ELSEVIER

Journal of Organometallic Chemistry 518 (1996) 105–113

Journal of Organometallic Chemistry

C–H and C–Cl bond activation in the formation of cyclometallated platinum(II) and platinum(IV) compounds with chlorinated N-benzylidenebenzylamines

Margarita Crespo [a,*], Xavier Solans [b], Mercè Font-Bardía [b]

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

[b] *Departament de Cristallografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franqués s/n, 08028 Barcelona, Spain*

Received 21 November 1995

Abstract

Platinum substrate $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) reacts with chlorinated imines $3,5\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2a**) and $3\text{-}ClC_6H_4CH{=}NCH_2C_6H_5$ (**2b**) to yield cyclometallated platinum(II) compounds $[PtMe(3,5\text{-}Cl_2C_6H_2CH{=}NCH_2C_6H_5)(SMe_2)]$ (**4a**) and $[PtMe(3\text{-}ClC_6H_3CH{=}NCH_2C_6H_5)(SMe_2)]$ (**4b**), arising from C–H bond activation followed by loss of methane. A reaction intermediate $[PtMe_2(3,5\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5)(SMe_2)]$ (**3a**) was detected by ^1H NMR. The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with chlorinated imine $2,4\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2c**) produces a mixture of cyclometallated platinum(II) compound $[PtMe(2,4\text{-}Cl_2C_6H_2CH{=}NCH_2C_6H_5)(SMe_2)]$ (**4c**) and cyclometallated platinum(IV) compound $[PtMe_2Cl(4\text{-}ClC_6H_3CH{=}NCH_2C_6H_5)(SMe_2)]$ (**4c'**) arising respectively from aryl C–H and aryl C–Cl bond activation. The reaction of complex **4a** with triphenylphosphine produces metallacycle cleavage and $[PtMe(3,5\text{-}Cl_2C_6H_2CH{=}NCH_2C_6H_5)(PPh_3)_2]$ (**5a**) is formed with the imine acting as a $[C^-]$ unidentate ligand. **5a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.899(5)$ Å, $b = 22.953(5)$ Å and $c = 17.588(9)$ Å, $\beta = 95.14(5)°$ and $Z = 4$. Compounds **4b**, **4c** and **4c'** react with PPh_3 to give cyclometallated compounds $[PtMe(3\text{-}ClC_6H_3CH{=}NCH_2C_6H_5)(PPh_3)]$ (**5b**), $[PtMe(2,4\text{-}Cl_2C_6H_2CH{=}NCH_2C_6H_5)(PPh_3)]$ (**5c**), and $[PtMe_2Cl(4\text{-}ClC_6H_3CH{=}NCH_2C_6H_5)(PPh_3)]$ (**5c'**) respectively. The stereo-electronic effect of chlorine substituents, as well as the NMR parameters, are discussed in relation to the observed reactivity of these compounds.

Keywords: Platinum; Cyclometallation; X-ray structure; Benzylidenebenzylamines; Imine; Cycloplatination

1. Introduction

Since the early reports of platinum complexes with *ortho*-metallated nitrogen donor ligands [1] many examples of cyclometallation involving aryl C–X (X = H, I, Br, Cl or F) bond fission have been described. While the mechanism for the more studied cyclopalladation reactions consists of an intramolecular electrophilic attack of the palladium at the carbon atom, platinum substrates may display nucleophilic behaviour [2]. Regardless of the operating mechanism, several features of this process are common to those described for other metal systems. In general, the reactivity of the aryl C–X bond follows the inverse order of C–X bond energies [3], but there are also reports of the activation of stronger bonds in the presence of weaker C–X bonds [4]. Another feature of metallation reactions is that non-coordinating substituents in the carbon atom adjacent to the metallation position hinder the process [5].

We are currently studying the cycloplatination reactions of N-benzylidenebenzylamines at the platinum substrate $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. Our previous results indicate that methyl or methoxy groups adjacent to the aryl C–H bonds inhibit the metallation [6]. However, the presence of fluorine substituents in such positions does not hinder the formation of platinocycles [7]. This result has been attributed to the small size of the fluorine atom as well as to its great electron-withdrawing ability since, in this system, the platinum substrate acts as a nucleophile.

In order to be able to discriminate between the steric and electronic factors, we extended our studies to chlorinated iminic ligands. Since chlorine and fluorine have a similar electron-withdrawing ability but differ in size, the comparative analysis of the results for these sub-

* Corresponding author.

PII S0022-328X(96)06221-3

stituents should be quite informative. Moreover, chlorinated imines should be useful to address the question of C–Cl versus C–H bond activation.

2. Results and discussion

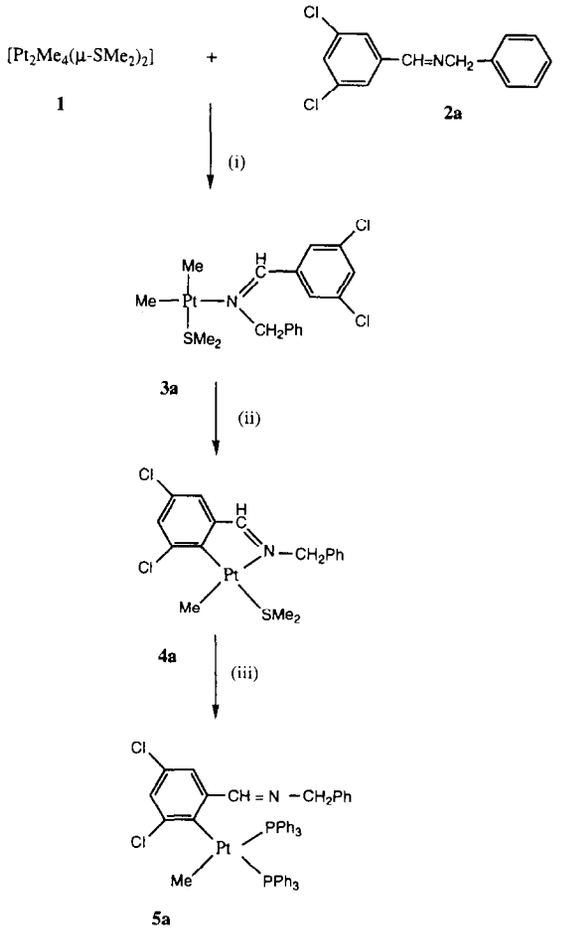
2.1. Cycloplatination of ligand 3,5-$Cl_2C_6H_3CH=NCH_2C_6H_5$ (2a)

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with chlorinated imine 3,5-$Cl_2C_6H_3CH=NCH_2C_6H_5$ (**2a**) was carried out in acetone solution at room temperature (Scheme 1) and yielded the cyclometallated platinum(II) compound $[PtMe(3,5\text{-}Cl_2C_6H_2CH=NCH_2C_6H_5)(SMe_2)]$ (**4a**) arising from C–H bond activation followed by loss of methane. We have previously shown for analogous systems that the formation of *endo*-metallacycles (containing the iminic group) is much more favoured than the formation of *exo*-metallacycles. In particular, the latter does not take place for C–H bonds, and thus the formation of *exo*-metallacycles can be ruled out [8].

