Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Vicente, José and Saura-Llamas, Isabel(2007) '*ORTHO*-PALLADATION OF PRIMARY AMINES: THE MYTH DISPELLED', Comments on Inorganic Chemistry, 28: 1, 39 — 72
To link to this Article: DOI: 10.1080/02603590701394766
URL: http://dx.doi.org/10.1080/02603590701394766

Comments on Inorganic Chemistry, 28: 39–72, 2007

ISSN: 0260-3594 print
DOI: 10.1080/02603590701394766

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ORTHO-PALLADATION OF PRIMARY AMINES: THE MYTH DISPELLED

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Cyclopalladation reactions are well known processes widely studied, because they represent a facile method for the activation of a C–H bond in aromatic rings and have potential applications in organic synthesis. A large variety of N-containing ligands has been cyclometalated, including tertiary amines. Nevertheless, only very recently, a general method to *ortho*-palladate primary aryl-alkylamines has been reported. This review deals mainly with the synthesis, but also with the structure and reactivity, of *ortho*-metalated complexes containing this kind of ligand. In addition, it will try to summarize the reasons that make so different the behavior of tertiary and primary amines towards direct palladation.

1. SCOPE AND LIMITATIONS

This review is devoted to cyclopalladated primary aryl-substituted alkylamines (primary aryl-alkylamines) in which a C_{sp^2}-Pd bond is present (Chart 1). Therefore, complexes with the NH_2 group directly bonded to an aryl ring (e.g., cyclopalladated anilines[1,2] or naphthylamines[3]) will not be considered. On the other hand, the nature of the aryl group is not restricted to phenyl rings and hence results with napthyl, cyclopentadienyl

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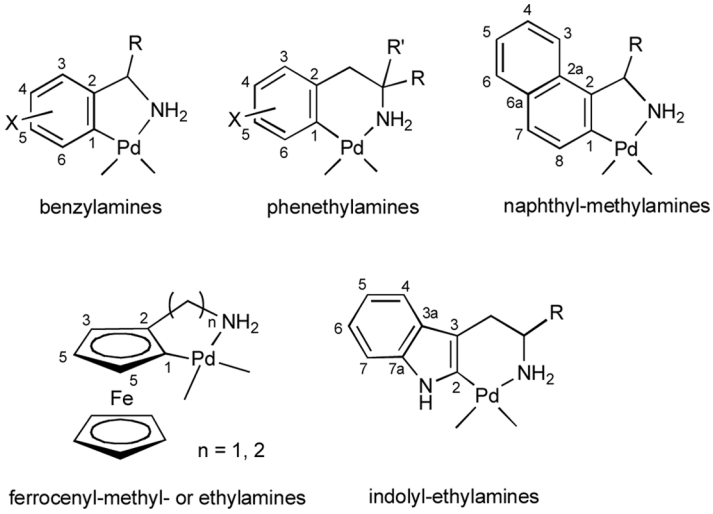


Chart 1. Types of *ortho*-metalated primary aryl-alkylamines and numbering schemes for the aryl rings.

or indolyl groups are included. In those cases, the resulting complexes are not strictly *ortho*-metalated, although this term is widely used in the literature and through this review.

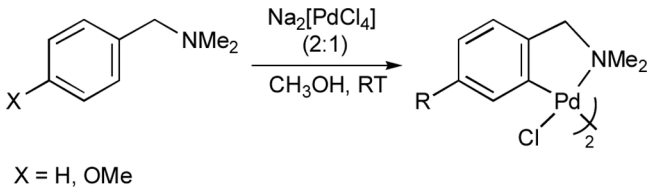
Compounds only reported to exist in solution are not collected; only isolated species are taken into account. Some of the complexes included in section 2.1 (historical aspects) are poorly characterized, due to the lack of adequate techniques in those times.

The use of the tittle complexes as agents for enantiomeric resolution will not be considered because, very recently, Granell *et al.* have published a review on the subject.[4] Dunina *et al.* have also reported the use of *ortho*-palladated primary benzylamines as chirality transfer reagents to synthesize other optically active palladacycles through ligand exchange reactions.[5]

2. SYNTHESIS OF *ORTHO*-METALATED ARYL-ALKYLAMINES

2.1. Historical Aspects

Since the early work of Cope and Friedrich on cyclopalladation of aryl-alkylamines,[6] it had been generally accepted[7,8] that this kind of ligand should meet three requirements to undergo *ortho*-metalation: (1) the nitrogen should be tertiary; (2) the metallacycle formed should be a



Scheme 1.

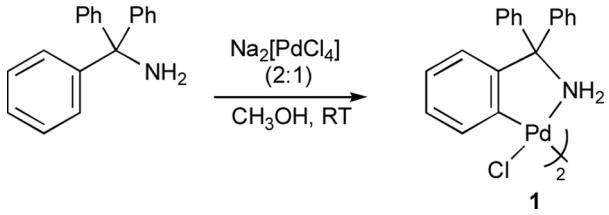
five-membered ring; and (3) the aromatic ring should not be deactivated towards electrophilic attack. For instance, N,N-dimethylbenzylamine or N,N-dimethyl-4-methoxy-benzylamine reacted with $[PdCl_4]^{2-}$ (molar ratio amine:Pd = 2:1) in methanol to give dinuclear chloro-bridged *ortho*-metalated complexes (Scheme 1), while benzylamine, N-methylbenzylamine, N,N-dimethyl-2-phenyl-1-ethylamine and N,N-dimethyl-4-nitrobenzylamine did not. Instead, coordination complexes $[PdCl_2(amine)_2]$ were obtained.

In the following 25 years (1968–1993), several exceptions to these rules were reported. Thus, in 1973, Lewis *et al.* published the cyclopalladation of triphenylmethylamine using Cope's reaction conditions (Scheme 2).[9] The presence of sterically hindered substituents at the α-carbon was postulated to promote the *Ortho*-metalation process.

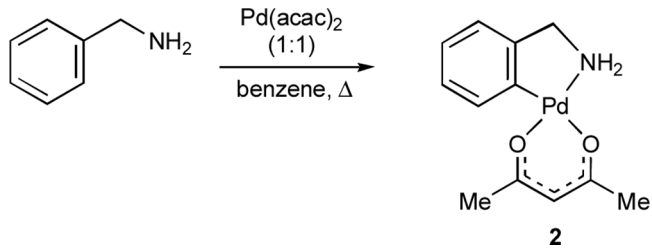
ortho-metalation of other primary amines was achieved by changing the nature of the metalating agent. For instance, in 1975, Baba *et al.*[10] used $Pd(acac)_2$ (acac = acetylacetonate) to *ortho*-metalate benzylamine itself (Scheme 3).

In 1983, Avshu and co-workers also succeeded in preparing the iodo-bridged *ortho*-palladated complex of benzylamine by treating the bis-amine complex $[PdI_2(NH_2CH_2Ph)_2]$ with a silver(I) salt (Scheme 4).[11]

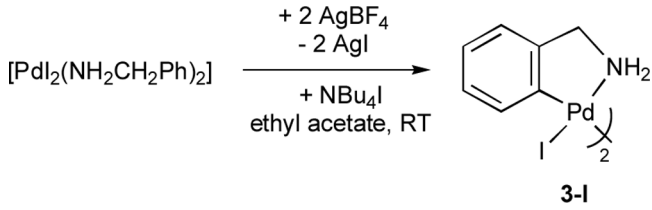
Similar reaction conditions were used in 1993 to prepare *ortho*-metalated derivatives of α-methylbenzylamine (Scheme 5).[12] Complex



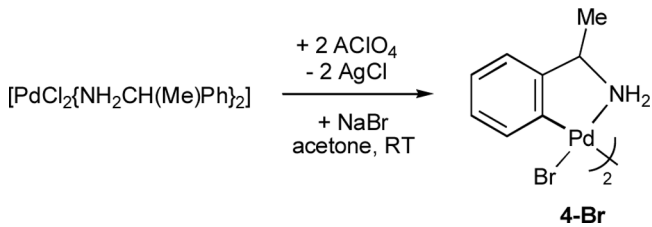
Scheme 2.



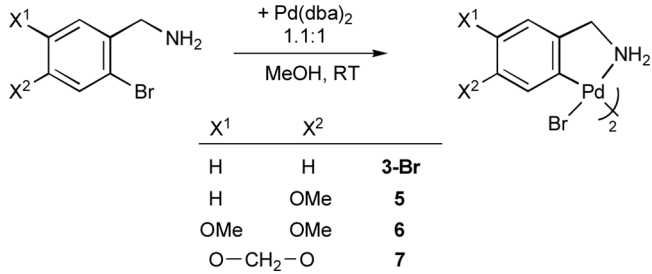
Scheme 3.



Scheme 4.

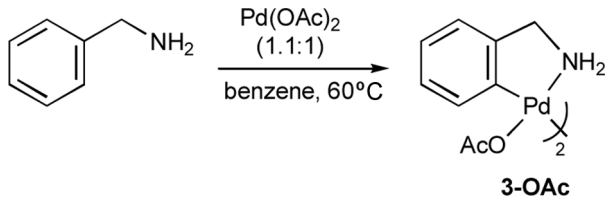


Scheme 5.



X^1	X^2	
H	H	**3-Br**
H	OMe	**5**
OMe	OMe	**6**
O−CH_2−O		**7**

Scheme 6.



3-OAc

Scheme 7.

4-Br could be obtained optically pure if (*R*)- or (*S*)-α-methylbenzylamine was used as starting material.

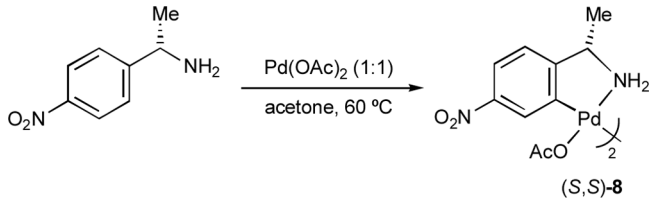
Finally, it is necessary to mention that Clark and Dyke prepared in 1983 some cyclopalladated primary benzylamines by oxidative addition of 2-bromo derivatives to $Pd(dba)_2$ (dba = dibenzylidenacetone) (Scheme 6).[13,14] As this is not a metalation reaction, the limitations imposed to the ligand by Cope's rules do not apply.

