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Oxidative addition of aryl–halogen bonds of *N*-benzylidenbenzylamines to palladium(0) compounds

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Abstract

The oxidative addition of imines 2-Cl,6-$XC_6H_3CH{=}NCH_2C_6H_4$-2′-Y, (X = H, Cl; Y = Cl, Br) and 4-$NO_2C_6H_4CH{=}NCH_2C_6H_4$-2′-Br to $[Pd(PPh_3)_4]$ and $[Pd(dba)_2]$ has been studied. *endo* Cyclometallated compounds are obtained if the carbon–halogen bonds to be activated are the same in both aromatic rings, and the *exo* derivatives are obtained only if the benzylic phenyl ring contains an *ortho*-C–Br bond. The activation of the stronger C–Cl bond, with formation of an endocyclic compound, takes place in preference to that of the weaker C–Br bond when the imine 2,6-$Cl_2C_6H_3CH{=}NCH_2C_6H_4$-2′-Br reacts with $[Pd(PPh_3)_4]$.

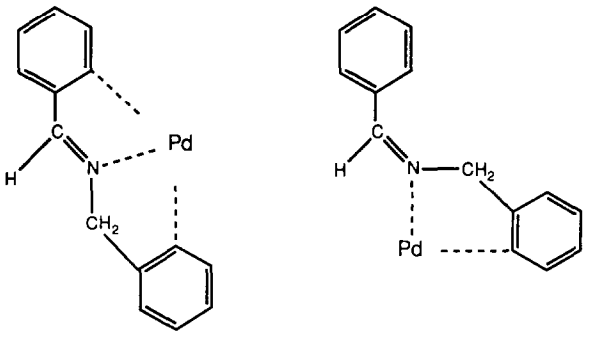
Introduction

Cyclometallations represent a rapidly growing area of organometallic chemistry, especially cyclopalladation of *N*-donor ligands [1]. Cyclopalladated compounds are valuable intermediates for organic synthesis. Carbonylation, vinylation, and insertion of alkynes have been reported for several cyclometallated complexes [2].

Recently, a new route to cyclometallated compounds involving oxidative addition of imines to palladium(0) complexes has been reported [3]. The cyclopalladation of *N*-benzylidenamines by palladium(II) salts has been extensively studied [4], but there are very few reports on oxidative addition of these ligands to palladium(0) compounds [3,5,6].

Since cyclometallation by palladium(II) involves an electrophilic attack of metal [1], and oxidative addition of aryl halides to phosphine complexes of palladium(0) seems to occur by an S_N2-type mechanism [7], it seemed of interest to study the oxidative addition of *ortho*-bromo- and *ortho*-chlorobenzylidenbenzylamines to palladium(0) complexes, to enable comparison with the results, previously described, of cyclopalladation of imines by palladium(II) salts.

These imines are polyfunctional in that they can give two different metallocycles, one in which the cycle contains the C=N group (*endo*) and the other in which it does not (*exo*). Furthermore, these imines can exist in two isomeric forms *E* or *Z*. Depending on the isomeric form, these imines can give different cyclometallated



E form Z form

Fig. 1.

derivatives; from the *E* form both *endo* and *exo* cyclometallated compounds can be obtained, whereas from the *Z* form only *exo* derivatives are formed (see Fig. 1).

All the *exo* cyclometallated imines obtained from palladium(II) salts contain the organic ligand in the *Z* form [8], but Dyke et al. [5] have recently obtained an *exo* cyclopalladated imine derivative that contains the imine in the *E* form by oxidative addition of benzyliden-2-bromobenzylamine on $[Pd(dba)_2]$.

We describe here a study of the oxidative addition of *ortho*-substituted benzylidenbenzylamines to $[Pd(dba)_2]$ and $[Pd(PPh_3)_4]$ undertaken in order to throw more light on the factors governing the metallation of imines and to reveal the rôle of the metallation reaction in the $E \rightarrow Z$ isomerization process.

