ELSEVIER

Journal of Organometallic Chemistry 549 (1997) 167–176

Journal of Organometallic Chemistry

Synthesis and reactivity of new palladium alkyl complexes containing PMe_3 ligands: Insertion reactions and formation of bis(pyrazolyl)borate derivatives

Enrique Gutiérrez [a], M. Carmen Nicasio [b,1], Margarita Paneque [b,*], Caridad Ruiz [a], Verónica Salazar [b]

[a] *Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, 28049 Madrid, Spain*
[b] *Instituto de Investigaciones Químicas-Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, C/Américo Vespucio s/n, Isla de la Cartuja, 41092 Sevilla, Spain*

Received 6 June 1997

Abstract

The complex $PdCl_2(cod)$ (cod = 1,4-cyclooctadiene) reacts with one equivalent of R(Mg)Cl (R = CH_2CMe_2Ph, CH_2SiMe_3, $CH_2C_6H_4$-*o*-Me) to yield monoalkyl derivatives of composition Pd(R)Cl(cod). The cyclooctadiene ligand is readily displaced by dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) and PMe_3 to generate $Pd(R)Cl(L_2)$ (L_2 = $(PMe_3)_2$, dmpe) of which, the complex $Pd(CH_2CMe_2Ph)Cl(PMe_3)_2$ thermally isomerizes to the palladium aryl $Pd(C_6H_4$-*o*-$CMe_3)Cl(PMe_3)_2$ in the presence of catalytic amounts of NEt_3. Carbonylation of the alkyl derivatives affords acyl complexes $Pd(COR)Cl(L_2)$ and related iminoacyl derivatives have also been obtained by the analogous reaction with *tert*-butyl-isocyanide. New alkyl and acyl species containing bis(pyrazolyl)borate ligands have been prepared by halide metathesis in the $Pd(R/COR)Cl(PMe_3)_2$ complexes. During the course of these reactions one equivalent of PMe_3 is liberated. The complex Bp' $Pd(CH_2SiMe_3)(PMe_3)$ has been structurally characterized by X-ray crystallography.

Keywords: Palladium alkyl complexes; Pd–C σ bonds; Organometallic chemistry; Ligands

1. Introduction

Interest in the organometallic chemistry of palladium derives largely from its pivotal role in a number of important catalytic cycles. These include, olefin oxidation, the oligomerization of olefins, dienes and acetylenes, carbonylation, vinylation, acetoxylation, isomerization, halogenation, coupling of arenes [1–3]. In most of these processes, intermediates containing Pd–C σ bonds are either known to be generated or are proposed as transients, and consequently the chemistry of palladium alkyl complexes remains an area of intense research activity [4–15]. In this paper, we report on the synthesis, characterization and reactivity of some alkyl derivatives of Pd(II) containing PMe_3 and dmpe as coligands.

2. Results and discussion

2.1. Synthesis of alkyl derivatives

When one equivalent of $Mg(CH_2CMe_2Ph)Cl$ is added to a cold suspension of $PdCl_2(cod)$ (cod = 1,4-cyclooctadiene) in Et_2O, a yellow solution results from which a yellow microcrystalline solid can be isolated in good yields. ^1H and $^{13}C\{^1H\}$ NMR and elemental analysis data indicate that metathesis of one chloride ligand has taken place with formation of the species $Pd(CH_2CMe_2Ph)Cl(cod)$ (**1**) (Eq. (1)) [16–18].

$$PdCl_2(cod) \xrightarrow[-MgCl_2]{Mg(CH_2CMe_2Ph)Cl} \underset{\mathbf{1}}{Pd(CH_2CMe_2Ph)Cl(cod)} \quad (1)$$

* Corresponding author.
[1] New address: Departamento de Química y Ciencia de los Materiales, Universidad de Huelva, 21819 Palos de la Frontera, Huelva, Spain.

0022-328X/97/$17.00
PII S0022-328X(97)00495-6

Complex **1** is moderately stable in solution and in the solid state, but the diolefin ligand may readily be displaced by other neutral donor molecules such as phosphines. Thus, the derivatives $Pd(CH_2CMe_2Ph)Cl(P_2)$ ($P_2 = (PMe_3)_2$, **2**; dmpe, **3** [dmpe = 1,2-bis(dimethylphosphino)ethane]) are prepared in moderate to good yields (Eq. (2)). Complex **2** can also be directly obtained by addition of

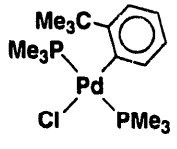
$$\underset{\mathbf{1}}{Pd(CH_2CMe_2Ph)Cl(cod)} \xrightarrow{2\,P} Pd(CH_2CMe_2Ph)Cl(P_2) \quad (2)$$

P = PMe_3, **2**; 1/2 dmpe, **3**

2 equivalents of PMe_3 to the reaction mixture of Eq. (1), without isolation of complex **1**. It is important to note that the addition of the phosphine should be accomplished only after all the starting $PdCl_2(cod)$ has been consumed. On several occasions, when the phosphine was added at the beginning of the reaction, the known [19] dialkyl *cis*-$Pd(CH_2CMe_2Ph)_2(PMe_3)_2$ was obtained instead. A related palladium bis-alkyl complex has been reported to result from the reaction of $PdCl_2(bipy)$ with 1 equiv of $LiCH_2CMe_3$ in which the dialkyl complex $Pd(CH_2CMe_3)_2(bipy)$ was isolated [20]. Presumably, the insolubility of the starting material leads to the observed dialkylation in this case. The characterization of complex **2** follows unambiguously from the analytical and NMR data. The two phosphine ligands occupy mutually trans positions, as can be deduced from the appearance of virtually coupled triplets [21,22], both in the ^1H and $^{13}C\{^1H\}$ NMR spectra, for the methyl groups of the PMe_3 ligands, and from the presence of a singlet in the $^{31}P\{^1H\}$ NMR spectrum ($\delta = -14.9$).

Obviously, complex **3** exhibits a cis disposition of the chloride and the neophyl groups. Two inequivalent and mutually coupled P nuclei are observed in the $^{31}P\{^1H\}$ NMR spectrum ($\delta_A = 24.2$, $\delta_X = 33.5$, $J(AX) = 29$ Hz). In this case, the methylene carbon of the neophyl ligand is evidenced by a doublet ($\delta = 40.6$, $^2J(CP) = 117$ Hz) as a result of its coupling with the P *trans* to it (consistent with these observations, phosphorus coupling is not resolved in the resonance of the analogous carbon atom in complex **2**).