However, the above works did not change esentially the fundamental believe that primary amines were inert toward direct activation of C−H bonds by palladium(II) to afford the corresponding palladacycles.

2.2. In Search of a General Method

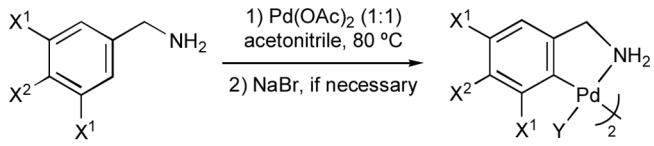
In 1993, Fuchita *et al.* used for the first time $Pd(OAc)_2$ (OAc = acetate) to successfully *ortho*-metalate benzylamine.[15,16] The reaction was carried out in benzene, at 60° C, using a molar ratio amine:$Pd(OAc)_2$ = 1.1:1 (Scheme 7). In these conditions, the cyclopalladated complex **3-OAc** was obtained in acceptable yield.

The same metalating agent, but using acetone as solvent and a molar ratio amine:Pd = 1:1, allowed us to *ortho*-metalate (*S*)-4-nitro-α-methylbenzylamine. This was the first cyclopalladated complex containing a primary benzylamine with an electron-withdrawing substituent on the aromatic ring (Scheme 8).[17]



(*S*,*S*)-**8**

Scheme 8.



X^1	X^2	Y	
H	H	OAc	**3-OAc**
H	Cl	Br	**9**
H	OMe	Br	**10**
OMe	H	Br	**11**

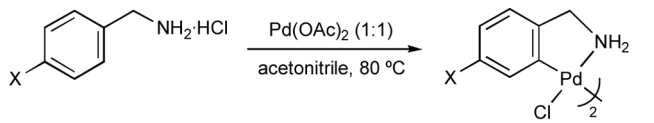
Scheme 9.

In both reactions, two significant changes had been made from Cope's reaction conditions: the use of (1) $Pd(OAc)_2$ instead $[PdCl_4]^{2-}$, and (2) a molar ratio amine:Pd(II) of ca. 1:1.

As will be discussed later, the choice of reaction solvent is not a trivial issue, and new reactions were tried using acetonitrile. These new conditions enabled preparation of a wide variety of *ortho*-metalated non-α-substituted primary benzylamines (Scheme 9).[18] When the acetato-bridged complexes were not isolable, methatesis reaction with NaBr led to the analogous bromo-bridged dimers.

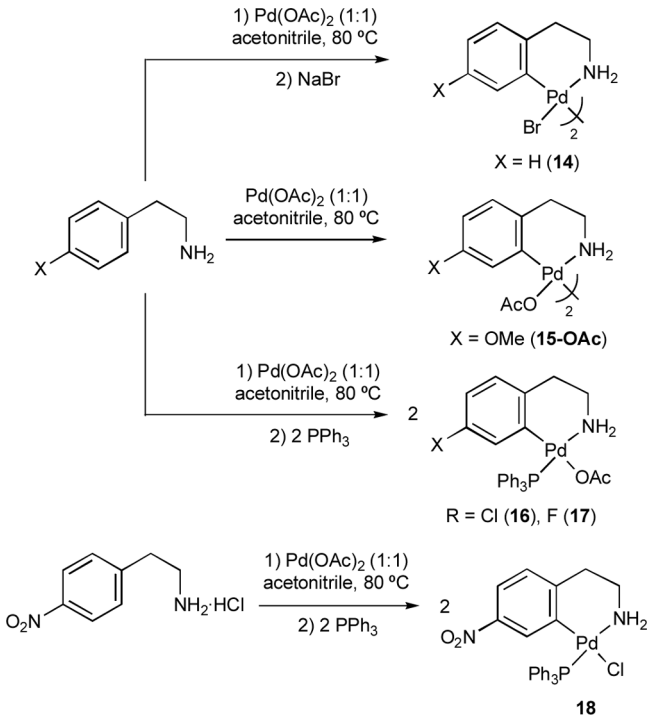
The reactions could also be carried out using the hydrochloride salts of the benzylamines as starting materials. In these cases, the corresponding chloro-bridged *ortho*-metalated complexes were obtained (Scheme 10).

The method proved to be quite general, as it also worked with phenethylamines, where six-membered palladacycles were formed (Scheme 11).[19] *Ortho*-palladation of 4-NO_2-phenethylamine was an important issue, as it transgressed simultaneously the three limits imposed by Cope's rules. When the acetato- or chloro-bridged dimers could not be isolated in pure forms, addition of a neutral ligand led to monomeric species, easier to purify.



X = F (**12-Cl**), NO_2 (**13-Cl**)

Scheme 10.



Scheme 11.

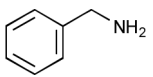
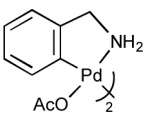
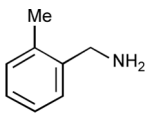
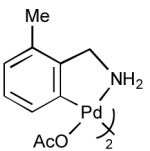
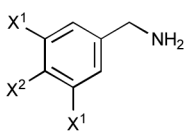
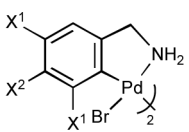
These reaction conditions have been successfully used to *ortho*-metalate other benzyl- and phenethylamines (summarized in Table 1), including amino acids, and to cyclopalladate cyclopentadienyl-, naphthyl- and indolyl-alkylamines.

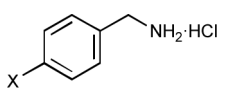
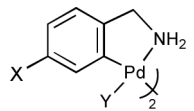
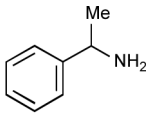
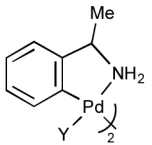
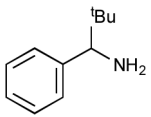
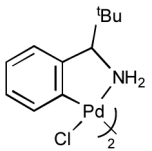
2.3. Reaction Intermediates

When $Pd(OAc)_2$ reacts at room temperature in acetonitrile with an excess of benzylamine (molar ratio amine:Pd $\geq$ 2:1), a bis-amine N-bound complex $[Pd(OAc)_2(NH_2CH_2Ph)_2]$ (**A**) is formed (Scheme 12). The reaction was monitored by UV-Vis spectroscopy and it was complete after 1 min. If the reaction mixture is heated at 60°C, complex **A** transforms slowly into the *ortho*-palladated material.[29]

When the reactions of primary benzylamines and $Pd(OAc)_2$ are carried out at 1:1 molar ratios, the bis-amine complexes of type **A**, $[Pd(OAc)_2(NH_2CH_2Ar)_2]$, are initially formed, but these react subsequently with

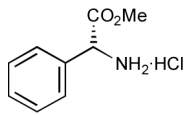
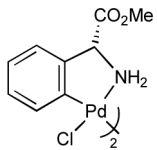
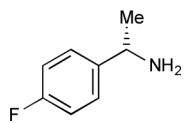
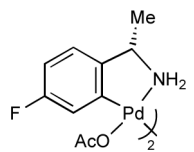
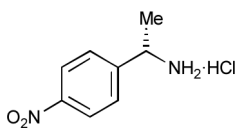
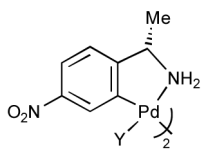
Table 1. Cyclopalladated complexes[a] containing primary aryl-alkylamines prepared by using $Pd(OAc)_2$

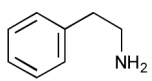
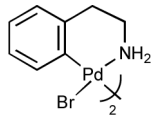
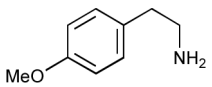
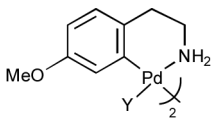
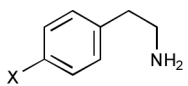
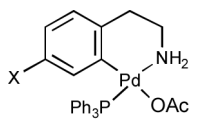
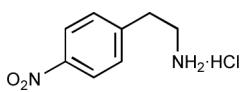
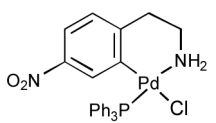
$Ar(CH_2)_nNH_2$ or $Ar(CH_2)_nNH_2 \cdot HCl$ (n = 1, 2)	Metalation conditions	Other reagents used after metalation	Cyclopalladated complex	Reference
	benzene, 60°C or acetonitrile, 80°C		 **3-OAc**	[15] [16] [18]
	acetonitrile, 80°C		 **19**	[20]
 $X^1 = H, X^2 = Cl$; $X^1 = H, X^2 = OMe$; $X^1 = OMe, X^2 = H$	acetonitrile, 80°C	+NaBr −NaOAc	 $X^1 = H, X^2 = Cl$ (**9**); $X^1 = H, X^2 = OMe$ (**10**); $X^1 = OMe, X^2 = H$ (**11**)	[18]

 X = F, NO_2	acetonitrile, 80°C	+NaBr − NaCl	 X = F, Y = Cl (**12-Cl**), Br (**12-Br**) X = NO_2, Y = Cl (**13-Cl**), Br (**13-Br**)	[18]
 (*R*) or (*S*)	benzene, 50°C or toluene, RT	+ NaCl or LiBr − NaOAc or LiOAc	 Y = OAc, (*R*,*R*)- and (*S*,*S*)-**4-OAc** Y = Cl, (*R*,*R*)-**4-Cl** and (*S*,*S*)-**4-Cl** Y = Br, (*R*,*R*)-**4-Br**	[1] [21] [22]
	benzene, RT or acetone, 50°C or metanol, RT	+ LiCl − LiOAc	 **20**	[23]

(*Continued*)

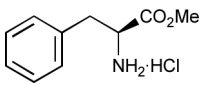
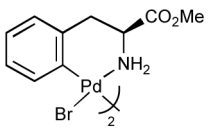
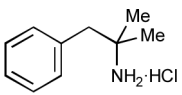
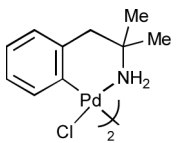
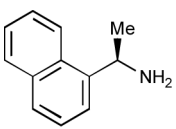
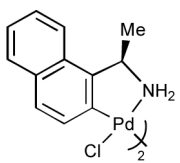
Table 1. Continued