When the reaction was monitored by ^1H NMR, compound $[PtMe_2(3,5\text{-}Cl_2C_6H_3CH=NCH_2C_6H_5)(SMe_2)]$ (**3a**), with the imine coordinated to platinum through the nitrogen atom, was detected. Compound **3a** could not be isolated in a pure form and was characterized by its ^1H NMR in solution. The two methyl–platinum resonances appeared as singlets with platinum satellites [^2J(HPt) = 82 Hz]. The coordination of the imine to platinum was confirmed by the coupling of the iminic proton with ^{195}Pt [^3J(HPt) = 51 Hz].

The coordination of the nitrogen donor ligand to platinum has been postulated as a previous step preceding the cyclometallation process [8]. For ligand **2a**, the two chlorine atoms in the adjacent positions to the C–H bond obstruct the cyclometallation process and, as a result, compound **3a** was detected. In spite of the presence of chlorine substituents, a further intramolecular process took place to yield the cycloplatinated compound $[PtMe(3,5\text{-}Cl_2C_6H_2CH=NCH_2C_6H_5)(SMe_2)]$ (**4a**).

Compound **4a** was characterized by elemental analysis and its ^1H NMR spectrum. In the ^1H NMR the resonances due to the methyl and to the iminic protons appeared coupled to ^{195}Pt [^2J(HPt) = 82 and 50 Hz respectively]. As observed for fluorinated metallacycles with a fluorine at carbon C(5) [9], the methyl resonance was downfield shifted (see Table 1) when compared with platinacycles without substituents at C(5), which indicates a CH · · · Cl interaction between the methyl hydrogens and the chlorine atom Cl(5), as shown in Fig. 1. Hydrogen bonding involving chlorine atoms has been

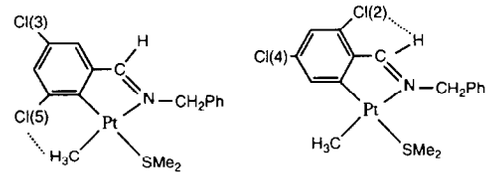


Scheme 1. (i) Acetone, room temperature, 30 min; (ii) acetone, room temperature, 16 h, ($-CH_4$); (iii) $+PPh_3$, acetone, room temperature, 16 h.

Table 1
Selected ^1H NMR data for compounds $[PtMe(RCH=NCH_2Ar)(SMe_2)]$ (**4**) and $RCH=NCH_2Ar$ (**2**) [a]

Imine	Compounds **4**		Compounds **2**
	δ(Me)[^2J(HPt)]	δ(CH=N)[^3J(HPt)]	δ(CH=N)
3,5-$Cl_2C_6H_3CHNCH_2C_6H_5$ (**2a**)	1.24[82]	8.96[50]	8.27
3-$ClC_6H_4CHNCH_2C_6H_5$ (**2b**)	0.84[82]	8.85[56]	8.34
2,4-$Cl_2C_6H_3CHNCH_2C_6H_5$ (**2c**)	0.82[81]	9.23[59]	8.80
2-$ClC_6H_4CHNCH_2C_6H_5$ [b]	[c]	[c]	8.83
3,5-$F_2C_6H_3CHNCH_2C_6H_5$ [d]	1.21[81]	9.03[53]	8.25
2,3-$F_2C_6H_3CHNCH_2C_6H_5$ [e]	0.84[82]	9.15[56]	8.63
$C_6H_5CHNCH_2$(2-ClC_6H_4) [b]	0.91[80]	8.81[53]	8.55

[a] δ in parts per million, J in Hertz, solvent acetone-d_6 for **4** and $CDCl_3$ for **2**. [b] Taken from Ref. [8]. [c] The reaction with **1** produces a platinum(IV) compound. [d] Taken from Ref. [7]. [e] Taken from Ref. [9].



4a 4c

Fig. 1. H · · · Cl interactions in compounds **4a** and **4c**.

described for both CH · · · Cl [10] and NH · · · Cl [11] systems.

As reported for fluorinated imine 3,5-$F_2C_6H_3CH$=$NCH_2C_6H_5$ [7], cycloplatination was achieved for chlorinated imine 3,5-$Cl_2C_6H_3CHNCH_2C_6H_5$ (**2a**), in spite of the presence of fluoro or chloro substituents in the adjacent positions of the C–H bonds. Since the size of chlorine is larger than that of the methoxy group and similar to that of the methyl group (see Table 2) [12] and no metallation occurs when these substituents are present, the electron-withdrawing ability of fluoro or chloro substituents seems therefore decisive.

As shown in Scheme 1, the reaction of compound **4a** with PPh_3 in acetone yielded compound [PtMe(3,5-$Cl_2C_6H_2CH$=$NCH_2C_6H_5$)(PPh_3)$_2$] (**5a**) even when a 1 : 1 molar ratio was used. Formation of compound **5a** arises from a displacement reaction of SMe_2 and the iminic nitrogen for two PPh_3 ligands, which produces the cleavage of the metallacycle. In an attempt to detect the formation of the cyclometallated compound [PtMe(3,5-$Cl_2C_6H_2CH$=$NCH_2C_6H_5$)(PPh_3)] containing only one PPh_3 ligand, the reaction of compound **4a** with less than the stoichiometric amount of PPh_3 was monitored by ^{1}H NMR, but this produced a mixture of compounds **4a** and **5a**.

Compound **5a** was characterized by elemental analysis, ^{1}H and ^{31}P NMR spectroscopies, and X-ray analysis. The methyl resonance appeared as a doublet of doublets, due to coupling to two non-equivalent phosphorus atoms. The value of the coupling constant with platinum is consistent with the presence of a phosphine ligand *trans* to the methyl group. Furthermore, the coupling constant of the iminic nitrogen to platinum is much lower than for cyclometallated compound **4a**, and

Table 2
Electronic and steric parameters for several substituents [a]

	σ_I	σ_R	E_S
F	0.50	−0.31	−0.46
Me	−0.05	−0.13	−1.24
OMe	0.27	−0.42	−0.55
Cl	0.46	−0.18	−0.97

[a] σ_I, σ_R and E_S are inductive (*para*), mesomeric (*para*) and steric parameters respectively, taken from Ref. [12]. H is taken as a standard, with value 0. Positive σ values indicate electron-withdrawing groups, negative σ values indicate electron-donating groups and negative E_S values indicate unfavourable steric effects.