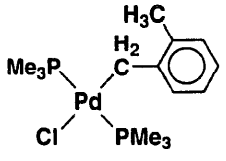
Interestingly, complex **2** isomerizes to the *o-tert*-butylphenyl derivative $Pd(C_6H_4\text{-}o\text{-}CMe_3)Cl(PMe_3)_2$ (**4**), when a toluene solution is heated to reflux in the presence of triethylamine as a catalyst. The NMR



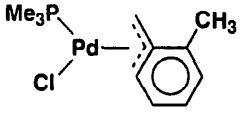
4

data of the yellow crystalline material isolated is clearly in accord with the proposed formulation. In addition to a pseudotriplet for the two trans PMe_3 ligands, the aliphatic region of the $^{13}C\{^1H\}$ NMR spectrum contains only the signals expected for a CMe_3 group. In addition, four aromatic C–H resonances and two signals for quaternary carbons are observed. Examples of this kind of rearrangement, which implies the transposition of an *ortho*-H to the methylene, have been previously described in related systems [23–28]. Probably, the formation of a stronger Pd–C(aryl) bond, compared with the Pd–C(alkyl), is in part responsible for the favourable thermodynamics.

The synthetic procedure used for **2** has also been employed for the preparation of other derivatives, such as the 2-methylbenzyl complexes **5** and **6**. Upon reaction of $PdCl_2(cod)$ with 1 equiv of $Mg(CH_2C_6H_4\text{-}o\text{-}Me)Cl$, the formation of a white microcrystalline precipitate was observed. This is assumed to be $Pd(CH_2C_6H_4\text{-}o\text{-}Me)Cl(cod)$, although it was not isolated. When 2 or 1 equiv of PMe_3 are added to the above mentioned suspension, the η^1-benzylic and the η^3-pseudoallylic derivatives **5** and **6** can be obtained in 55 and 50% yield, respectively. These complexes are



5



6

yellow (**5**) and orange (**6**) microcrystalline materials, stable to air in the solid state but not in solution, and soluble in most common organic solvents, with the exception of petroleum ether.

The NMR data for the η^1 derivative **5** are similar to those of the neophyl complex **2** and in agreement with the structure proposed. Some related benzylic complexes have been reported previously [29–31]. For the pseudoallylic complex **6**, doublets are observed in the ^1H NMR spectrum for the PMe_3 (δ 1.29 ppm, $^2J(HP) = 11.1$ Hz) and for the Pd–CH_2 groups (δ 2.83 ppm, $^3J(HP) = 2.7$ Hz). A comparison of the spectroscopic data of **6** with those of the Ni complex $Ni(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$, previously prepared and

fully characterized by our group [32] strongly supports the proposed η^3-pseudoallylic structure of **6** [33,34].

Related Pd(II) alkyl derivatives can also be obtained, for example the complex $Pd(CH_2SiMe_3)Cl(PMe_3)_2$ (**7**) (Eq. (3)). It is worth mentioning

$$PdCl_2(cod) \xrightarrow[\text{2) } Mg(CH_2SiMe_3)Cl]{\text{1) 2 } PMe_3} \underset{\mathbf{7}}{Pd(CH_2SiMe_3)Cl(PMe_3)_2} \quad (3)$$

that the synthesis of complex **7** requires the addition of the phosphine to be carried out at the beginning of the reaction, i.e., prior to the addition of the Grignard reagent. Otherwise, reduction to metallic palladium competes with the desired alkylation, leading to a concomitant decrease in the isolated yield of **7**.

Complex **7** is characterized, by ^1H NMR spectroscopy, for instance by a pseudotriplet for the methyl protons of the phosphines and by a triplet for the methylene.

2.2. *Insertion reactions*

The reaction of some of the alkyl derivatives already described with CO has been studied, these reactions are summarized in Eq. (4), the products in all cases being η^1-acyl complexes. The conditions required for achieving optimum yields of the insertion products are somewhat variable. Thus, whilst the reaction of **2** is essentially complete after 15 min at room temperature and 1 atm, the analogous reaction of complex **7** which contains the CH_2SiMe_3 group requires 20 h at 2 atm. For the cyclooctadiene derivative **1**, the reaction is particularly facile and may be carried out at −50°C (1 atm CO, 15 min) due probably to the lability of the coordinated olefin.

$$Pd(R)Cl(L_2) \xrightarrow{CO} Pd(COR)Cl(L_2) \quad (4)$$

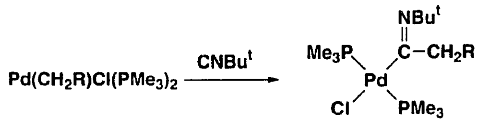
R = CH_2CMe_2Ph, L_2 = cod, **8**
R = CH_2CMe_2Ph, L = PMe_3, **9**
R = CH_2SiMe_3, L = PMe_3, **10**

In addition, a related acyl complex **11** containing the chelating dmpe ligand, has been obtained by the metathesis reaction depicted in Eq. (5).

$$Pd(COCH_2CMe_2Ph)Cl(cod) \xrightarrow{dmpe} \underset{\mathbf{11}}{Pd(COCH_2CMe_2Ph)Cl(dmpe)} \quad (5)$$

The new acyl derivatives are readily characterized by spectroscopic methods. They all display a strong absorbance in their IR spectra, assigned to ν(COR), which ranges from 1650 cm^{-1} for the PMe_3 derivatives **9** and **10** to 1730 cm^{-1} for the *cis* complexes **8** and **11**. The latter value, although towards the higher extreme of the range of frequencies found for Pd(II)-η^1-acyls, is similar to other values reported for the CO stretching frequency of some *cis*-acetylpalladium complexes [35]. For the *trans* species **9** and **10**, the methylenic carbon is evidenced in the $^{13}C\{^1H\}$ NMR spectra as a triplet, coupling to two equivalent phosphorous nuclei, with coupling constants of 15 Hz (**10**) and 17 Hz (**9**), while the acyl $C{=}O$ carbon atom resonates as a singlet in both cases at ca. 235 ppm, indicating that ^3J(CP) is larger than ^2J(CP) for the acyl group of these *trans* complexes [36]. For the related nickel derivatives of composition *trans*-$Ni(COCH_2R)X(PMe_3)_2$ [37], the situation is in general the opposite, with ^2J(CP) being of the order of ca. 25 Hz, while ^3J(CP) is close to zero. On the other hand, the carbonyl carbon nucleus of the *cis* derivative $Pd(COCH_2CMe_2Ph)Cl(dmpe)$ **11** resonates as a doublet of doublets with ^2J(CP) values of 10 and 141 Hz, attributed respectively to the coupling with the *cis* and *trans* P nuclei, in good agreement with other values reported previously in the literature [38–40].