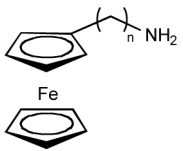
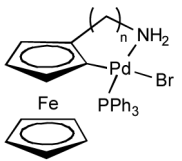
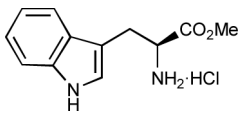
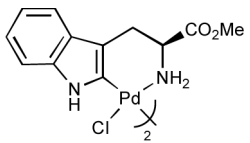
$Ar(CH_2)_nNH_2$ or $Ar(CH_2)_nNH_2 \cdot HCl$ (n = 1, 2)	Metalation conditions	Other reagents used after metalation	Cyclopalladated complex	Reference
	acetone, 60°C		 (*R*,*R*)-**21**	[21]
	benzene, 50°C or acetonitrile, 80°C		 (*S*,*S*)-**22-OAc**	[24]
	acetone, 60°C	+NaY −NaCl	 Y = Cl, (*S*,*S*)-**8-Cl**; Br, (*S*,*S*)-**8-Br**; I, (*S*,*S*)-**8-I**	[17]

	acetonitrile, 80°C	+ NaBr −NaOAc	 **14**	[18]
	acetonitrile, 80°C	+LiCl or NaBr −LiOAc or NaOAc	 Y = OAc, **15-OAc**; Cl, **15-Cl**; Br, **15-Br**	[19]
 X = Cl, F	acetonitrile, 80°C	+PPh_3	 X = Cl, **16**; F, **17**	[19]
	acetonitrile, 80°C	+PPh_3	 **18**	[19]

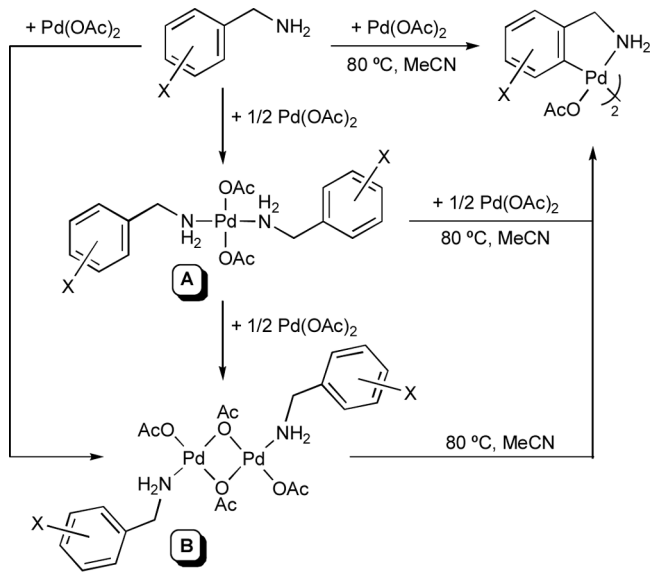
(*Continued*)

Table 1. Continued

$Ar(CH_2)_nNH_2$ or $Ar(CH_2)_nNH_2 \cdot HCl$ (n = 1, 2)	Metalation conditions	Other reagents used after metalation	Cyclopalladated complex	Reference
	acetonitrile, 80° C	+NaBr −NaOAc	 (*S*,*S*)-**26**	[25]
	acetonitrile, 80° C		 **27**	[26]
	acetic acid, 60° C	+LiBr −LiOAc	 (*R*,*R*)-**28**	[27]

	toluene, 60°C	1) +LiBr, −LiOAc 2) +PPh_3	 n = 1, **29**; 2, **30**	[28]
	acetonitrile, 80°C		 (*S*,*S*)-**31**	[26]

[a]When the halogeno- or acetato-bridged dimers could not be prepared in pure form, the first-isolated products containing the *ortho*-palladated amines are included.



Scheme 12.

more $Pd(OAc)_2$ to give the dimeric acetato-bridged species $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2Ar)]_2$ (**B**) (Scheme 12).[18,30] Again, if the reaction mixture is heated at 80 °C, the *ortho*-palladated complex is formed.

The reaction between $Pd(OAc)_2$ and benzylamine (1:1) was monitored by ^1H NMR in $CDCl_3$ at room temperature. Formation of complex **A** was almost immediate, and after 1–2 min only signals corresponding to this complex and unreacted $Pd(OAc)_2$ were present. After 5 min, complex **B** started to form. With time, signals corresponding to complex **A** decreased in intensity while the signal corresponding to complex **B** became stronger. After 1.5 h, the reaction was complete and only complex **B** was present in solution. In acetonitrile at room temperature, the reaction is analogous but slower and thus formation of $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2Ar)]_2$ is not complete after 2 h. In acetonitrile at 80 °C, the same intermediates are detected and, if not isolated, reaction continues and *ortho*-metalated primary benzylamines are formed.[18] Analogous results are obtained when phenethylamines are used.[19] Interestingly, when the reaction between the primary aryl-alkylamines, except benzylamine itself (see Section 3.1), and palladium(II) acetate was performed in molar ratio 2:1, in acetonitrile at 80 °C, only formation of complexes $[Pd(OAc)_2(NH_2CH_2Ar)_2]$ (**A**) was observed after 4 hours.

To prove that $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2Ar)]_2$ could be an intermediate, solutions of complexes **B** (prepared independently by reaction of $[Pd(OAc)_2(NH_2CH_2Ar)_2]$ and $Pd(OAc)_2$ in CH_2Cl_2 at room temperature) in acetonitrile were heated at 80 °C. In these conditions, cyclopalladated benzylamines were also obtained. Curiously, *ortho*-metalation from complexes **B** (Ar = 4-MeO-C_6H_4 and 2,5-$(MeO)_2$-C_6H_3) also occurred in the solid state at room temperature or on heating at 80 °C.[18]

The ^1H and ^{13}C NMR spectra of the few soluble bis-amine complexes **A** clearly indicated that only one isomer (*cis* or *trans*) was obtained, because only one set of signals was observed. We assumed the products have a *trans* geometry since this would be the thermodynamically most stable form, as proved for other bis(amine)dihalogenopalladium(II) complexes.[31] The crystal structure of complex $[Pd(OAc)_2\{NH_2CH(Me)C_6H_4\text{-}F\text{-}4\}_2]$ has been determined by X-ray diffraction and confirms the mutually *trans* disposition of the amine ligands.[24]

^1H and ^{13}C NMR spectra of complexes **B** showed only two signals for the acetate methyl groups: one for the bridging and the other for the terminal acetate methyl groups. Thus, both ligands must have the same chemical environment and must adopt a *trans* disposition. This is proved by the crystal structure of complex $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2C_6H_4NO_2\text{-}4)]_2$, which was determined by X-ray diffraction.[18] Each palladium atom is bonded to four atoms in a square-planar coordination. The nitrogen of the amine and the oxygen atom from a terminal acetate group are mutually *cis*. The distances between one of the oxygen atoms of the mono-coordinated acetato ligand bonded to one palladium atom and the *ortho* hydrogen atom of the amine coordinated to the other palladium atom (2.429 and 2.540 Å) are shorter than the sum of the van der Waals radii of O and H (2.7 Å). This feature is relevant to the mechanism and it suggests that *ortho*-metalation reactions in the solid state starting from dimers **B** could occur through an intramolecular process involving the mentioned pair of oxygen and hydrogen atoms.

When an amine hydrochloride salt is used as starting material, its reaction with $Pd(OAc)_2$ in a 1:1 molar ratio gives acetic acid and mixed $[PdCl(OAc)(NH_2CH_2Ar)]_2$ complexes. Unfortunately, none of these chloro- or acetato-bridged intermediates have been isolated, and thus their structure remains uncertain. Nevertheless, when these complexes are heated in acetonitrile at 80 °C, only the chloro-bridged derivatives of the *ortho*-metalated amines are obtained, as proved by IR and NMR spectroscopy. Since in complexes $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2Ar)]_2$

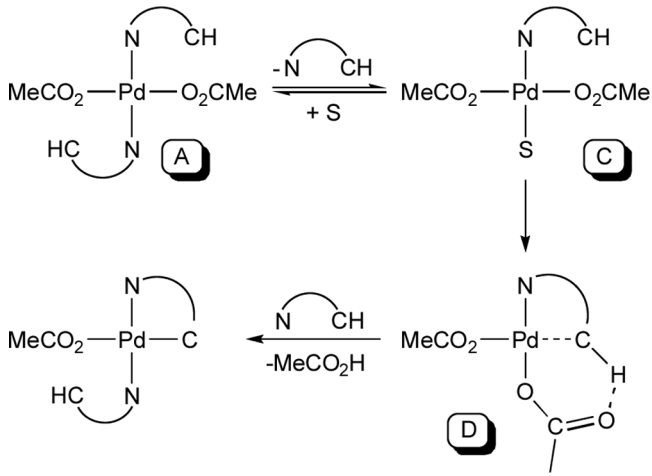
(B) the interactions that lead to *ortho*-metalation seem to be those between the terminal acetates and the coordinated amines, it is reasonable to propose that in the mixed $[PdCl(OAc)(NH_2CH_2Ar)]_2$ complexes, the chloro ligands act as bridges.

3. MECHANISM

3.1. Proposed Mechanism

The mechanism of *ortho*-metalation of benzylamine has been investigated by Ryabov *et al.* using acetonitrile solutions of palladium(II) acetate and an excess of the amine.[29] In these conditions, palladium(II) acetate reacts with benzylamine to give the N-bound coordination complex $[Pd(OAc)_2(amine)_2]$ **(A)**, as stated in section 2.3. If this reaction mixture is heated at 60°C, the complex **A** transforms slowly into the *Ortho*-palladated material. This process takes place in two steps: (1) reversible solvolysis of the amine ligand (Scheme 13, **A** → **C**); and (2) electrophilic attack of Pd(II) at the *ortho* carbon of the aryl ring followed by proton elimination (Scheme 13, **C** → **D**). Although high concentrations of benzylamine favor the formation of complex **A** from $Pd(OAc)_2$, the rate of the *ortho*-metalation reaction is strongly decreased by the excess of amine.