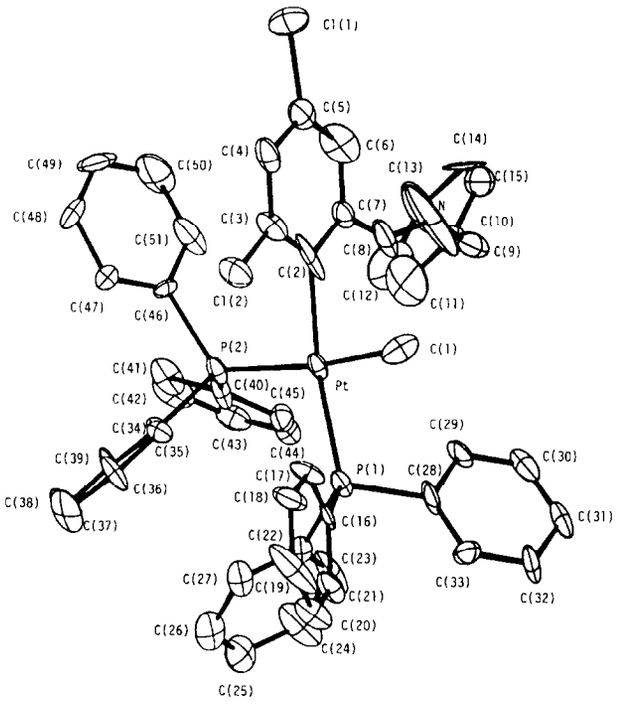


Fig. 2. Molecular structure of **5a**.

the methylene resonance appeared as an *AB* quartet. The ^{31}P NMR spectrum showed two sets of resonances due to the non-equivalent phosphorus atoms, both coupled to platinum.

We have previously reported a similar reactivity with PPh_3 for fluorinated platinacycles containing a fluorine atom at C(5) [9]. Unfavourable steric effects between the methyl group and the chlorine atom at C(5) may account for the easy formation of compound **5a**. The chelating nature of the iminic ligand in compound **4a** implies that the chlorine should be in the coordination plane, and formation of compound **5a** with cleavage of the metallacycle would relieve the steric crowding in the coordination sphere of platinum. Moreover, the presence of the chlorine atoms reduces the basicity of the iminic nitrogen and, as a result, cleavage of the Pt–N bond occurs more readily.

2.2. Molecular structure of 5a

Crystals of **5a** were grown from acetone solution and used for an X-ray study. The molecular structure is shown in Fig. 2. Crystallographic data are given in the Experimental section, atomic coordinates in Table 3 and selected bond distances and angles in Table 4.

The crystal structure consists of discrete molecules separated by van der Waals distances. The crystal structure confirms the square-planar coordination around the platinum, completed with two mutually *cis* PPh_3 ligands, the methyl and the aryl groups, as well as the presence of a chlorine atom [Cl(2)] adjacent to the metallation position in the aryl group. Pt–C and Pt–P

Table 3
Atomic coordinates ($\times 10^4$) and equivalent displacement parameters ($Å^2 \times 10^3$) with e.s.d.s in parentheses for non-hydrogen atoms for **5a**

Atom	x	y	z	U_{eq} [a]
Pt	1349(1)	1455(1)	2296(1)	38(1)
P(1)	−325(2)	845(1)	1984(1)	39(1)
P(2)	1653(2)	1251(1)	3576(1)	40(1)
Cl(1)	6147(3)	3266(1)	2618(2)	81(1)
Cl(2)	4347(2)	1133(1)	2153(2)	68(1)
N	918(29)	3381(4)	2459(7)	225(14)
C(1)	1421(5)	1627(4)	1145(4)	50(2)
C(2)	2827(4)	2040(2)	2400(3)	84(4)
C(3)	4013(5)	1830(2)	2350(3)	50(2)
C(4)	5005(4)	2213(2)	2397(3)	72(3)
C(5)	4810(5)	2806(2)	2493(3)	59(2)
C(6)	3623(6)	3016(2)	2543(4)	87(4)
C(7)	2632(4)	2633(2)	2496(3)	45(2)
C(8)	1555(13)	2865(4)	2478(6)	79(4)
C(9)	−109(11)	3583(5)	2380(9)	77(4)
C(10)	−558(7)	3865(3)	3148(4)	63(2)
C(11)	−1003(10)	3575(3)	3761(6)	153(9)
C(12)	−1273(11)	3886(5)	4404(5)	126(6)
C(13)	−1099(10)	4486(5)	4433(5)	158(9)
C(14)	−654(8)	4775(3)	3820(6)	119(7)
C(15)	−384(6)	4465(3)	3177(5)	77(3)
C(16)	164(5)	215(2)	1430(3)	46(2)
C(17)	1377(5)	169(2)	1252(3)	50(2)
C(18)	1774(5)	−335(2)	911(4)	72(3)
C(19)	958(6)	−793(2)	748(4)	131(7)
C(20)	−255(6)	−747(2)	927(4)	65(3)
C(21)	−652(4)	−243(2)	1268(3)	61(2)
C(22)	−1284(5)	500(2)	2671(3)	38(2)
C(23)	−2384(6)	752(2)	2846(3)	94(4)
C(24)	−3113(6)	472(3)	3343(4)	104(5)
C(25)	−2742(6)	−60(3)	3665(3)	72(3)
C(26)	−1643(7)	−312(2)	3489(3)	74(3)
C(27)	−914(5)	−32(2)	2992(3)	58(2)
C(28)	−1504(5)	1240(2)	1392(4)	70(3)
C(29)	−1636(6)	1833(2)	1523(4)	58(2)
C(30)	−2572(6)	2144(2)	1115(4)	67(3)
C(31)	−3375(6)	1862(6)	577(4)	71(3)
C(32)	−3243(5)	1269(3)	447(4)	79(3)
C(33)	−2308(5)	958(2)	855(4)	53(2)
C(34)	1797(5)	480(1)	3753(2)	35(1)
C(35)	2369(5)	166(2)	3208(2)	40(2)
C(36)	2565(6)	−429(2)	3303(3)	69(3)
C(37)	2190(8)	−710(2)	3943(3)	99(5)
C(38)	1618(7)	−396(2)	4488(3)	74(3)
C(39)	1422(6)	199(2)	4393(2)	64(3)
C(40)	527(5)	1545(2)	4202(3)	67(3)
C(41)	793(5)	1576(2)	4988(3)	71(3)
C(42)	−59(7)	1818(3)	5440(2)	83(4)
C(43)	−1176(6)	2027(3)	5106(3)	61(2)
C(44)	−1442(4)	1996(3)	4319(4)	62(2)
C(45)	−590(5)	1754(3)	3867(2)	50(2)
C(46)	3116(4)	1516(2)	4088(4)	44(2)
C(47)	4123(6)	1166(2)	4315(4)	66(3)
C(48)	5178(5)	1411(3)	4687(5)	88(4)
C(49)	5225(6)	2006(4)	4833(5)	85(4)
C(50)	4218(8)	2356(2)	4607(5)	124(6)
C(51)	3163(6)	2112(2)	4234(4)	83(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Selected bond lengths (Å) and angles (°) for compounds **5a**