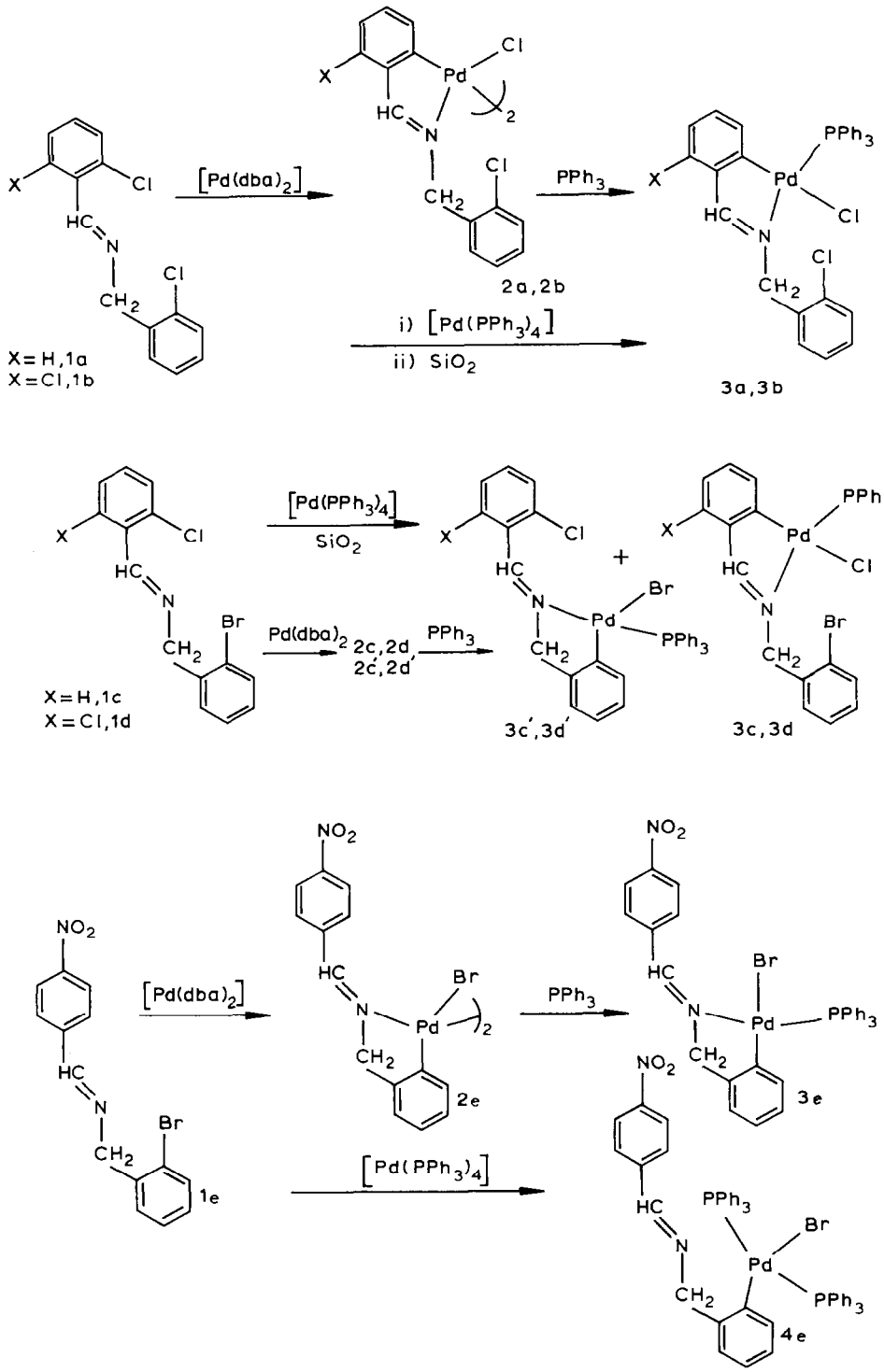
Results and discussion

Imines **1a–e** were treated in refluxing benzene under nitrogen in a 1/1 ratio with $[Pd(dba)_2]$ (2 h) or with $[Pd(PPh_3)_4]$ (24 h), see Scheme 1. The yield of the reactions and the *endo* or *exo* nature of the metallated compounds are shown in Table 1.

The oxidative addition of imines to $[Pd(dba)_2]$ affords the cyclopalladated dimers **2**. The action of PPh_3 in a 1/1 ratio affords compounds **3** $[PdX(\overline{C-N})(PPh_3)]$. The oxidative addition of imines to $[Pd(PPh_3)_4]$ gives the metallated compounds **4**, $[PdX(C-N)(PPh_3)_2]$, $[Pd(PPh_3)_4]$, and decomposition products.