When chloroform is used as solvent, a three-coordinated $14e^-$ intermediate $[Pd(OAc)_2(amine)]$ has been proposed,[32] although species such



Scheme 13.

as [Pd(μ-OAc)(OAc)(amine)]$_2$ (**B** in Scheme 12) or [Pd(κ^2-*O, O*-OAc)(OAc)(amine)] cannot be ruled out, as dissociative pathways are very uncommon in Pd(II) chemistry.[33] The existence of such species in stronger coordinating solvents (such as acetonitrile) appears unlikely, and the solvento species [Pd(OAc)$_2$(amine)(S)] (**C**) must be formed.[29]

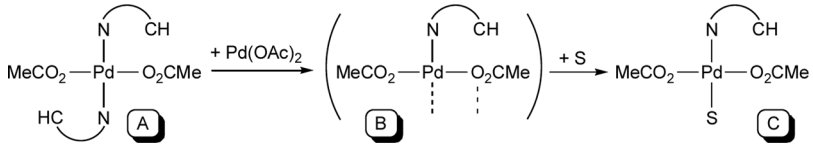
Two of Cope's rules imposed on the amine to be *ortho*-metalated can be explained based on this mechanism. Thus, primary amines are inert towards *ortho*-palladation because the enhanced stability of the [PdX$_2$-(amine)$_2$] complexes ruled out the easy formation of [PdX$_2$(amine)(S)] (**C**) in many commonly used solvents.[8] On the other hand, if the aryl ring bears electron-withdrawing substituents, the electrophilic attack of Pd(II) is disfavored. The last of Cope's conditions has a thermodynamic reason, as five-membered metallacycles are more stable than six-membered ones.[34]

This mechanism also explains *ortho*-metalation of tribenzylmethylamine, which is attributable to steric promotion. When bulky amines are used, the large effective volume of the ligand must increase the internal energy of the bis-amine complex [PdX$_2$(amine)$_2$] (**A**) due to a set of unfavorable non-bonding interactions,[7,23] thus stimulating the formation of intermediate **C**. The electrophilicity of the palladium center is also enhanced by the use of sterically hindered amines, because the large effective volume of the ligand weakens the Pd–N bond in the intermediate **C**.[23]

3.2. Key Factors that Facilitate *Ortho*-Metalation of Primary Amines

The key factors that allow the easy *ortho*-metalation of primary arylalkylamines seem to be:

a) The use of a molar ratio amine:Pd = 1:1. In these conditions, the initial bis-amine complex formed (**A**) reacts with more Pd(OAc)$_2$ to give intermediate **B**, as stated in section 2.3. From this intermediate, formation of solvento complex **C** becomes easier, as it requires only breaking of a weak Pd-(μ-OAc) bond, (Scheme 14, **B** $\rightarrow$ **C**) instead dissociation of a coordinated amine (Scheme 13, **A** $\rightarrow$ **C**).
b) The use of Pd(OAc)$_2$ as palladating agent. The acetato ligand seems to play a triple role: (1) it facilitates the solvolysis process of intermediate **A** due to a larger effective volume; (2) it enhances the electrophilicity of the palladium(II) center, as intermediate **C**,



Scheme 14.

$[Pd(OAc)_2(amine)(S)]$, is more electrophilic than $[PdCl_2(amine)(S)]$, formed when Cope's conditions are used;[8] and (3) it acts as an intramolecular base for deprotonation: the acetato helps the C–H bond breaking by nucleophilic assistance (Scheme 13, intermediate **D**).[35] In fact, as stated in section 2.3, the crystal structure of $[Pd(OAc)(\mu\text{-}OAc)(NH_2CH_2C_6H_4NO_2\text{-}4)]_2$ shows interactions between one of the oxygen atoms of a terminal acetate and the *ortho* hydrogen atom of the amine coordinated to the other palladium, suggesting that the *ortho*-metalation reactions could occur through an intramolecular process involving these atoms.

c) The use of polar solvents. Polar solvents, as acetonitrile or methanol, favor the solvolysis process (**A** → **C**, Scheme 13, or **B** → **C**, Scheme 14) because of their increased donicity toward metal centers.[29] As reported by Dunina et al.,[23] cyclopalladation of α-^{t}butylbenzylamine th $Pd(OAc)_2$ could be performed in benzene at room temperature (24 h, 43% yield), but the best results were achieved using methanol as solvent (24 h, 71% yield).

d) Temperature. Most cyclopalladation reactions of primary aryl-alkylamines are carried out at 60–80°C (Table 1). As is known, dissociation of ligands from Pd(II) is facilitated by increasing the temperature.[36]

3.3. Nature of Intermediate D

For the final ring-closure process, a metal arenium intermediate that transfers a proton to a bound acetato via a highly ordered six-membered transition state has been proposed (Chart 2, **D1**).[29] However, very recently, based on density functional calculations, Davies *et al.*[37] have postulated that cyclometalation reactions proceed *via* the formation of an agostic C–H complex (Chart 2, **D2**), which also exhibits an hydrogen-bonding interaction between the *ortho*-H and a coordinated acetato ligand. The formation of this agostic complex is also consistent with the

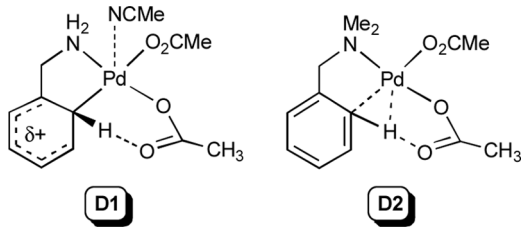


Chart 2.

effects of substituents on the aryl ring, as it involves some elongation of the C−H bond and this is facilitated by electron-donating groups.

3.4. Mechanism in Acetic Acid

The mechanism of cyclopalladation reactions of primary amines using acetic acid as solvent has also been studied.[20,38,39] The process is quite complicated and other reactions, such as acidolysis of Pd−C bond, take place. Dimeric cyclopalladated complexes are initially formed, but the existence of dynamic processes affords some final polynuclear species.

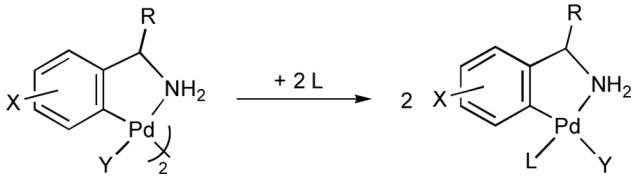
4. REACTIVITY

4.1. Substitution Reactions

The halogeno or acetato-bridges in dimeric *ortho*-palladated complexes containing primary aryl-alkylamines are easily cleaved by various neutral ligands, including pyridines, phosphines or isocyanides, to afford mononuclear metallacycles (Tables 2 and 3 and Scheme 15). This classical reaction has been used for the structural characterization of cyclometalated species (as monomers are usually more soluble that the corresponding dimers),[16,18,19,38] and for the resolution of chiral ligands.[4,27,40] The mechanism of these reactions has been studied for tertiary amines.[41] In addition, reactions of this type are postulated as key pre-equilibria in synthetically important insertion reactions of alkenes, alkynes and other unsaturated molecules into the Pd−C bonds of dimeric palladacycles (e.g., insertion of isocyanides).[42]

Usually, an excess of the neutral ligand does not cleave the Pd−N bond of the resulting five- or six-membered ring,[1,19] in contrast to other palladacycles that contain weaker Pd−N bonds; for example, tertiary amines,[14] benzylideneamines,[46] or 2-phenylaniline.[1] An exception is

Table 2. Neutral mononuclear derivatives of *ortho*-metalated primary benzylamines



Compound	X	R	Y	L	Ref.
32a	H	H	Cl	2-picoline	[16]
32b	H	H	Cl	3,5-lutidine	[16]
32c	H	H	Cl	quinoline	[16]
33-Cl	H	H	Cl	PPh_3	[16]
33-OAc	H	H	OAc	PPh_3	[18,30]
34a	H	H	Br	2,4-Me_2-C_4H_3NC	[42]
34b	H	H	Br	^{t}BuNC	[42]
(*R*)-**35a**	H	Me	Cl	pyridine	[22]
(*R*)-**35b** and (*S*)-**35b**	H	Me	Cl	3,5-lutidine	[21,43]
(*S*)-**35c** and *rac*-**35c**	H	Me	Cl	2,6-lutidine	[43]
(*R*)-**35d** and *rac*-**35d**	H	Me	Cl	2,4,6-trimethylpyridine	[43]
(*S*)-**35e**[a]	H	Me	Cl	2,3,4-trichloropyridine	[44]
(*R*)-**36**	H	Me	Br	$NH_2CH(Me)C_6H_4$	[1]
(*R*)-**37**, (*S*)-**37** and *rac*-**37**	H	Me	Br	PPh_3	[1,12]
38	H	^{t}Bu	Cl	PPh_3	[23]
(*R*)-**39**	H	CO_2Me	Cl	3,5-lutidine	[21]
(*R*)-**40**	H	CO_2Me	Cl	PPh_3	[21]
41	3-Me	H	Br	PPh_3	[20]
42	4,6-$(OMe)_2$	H	Br	PPh_3	[18]
43	5-OMe	H	Br	PPh_3	[18]
44a	5-OMe	H	Br	2,4-Me_2-C_4H_3NC	[42]
44b	5-OMe	H	Br	^{t}BuNC	[42]
45	5-Cl	H	Br	PPh_3	[18]
46-Cl	5-F	H	Cl	PPh_3	[18]
46-Br	5-F	H	Br	PPh_3	[18]
47a	5-F	H	Br	2,4-Me_2-C_4H_3NC	[42]
47b	5-F	H	Br	^{t}BuNC	[42]
48-Cl	5-NO_2	H	Cl	PPh_3	[18]
48-Br	5-NO_2	H	Br	PPh_3	[18]
49a	5-NO_2	H	Br	2,4-Me_2-C_4H_3NC	[42]
49b	5-NO_2	H	Br	^{t}BuNC	[42]
(*S*)-**50-Cl**	5-NO_2	Me	Cl	PPh_3	[17]
(*S*)-**50-Br**	5-NO_2	Me	Br	PPh_3	[17]

(*Continued*)

Table 2. Continued

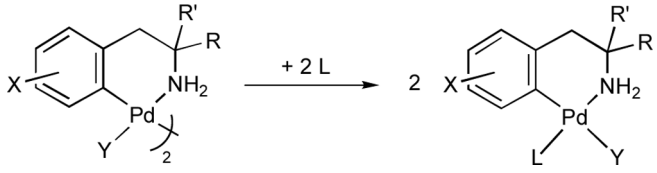
Compound	X	R	Y	L	Ref.
(*R*)-**23**	5-Me	Me	Cl	pyridine	[45]
(*R*)-**24** and (*S*)-**24**	5-Br	Me	Cl	pyridine	[45]
(*S*)-**25**	5-Cl	Me	Cl	pyridine	[45]
(*S*)-**51**	5-F	Me	Cl	pyridine	[45]

[a]In this complex, L is in *trans* position to the *ortho*-metalated carbon.