Bond lengths			
Pt–C(1)	2.070(8)	P(1)–C(16)	1.848(4)
Pt–C(2)	2.092(4)	P(2)–C(34)	1.801(4)
Pt–P(2)	2.295(2)	P(2)–C(40)	1.847(4)
Pt–P(1)	2.326(2)	P(2)–C(46)	1.862(4)
P(1)–C(28)	1.821(4)	Cl(1)–C(5)	1.797(5)
P(1)–C(22)	1.845(4)	Cl(2)–C(3)	1.683(4)
Bond angles			
C(1)–Pt–C(2)	82.3(2)	C(1)–Pt–P(1)	89.0(2)
C(1)–Pt–P(2)	169.5(2)	C(2)–Pt–P(1)	171.2(2)
C(2)–Pt–P(2)	90.1(2)	P(2)–Pt–P(1)	98.62(8)

bond lengths are well within the range of values reported for analogous compounds. As observed for square-planar aryl complexes of platinum(II) the metallated phenyl ring is nearly perpendicular to the coordination plane, the dihedral angle being 88.1°. As suggested from the high value of U_{eq} for the nitrogen atom, the molecule shows considerable disorder, which could not be located, around the uncoordinated iminic group. As a result, anomalous bond lengths and angles result in the dangling iminic moiety, and parameters in this fragment of the molecule will not be discussed any further.

2.3. Cycloplatination of ligand 3-$ClC_6H_4CH=NCH_2C_6H_5$ (2b)

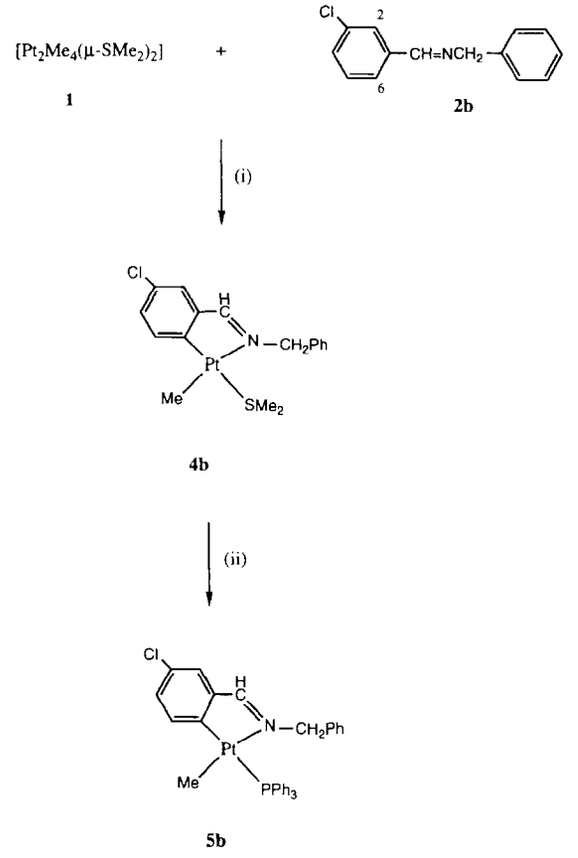
For ligand 3-$ClC_6H_4CH=NCH_2C_6H_5$ (**2b**), two distinct *endo*-metallacycles may be obtained since the two *ortho*-positions of the benzal ring (C(2) and C(6)) are not equivalent. However, upon reaction with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) in acetone solution, only one cyclometallated platinum(II) compound was formed, indicating that C–H bond activation occurred regioselectively at one of the two positions. Metallation at position C(6) yielding [PtMe(3-$ClC_6H_3CH=NCH_2C_6H_5$)-(SMe_2)] (**4b**) seems more likely for reasons discussed below. As shown in Scheme 2, the reaction of compound **4b** with PPh_3 in acetone yielded cyclometallated compound [PtMe(3-$ClC_6H_3CH=NCH_2C_6H_5$)(PPh_3)] (**5b**). In this case, cleavage of the metallacycle was not achieved, even with a large excess of PPh_3.

Compounds **4b** and **5b** were characterized by elemental analysis and ^1H NMR spectra, together with ^{31}P NMR for the phosphine derivative. In the ^1H NMR spectra, the resonance for the methyl–platinum group appeared as a singlet for **4b** and as a doublet, owing to coupling with the phosphorus atom, for **5b**. In both cases, the methyl group was coupled to platinum [^2J(HPt) = 82–83 Hz]. The iminic and benzylic protons

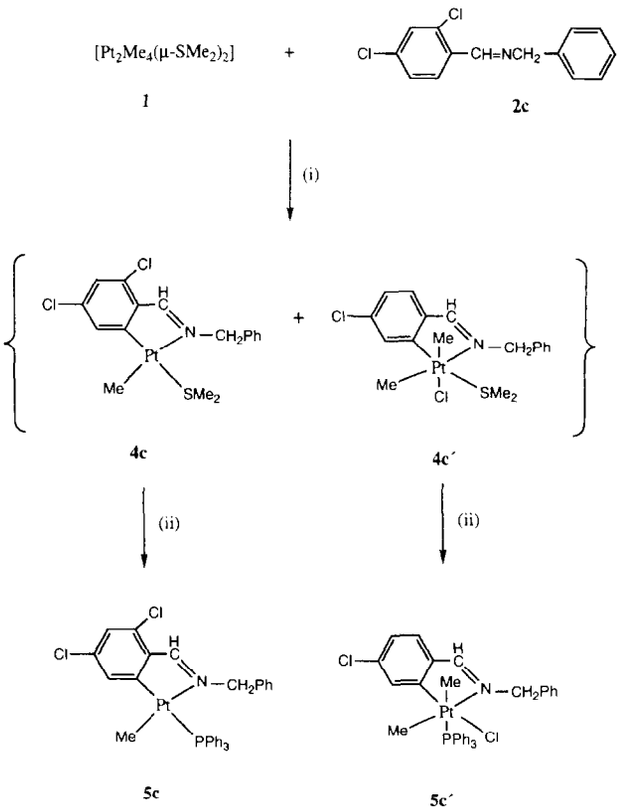
were coupled to platinum, thus indicating that the imine is bound to platinum in a bidentate (C,N) fashion.