Iminoacyl complexes can also be prepared by insertion of *tert*-butylisonitrile into the Pd–C bond of complexes **2** and **5**. Thus, the addition of 1 equiv of $CNBu^t$ to a THF solution of complexes **2** or **5** yields the new yellow crystalline compounds **12** and **13**, formulated as shown in Eq. (6). The IR spectra of these materials display strong absorptions at 1650 (**12**)



(6)

R = CMe_2Ph, **12**
C_6H_4-*o*-Me, **13**

and 1610 cm^{-1} (**13**). NMR data are also in agreement with the η^1-iminoacyl structure proposed for these complexes and are similar to analogous compounds previously described [41]. Thus, the $^{13}C\{^1H\}$ NMR spectrum of **13** shows the Pd–*C*(NR)R′ resonance as a singlet at 171.2 ppm, while the methylene carbon appears at 61.5 ppm (t, $^3J(CP) = 13$ Hz). Once again, $^3J(CP) > {}^2J(CP)$ for the iminoacyl group in these Pd complexes, while for the Ni analogues [42] the opposite trend is observed (^2J(CP) (20–25 Hz) > ^3J(CP) (6–8 Hz)).

2.3. *Reactivity towards bis(pyrazolyl)borates*

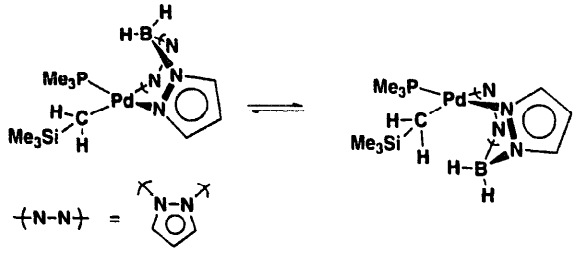
Finally, we have studied the reactivity of some of the alkyl complexes described above towards the pyrazolylborate anions Bp (dihydrobis(pyrazolyl)borate) and Bp^* (dihydrobis(3,5-dimethylpyrazolyl)borate).

Poly(pyrazolyl)borates have become an important class of ligands with unique properties, as indicated by the variety of species they form with most metals and metalloids [43]. A number of such derivatives of Pd(II)

have been prepared [44,45] and we have previously reported the reactivity of the palladium aryl complex $Pd(Ph)Br(PMe_3)_2$ towards the bulky hydrotris(3-*tert*-butylpyrazolyl)borate anion; in that case, η^1 coordination of the tridentate ligand was achieved [46], the adoption of such a coordination mode undoubtedly is steric in origin. When 1 equiv of the KBp' salt (Bp' = Bp or Bp*) is added to cold (−20°C) THF solutions of the alkyls **2** or **7**, a smooth reaction takes place with formation of yellow suspensions. After work-up, yellow crystals of the new complexes **14–17** can be isolated, in moderate yields. Elemental analysis and NMR data show that, in all cases, the halide has been substituted by Bp' and that one equivalent of PMe_3 has been liberated in each case (Eq. (7)).

$$\underset{\text{R = CMe}_2\text{Ph, 2; SiMe}_3\text{, 6}}{Pd(CH_2R)Cl(PMe_3)_2} \xrightarrow{KBp'} \underset{\text{R = CMe}_2\text{Ph, Bp' = Bp, 14; CMe}_2\text{Ph, Bp*, 16; SiMe}_3\text{, Bp, 15; SiMe}_3\text{, Bp*, 17}}{(Bp')Pd(CH_2R)(PMe_3)} \quad (7)$$

The NMR data obtained for complexes **14–17** show clear differences depending upon the nature of the Bp' ligand. Thus, complexes **14** and **15**, of composition $BpPd(CH_2R)(PMe_3)$, display, in their room temperature ^1H NMR spectra, broad singlets for the two protons of the methylene Pd–CH_2. This observation requires the coordination plane to be an effective plane of symmetry and we propose the existence of a fast exchange, on the NMR time scale, between the two degenerated boat configurations [47–52] to explain the observed equivalence of the methylenic protons (Scheme 1). Actually, under the conditions of the NMR experiment (20°C, 500 MHz) the fast exchange limit has not been completely reached, since the Pd–CH_2 signals are still broad, with ^3J(HP) remaining unresolved. In accord with the fluxional mechanism proposed, each pyrazolyl ring displays distinct well-resolved resonances. Also, the observation of a sharp doublet (^2J(CP) = 7 Hz) for the methylene carbon nucleus of **15** indicates that no PMe_3 interchange is taking place under these conditions. As expected, for the more sterically crowded Bp* derivatives **16** and **17**, the inversion of the boat configuration is considerably slower and this is evidenced by the chemi-



Scheme 1.

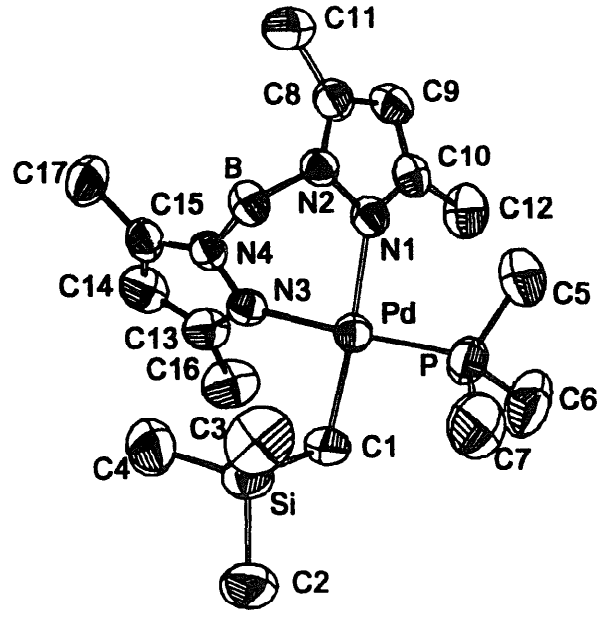


Fig. 1. Molecular structure and numbering scheme for **17**.