It was not possible to purify compounds **4** by recrystallization, except in the case of compound **4e** (see Experimental section). Chromatography of the product mixture on a SiO_2 column, with chloroform–methanol (100/1) as the eluent, gave cyclometallated compounds **3** and free PPh_3. This result can be accounted for in terms of an intramolecular attack of nitrogen atom on palladium to form the cyclometallated compound (see Fig. 2). A similar mechanism was proposed previously to account for the ^1H NMR spectra of metallated azobenzenes [9].

Table 1 shows that $[Pd(dba)_2]$ is a better starting material than $[Pd(PPh_3)_4]$ because the reaction takes place quickly and with better yields, and the metallated complexes are easily purified. The oxidative addition takes place better with 2,6-dichlorobenzalimines than with 2-chlorobenzalimines (see reactions i and iii, ii and iv). These results can be accounted for in terms of the electronic effect of substituents. The oxidative addition of $[Pd(PR_3)_4]$ seems to involve a nucleophilic


X=H,1a
X=Cl,1b
[Pd(dba)2]
2a,2b
PPh3
3a,3b
i) [Pd(PPh3)4]
ii) SiO2
X=H,1c
X=Cl,1d
Pd(dba)2
2c,2d,
2c',2d'
3c',3d'
3c,3d
1e
2e
3e
4e

Scheme 1.

Table 1

Results of oxidative addition reactions

Reaction	Imine	Pd^0 compound	Product	Yield (%)
i	**1a**	$[Pd(dba)_2]$	*endo*	10
ii	**1a**	$[Pd(PPh_3)_4]$	*endo*	5
iii	**1b**	$[Pd(dba)_2]$	*endo*	30
iv	**1b**	$[Pd(PPh_3)_4]$	*endo*	20
v	**1c**	$[Pd(dba)_2]$	*exo*	30
vi	**1c**	$[Pd(PPh_3)_4]$	*exo*–*endo* (8/1)	20
vii	**1d**	$[Pd(dba)_2$	*exo*–*endo* (1/1)	40
viii	**1d**	$[Pd(PPh_3)_4]$	*endo*	30
ix	**1e**	$[Pd(dba)_2]$	*exo*	40
x	**1e**	$[Pd(PPh_3)_4]$	*exo*	15

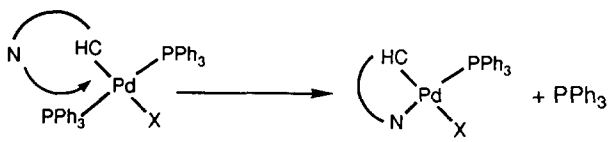


Fig. 2.

attack by the metal complex [7] and a chloride atom on an aromatic ring promotes the nucleophilic attack at the *meta* position.

Schiff bases can exist in two isomeric forms, *E* and *Z*. In general imines exist only in the more stable *E* form, but in some cases there is a significant equilibrium concentration of the less stable *Z* form [10]. It has been shown [8] that all the *exo* cyclopalladated derivatives obtained from palladium(II) salts and imines, in AcOH as solvent contain the imine in the *Z* form. In contrast, *exo* cyclopalladated derivatives obtained from palladium(II) in toluene as solvent contain the imine in the *E* form [11]. These results show that protonation of the imine is essential to promote the $E \rightarrow Z$ isomerization, and suggest that isomerization can be attributed

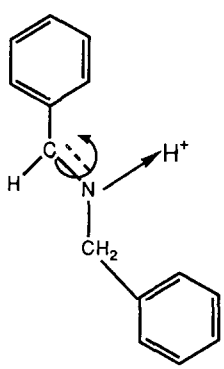


Fig. 3.

to a decrease in the bond order of the C=N bond caused by protonation of the imine (see Fig. 3).

All the *exo* cyclometallated compounds obtained by oxidative additon during this study have the imine in the *E* form. This shows that isomerization of imine does not take place in an aprotic solvent such as benzene, in agreement with the previously proposed mechanism.

It has been shown previously that *endo* cyclometallated compounds are more stable than corresponding *exo* compounds. The reactivity of cyclometallated compounds towards phosphines, CO, and acetylenes [12], and in the ligand exchange reactions between free imines and cyclometallated compounds [13], and especially the cyclopalladation of bifunctional imines [14], show that *endo* cyclometallated compounds are more stable than the corresponding *exo* species. The action of palladium(II) on bifunctional imines always gives the *endo* compound, and the *exo* derivatives are obtained only if the *ortho* positions of the methinic phenyl ring are protected from electrophilic attack [8]. The oxidative addition of imines to palladium(0) complexes affords the *endo* derivatives when the C–X bonds to be activated are the same in both aromatic rings (reactions i, ii, iii and iv). *exo* Compounds, or mixtures of both *exo* (**3c′**, **3d′**) and *endo* (**3c**, **3d**) compounds, are obtained when the *ortho*-C–X bond in the benzylic ring is weaker (reactions v, vi and vii). These results can be attributed to the great stability of *endo* compounds, but the possibility that the electronic effects of groups HC=N and CH_2N are important cannot be excluded.