The chemical shift of the methyl resonance for **4b** [δ 0.84 ppm], and the fact that metallacycle cleavage was not observed upon reaction with PPh_3, indicate the absence of a chlorine atom adjacent to the metallated carbon, in contrast to the results observed for **4a**. Moreover, when the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with $3\text{-}ClC_6H_4CH{=}NCH_2C_6H_5$ (**2b**) was monitored by ^1H NMR, a compound analogous to **3a** was not detected, indicating that the cyclometallation process from the corresponding compound **3** is fast on the NMR scale.

As observed for ligand $3,5\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2a**), chlorine substituents in the carbon atoms adjacent to the metallation positions do not inhibit the reaction; however, for asymmetric ligand $3\text{-}ClC_6H_4CH{=}NCH_2\text{-}C_6H_5$ (**2b**), metallation at the less hindered C(6) position is preferred. Previous work with related fluorinated ligands has shown that metallation occurs in spite of the presence of fluorine substituents adjacent to the activated bond, and the position having a vicinal fluorine atom (C(2)) is exclusively activated for $3\text{-}FC_6H_4CH{=}NCH_2(2\text{-}ClC_6H_4)$ [7]. Thus, the results are not entirely similar for chlorine and fluorine substituents and the different behaviour can be attributed to the larger size of the chlorine atom.



Scheme 2. (i) Acetone, room temperature, 16 h, $(-CH_4)$; (ii) $+PPh_3$, acetone, room temperature, 16 h.

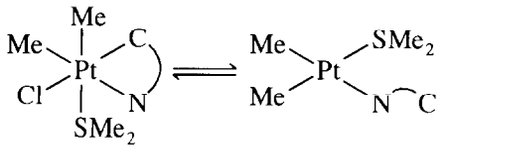


Scheme 3. (i) Acetone, room temperature, 16 h, $(-CH_4)$; (ii) $+PPh_3$, acetone, room temperature, 16 h.

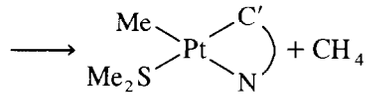
2.4. Cycloplatination of ligand $2,4\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (2c)

The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with chlorinated imine $2,4\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2c**) was carried out in acetone solution at room temperature (Scheme 3) and yielded a mixture of cyclometallated platinum(II) compound $[PtMe(2,4\text{-}Cl_2C_6H_2CH{=}NCH_2\text{-}C_6H_5)(SMe_2)]$ (**4c**) arising from *ortho* aryl C–H bond activation followed by loss of methane, and cyclometallated platinum(IV) compound $[PtMe_2Cl(4\text{-}ClC_6H_3\text{-}CH{=}NCH_2C_6H_5)(SMe_2)]$ (**4c′**) arising from *ortho* aryl C–Cl bond activation.

Early stages of the reaction were monitored by ^1H NMR and no evidence of coordination of the imine to platinum through the nitrogen atom was observed. Instead, methane formation occurred readily and NMR signals corresponding to compounds **4c** and **4c′** were observed. The proportions, averaged from all signals, in which compounds **4c** and **4c′** were formed are 65% and 35% respectively. Compound **4c** crystallized as an orange solid from the acetone solution and, upon addition of hexane, compound **4c′** was isolated as a pale yellow solid. Conversion of compound **4c′** to compound **4c**, which is in principle possible according to the reaction below, was not observed.



4c′



4c

Compounds **4c** and **4c′** were characterized by elemental analysis and ^{1}H NMR spectra. In the ^{1}H NMR spectra, both the methyl and iminic resonances were coupled with ^{195}Pt. The values of the coupling constants were smaller for **4c′** than for **4c**, which is consistent with the higher oxidation state of platinum. Both sets of values are in good agreement with those reported for platinum(II) and platinum(IV) compounds [13]. For compound **4c**, as well as for the free imine **2c**, the iminic resonance was shifted slightly downfield when compared with analogous compounds (see Table 1), and this can be taken as an indication of a CH · · · Cl interaction between the imine proton and the chlorine atom Cl(2), as shown in Fig. 1. A similar shift has been observed for compounds with a fluorine atom at C(2).

Compounds **4c** and **4c′** were treated with PPh_3 in acetone solution and yielded cyclometallated phosphine derivatives $[PtMe(2,4\text{-}Cl_2C_6H_2CH{=}NCH_2C_6H_5)(PPh_3)]$ (**5c**) and $[PtMe_2Cl(4\text{-}ClC_6H_3CH{=}NCH_2C_6H_5)(PPh_3)]$ (**5c′**) as yellow and white solids respectively. For these compounds, cleavage of the metallacycle was not achieved even with a large excess of PPh_3. For compound **4c** this can be related, in line with the result for compounds **4a** and **4b**, to the fact that the adjacent position to the aryl C–Pt bond does not bear any bulky substituent. Concerning compound **4c′**, it is worth noting that displacement of the iminic nitrogen for PPh_3 has not been achieved for platinum(IV) cyclometallated compounds [8], regardless of the substituents in the aryl group. It has been suggested that the harder nature of platinum(IV) versus platinum(II) would increase the affinity of platinum for the nitrogen atom.

Compounds **5c** and **5c′** were characterized by elemental analysis and ^{1}H and ^{31}P NMR spectra. As mentioned for compounds **4c** and **4c′**, reduced coupling constants to ^{195}Pt were observed for methyl and iminic protons of the platinum(IV) versus the platinum(II) compound. The methyl resonances appeared as doublets due to coupling with ^{31}P. For compound **5c′**, two distinct methyl resonances appeared; the one at higher field with the smaller ^2J(HPt) value is assigned to the axial methyl group in a *trans* position to PPh_3, and the other to the equatorial methyl group. For both compounds, a single resonance appeared in the ^{31}P NMR and the ^1J(PPt) values were consistent with the oxidation state of platinum [14].

Activation of both aryl C–H and aryl C–Cl bonds of ligand **2c** took place to yield, respectively, platinum(II) and platinum(IV) *endo*-metallocycles. A comparison with the results previously obtained for analogous ligands is shown in Chart 1. Activation of C–X bonds (X = Br, Cl) takes place exclusively for $2\text{-}XC_6H_4CH{=}NCH_2C_6H_5$ [8], while C–H bond activation is selectively activated for $2\text{-}FC_6H_4CH{=}NCH_2C_6H_5$ [7]. These results are consistent with the order of C–X bond energies. However, for ligand $C_6H_5CH{=}NCH_2(2\text{-}ClC_6H_4)$ [8], activation of a C–H bond to give a more stable *endo*-metallacycle is easier than activation of the weaker C–Cl bond to give an *exo*-metallacycle, and exclusive activation of a C–H bond in the presence of a C–Cl bond has also been reported at platinum(II) for $PPh_2CH_2C(^tBu){=}N{-}N{=}CH(2\text{-}ClC_6H_4)$ [4b]. For ligand $2,4\text{-}Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2c**), it is likely that the presence of an electron-withdrawing chlorine atom at position 4 increases the reactivity of the aryl C–H bond and the fission of this bond, in spite of its greater bond energy, becomes competitive with the C–Cl bond fission.