Table 1
Crystal and refinement data for complex **17**

	3a
Formula	$C_{17}H_{30}BN_4PPdSi$
Formula weight	472.7
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	10.692(2)
b (Å)	20.536(2)
c (Å)	11.326(2)
β (deg)	99.06(2)
V (Å3)	2455.9(6)
Z	4
Crystal dimensions (mm^3)	0.1×0.15×0.15
D_{calc} (g cm^{-3})	1.28
μ (cm^{-1})	8.6
Temperature (K)	295
Diffractometer	Enraf-Nonius
Monochromator	graphite
Radiation	Mo Kα (λ = 0.71069 Å)
2θ range (deg)	2–50
Scan technique	$\omega/2\theta$
Data collected	(−12, 0, 0) to (12, 24, 13)
Unique data	4306
Observed reflections, $I_o > 3\sigma(I_o)$	2613
R_{int} (%)	3.1
Standard reflections	2/57
Weighting scheme	unit
$R = \Sigma\|\Delta^2F\|/\Sigma\|F_o\|$	3.6
$R_w = (\Sigma w\Delta^2F/\Sigma w\|F_o\|^2)^{1/2}$	3.8
Maximum shift/error	0.03
Absorption correction range	0.82–1.12

Table 2
Selected bond distances (Å) and angles (deg) for compound **17**

Pd–P	2.224(2)	N(3)–Pd–C(1)	92.0(2)
Pd–N(1)	2.123(5)	N(1)–Pd–C(1)	174.6(2)
Pd–N(3)	2.098(4)	N(1)–Pd–N(3)	82.6(2)
Pd–C(1)	2.045(6)	P–Pd–C(1)	87.9(2)
		P–Pd–N(3)	176.7(1)
		P–Pd–N(1)	97.5(1)

cal inequivalence of the methylenic CH_2R protons at room temperature.

We have carried out a single crystal X-ray study of the derivative $Bp^*Pd(CH_2SiMe_3)(PMe_3)$ (**17**). Fig. 1 shows an ORTEP [53] perspective view of the molecule and Tables 1 and 2 collect relevant structural data. Complex **17** has a distorted square planar structure, in the solid state, the angles N(1)–Pd–C(1) (174.6(2)°) and P–Pd–N(3) (176.7(1)°) display slight deviations from the ideal value of 180°. The two Pd–N distances (2.123(5) and 2.098(4) Å) are very similar and in the range found for other Pd–N distances in poly(pyrazolyl)borate derivatives (2.17 average for the Pd–N distances in the Pd(IV) complexes $Tp'PdR_3$ [45] or 2.02 average for the Pd–N distances in Tp_2Pd [54]). The distance Pd–P of 2.224(2) Å compares well with other examples in the literature [6], while the Pd–C(1) separation of 2.045(6) Å is within the usual range for Pd(II)–C(sp^3) σ bonds [45,55–58].

Finally, acyl compounds derived from complexes **14–17** have been prepared by two different synthetic methods, as summarized in Eqs. (8) and (9). Thus, the parent acyls **9** and **10** have been employed for the synthesis of complexes **18** and **19**, by reaction with the corresponding KBp'

$$Pd(COCH_2R)Cl(PMe_3)_2 \xrightarrow{KBp'} (Bp')Pd(COCH_2R)(PMe_3)$$

R = CMe_2Ph, Bp' = Bp*, **18**; $SiMe_3$, Bp, **19** (8)

$$(Bp')Pd(CH_2R)(PMe_3) \xrightarrow{CO} (Bp')Pd(COCH_2R)(PMe_3)$$

R = CMe_2Ph, Bp' = Bp, **20**; $SiMe_3$, Bp*, **21** (9)

salt. Alternatively, the Bp' derivatives **14** and **17** were reacted with CO (2 atm) at room temperature, to yield complexes **20** and **21**. Spectroscopic data and elemental analyses are in accord with the formulation proposed. The product acyl derivatives contain a strong absorbance at 1640–1680 cm^{-1} in their IR spectra assigned to ν(COR). All these complexes display separate and sharp NMR resonances for the two inequivalent pyrazolyl rings, indicating that the square planar geometry is configurationally stable. However, and consistent with our findings during the study of the parent alkyl compounds **14–17**, the inversion of the boat configuration in the Bp complexes **19** and **20** occurs at appreciable rates at room temperature, while for the Bp* derivatives **18** and **21**, this inversion process is suppressed on the NMR time scale, under the same conditions.

Table 3
Microanalyses and IR data for compounds **1–21**

Compound	Microanalyses[a]			IR (cm^{-1})[b]	
	C (%)	H (%)	N (%)	ν(C=O)	ν(C=N)
$Pd(CH_2CMe_2Ph)Cl(cod)$, **1**	56.3 (56.6)	6.7 (6.5)			
$Pd(CH_2CMe_2Ph)Cl(PMe_3)_2$, **2**	45.5 (45.0)	7.5 (7.3)			
$Pd(CH_2CMe_2Ph)Cl(dmpe)\cdot 0.5\ CH_2Cl_2$, **3**	41.9 (42.4)	6.3 (6.4)			
$Pd(C_6H_4$-*o*-$CMe_2)Cl(PMe_3)_2$, **4**	44.8 (45.0)	7.7 (7.3)			
$Pd(\eta^1$-$CH_2C_6H_4$-*o*-Me)$Cl(PMe_3)_2$, **5**	42.4 (42.1)	7.2 (6.7)			
$Pd(\eta^3$-$CH_2C_6H_4$-*o*-Me)$Cl(PMe_3)$, **6**	41.6 (40.9)	6.0 (5.6)			
$Pd(CH_2SiMe_3)Cl(PMe_3)_2$, **7**	31.6 (31.5)	7.6 (7.6)			
$Pd[C(O)CH_2CMe_2Ph]Cl(cod)$, **8**	55.4 (55.5)	6.1 (6.1)		1725	
$Pd[C(O)CH_2CMe_2Ph]Cl(PMe_3)_2$, **9**	44.6 (44.9)	6.9 (6.8)		1650	
$Pd[C(O)CH_2SiMe_3]Cl(PMe_3)_2$, **10**	32.1 (32.3)	7.0 (7.1)		1646	
$Pd[C(O)CH_2CMe_2Ph]Cl(dmpe)$, **11**[c]				1720	
$Pd[C(NBu^t)CH_2CMe_2Ph]Cl(PMe_3)_2$, **12**	50.0 (49.4)	8.0 (7.9)	2.7 (2.8)		1660
$Pd[C(NBu^t)CH_2C_6H_4$-*o*-Me$]Cl(PMe_3)_2$, **13**	47.3 (47.3)	7.8 (7.5)	2.5 (2.9)		1620
$BpPd(CH_2CMe_2Ph)(PMe_3)$, **14**	49.1 (49.3)	6.7 (6.5)	12.5 (12.1)		1500
$BpPd(CH_2SiMe_3)(PMe_3)$, **15**	37.9 (37.5)	6.9 (6.7)	13.6 (13.4)		1497
$Bp^*Pd(CH_2CMe_2Ph)(PMe_3)$, **16**	52.9 (52.9)	7.3 (7.2)	10.7 (10.7)		1539
$Bp^*Pd(CH_2SiMe_3)(PMe_3)$, **17**	43.2 (43.2)	7.8 (7.6)	11.7 (11.9)		1539
$Bp^*Pd[C(O)CH_2CMe_2Ph](PMe_3)$, **18**	52.1 (52.8)	7.2 (7.0)	9.9 (10.3)	1662	1536
$BpPd[C(O)CH_2SiMe_3](PMe_3)$, **19**	38.4 (37.8)	6.6 (6.3)	12.4 (12.6)	1655	1500
$BpPd[C(O)CH_2CMe_2Ph](PMe_3)$, **20**	48.8 (49.0)	6.3 (6.1)	11.2 (11.4)	1681	1495
$Bp^*Pd[C(O)CH_2SiMe_3](PMe_3)$, **21**	43.1 (43.2)	6.9 (7.2)	11.1 (11.2)	1638	1538