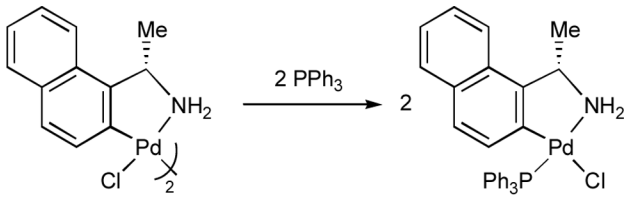
the case of metalated ferrocenyl-alkylamines, as the palladacycle in complexes **29** and **30** can be cleaved by PPh_3 to give compounds in which a second phosphine is coordinated to palladium(II) and the amine acts as a C-monodentate anionic ligand bound through the ferrocenyl fragment.[28]

Reaction of cyclometalated dimers with Tl(acac) or Na(acac) affords the corresponding κ^2-*O,O*-acetylacetonato complexes (Scheme16).[12,16,47,48] Cationic mononuclear derivatives can also be

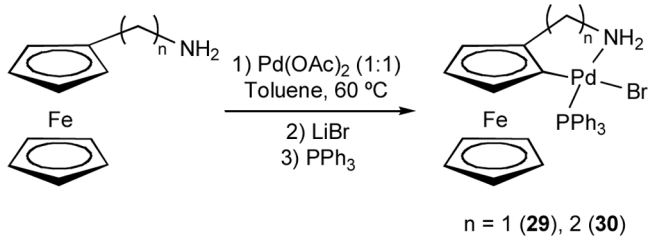
Table 3. Mononuclear derivatives of *ortho*-metalated phenethylamines



Compound	X	R	R′	Y	L	Ref.
52	H	H	H	Br	PPh_3	[18]
(*S*)-**53**	H	H	CO_2Me	Br	4-picoline	[25]
54-OAc	5-OMe	H	H	OAc	PPh_3	[19]
54-Br	5-OMe	H	H	Br	PPh_3	[19]
16	5-Cl	H	H	OAc	PPh_3	[19]
17	5-F	H	H	OAc	PPh_3	[19]
18	5-NO_2	H	H	Cl	PPh_3	[19]



(*R*,*R*)-**28** **55**

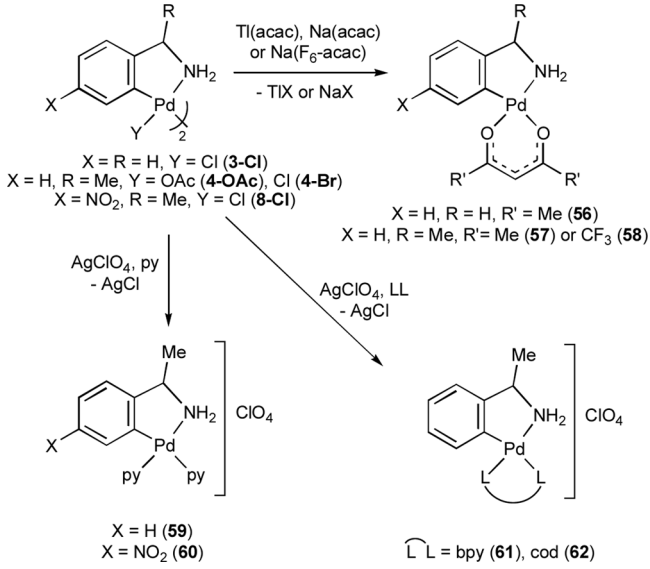


Scheme 15. Mononuclear derivatives of *ortho*-metalated 1-(1-naphthyl)ethylamine and primary ferrocenyl-alkylamines.

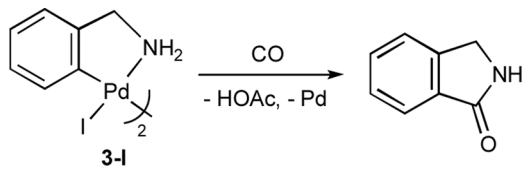
obtained by reacting the acetato- or chloro-bridged dimers with neutral mono- (pyridine, py) or bidentate ligands (2,2′-bipyridine, bpy, or 1,5-cyclooctadiene, cod) and $AgClO_4$.[12,17]

4.2. Insertion Reactions

Insertion of unsaturated reagents into the Pd–C bond of *ortho*-palladated tertiary amines has been widely investigated,[49–51] but only a few examples of these reactions with primary amines have been reported.



Scheme 16. Acetylacetonato and cationic mononuclear derivatives of *ortho*-metalated primary amines.



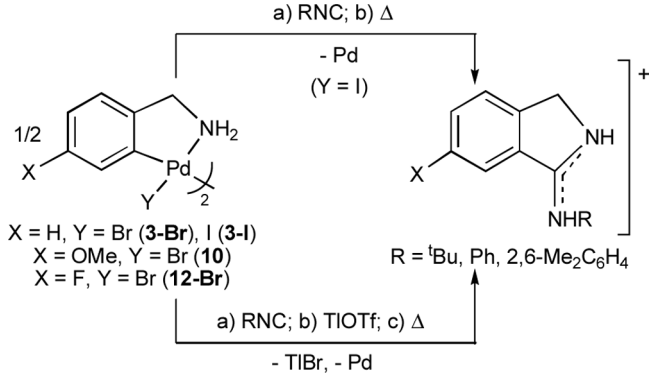
Scheme 17.

A preliminary communication by Parkins *et al.* in 1984 described the reaction of $[Pd_2(\kappa^2\text{-}C,N\text{-}NH_2CH_2C_6H_4\text{-}2)_2I_2]$ with CO in methanol at room temperature to give phthalimidine and palladium metal (Scheme 17).[52] Dyke *et al.* in 1986 observed a similar reaction, although the expected phthalimidine was not obtained pure.[53]

Orito *et al.* have reported a Pd(II)-catalyzed carbonylation of N-alkyl-ω-arylalkylamines to afford five- or six-membered benzolactams. In these conditions, carbonylation of primary amines does not produce benzolactams but ureas.[54] This result is not surprising since the required *ortho*-metalation of primary amines does not occur in the used reaction conditions when an excess of amine is present.[30]

Similarly, the reactions of cyclopalladated benzylamines with isocyanides in refluxing toluene allow the isolation of the corresponding isoindolinium salts (Scheme 18).[42,52]

The suggested mechanism for these reactions is analogous to that proposed for the insertion of CO or isocyanides into the Pd–C bond of *ortho*-metalated tertiary amines: (1) bridge-splitting of the dimer and

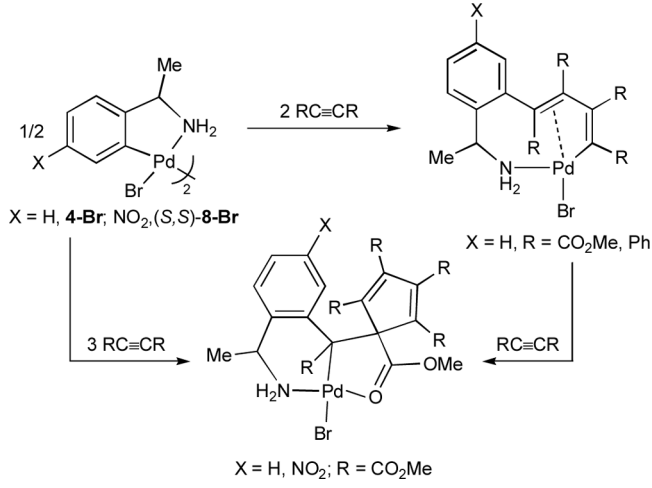


Scheme 18.

coordination of CO or isocyanide to palladium(II); (2) insertion of coordinated CO or isocyanide into the Pd–C bond of the resulting monomer; and (3) decomposition of the acyl or iminoacyl derivative to give Pd(0) and the organic compound.[42,55,56]

Recently, Saluste *et al.* have reported the palladium catalyzed synthesis of cyclic amidines, starting from 2-bromo-benzylamine or 2-bromo-phenethylamine, ^{t}BuNC and Cs_2CO_3.[57] The catalytic reaction must proceed through the oxidative addition of the haloamine to a Pd(0) species, and the subsequent insertion of RNC into the Pd–C bond of the cyclopalladated complex.

Insertion of alkynes in *ortho*-metalated primary amines has also been reported. The reaction of complex **4-Br** with RC≡CR (R=CO_2Me or Ph, Scheme 19) gives the nine-membered cyclometalated complexes resulting from insertion of two alkyne molecules into the Pd–C bond.[58] Attempts to obtain the mono-insertion products were unsuccessful. When $MeO_2CC{\equiv}CCO_2Me$ is used, an excess of alkyne leads to a tri-inserted complex.[58] Isolation of di- and tri- inserted compounds of this type with other cyclopalladated complexes is well documented.[50,59,60] Complex (*S*,*S*)-**8-Br** also reacts with three equivalents of RC≡RC (R = CO_2Me) to give the tri-insertion product, the crystal structure of which has been determined by X-ray diffraction studies.[17]

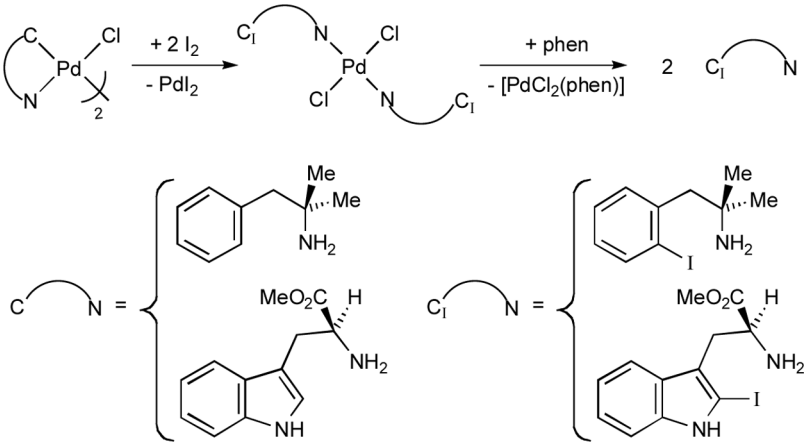


Scheme 19.