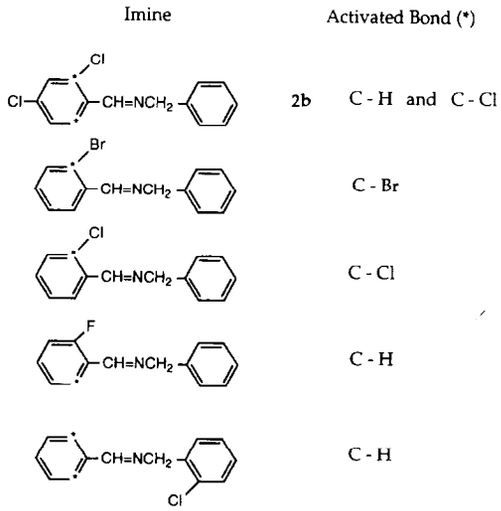


Chart 1.

As suggested for the Schiff base $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)CH_2{-}N{=}CH(2\text{-}ClC_6H_4)\}]$ [15], of the two possible planar conformations (A and B in Fig. 3) of the more stable E-form of imine **2c**, A is less likely due to the repulsion of the nitrogen lone pair with the chlorine

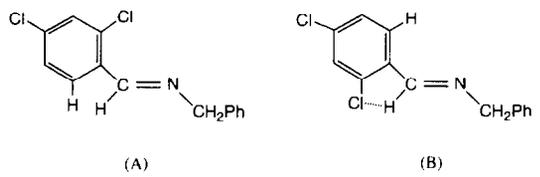


Fig. 3. Conformers of the E-form of 2,4-dichlorobenzylidenbenzylamine.

atom, while B is stabilized by a Cl · · · H interaction. Conformation B favours C–H bond activation versus C–Cl bond activation. Although the Cl · · · H interaction is consistent with the shift of the iminic proton and the reactivity of imine **2c**, this factor is not decisive since exclusive C–Cl bond activation was achieved for ligand 2-$ClC_6H_4CH{=}NCH_2C_6H_5$. In fact, studies of CH · · · Cl hydrogen bonds indicate that these are relatively weak interactions due to the relatively low electronegativity of carbon and to the size of chlorine atom [10].

The results reported in this paper for chlorinated N-benzylidenebenzylamines indicate that the stereoelectronic effects of the chlorine substituents are quite important in the reactivity of the aryl C–H bonds, while the CH · · · Cl interactions detected by NMR do not seem to be decisive. The electron-withdrawing ability of the chlorine substituents facilitates the intramolecular C–H bond activation in spite of the presence of two bulky chlorine atoms adjacent to the metallation positions for ligand **2a**. In contrast, the unfavourable steric effect of the chlorine atom is evidenced for ligand **2b** since metallation at the less hindered position is preferred in spite of the electron-withdrawing ability of the chlorine atom. For ligand **2c**, electronic effects of the chlorine atoms at positions 2 and 4 render C–H bond activation competitive with C–Cl bond activation.

3. Experimental details

^1H and ^{31}P-{^1H} NMR spectra were recorded using Varian Gemini 200 (^1H, 200 MHz), Bruker WP80SY (^{31}P, 32.4 MHz) and Varian XL 300FT (^{31}P, 121.4 MHz) spectrometers, and referenced to $SiMe_4$(^1H) and H_3PO_4 (^{31}P). δ values are given in parts per million and J values in Hertz. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and by the Serveis Científico-Tècnics de la Universitat de Barcelona. Decomposition points were obtained with a Buchi 510 melting point instrument.

3.1. Preparation of the compounds

The complex [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**) was prepared by the method reported in the literature [16].

Compounds **2** were prepared by reaction of 5 mmol of the corresponding aldehyde with an equimolar amount of benzylamine in ethanol [17]. The mixture was refluxed for 2 h and the solvent was removed in a rotary evaporator to yield yellow oils (**2a**, **2b**) or a white solid (**2c**).

*3,5-$Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2a**).* ^1H NMR ($CDCl_3$): δ 4.82 [s, CH_2], {7.36 [m], 7.67 [m], aromatics}, 8.27 [s, CHN].

*3-$ClC_6H_4CH{=}NCH_2C_6H_5$ (**2b**).* ^1H NMR ($CDCl_3$): δ 4.83 [s, CH_2], {7.37 [m], 7.60 [m, 1H], 7.81 [m, 1H], aromatics}, 8.34 [s, CHN].

*2,4-$Cl_2C_6H_3CH{=}NCH_2C_6H_5$ (**2c**).* ^1H NMR ($CDCl_3$): δ 4.85 [s, CH_2], {7.34 [m], 7.41 [m], 8.10 [d], aromatics}, 8.80 [s, CHN].

Compound **3a** was detected using the following procedure: 20.0 mg (0.035 mmol) of compound [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**) and 0.08 mmol of imine **2b** were dissolved in 0.6 ml of acetone-d_6 and the ^1H NMR spectrum was recorded.

*[$PtMe_2${3,5-$Cl_2C_6H_3CH{=}NCH_2C_6H_5$}($SMe_2$)] (**3a**).* ^1H NMR (acetone-d_6): δ 0.47 [s, ^2J(HPt) = 82, Me], 0.94 [s, ^2J(HPt) = 82, Me], 2.31 [s, ^3J(HPt) = 26, SMe_2], {4.20(d), 4.35(d), ^2J(HH) = 13, CH_2, *AB* pattern}, 9.10 [s, ^3J(HPt) = 51, CHN].

Compounds **4a** and **4b** were prepared by reaction of 100 mg (0.17 mmol) of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (**1**) with 0.35 mmol of the corresponding imine in acetone. The mixture was stirred for 48 h (**4a**) or 16 h (**4b**) and the solvent was removed in a rotary evaporator. The residue was washed with hexane and recrystallized in acetone/hexane to yield yellow–orange solids, which were filtered and washed with hexane.

*[$PtMe$(3,5-$Cl_2C_6H_2CH{=}NCH_2C_6H_5$)($SMe_2$)] (**4a**).* Yield 150 mg (80%), m.p. 82–87°C (d). Anal. Found: C, 38.74; H, 3.48; N, 2.72. $C_{17}H_{19}Cl_2NSPt$ Calc.: C, 38.14; H, 3.58; N, 2.62%. ^1H NMR (acetone-d_6): δ 1.24 [s, ^2J(HPt) = 82, Me], 1.98 [s, ^3J(HPt) = 30, SMe_2], 5.20 [s, ^3J(HPt) = 14, CH_2], {7.20 [m], 7.23 [m], 7.65 [m], aromatics}, 8.96 [s, ^3J(HPt) = 50, CHN].