[a] Calculated values in parentheses.
[b] In nujol mull.
[c] Due to the high instability of this compound in air, analytical data were not obtained.

3. Experimental details

Microanalyses were performed by the Microanalytical Service of the University of Seville. Perkin-Elmer Models 577 and 684 spectrometers were used for IR spectra, and Varian XL-200 and Bruker AMX 300 and AMX 500 instruments were used for NMR studies. The ^{13}C resonance of the solvent was used as an internal reference, but chemical shifts are reported with respect to $SiMe_4$. ^{31}P NMR shifts are relative to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenck techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60°C. The salts KBp' were prepared following literature procedures [59,60]. Tables 3–9 contain the analytical and spectroscopic data for the complexes prepared.

3.1. Synthesis of alkyl complexes

3.1.1. Pd(CH_2CMe_2Ph)Cl(cod) (1)

$PdCl_2$(cod) (0.28 g, 1 mmol) is suspended in Et_2O (25 ml) at −50°C. To the suspension

Table 4
^1H and $^{31}P\{^1H\}$ NMR data for compounds **1–7**

Compound	$^{31}P\{^1H\}$[a]	^1H				
		P(CH_3)[b]	CH_2[b]	Me	Ph[c]	others
1[d]			2.66s	1.70s	7.08m, 7.17t, 7.52d (7.6)	cod: 1.5–1.6m, 3.93m, 5.85m
2[d]	−14.9s	1.06pt (3.3)	1.95t (3.3)	1.48s	7.0–7.5m	
3[e]	33.5d, 24.2d (29)	1.06d (10.6), 1.44d (9.0)	1.86dd (8.1, 5.4)	1.51s	7.1brt, 7.2brd, 7.6brd	1.53–1.80m (PCH_2)
4[d]	−15.7s	0.93pt (3.3)		1.57s	6.8–7.6m	
5[d]	−14.5s	0.98pt (3.3)	2.60t (6.7)	2.36s	7.0–8.0m	
6[f]	3.8s	1.29d (11.1)	2.83d (2.7)	2.46s	6.9–7.4m	
7[g]	−14.6s	1.40pt (3.4)	0.35t (8.9)	0.02s		

Values of J in Hz.
[a] J(PP) in parentheses. [b] J(HP) in parentheses. [c] J(HH) in parentheses. [d] In C_6D_6. [e] In CD_2Cl_2. [f] In CD_3COCD_3. [g] In $CDCl_3$.

Table 5
$^{13}C\{^1H\}$ NMR data for compounds **1–7**

Compound	$^{13}C\{^1H\}$[a]				
	P(CH_3)	CH_2	Me	Ph	others
1[b]		46.3s	30.4s	124.5s, 125.4s, 126.1s, 151.9s (Cq)	26.5s, 29.8s (CH_3), 100.3s, 128.0s (CH), 41.9 (CMe_3)
2[b]	14.0pt (14)	30.8s	32.2s	125.2s, 126.3s, 127.9s, 152.7s (Cq)	41.8s (CMe_3)
3[c]	13.1d (30), 11.9d (17)	41.8d (72)	34.0d (6)	124.8s, 126.6s, 127.7s, 154.9s (Cq)	23.6dd (9, 24) (PCH_3) 32.0dd (24, 35) (PCH_3) 39.8s (CMe_3)
4[b]	13.1pt (14)		32.7s	122.7s, 124.2s, 127.3s, 135.2t (6), 150.0t (4) (Cq), 152.6s	36.0 CMe_3
5[b]	13.1pt (14)	15.4s	21.2s	124.7s, 125.4s, 129.4s, 131.8brs, 137.7s (Cq), 147.5s (Cq)	
6[d]	13.9d (32)	22.2s	22.2s	124.6s, 125.3s, 130.1s, 130.2brs, 136.3s (Cq), 146.2s (Cq)	
7[e]	14.4pt (14)	0.21s	3.1s		

[a] J(CP), in Hz, in parentheses. [b] In C_6D_6. [c] In CD_2Cl_2. [d] In CD_3COCD_3. [e] In $CDCl_3$.

Table 6
^1H and $^{31}P\{^1H\}$ NMR data for compounds **8–13**

Compound	$^{31}P\{^1H\}$[a]	^1H				
		P(CH_3)[b]	CH_2[b]	Me	CH(Ph)[c]	others
8[d]			3.52s	1.37s	7.1–7.5m	2.3–2.5m, 4.70brs, 5.70brs (cod)
9[e]	−14.8s	1.26pt (3.5)	3.15s	1.40s	7.1–7.4m	
10[f]	−21.0s	1.36pt (3.6)	2.39s	0.03s		
11[g]	22.3d, 12.3d (22)	1.21d (10.7) 1.34d (8.5)	3.40s	1.36s	7.11t, 7.25d, 7.37d (7.4)	1.70–1.79m, 1.50–1.59m (PCH_2)
12[d]	−19.9 s	1.07pt (3.5)	2.86s	1.59s	7.0–7.5m	1.30s (N–CMe_3)
13[d]	−17.1 s	0.99pt (3.3)	3.84t (1.5)	2.61s	6.9–7.7m	1.46s (N–CMe_3)

Values of J in Hz.
[a] J(PP) in parentheses. [b] J(HP) in parentheses. [c] J(HH) in parentheses. [d] In C_6D_6. [e] In CD_3COCD_3. [f] In $CDCl_3$. [g] In CD_2Cl_2.