It is noteworthy that the activation of the stronger C–Cl bond (96 kcal/mol) of the methynic phenyl ring, with formation of an endocyclic compound, takes place in preference to the activation of the weaker C–Br (81 kcal/mol) when imine **1d** is treated with $[Pd(PPh_3)_4]$ (reaction viii). Related observations have been reported previously. The action of $[W(CO)_3(NCEt)_3]$ on the ligand **A** (see Fig. 4) affords the corresponding *endo*-metallocycle by oxidative addition of the stronger C–Cl bond (96 kcal/mol) rather than the weaker C–I bond (65 kcal/mol) [15]. Furthermore, the ligands B and C permit the activation of C–F bonds (126 kcal/mol) by

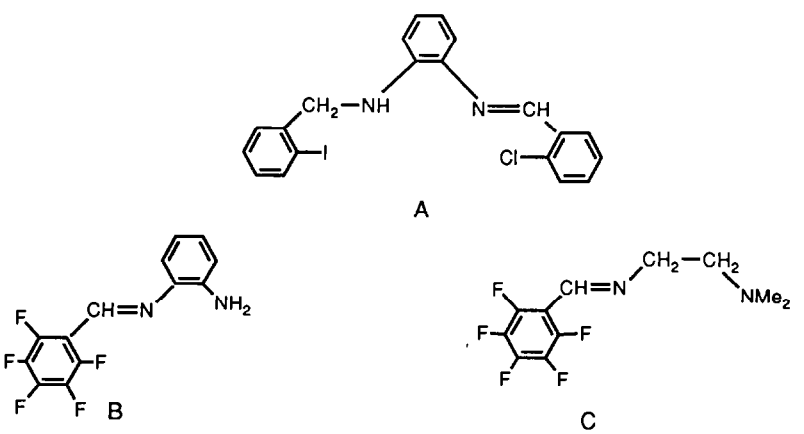


Fig. 4.

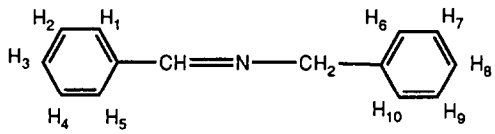


Fig. 5.

oxidative addition to $[W(CO)_3(NCEt)_3]$ [16] and $[PtMe_2(\mu\text{-}SMe_2)]_2$ [17] respectively, to give the corresponding compounds with an *endo* type structure.

It should be noted that $[Pd(PPh_3)_4]$ shows a stronger tendency than $[Pd(dba)_2]$ to form endocyclic compounds (reactions v and vi, vii and viii). These results can be accounted for in terms of steric considerations. The $E \rightarrow Z$ isomerization does not take place during the oxidative addition and so the methynic phenyl ring is *cis* to the nitrogen lone pair. The steric repulsion present when the bulky $[Pd(PPh_3)_4]$ is used would be minimized because of the flexibility of CH_2 group when the endocyclic compound is formed.

Characterization

All the new compounds are pale-yellow air stable solids. The analytical data are shown in Table 2. The IR spectra show the typical bands of phosphines and imines.

The proton NMR data for compounds **3** are listed in Table 3. The assignment of the aromatic signals affords conclusive evidence of the palladation position (*endo* or *exo* cyclometallated compounds). The aromatic protons of the metallated benzene ring are shifted to high field; this effect must be caused by a phosphine phenyl ring, in accord with a *cis* arrangement between the phosphine and the metallated ring, and thus a *trans* disposition of the phosphorus and nitrogen atoms. The ^{31}P chemical shifts for compounds **3** ($\delta \approx 41$–42 ppm) (see Table 2) are consistent with a *trans* disposition of the phosphorus and nitrogen atom [8].