*[$PtMe$(3-$ClC_6H_3CH{=}NCH_2C_6H_5$)(SMe_2)] (**4b**).* Yield 140 mg (80%), m.p. 140–5°C (d). Anal. Found: C, 40.63; H, 4.09; N, 2.82. $C_{17}H_{20}ClNSPt$ Calc.: C, 40.76; H, 4.02; N, 2.79%. ^1H NMR (acetone-d_6): δ 0.84 [s, ^2J(HPt) = 82, Me], 1.97 [s, ^3J(HPt) = 27, SMe_2], 5.22 [s, ^3J(HPt) = 13, CH_2], {7.18 [m], 7.30 [m], 7.45 [m], aromatics}, 8.85[s, ^3J(HPt) = 56, CHN].

A similar reaction using **2c** yielded a mixture of **4c** and **4c'**.

*[$PtMe$(2,4-$Cl_2C_6H_2CH{=}NCH_2C_6H_5$)($SMe_2$)] (**4c**).* M.p. 147–152°C (d). Anal. Found: C, 38.77; H, 3.71; N, 2.84. $C_{17}H_{19}Cl_2NSPt$ Calc.: C, 38.14; H, 3.58; N, 2.62%. ^1H NMR (acetone-d_6): δ 0.82 [s, ^2J(HPt) = 81, Me], 1.97 [s, ^3J(HPt) = 29, SMe_2], 5.31 [s, ^3J(HPt) = 13, CH_2], {7.07 [m], 7.31 [m], 7.45 [d], aromatics}, 9.23 [s, ^3J(HPt) = 59, CHN].

*[$PtMe_2Cl$(4-$ClC_6H_3CH{=}NCH_2C_6H_5$)(SMe_2)] (**4c'**).* Anal. Found: C, 40.08; H, 3.93; N, 2.52. $C_{18}H_{23}Cl_2NSPt$ Calc.: C, 39.21; H, 4.20; N, 2.54%. ^1H NMR (acetone-d_6): δ 0.80 [s, ^2J(HPt) = 70, Me], 1.16 [s, ^2J(HPt) = 68, Me], 1.97 [s, ^3J(HPt) = 13, SMe_2], {5.23 [d], 5.36 [d], ^2J(HH) = 13, *AB* pattern, CH_2}, {7.32 [m], 7.58 [m], aromatics}, 8.72 [s, ^3J(HPt) = 46, CHN].

Compound **5a** was prepared by reaction of 50 mg of compound **4a** with two equivalents of PPh_3 in acetone. Within 1 h, the colour of the solution faded and a white precipitate was formed. After addition of hexane, the

white solid was collected by filtration, washed with hexane and dried in vacuo.

[PtMe(3,5-$Cl_2C_6H_2CH=NCH_2C_6H_5$)(PPh_3)$_2$] (5a). Yield 75 mg (80%), m.p. 227°C (d). Anal. Found: C, 61.08; H, 4.43; N, 1.40. $C_{51}H_{43}Cl_2NP_2Pt$ Calc.: C, 61.38; H, 4.34; N, 1.40%. ^{1}H NMR (acetone-d_6): δ 0.30 [dd, ^2J(HPt) = 65, $^3J(HP_a)$ = 8, $^3J(HP_b)$ = 7, Me], {4.75 [d], 4.88 [d], ^2J(HH) = 14, *AB* pattern, CH_2}, {6.90 [m], 7.11 [m], 7.21 [m], aromatics}, 9.63 [s, ^4J(HPt) = 10, CHN]. ^{31}P NMR (acetone): δ 20.69 [d, ^1J(PPt) = 2167, ^2J(PP) = 15], 20.37 [d, ^1J(PPt) = 1921, ^2J(PP) = 15].

Compound **5b** was prepared by reaction of 50 mg of compound **4b** with the equimolar amount of PPh_3 in acetone. The mixture was stirred at room temperature for 16 h. On addition of hexane, yellow crystals were formed, and they were collected by filtration, washed with hexane and dried in vacuo.

[PtMe(3-$ClC_6H_3CH=NCH_2C_6H_5$)(PPh_3)] (5b). Yield 45 mg (64%), m.p. 205°C (d). Anal. Found: C, 56.08; H, 4.21; N, 2.03. $C_{33}H_{29}ClNPPt$ Calc.: C, 56.53; H, 4.17; N, 2.00%. ^{1}H NMR (acetone-d_6): δ 0.65 [d, ^2J(HPt) = 83, ^3J(HP) = 7, Me], 4.35 [s, ^3J(HPt) = 9, CH_2], {6.85 [d], 7.17 [m, 1H], 7.41 [m], 7.65 [m], aromatics}, 8.55 [s, ^3J(HPt) = 56, CHN]. ^{31}P NMR (acetone): δ 26.62 [s, ^1J(PPt) = 2227].

Compounds **5c** and **5c′** were prepared by reaction of 50 mg of compounds **4c** and **4c′** respectively with the equimolar amount of PPh_3 in acetone. The mixture was stirred at room temperature for 16 h. On addition of hexane, the solid was collected by filtration, washed with hexane and dried in vacuo.

[PtMe(2,4-$Cl_2C_6H_2CH=NCH_2C_6H_5$)(PPh_3)] (5c). M.p. 205–210°C (d). Anal. Found: C, 52.97; H, 3.80; N, 1.94. $C_{33}H_{28}Cl_2NPPt$ Calc.: C, 53.88; H, 3.84; N, 1.90%. ^{1}H NMR (acetone-d_6): δ = 0.63 [d, ^2J(HPt) = 82, ^3J(HP) = 7, Me], 4.40 [s, ^3J(HPt) = 9, CH_2] {6.80 [m, 1H], 7.20 [m, 1H], 7.55–7.65 [m], aromatics}, 8.95 [s, ^3J(HPt) = 58, CHN]. ^{31}P NMR (acetone): δ 30.85 [s, ^1J(PPt) = 2341].

