Sheldrick, *Acta Crystallograph., Sect. A*, 1990, **46**, 467.

20 G. M. Sheldrick, SHELX, a Computer Program for Crystal Structure Determination, University of Cambridge, 1976.

21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 100, 149.

Received 16th October 1992; *Paper* 2/05540F