The chemical shift of the methynic protons is a useful item of information for the structural characterization of imine cyclopalladated derivatives. This signal is shifted to high field, relative to that for free imines, in the *endo* metallocycles, where the imines must be in *E* form (see Fig. 1). For the *exo* derivatives obtained from imines

Table 2

Analytical data and ^{31}P NMR spectra [a]

Compound	Analytical data (found (calc) (%))			^{31}P
	C	H	N	
3a	60.8 (60.69)	4.0 (4.11)	2.2 (2.21)	42.67
3b	58.0 (57.55)	3.7 (3.74)	2.1 (2.09)	42.26
3c	56.9 (56.71)	3.5 (3.83)	2.1 (2.07)	42.80
3d	53.3 (53.96)	3.6 (3.51)	2.0 (1.96)	42.40
3e	55.6 (55.84)	3.5 (3.78)	4.0 (4.07)	41.62
3c′	56.4 (56.71)	3.7 (3.87)	2.0 (2.07)	41.81
3d′	53.8 (53.96)	3.5 (3.51)	2.0 (1.96)	41.74
4e	63.0 (63.18)	4.2 (4.32)	2.8 (2.95)	22.81

[a] In $CHCl_3$; chemical shifts in ppm with respect H_3PO_4.

Table 3

Proton NMR data [a]

Compound	aromatic, HC=N	CH_2N
3a	7.88–7.24 (br m, H_7, H_8, H_9, H_{10}, HC=N); 6.85 (br m, H_4, H_5); 6. 43 (br m, H_2, H_3)	5.39 s
3b	8.42 (d, ^4J(HP) = 7.99, HC=N); 7.89–7.24 (br m, H_7, H_8, H_9, H_{10}); 6.80 (d, ^3J(HH) = 7.0, H_4); 6.45 (t, ^3J(HH) = 7.0, H_3); 6.27 (t, ^3J(HH) = ^4J(HP) = 6.9, H_2)	5.41 s
3c	7.89–7.24 (br m, H_7, H_8, H_9, H_{10}, HC=N); 6.84 (br m, H_4, H_5); 6.43 (br m, H_2, H_3)	5.39 s
3d	8.42 (d, ^4J(HP) = 7.8, HC=N); 7.89–7.24 (br m, H_7, H_8, H_9, H_{10}); 6.80 (d, ^3J(HH) = 7.0, H_4); 6.46 (t, ^3J(HH) = 7.2, H_3); 6.27 (t, ^3J(HH) = ^4J(HP) = 6.9, H_2)	5.45 s
3c′	7.88–7.24 (br m, H_1, H_2, H_3, H_4, HC=N); 6.90 (br m, H_7, H_8); 6.44 (br m, H_9, H_{10})	4.30 s
3d′	8.42 (d, ^4J(HP) = 7.7, HC=N); 7.88–7.24 (br m, H_2, H_3, H_4); 6.90 (br m, H_7, H_8); 6.44 (br m, H_9, H_{10})	4.30 s
3e	8.37 (d, ^3J(HH) = 8.4, H_2, H_4); 8.0–7.25 (br m, HC=N, H_1, H_3); 6.90 (br m, H_7, H_8); 6.48 (br m, H_9, H_{10})	4.37 s
4e	8.13 (d, H_2, H_4); 8.05–7.25 (br m, HC=N, H_1, H_3); 6.30–6.90 (br m, H_7, H_8, H_9, H_{10})	4.64 s

[a] In $CDCl_3$; chemical shifts in ppm with respectal internal TMS; coupling constants in Hz; numbering as in Fig. 5.

and palladium(II) salts in acetic acid as solvent this signal is shifted to low field by 0.5–1.1 ppm relative to that for the corresponding free imine. This shift can be attributed to the paramagnetic anisotropy of palladium, and indicates a close disposition of the metal and methinic proton, suggesting a *Z* form for the ligand, as was confirmed by X-ray study of *exo* cyclopalladated derivatives [8].

All the *exo* cyclopalladated derivatives obtained in this work have the methynic signal shifted to high field, in accord with an *E* form for the ligand. A similar high field shift has been observed previously for the *exo* cyclopalladated compound [Pd(acac)($C_6H_4CH_2$N=CHPh], obtained by oxidative addition of benzyliden-2-bromobenzylamine to [Pd(dba)$_2$]; the *E* form of the imine in the product, was confirmed by an X-ray study [5].

The chemical shifts of CH_2 protons confirm the *endo* or *exo* structure of the compounds. This signal is shifted to low field in all the endocyclic compounds, probably due to the anisotropy of palladium atom.