Preliminary results indicate that other benzyl or phenethylamines can insert three molecules of $MeO_2CC{\equiv}CCO_2Me$ to give analogous complexes, while only di-insertion products are obtained when 2-butyne or 3-hexyne are used.[61]

4.3. Reactions with Halogens

Stoichiometric bromination or iodination of cyclopalladated complexes is a known process, but very few studies are dedicated to halogenation of *ortho*-palladated tertiary benzylamines.[49,62] Complexes **27** and (*S*,*S*)-**31** (Table 1) are the only cyclopalladated primary amines that have been reacted with I_2. The reaction in CH_2Cl_2 at room temperature gives *trans*-[$PdCl_2$(2-iodo-amine)$_2$] in good yields (Scheme 20).[26] It has been proposed that the initial step of the reaction is the oxidative addition of iodine to give a Pd(IV) complex that would then undergo a reductive elimination followed by a symmetrization process, leading to the bis-iodo-amine complexes and PdI_2. 2-I-phentermine (2-1-α,α-dimethyl-phenethylamine) and (*S*)-2-I-tryptophan methyl ester are conveniently prepared in high yield by reacting these precursors with 1,10-phenanthroline (phen). The by-product in these reactions, [$PdCl_2$(phen)], precipitates from the mixtures and can be easily separated.



Scheme 20.

5. STRUCTURES OF *ORTHO*-METALATED COMPLEXES

5.1. Halogeno-Bridged Dinuclear Cyclopalladated Complexes

The crystal structure of complex (*R*,*R*)-**4-Cl** has been determined by X-ray diffraction studies, and it shows a *transoid* geometry (Chart 3).[22] This isomer is also the most common for similar cyclopalladated dimers containing secondary[60] and tertiary amines,[63–65] although in some cases the *cis* isomer can be isolated.[65,66a] The chloro bridges are non-symmetric due to the different *trans* influence of the chloro and nitrogen atoms [Cl–Pd *trans* to carbon, 2.447(2) and 2.4781(19) Å; Cl–Pd *trans* to nitrogen, 2.332(2) and 2.333(2) Å]. The shorter value of the Pd–N bonds [2.020(6) and 2.019(5)Å], compared to that reported for related tertiary benzylamines [2.075(4) Å for chloro-bridged dimer of N,N-dimethyl-2-methoxy-benzylamine, 2.069(3) Å for N,N-dimethyl-3-methoxy-benzylamine, and 2.068(5) and 2.072(5)2 Å for N,N-dimethyl-4-methoxy-benzylamine],[63] may serve as reliable evidence in favor of a tighter coordination of the primary amine group to the palladium center. The coordination geometry around the palladium atom is planar and the "Pd_2Cl_2" four-membered ring is esentially flat; the best planes through the two Pd centers and their coordinating atoms subtend a dihedral angle of 5.9(2)°.[66b] The C,N-chelate ring has an envelope shape.

Among all the halogeno-bridged dimers reported, complexes (*R*,*R*)- and (*S*,*S*)-**4-Br**, (*R*,*R*)- and (*S*,*S*)-**4-Cl**, **10**, **14**, **15-Cl**, **15-Br**, (*R*,*R*)-**21**, and **27** (Table 1) are soluble enough in $CDCl_3$ to be characterized in this solvent by ^1H NMR spectroscopy. For these complexes, one set of signals is observed, indicating that only one geometric isomer (probably the

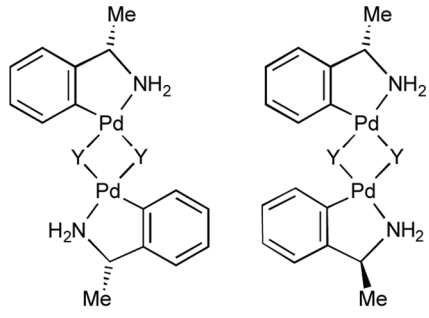


Chart 3.

transoid) is present in solution. Tables with ^{1}H NMR data for all reported complexes containing *ortho*-metalated primary benzyl- and phenethylamines are given in the Supporting Information.

Complexes *rac*-**4-Br**, (*S*,*S*)-**8-Br**, (*S*,*S*)-**8-Cl**, (*S*,*S*)-**8-I**, **12-Br**, **12-Cl**, and **13** are not very soluble in $CDCl_3$ but soluble in acetone-d^6 or dmso-d^6. Probably, coordinating solvents break the halogeno bridges, leading to the formation of mononuclear species. This process should be responsible for the absence of two sets of signals (corresponding to a mixture of *RR* + *RS* and *SR* diastereoisomers) in the NMR spectra of racemic complexes containing primary amines with a chiral center. The optically active isomers (*R*,*R*)- and (*S*,*S*)-**4-Br** are remarkably more soluble in CH_2Cl_2 than the corresponding (*R*,*S*) diastereoisomer.

The ^{1}H NMR spectra of halogeno-bridged dimers clearly show that cyclometalation has taken place. For complexes containing unsubstituted phenyl rings, a set of four different signals (sometimes described as a multiplet) in the aromatic region corresponding to the four protons in the *ortho*-metalated ring is found. For *ortho*-metalated 4-substituted-aryl-alkylamines, a set of three different signals, corresponding to the H3, H4, and H6 aryl protons (see Chart 1 for numbering scheme), are observed. When ^{13}C NMR data are reported, the carbon bonded to palladium(II) is deshielded with respect to that of the corresponding free ligand, as observed in other cyclopalladated complexes.[67]

5.2. Acetato-Bridged Dinuclear Cyclopalladated Complexes

These complexes have a folded arrangement and two geometrical isomers are expected, the *anti* and the *syn* isomers (Chart 4). In practice,

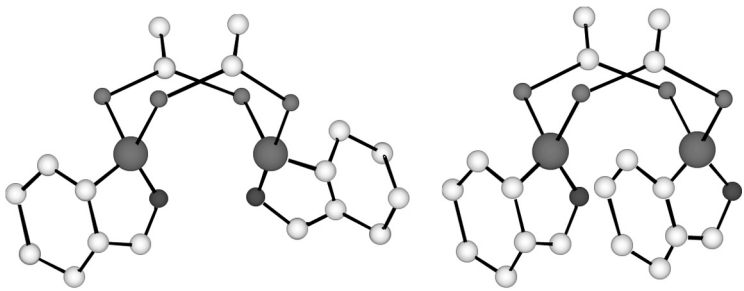


Chart 4.

the *anti* isomer is usually obtained, and all crystallographically characterized acetato-bridged C,N-cyclopalladated dimers containing tertiary amines have this structure.[30,56,68,69] It is assumed that the *syn* isomer is thermodynamically less favorable because the two amino groups are located close to each other.[70] Nevertheless, the *syn*-type isomer has been detected in solution for acetato-bridged cyclopalladated complexes containing N-methylbenzylamine.[16]

The structures of the acetato-bridged dinuclear complexes (*R*,*R*)-**4-OAc**,[22] (*S*,*S*)-**4-OAc**,[71] **15-OAc**,[19] and (*S*,*S*)-**22-OAc**[24] (Table 1) have been determined by X-ray diffraction. The bridging acetato ligands force the two palladium planes to adopt a nonplanar open-book shape. In all complexes, coordination around palladium atoms is essentially square-planar with each nitrogen atom in *trans* position to a different acetate (*anti* isomer). The five-membered palladacycles have typical envelope-type structures, while the six-membered metallacycles are in a boat conformation.

These complexes are usually less soluble in commonly used organic solvents than halogeno-bridged complexes and only a few have been characterized by NMR spectroscopy. At room temperature, ^{1}H NMR spectra of complexes **3-OAc**, **15-OAc** and **19** (Table 1) in $CDCl_3$ exhibited only one singlet due to the acetate methyl protons, supporting that only one isomer (probably the *anti*) is present in solution.

Complexes (*R*,*R*)- and (*S*,*S*)-**4-OAc** (Table 1) exhibit dynamic behavior in solution (acetone-d^6) and at -60°C two isomers are detected.[21] They can be attributable to a change of the ring conformation, as will be discussed in the next section for mononuclear derivatives. Conformational isomers have been detected for complex (*S*,*S*)-**4-OAc** in solid state.[71]

5.3. Mononuclear Derivatives

Molecular structures of mononuclear complexes **16** (Table 1),[19] (*R*)-**23**, (*R*)- and (*S*)-**24**, (*S*)-**25**,[43] (*R*)-**35a**, (*R*)- and (*S*)-**35b**, (*S*)- and *rac*-**35c**, (*R*)- and *rac*-**35d**,[22] (*S*)-**35e**,[45] (*R*)-**37**,[12] *rac*-**38**,[23] (*R*)-**40**,[21] **47b**,[42] (*S*)-**51** (Table 2),[43] **52** (Table 3),[18] (*S*)-**53** (Table 3),[25] (*S*)-**57**,[47] (*S*)- and *rac*-**58**,[48] and *rac*-**62** (Scheme 16),[12] were established by X-ray diffraction studies.