[$PtMe_2Cl$(4-$ClC_6H_3CH=NCH_2C_6H_5$)(PPh_3)] (5c′). M.p. 106–112°C (d). Anal. Found: C, 54.05; H, 4.30; N, 1.76. $C_{34}H_{32}Cl_2NPPt$ Calc.: C, 54.33; H, 4.29; N, 1.86%. ^{1}H NMR (acetone-d_6): δ 0.75 [d, ^2J(HPt) = 59, ^3J(HP) = 8, Me], 1.27 [d, ^2J(HPt) = 69, ^3J(HP) = 8, Me], {4.50 [d], 5.29 [d], ^3J(HH) = 15, *AB* pattern, CH_2}, {6.42 [s, ^3J(HPt) = 47, 1H], 7.27 [m], 7.30–7.35 [m], 7.54–7.58 [m], aromatics}, 8.18 [s, ^3J(HPt) = 52, CHN]. ^{31}P NMR (acetone): δ −4.04 [s, ^1J(PPt) = 1009].

3.2. X-ray structure analysis

3.2.1. Data collection

A prismatic crystal (0.1 × 0.1 × 0.2 mm^3) was selected and mounted on an Enraf-Nonius CAD-4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($12° < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using an $\omega/2\theta$ scan technique. A total of 10901 reflections were measured in the range $1.46° < \theta < 29.97°$, 7445 of which were assumed as observed, applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control and significant intensity decay was not observed. Lorentz polarization and absorption corrections were made.

Table 5
Crystallographic data and details of the refinements for compound **5a**

Formula	$C_{51}H_{43}Cl_2NP_2Pt$
FW	997.79
Crystal system, space group	monoclinic, $P2_1/n$
a, b, c (Å)	10.899(5), 22.953(5), 17.588(9)
α, β, γ (°)	90, 95.14(5), 90
V (Å^3)	4382(3)
D_c (g cm^{-3})	1.512
Z	4
F(000)	1992
Crystal size (mm^3)	0.1 × 0.1 × 0.2
μ (Mo Kα)	54.14
λ (Mo Kα) (Å)	0.71069
T (K)	293(2)
Reflections collected	10901
$R[I > 2\sigma(I)]$, $wR(F^2)$	0.0566, 0.1657
R (all data), $wR(F^2)$	0.0833, 0.2095
Refined parameters	419
Max shift/e.s.d.	0.02
max., min. difference peaks, (e Å^{-3})	3.182, −4.108

3.2.2. Structure solution and refinement

The structure was solved by Patterson synthesis, using the SHELXS computer program [18] and refined by the full-matrix least-squares method with the SHELX93 computer program [19] using 10.901 reflections. The function minimized was $\sum w || F_o |^2 - | F_c |^2 |^2$, where $w = [\sigma^2(I) + (0.2685P)^2]^{-1}$ and $P = (| F_o |^2 + 2 | F_c |^2)/3$. f, f' and f'' were taken from *International Tables of X-Ray Crystallography* [20]. Hydrogen atoms were not included in the refinement. The final R factor, the number of refined parameters and the maximum and minimum peaks in the final difference synthesis are given in Table 5.

4. Supplementary material available

Tables of anisotropic displacement parameters and observed and calculated structure factors, and complete lists of bond lengths and angles are available from the authors on request and have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We acknowledge financial support from the DGICYT (Dirección General de Investigación Científica y Técnica, Ministerio de Educación y Ciencia, Spain).

References

[1] (a) A.C. Cope and R.W. Siekman, *J. Am. Chem. Soc.*, *87* (1965) 3272; (b) R.C. Elder, R.D. Cruea and R.F. Morrison, *Inorg. Chem.*, *5* (1976) 1623; (c) A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc.*, *90* (1968) 909.

[2] A.D. Ryabov, *Chem. Rev.*, *90* (1990) 403.

[3] (a) T.G. Richmond, *Coord. Chem. Rev.*, *105* (1990) 221; (b) C.M. Anderson, R.J. Puddephatt, G. Ferguson and A.J. Lough, *J. Chem. Soc., Chem. Commun.*, (1989) 1297; (c) C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson and R.J. Puddephatt, *Organometallics*, *10* (1991) 2672.

[4] (a) B.L. Lucht, M.J. Poss, M.A. King and T.G. Richmond, *J. Chem. Soc., Chem. Commun.*, (1991) 400; (b) S.D. Perera and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1995) 641; (c) M. Crespo, M. Martinez and J. Sales, *J. Chem. Soc., Chem. Commun.*, (1992) 822.

[5] (a) J. Albert, R.M. Ceder, M. Gómez, J. Granell and J. Sales, *Organometallics*, *11* (1992) 1536; (b) S.F. Dyke and S.N. Quessy, *Transition Met. Chem.*, *7* (1982) 233; (c) J.M. Vila, M.T. Pereira, E. Gayoso and M. Gayoso, *Transition Met. Chem.*, *11* (1986) 342; (d) J.M. Vila, A. Suarez, M.T. Pereira, E. Gayoso and M. Gayoso, *Polyhedron*, *6* (1987) 1003; (e) M. Pfeffer, E.P. Urriolabeitia and J. Fischer, *Inorg. Chem.*, *34* (1995) 643.

[6] M. Crespo, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, *509* (1996) 29.

[7] M. Crespo, M. Martinez and J. Sales, *Organometallics*, *12* (1993) 4297.

[8] M. Crespo, M. Martinez, J. Sales, X. Solans and M. Font-Bardía, *Organometallics*, *11* (1992) 1288.

[9] M. Crespo, X. Solans and M. Font-Bardía, *Organometallics*, *14* (1995) 355.

[10] L. Brammer, J.M. Charnock, P.L. Goggie, R.J. Goodfellow, A.G. Orpen and T.F. Koetzle, *J. Chem. Soc., Dalton Trans.*, (1991) 1789.

[11] G.P.A. Yap, A.L. Rheingold, P. Das and R.H. Crabtree, *Inorg. Chem.*, *34* (1995) 3474.

[12] J. March, in *Advanced Organic Chemistry*, Wiley, New York, 1995, pp. 242–250.

[13] J.A.M. van Beek, G. van Koten, I.C.M. Wehman-Ooyevaar, W.J.J. Smeets, P. van der Sluis and A.L. Spek, *J. Chem. Soc., Dalton Trans.*, (1991) 883.

[14] P.S. Pregosin and R.W. Kunz, in P. Diehl, E. Fluck and R. Kosfeld (eds.), *^{31}P and ^{13}C NMR of transition metal phosphine complexes*, Springer, Berlin, 1979.

[15] R. Bosque, C. López and J. Sales, *J. Organomet. Chem.*, *498* (1995) 147.

[16] J.D. Scott and R.J. Puddephatt, *Organometallics*, *2* (1983) 1643.

[17] L.A. Bigelow and H. Ealough, in A.H. Blatt (ed.), *Organic Syntheses*, Vol. 1, Wiley, New York, 1994.

[18] G.M. Sheldrick, *Acta Crystallogr.*, *A46* (1990) 467.

[19] G.M. Sheldrick, *SHELX93, A Computer Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1993.

[20] *International Tables of X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, UK, 1974, pp. 99–100 and 149.