Table 7
$^{13}C\{^1H\}$ NMR data for compounds **8–13**

Compound	$^{13}C\{^1H\}$[a]				
	$P(CH_3)$	CH_2	Me	Ph	others
8[b]		64.3s	28.7s	125.7s, 126.1s, 128.4s, 148.1s (Cq)	27.3s, 30.5s (CH_2), 105.9s, 172.9s (CH), 215.2s (CO), 38.6s (CMe_2)
9[c]	13.6pt (14)	70.0t (17)	28.6s	126.0s, 126.7s, 128.4s, 149.6s (Cq)	38.4s (CMe_2), 233.5s (CO)
10[d]	14.3pt (13)	48.9t (16)	−0.5s		235.6s (CO)
11[c]	12.1d (29) 11.2d (14)	67dd (36, 17)	29.4s	125.3s, 125.9s, 127.9s, 154.9s (Cq)	24.7dd (24, 9) (PCH_2) 29.9dd (35, 24) (PCH_2), 248.2dd (10, 141) 37.6d (5) (CMe_2)
12[b]	14.2pt (13)	61.5t (13)	28.7s	125.0s, 126.5s, 127.4s, 150.5s (Cq)	30.6s ($NCMe_3$), 39.4brs, CMe_2, 55.8s (CMe_3), 171.2s (CN)
13[b]	14.5pt (14)	54.7t (12)	20.7s	125.9s, 126.3s, 130.7s, 131.8s, 137.5s, (Cq)	31.2s ($NCMe_3$), 65.6s, (CMe_3), 176.2s (CN)

[a] J(CP), in Hz, in parentheses. [b] In C_6D_6. [c] In CD_3COCD_3. [d] In $CDCl_3$. [e] In CD_2Cl_2.

$Mg(CH_2CMe_2Ph)Cl$ (1.1 ml, 0.9 M solution in Et_2O) is added. The reaction is stirred for 30 min at −50°C, then it is left to reach room temperature and stirred for an additional 4 h. A yellow solution and a microcrystalline yellow solid are formed. The suspension is filtered off and the solid residue is washed with Et_2O (30 ml). The combined liquids are pumped off, the resulting white solid is dissolved in Et_2O (40 ml) and the solution is concentrated and cooled down to −20°C to give pale yellow crystals of **1**. Yield, 0.22 g, 60%.

3.1.2. Synthesis of complexes 2, 3, 5, 6 and 7

To a suspension of $PdCl_2$(cod) (0.28 g, 1 mmol) in Et_2O (20 ml) cooled to −50°C, $Mg(CH_2CMe_2Ph)Cl$ (0.8 ml, 1.3 M solution in Et_2O) is added. The mixture is stirred for 30 min at low temperature and 4 h at room temperature. PMe_3 (2 ml, 1 M solution in THF) is then added to the reaction and after stirring the mixture for 30 min the resulting suspension is filtered off and the solution pumped to dryness. The residue is extracted in Et_2O (40 ml), centrifuged and the solution is concentrated under reduced pressure. Complex **2** is isolated as white crystals by cooling the solution at −20°C overnight. Yield, 0.28 g, 70%.

Complexes **3** and **5** are obtained as yellow or white crystals in 50–55% yield following the preparation described above for **2**. $Pd(\eta^3\text{-}CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)$ (**6**) is prepared in a similar fashion but the reaction mixture is treated with only 1 equivalent of PMe_3. Orange crystals of **6** can be isolated from Et_2O–CH_2Cl_2 (1:1) solutions in 50% yield.

The synthesis of **7** is carried out in low temperature THF solutions and the addition of the PMe_3 must be done prior to the addition of 1 equivalent of

Table 8
^1H and $^{31}P\{^1H\}$ NMR data for compounds **14–21**[a]

Compound	$^{31}P\{^1H\}$	^1H				
		$P(CH_3)$[b]	CH_2[c]	Me	Ph[c]	Bp'[c]
14	−10.5s	0.52d (9.6)	2.05brs	1.39s	6.98t, 7.20t, 7.99brd (7.4)	5.99t, 5.96t, 7.65brd, 7.54brs, 7.03brs (*CH*-pz) (2.0)
15	−8.8s	0.78d (9.9)	0.82br, 0.60br	0.15s		5.95m, 7.00d, 7.44d, 7.57d, 7.61d (1.5)
16	−9.5s	0.68d (9.6)	1.48dd, 2.73m (10.1) (19.6)[b]	1.61s 1.37s	7.06t, 7.25t, 7.78d (7.2)	2.00s, 2.33s, 2.38s, (1:2:1) (Me-pz), 5.57s, 5.59s (*CH*-pz)
17	−8.7s	0.84d (9.7)	−0.09dd (12) (15.9)[b], 1.23dd (2.4)[b] (11.9)	0.21s		2.01s, 2.30s , 2.32s, (1:2:1) (Me-pz), 5.58s, (*CH*-pz)
18	−16.3s	0.70d (9.6)	3.27d, 3.38d, (19.6)[b]	1.23s 1.39s	7.05m, 7.10m, 7.30m	1.89s, 2.08s, 2.32s, 2.33s (Me-pz), 5.58s, 5.60s (*CH*-pz)
19	−16.2s	0.76d (9.6)	2.65brs	0.01s		5.97s, 5.89brs, 6.91s, 7.55s, 7.60s, 7.65s
20	−16.6s	0.63d (9.8)	3.26brs	1.30s	7.15t, 7.22t, 7.27d (7)	5.91brs, 5.95brs, 6.94brs, 7.66brs, 7.72brs (*CH*-pz)
21	−15.8s	0.85d (9.7)	2.54d, 2.89d (15.6)[b]	0.04s		1.92s, 2.28s, 2.30s, 2.35s (Me-pz), 5.57s, 5.59s (*CH*-pz)

J values in Hz.
[a] In C_6D_6. [b] J(HP) in parentheses. [c] J(HH) in parentheses.