Disregarding optical isomers, ten crystal structures of mononuclear *ortho*-metalated complexes containing primary amines and pyridine derivatives have been reported. Nine of these crystal structures (**35a–d**, **23–25** and

51, Table 2, and **53**, Table 3) show a *cis* disposition of the pyridine ligand and the carbon atom of the cyclopalladated ring, with the pyridine rotated ca. 60° with respect to the phenyl ring in order to avoid steric hindrance. This isomer is thermodynamically favored in monomeric cyclopalladated compounds.[41,68] For complex (*S*)-[PdCl(κ^2-*C,N*-$C_6H_4CHMeNH_2$)(3,4,5-trichloropyridine)] (**35e**), single-crystal X-ray diffraction studies show that it exists in solid state as an essentially planar *trans* isomer.[44] For steric reasons an alternative *cis* isomer would be restricted to a non-planar geometry, as a planar geometry would necessarily result in prohibitively short $H_{py}\cdots H_{Ph}$ distances and a distorted square-planar environment around the central Pd atom.[44]

In complexes **16** (Table 1), (*R*)-**37**, **38**, (*R*)-**40** (Table 2) and **52** (Table 3) the phosphine ligand is in *trans* position to the amine group, in agreement with the well-established *transphobia* between PPh_3 and aryl ligands.[72] Likewise, in complex **47b** (Table 2) the isocyanide is in *cis* position with respect to the aryl group, according to the greater *transphobia* between two carbon donor ligands than between a C– and a N–donor ligand.

The coordination around the palladium atom is essentially square-planar in all complexes except in **52**, which has a very distorted geometry: the angle between the Br−Pd−P and N−Pd−C planes is 18.6°. As expected, the palladacycles are not planar but have an envelope (five-membered) or a boat (six-membered) conformation.

Analysis of the aromatic region of the ^{1}H NMR spectra confirms the metalation. Moreover, for pyridine and PPh_3 derivatives, the aromatic proton H6 appears at a considerably lower frequency relative to the free amine (average value $\Delta\delta = 0.8$ ppm) due to the anisotropic shielding by the adjacent pyridine, that is coordinated nearly perpendicular to the square-planar palladium(II) plane, or the P-phenyl rings. This effect supports the mutually *trans* position of the pyridine or phosphine ligand and the NH_2 group in solution.[73] For complex **35e** (Table 2), H6 is not shielded and therefore it must retain the *trans* configuration in solution. Long-range couplings of protons to ^{31}P-nucleus have also been observed: the ^{31}P−H6 coupling lies in the range 5.1–6.9 Hz for five-membered palladacycles and in the range 4.3–5.4 Hz for the six-membered ones.

In the mononuclear complexes derived from benzylamine, the NH_2 protons resonate as one broad signal. As the cyclometalated ring is not planar, H_{ax} should be distinguished from H_{eq}. Moreover, there must be two different conformations (δ and λ) for the five-membered cyclopalladated ring. At room temperature, conformational inversion of the

palladacycle lies in the fast range and, if the ligand is symmetric or it can freely rotate around the Pd–L bond, the two NH_2 protons become equivalent through an average symmetry plane. However, when unsymmetric ligands such as 2-picoline or quinoline are ligated to the palladium atom, although conformational inversion still exchanges equatorial and axial positions, the two protons are in different chemical environments and resonate separately.

The presence of a chiral center in the molecule also makes the NH_2 group diastereotopic, and both hydrogen atoms become different for each conformation. As stated by Dunina *et al.*, when there is a bulky substituent on the α-carbon, the conformation in which the group is located in the axial position must be favored. They proposed that mononuclear complexes containing *ortho*-metalated ^{t}Bu-benzylamine exist in a $\lambda(S)$ or $\delta(R)$ conformation.[23] The stereochemistry of the palladacycle in complex **38** (Table 2), as shown by X-ray diffraction studies, is in agreement with the ^{1}H NMR data in solution, namely, λ for the *S*, and δ for the *R* enantiomer. The bulky α-^{t}Bu substituent is situated close to the axial position and the α-methine proton is arranged nearly equatorial.

^{31}P NMR spectra of complexes containing five-membered palladacycles showed a singlet at 37.0–43.3 ppm, while this signal is shifted to lower frequencies for complexes containing six-membered palladacycles (31.4–34.3 ppm). This difference may be used as an indication of the effect of the chelate bite of the *ortho*-metalated amine upon the phosphine ligand (80.6–81.8° for five-membered rings and 84.29–87.97° for six-membered ones).[28,74]

6. CONCLUSIONS

Primary aryl-alkylamines can be *ortho*-metalated using the appropriate reaction conditions, even if the aryl ring bears electron-withdrawing substituents and a six-membered palladacycle is formed. The most successful reaction conditions include the use of: (1) $Pd(OAc)_2$ as palladating agent; (2) a molar ratio Pd:amine = 1:1; (3) polar solvents (acetonitrile, methanol); and (4) temperatures above 25 °C. Structural features of *ortho*-metalated complexes containing primary aryl-alkylamines are similar to analogous compounds with tertiary amines, but their reactivity seems more limited due to the greater stability of the resulting cyclometalated ring.

ACKNOWLEDGEMENT

We thank Ministerio de Educación y Ciencia (Spain) and FEDER (CTQ2004-05396) for financial support.

REFERENCES

1. Albert, J., J. Granell, A. Luque, J. Minguez, R. Moragas, M. Font-Bardia, and X. Solans, 1996. *J. Organomet. Chem.*, **522**, 87.
2. Driver, M. S. and J. F. Hartwig, 1997. *J. Am. Chem. Soc.*, **119**, 8232. Albert, J., J. Granell, J. Zafrilla, M. Font-Bardia, and X. Solans, 2005. *J. Organomet. Chem.*, **690**, 422.
3. Pfeffer, M., N. Sutter-Beydoun, A. De Cian, and J. Fisher, 1993. *J. Organomet. Chem.*, **453**, 139.
4. Albert, J., J. Granell, and G. Muller, 2006. *J. Organomet. Chem.*, **691**, 2101.
5. Dunina, V. V., E. D. Razmyslova, O. N. Gorunova, M. V. Livantsov, and Y. K. Grishin, 2003. *Tetrahedron Asymm.*, **14**, 2331. Dunina, V. V., O. N. Gorunova, E. D. Kuznetsova, E. I. Turubanova, M. V. Livantsov, and Y. K. Grishin, 2006. *Russian Chemical Bulletin* 2007, **55**, 12.
6. Cope, A. C. and E. C. Friedrich, 1968. *J. Am. Chem. Soc.*, **90**, 909.
7. Dunina, V. V., O. A. Zalevskaya, and V. M. Potapov, 1988. *Russ. Chem. Rev.*, **57**, 250.
8. Ryabov, A. D. 1990. *Chem. Rev.*, **90**, 403.
9. Cockburn, B. N., D. V. Howe, T. Keating, B. F. G. Johnson, and J. Lewis, 1973. *J. Chem. Soc., Dalton Trans.*, 404.
10. Baba, S. and S. Kawaguchi, 1975. *Inorg. Nucl. Chem. Lett.*, **11**, 415.
11. Avshu, A., R. D. O'Sullivan, A. W. Parkins, N. W. Alcock, and R. M. Countryman, 1983. *J. Chem. Soc., Dalton Trans.*, 1619.
12. Vicente, J., I. Saura-Llamas, and P. G. Jones, 1993. *J. Chem. Soc., Dalton Trans.*, 3619.
13. Clark, P. W. and S. F. Dyke, 1983. *J. Organomet. Chem.*, **259**, C17.
14. Clark, P. W. and S. F. Dyke, 1985. *J. Organomet. Chem.*, **281**, 389.
15. Fuchita, Y. and H. Tsuchiya, 1993. *Polyhedron*, **12**, 2079.
16. Fuchita, Y., H. Tsuchiya, and A. Miyafuji, 1995. *Inorg. Chim. Acta*, **233**, 91.
17. Vicente, J., I. Saura-Llamas, M. G. Palin, and P. G. Jones, 1995. *J. Chem. Soc., Dalton Trans.*, 2535.
18. Vicente, J., I. Saura-Llamas, M. G. Palin, P. G. Jones, and M. C. Ramírez de Arellano, 1997. *Organometallics*, **16**, 826.
19. Vicente, J., I. Saura-Llamas, J. Cuadrado, and M. C. Ramírez de Arellano, 2003. *Organometallics*, **22**, 5513.
20. Gómez, M., J. Granell, and M. Martínez, 2000. *Eur. J. Inorg. Chem.*, 217.
21. Fuchita, Y., K. Yoshinaga, Y. Ikeda, and J. Kinoshita-Kawashima, 1997. *J. Chem. Soc., Dalton Trans.*, 2495.

22. Calmuschi, B. and U. Englert, 2002. *Acta Cryst.*, **C58**, m545.
23. Dunina, V. V., L. G. Kuz'mina, M. Y. Kazakova, O. N. Gorunova, Y. K. Grishin, and E. I. Kazakova, 1999. *Eur. J. Inorg. Chem.*, 1029.
24. Calmuschi, B., A. Erik, and U. Englert, 2004. *Acta Cryst.*, **C60**, m320.
25. Vicente, J., I. Saura-Llamas, J.-A. García-López, B. Calmuschi-Cula, and D. Bautista, 2007, *Organometallics*, **26**, 2768.
26. Vicente, J., I. Saura-Llamas, and D. Bautista, 2005. *Organometallics*, **24**, 6001.
27. Albert, J., J. M. Cadena, and J. Granell, 1997. *Tetrahedron Asymm.*, **8**, 991.
28. Bosque, R. and C. López, 1999. *Polyhedron*, **18**, 135.
29. Kurzeev, S. A., G. M. Kazankoz, and A. D. Ryabov, 2002. *Inorg. Chim. Acta*, **340**, 192.
30. Fuchita, Y., K. Yoshinaga, T. Hanaki, H. Kawano, and J. Kinoshita-Kawashima, 1999. *J. Organomet. Chem.*, **580**, 273.
31. Cattalini, L. and M. Martelli, 1969. *J. Am. Chem. Soc.*, **91**, 312.
32. Ryabov, A. D., I. K. Sakodinskaya, and A. K. Yatsimirsky, 1985. *J. Chem. Soc., Dalton Trans.*, 2629.
33. Yagyu, T., S. Aizawa, and S. Funahashi, 1998. *Bull. Chem. Soc. Jpn.*, **71**, 619.
34. Bosque, R. and F. Maseras, 2005. *Eur. J. Inorg. Chem.*, 4040.
35. Canty, A. J. and G. van Koten, 1995. *Acc. Chem. Res.*, **28**, 406.
36. Ryabov, A. D. 1987. *Inorg. Chem.*, **26**, 1252
37. Davies, D. L., S. M. A. Donald, and S. A. Macgregor, 2005. *J. Am. Chem. Soc.*, **127**, 13754.
38. Albert, J., J. Granell, and R. Tavera, 2003. *Polyhedron*, **22**, 287.
39. Albert, J., J. Granell, and R. Tavera, 2003. *J. Organomet. Chem.*, **667**, 192.
40. Albert, J., J. M. Cadena, J. Granell, G. Muller, J. I. Ordinas, D. Panyella, C. Puerta, C. Sanudo, and P. Valerga, 1999. *Organometallics*, **18**, 3511. Albert, J., J. M. Cadena, J. Granell, G. Muller, D. Panyella, and C. Sañudo, 2000. *Eur. J. Inorg. Chem.*, 1283. Albert, J., J. M. Cadena, S. Delgado, and J. Granell, 2000. *J. Organomet. Chem.*, **603**, 235. Albert, J., R. Bosque, J. M. Cadena, J. R. Granell, G. Muller, and J. I. Ordinas, 2000. *Tetrahedron Asymm.*, **11**, 3335. Durán, E., E. Gordo, J. Granell, M. Font-Bardia, X. Solans, D. Velasco, and F. López-Calahorra, 2001. *Tetrahedron Asymm.*, **12**, 1987. Albert, J., R. Bosque, J. M. Cadena, S. Delgado, J. Granell, G. Muller, J. I. Ordinas, M. F. Bardia, and X. Solans, 2002. *Chem. Eur. J.*, **8**, 2279. Camus, J.-M., P. Roy-García, J. Andrieu, P. Richard, and R. Poli, 2005. *J. Organomet. Chem.*, **690**, 1659.
41. Ryabov, A. D., L. G. Kuz'mina, V. A. Polyakov, G. M. Kazankov, E. S. Ryabova, M. Pfeffer, and R. van Eldik, 1995. *J. Chem. Soc., Dalton Trans.*, 999.
42. Vicente, J., I. Saura-Llamas, C. Grünwald, C. Alcaraz, P. G. Jones, and D. Bautista, 2002. *Organometallics*, **21**, 3587.
43. Calmuschi, B., M. Alesi, and U. Englert, 2004. *Dalton Trans.*, 1852.