Experimental

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

Materials and synthesis

Solvents were dried and distilled before use. The benzylidenbenzylamines were made from the corresponding benzaldehydes and the appropriate benzylamines

under standard conditions (refluxing ethanol), $[Pd(dba)_2]$ and $[Pd(PPh_3)_4]$ were prepared as previously described [18,19]. The yields of reactions are shown in Table 1.

Oxidative addition of imines to $[Pd(dba)_2]$

A stirred mixture of imine (1 mmol) and $[Pd(dba)_2]$ (0.26 g, 1 mmol) in benzene under nitrogen was refluxed for 2 h. The precipitate formed was filtered off and recrystallized from chloroform–methanol to give compounds **2**. A stirred mixture of **2** (0.5 mmol) and PPh_3 (1 mmol) was refluxed in acetone for 30 min and then filtered. The filtrate was concentrated *in vacuo* and ether was added. The solid obtained, after addition of ether was recrystallized from chloroform–methanol to give compounds **3**. The mixture (1/1) of compounds **3d** and **3d′** was separated by a SiO_2 column chromatography with chloroform–methanol (100/1) as eluent. Compound **3d** was eluted in the less polar and compound **3d′** in the more polar fractions.

Oxidative addition of imines to $[Pd(PPh_3)_4]$

A stirred mixture of imine (1 mmol) and $[Pd(PPh_3)_4]$ (1.15 g, 1 mmol) in benzene was refluxed for 24 h, under nitrogen and then filtered. The filtrate was concentrated *in vacuo* and ether was added to precipitate a yellow solid, which was a mixture of compound **4**, $[Pd(PPh_3)_4]$, and decomposition products. Recrystallization from benzene–ether of the solid obtained from the reaction of imine **1e** gave pure **4e** in 15% yield. In all the other cases the mixture obtained was chromatographed on SiO_2 with chloroform–methanol (100/1) as eluent to afford compounds **3**. In reaction vi, which gives both *endo* and *exo* compounds, compound **3c** with the *endo* structure, was eluted in the less polar and compound **3c**, with the *exo* structure, in the more polar fractions.

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References

1 I. Omae, Coord. Chem. Rev., 83 (1988) 137; V.V. Dunina, O.A. Zalevskaya and V.M. Potatov, Russ. Chem. Rev., 57 (1988) 250.
2 A.D. Ryabov, Synthesis, (1985) 233.
3 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 259 (1983) C17.
4 H. Onoue and I. Moritani, J. Organomet. Chem., 43 (1972) 431; J. Granell, D. Sainz, J. Sales, X. Solans and M. Font, J. Chem. Soc., Dalton Trans., (1986) 1785; P.S. Pregosin and P. Ruedi, J. Organomet. Chem., 273 (1984) 401; M.T. Pereira, J.M. Vila, A. Suarez, E. Gayoso and M. Gayoso, Gazz. Chim. It., 118 (1988) 783.
5 P.W. Clark, S.F. Dyke, G. Smith and C.H.L. Kennard, J. Organomet. Chem., 330 (1987) 427.
6 P.W. Clark and S.F. Dyke, J. Organomet. Chem., 276 (1984) 421.
7 C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brooks/Cole, CA, 1985, p. 285.
8 J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, Organometallics, 9 (1990) 1407.
9 G.K. Anderson, R.J. Cross, S.A. Leaman, F.J. Robertson, D.S. Rycroft and M. Rocamora, J. Organomet. Chem., 388 (1990) 221.
10 G. Tennand, Comprehensive Organic Chemistry, Vol. 12, Pergamon, Oxford, 1979, Chap. 8.

11 J. Albert, J. Granell and J. Sales, unpublished results.
12 J. Albert, J. Granell, J. Sales and X. Solans, J. Organomet. Chem., 379 (1989) 177.
13 R.M. Ceder, M. Gómez and J. Sales, J. Organomet. Chem., 361 (1989) 391.
14 J. Albert, J. Granell and J. Sales, J. Organomet. Chem., 273 (1984) 393.
15 M.J. Ross, A.M. Arif and T.G. Richmond, Organometallics, 7 (1988) 1669.
16 T.G. Richmond, C.E. Osterberg and A.M. Arif, J. Am. Chem. Soc., 109 (1987) 8091.
17 C.M. Anderson, R.J. Pudephatt, G. Ferguson and A.J. Lough, J. Chem. Soc., Chem. Commun., (1989) 1297.
18 M.F. Rethy and P.M. Maitlis, Inorg. Synth., 17 (1977) 135.
19 D.R. Coulson, Inorg. Synth., 13 (1972) 121.