$Mg(CH_2SiMe_3)Cl$. Colorless crystals of **7** are obtained from concentrated ether solutions in 74% yield.

3.1.3. Reaction of $Pd(CH_2CMe_2Ph)Cl(PMe_3)_2$ with NEt_3: Synthesis of $Pd(C_6H_4\text{-}o\text{-}CMe_2)Cl(PMe_3)_2$ (4)

A toluene solution (20 ml) of **2** (0.1 g, 0.23 mmol) is treated with excess of NEt_3 (0.2 ml, 2 mmol). The mixture is refluxed for 3 h under nitrogen. The solvent is removed under reduced pressure and the residue dissolved in Et_2O (20 ml). The ether solution is concentrated and cooled to −20°C to give pale yellow crystals of **4**. Yield, 60%.

3.2. Reactions of alkyl–Pd(II) complexes with CO: Formation of acyl–Pd(II) derivatives

3.2.1. $Pd[C(O)CH_2CMe_2Ph]Cl(cod)$ (8) and $Pd[C(O)CH_2CMe_2Ph]Cl(PMe_3)_2$ (9)

Complex **1** (0.2 g, 0.52 mmol) is dissolved in THF (30 ml) and the solution is cooled to −50°C. CO is bubbled through the solution for 15 min. The solvent is then removed under vacuum and the white solid residue is extracted in 30 ml of a CH_2Cl_2:Et_2O (1:1) mixture. Pale yellow crystals of **8** are obtained, in 93% yield, by cooling the solution at −20°C.

The same procedure is employed for the synthesis of **9**, starting from the corresponding alkyl **2**. **9** is isolated, quantitatively, as white crystals from Et_2O solutions.

3.2.2. $Pd[C(O)CH_2SiMe_3]Cl(PMe_3)_2$ (10)

Compound **7**, (0.1 g, 0.26 mmol) is dissolved in THF (40 ml). The solution is transferred, via cannula, to a pressure vessel which is charged with 2 atm of CO. The reaction is stirred for 20 h and after removing the excess of pressure, the solvent is evaporated under vacuum. The solid residue is dissolved in Et_2O (20 ml) and the solution is filtered off and pumped off to dryness, resulting in analytically pure pale brown solid in quantitative yield.

3.2.3. Synthesis of $Pd(COCH_2CMe_2Ph)Cl(dmpe)$ (11)

To a THF (30 ml) solution of **1**, (0.2 g, 0.5 mmol), cooled to −50°C, dmpe (5.5 ml, 0.1 solution M in Et_2O) is added. The reaction is stirred at −50°C for 30 min and 2 h at room temperature. The solvent is pumped off and the residue is extracted in a 1:1 mixture of CH_2Cl_2: petroleum ether (30 ml). The volume is reduced under vacuum and the concentrated solution is kept at −20°C overnight, yielding colourless crystals of **11** in quantitative yield.

3.3. Reactions with $CNBu^t$: Synthesis of iminoacyl complexes

3.3.1. $Pd[C(NBu^t)CH_2CMe_2Ph]Cl(PMe_3)_2$ (12)

$Pd(CH_2CMe_2Ph)Cl(PMe_3)_2$ (**2**) (0.15 g, 0.35 mmol) is dissolved in 20 ml of THF and $CNBu^t$ (0.35 ml, 1 M

Table 9
$^{13}C\{^1H\}$ NMR data for compounds **14–21**[a]

Compound	$^{13}C\{^1H\}$					
	$P(CH_3)$	CH_2	Me	CH(Ph)	Bp'	others
14	14.3d (31)	34.7brs	31.7s	127.1s, 124.9s, 153.6s (Cq)	104.3s, 104.0s, 139.0s, 138.6s, 135.6s, 135.3s (*C*H-pz)	41.7s (CMe_2)
15	15.0d (32)	3.3d (7)	2.2s		104.1s, 104.2s, 135.2s, 138.5 s, 139.1s (*C*H-pz)	
16	15.1d (31)	31.4s	27.9s, 28.0s	124.8s, 126.2s, 127.9s, 154.0s (Cq)	12.6s, 12.7s, 14.5s, 14.8s (*Me*-pz), 104.8s, 105.4s (*C*H-pz); 143.8s, 144.4s, 145.8s, 147.0s (Cq-pz)	41.1s (CMe_2)
17	16.1d (32)	−2.0d (8)	1.5s		12.5s, 12.7s, 14.4s, 14.8s (*Me*-pz), 104.2s, 104.7s (*C*H-pz), 143.5s, 143.9s, 145.4s, 146.9s (Cq-pz)	
18	14.0d (29)	63.3d (16)	29.8s, 28.1s	125.1s, 126.1s, 143.7 (Cq)	12.5s, 12.7s, 13.4s, 14.4s (*Me*-pz), 104.6s, 104.9s (*C*H-pz), 143.6s, 144.3s, 146.4s, 147.5s (Cq-pz)	37.3s (CMe_2) 233.0s (*C*O)
19	14.8d (29)	47.0d (16)	−1.0s		104.1s, 104.4s, 135.2s, 135.6s, 139.5s, 140.0s (*C*H-pz)	233.3s (*C*O)
20	14.0d (30)	66.6d (16)	28.5s	125.3s, 125.9s, 148.8s (Cq)	104.2s, 104.5s, 135.1s, 139.5s, 140.2s, 145.7s (*C*H-pz)	37.4s (CMe_2) 232.3s (*C*O)
21	14.5d (29)	46.3d (14)	−0.8s		12.4s, 12.6s, 13.7s, 14.5s (*Me*-pz), 104.7s, 105.1s (*C*H-pz), 143.7s, 144.3s, 146.4s, 147.4s (Cq-pz)	235.5s (*C*O)

[a] In C_6D_6; *J*(CP) values, in Hz, in parentheses.

solution in THF) is added to the solution at room temperature. After stirring for 2 h, the solution is pumped to dryness and the remaining solid is dissolved in Et_2O (15 ml). Cooling the yellow solution to −20°C produces yellow crystals of **12** (0.14 g) in 80% yield.

Compound **13** is isolated as yellow crystals (60% yield) following the same procedure.

3.4. Synthesis of derivatives containing bis(pyrazolyl)borate ligands

3.4.1. BpPd(CH_2CMe_2Ph)(PMe_3) (14)

To a THF solution (40 ml) of **2** (0.1 g, 0.23 mmol) at −20°C, a solution of KBp (0.05 g, 0.26 mmol) in THF (10 ml) is added. The resulting yellow suspension is stirred for 1 h at low temperature and 4 h at room temperature. The solvent is evaporated under reduced pressure and the remaining solid is extracted in petroleum ether (30 ml). The solution is filtered off to eliminate the inorganic salts and kept at −20°C for several hours. Complex **14** is isolated as pale yellow crystals. Yield: 48%.