44. Calmuschi-Cula, B., I. Kalf, R. Wang, and E. Englert, 2005. *Organometallics*, **24**, 5491.
45. Calmuschi, B. and U. Englert, 2005. *Cryst. Eng. Comm.*, **7**, 171.
46. Clark, P. W. and H. J. Dyke, 1984. *J. Organomet. Chem.*, **276**, 421.
47. Calmuschi, B. and U. Englert, 2005. *Acta Cryst.*, **E61**, m164.
48. Calmuschi, B. and U. Englert, 2005. *Acta Cryst.*, **E61**, m166. Calmuschi, B. and U. Englert, 2005. *Acta Cryst.*, **E61**, m168.
49. Ryabov, A. D. 1985. *Synthesis*, 233. Omae, I. 2004. *Coord. Chem. Rev.*, **248**, 995.
50. Tao, W., L. J. Silverberg, A. L. Rheingold, and F. Heck, 1989. *Organometallics*, **8**, 2550. Pfeffer, M. 1990. *Recl. Trav. Chim. Pays-Bas*, **109**, 567.
51. Pfeffer, M. 1992. *Pure Appl. Chem.*, **64**, 335.
52. O'Sullivan, R. D. and A. W. Parkins, 1984. *J. Chem. Soc., Chem. Commun.*, 1165.
53. Barr, N., J. P. Bartley, P. W. Clark, P. Dunstan, and S. F. Dyke, 1986. *J. Organomet. Chem.*, **302**, 117.
54. Orito, K., A. Horibata, T. Nakamura, H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, and M. Tokuda, 2004. *J. Am. Chem. Soc.*, **126**, 14342. Orito, K., M. Miyazawa, T. Nakamura, A. Horibata, H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, H. Yamazaki, and M. Tokuda, 2006. *J. Org. Chem.*, **71**, 5951.
55. Yamamoto, Y. and H. Yamazaki, 1976. *Synthesis*, 750. Yamamoto, Y. and H. Yamazaki, 1980. *Inorg. Chim. Acta*, **41**, 229. Dupont, J. and M. Pfeffer, 1990. *J. Chem. Soc., Dalton Trans.*, 3193.
56. Böhm, A., K. Polborn, K. Sünkel, and W. Beck, 1998. *Z. Naturforsh.*, **53b**, 448.
57. Saluste, C. G., S. Crumpler, M. Furber, and R. J. Whitby, 2004. *Tetrahedron Lett.*, **45**, 6995.
58. Vicente, J., I. Saura-Llamas, and M. C. Ramírez de Arellano, 1995. *J. Chem. Soc., Dalton Trans.*, 2529.
59. Bahsoun, A., J. Dehand, M. Pfeffer, M. Zinsius, S.-E. Bouaoud, and G. Le Borgne, 1979. *J. Chem. Soc., Dalton Trans.*, 547. Wu, G. Z., A. L. Rheingold, and F. Heck, 1986. *Organometallics*, **5**, 1922. Maassarani, F., M. Pfeffer, and G. Le Borgne, 1987. *Organometallics*, **6**, 2029. Pfeffer, M., J.-P. Sutter, M. A. Rotteveel, A. De Cian, and J. Fischer, 1992. *Tetrahedron*, **48**, 2427. Sutter, J.-P., M. Pfeffer, A. De Cian, and J. Fischer, 1992. *Organometallics*, **11**, 386. Ryabov, A. D., R. van Eldik, G. Le Borgne, and M. Pfeffer, 1993. *Organometallics*, **12**, 1386.
60. Vicente, J., I. Saura-Llamas, J. Turpín, M. C. Ramírez de Arellano, and P. G. Jones, 1999. *Organometallics*, **18**, 2683.
61. Turpín, J. 1999. Ph. D. Thesis. University of Murcia.
62. Bartolome, C., P. Espinet, J. M. Martín-Álvarez, and F. Villafañe, 2003. *Inorg. Chim. Acta*, **347**, 49. Dunina, V. V., O. N. Gorunova, Y. K. Grishin,

L. G. Kuz'mina, A. V. Churakov, A. V. Kuchin, and J. A. K. Howard, 2005. *Russ. Chem. Bull. Int. Ed.*, **54**, 2073.

63. Barr, N., S. F. Dyke, G. Smith, C. H. L. Kennard, and V. McKee, 1985. *J. Organomet. Chem.*, **288**, 109.
64. Dunina, V. V., L. G. Kuzmina, M. Y. Kazakova, Y. K. Grishin, Y. A. Veits, and E. I. Kazakova, 1997. *Tetrahedron Asymm.*, **8**, 2537. Li, Y., K.-H. Ng, S. Selvaratnam, G.-K. Tan, J. J. Vittal, and P.-H. Leung, 2003. *Organometallics*, **22**, 834. Li, Y., S. Selvaratnam, J. J., Vittal, and P.-H. Leung, 2003. *Inorg. Chem.*, **42**, 3229. Apfelbacher, A., P. Braunstein, L. Brissieux, and R. Welter, 2003. *J. Chem. Soc., Dalton Trans.*, 1669. Mentes, A., R. D. W. Kemmitt, J. Fawcett, and D. R. Russell, 2004. *J. Mol. Struct.*, **693**, 241.
65. Jain, V. K. and L. Jain, 2005. *Coord. Chem. Rev.*, **249**, 3075.
66. (a) Kuz'mina, L. G., O. Y. Burtseva, M. A. Porai-Koshits, V. V. Dunina, O. A. Zalevskaya, and V. M. Potapov, 1989. *Zh. Obshch. Khim.*, **59**, 2525. Hockless, D. C. R., P. A. Gugger, P.-H. Leung, R. C. Mayadunne, M. Pabel, and S. B. Wild, 1997. *Tetrahedron*, **53**, 4083. Gül, N. and J. H. Nelson, 2000. *Organometallics*, **19**, 91. (b) Aullón, G., G. Ujaque, A. Lledós, S. Alvarez, and P. Alemany, 1998. *Inorg. Chem.,* **37**, 804.
67. Martinez-Viviente, E., P. S. Pregosin, and M. Tschoerner, 2000. *Magn. Reson. Chem.*, **38**, 23.
68. O'Keefe, B. J., and P. J. Steel, 1998. *Organometallics*, **17**, 3621.
69. Bedford, R. B., C. S. J. Cazin, S. J. Coles, T. Gelbrich, P. N. Horton, M. B. Hursthouse, and M. L. Light, 2003. *Organometallics*, **22**, 987.
70. Hiraki, K., Y. Fuchita, and K. Takechi, 1981. *Inorg. Chem.*, **20**, 4316.
71. Yang, F., Y. P. Li, J. Nie, J. Tang, and M. Y. He, 2003. *Chin. J. Chem*, **21**, 1039.
72. Vicente, J., A. Arcas, D. Bautista, and P. G. Jones, 1997. *Organometallics*, **16**, 2127. Vicente, J., J. A. Abad, A. D. Frankland, and M. C. Ramírez de Arellano, 1999. *Chem. Eur. J.*, **5**, 3066. Vicente, J., J. A. Abad, E. Martínez-Viviente, and P. G. Jones, 2002. *Organometallics*, **21**, 4454. Amatore, C., A. A. Bahsoun, A. Jutand, G. Meyer, A. N. Ntepe, and L. Ricard, 2003. *J. Am. Chem. Soc.*, **125**, 4212. Crespo, M., J. Granell, X. Solans, and M. Font-Bardia, 2003. *J. Organomet. Chem.*, **681**, 143. Rodríguez, N., A. Cuenca, C. Ramírez de Arellano, M. Medio-Simón, D. Peine, and G. Asensio, 2004. *J. Org. Chem.*, **69**, 8070. Vicente, J., A. Arcas, M. D. Gálvez-López, and P. G. Jones, 2006. *Organometallics*, **25**, 4247.
73. Deeming, J. A., I. A. Rothwell, M. B. Hursthouse, and L. New, 1978. *J. Chem. Soc., Dalton Trans.*, 1490. Elder, R. C., R. D. P. Cruea, and R. F. Morrison, 1976. *Inorg. Chem.*, **15**, 1623.
74. Garrou, P. E. 1991. *Chem. Rev.*, **81**, 229.