Compounds **15–17** are prepared according to the same procedure.

3.4.2. Bp*Pd[C(O)CH_2CMe_2Ph](PMe_3) (18)

To a solution of **9** (0.19 g, 0.42 mmol) in THF (40 ml), cooled to −20°C, KBp* (0.10 g, 0.42 mmol) in THF (10 ml) is added. A yellow suspension is inmediately formed and is stirred for ca. 6 h at room temperature. The solvent is pumped off and the solid residue is extracted in petroleum ether (20 ml). The solution is, after centrifugation, concentrated under vacuum and kept at −20°C overnight to give colourless crystals of **18** in 35% yield.

Complex **19** (43% yield) is obtained following the same preparation.

3.4.3. BpPd[C(O)CH_2CMe_2Ph](PMe_3) (20)

Complex **14** (0.15 g, 0.33 mmol) is dissolved in THF (40 ml) and CO is bubbled through the solution for 15 min. The resulting colourless solution is taken to dryness and the solid residue is dissolved in a (2:1) mixture of pentane:petroleum ether (30 ml). Colorless crystals of **20** are obtained by cooling the solution down to −20°C. Yield, 0.08 g, 50%.

Compound **21** is prepared in the same fashion in 60% yield

3.5. X-ray structure determination

A colorless crystal of prismatic shape was resin epoxy coated and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of the 25 reflections with a 2θ range of 17–30°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Pd, P and Si were taken from the literature [61]. The structure was solved by Patterson and Fourier methods in the centrosymmetric $P2_1/n$ space group. An empirical absorption correction [62] was applied at the end of the isotropic refinements. A final refinement was undertaken with unit weight and anisotropic thermal motion for all atoms except the hydrogen atoms that have been refined isotropically. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in ΔF vs. F_o or sin θ/λ was observed. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system [63]. Atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallography Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

The Dirección General de Investigación Científica y Técnica (Proyecto PB94-1445) and the Junta de Andalucía are thanked for financial support. Thanks are also due to the Instituto Nacional de Cooperación Iberoamericana (V.S.) and to the Ministerio de Educación y Ciencia (M.C.N.) for research fellowships. Prof. E. Carmona and Dr. M.L. Poveda are thanked for help and encouragement.

References

[1] P.M. Maitlis, The Organic Chemistry of Palladium, Academic Press, New York, 1971.
[2] P.M. Maitlis, P. Espinet, M.J.H. Russel, Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, Oxford, 1982.
[3] A.J. Canty, Comprehensive Organometallic Chemistry II, Vol. 9, Pergamon, Oxford, 1995.
[4] J.H. Groen, J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, Organometallics 16 (1997) 68.
[5] A.M. LaPointe, F.C. Rix, M. Brookhart, J. Am. Chem. Soc. 119 (1997) 906.
[6] F.M. Alías, T.R. Belderraín, M. Paneque, M.L. Poveda, E. Carmona, P. Valerga, Organometallics 16 (1997) 301.
[7] F.C. Rix, M. Brookhart, P.S. White, J. Am. Chem. Soc. 118 (1996) 4746.
[8] J. Andrieu, P. Braunstein, F. Naud, J. Chem. Soc., Dalton Trans. (1996) 2903.
[9] J.-M. Valk, J. Boersma, G. van Koten, Organometallics 15 (1996) 4366.
[10] A.C. Albéniz, P. Espinet, Y.-S. Lin, A.G. Orpen, A. Martín, Organometallics 15 (1996) 5003.
[11] S. Ramdeehul, L. Barloy, J.A. Osborn, A.D. Cian, J. Fischer, Organometallics 15 (1996) 5442.
[12] A.J. Canty, H. Jin, A.S. Roberts, B.W. Skelton, A.H. White, Organometallics 15 (1996) 5713.

[13] R.A. Widenhoefer, H.A. Zhong, S.L. Buchwald, Organometallics 15 (1996) 2745.
[14] J.H. Groen, C.J. Elsevier, K. Vrieze, W.J.J. Smeets, A.L. Spek, Organometallics 15 (1996) 3445.
[15] J. Vicente J.A. Abad, R. Fernández de Bobadilla, P.G. Jones, M.C. Ramírez de Arellano, Organometallics 15 (1996) 24.
[16] K. Itoh, M. Fukui, Y. Ishii, J. Organomet. Chem. 129 (1977) 259.
[17] M. Rudler-Chauvin, H. Rudler, J. Organomet. Chem. 134 (1977) 115.
[18] R.E. Rülke, I.M. Han, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, C.F. Roobeek, M.C. Zoutberg, Y.F. Wang, C.H. Stam, Inorg. Chim. Acta 169 (1990) 5.
[19] R. Tooze, K.W. Chiu, G. Wilkinson, Polyhedron 3 (1984) 1025.
[20] P. Diversi, D. Fasce, R. Santini, J. Organomet. Chem. 269 (1984) 285.
[21] R.K. Harris, Can. J. Chem. 42 (1964) 2275.
[22] D.A. Redfield, J.H. Nelson, L.W. Cary, Inorg. Nucl. Chem. Lett. 10 (1974) 727.
[23] A. Akermark, A. Ljungkist, J. Organomet. Chem. 149 (1978) 97.
[24] A. Akermark, A. Ljungkist, J. Organomet. Chem. 182 (1979) 47.
[25] S.I. Black, G.B. Young, Polyhedron 8 (1989) 585.
[26] B.P. Clearly, R. Eisenberg, Organometallics 11 (1992) 2335.
[27] D.C. Griffiths, L.G. Joy, A.C. Skapski, D.J. Wilkes, G.B. Young, Organometallics 5 (1986) 1744.
[28] R.F. Heck, J. Organomet. Chem. 37 (1972) 389.
[29] A.J. Canty, H. Jin, A.S. Roberts, B.W. Skelton, P.R. Traill, A.H. White, Organometallics 14 (1995) 199.
[30] D. Milstein, J. Chem. Soc., Chem. Commun. (1986) 817.
[31] P. Fitton, J.E. McKeon, B.C. Ream, J. Chem. Soc., Chem. Commun. (1969) 370.
[32] E. Carmona, J.M. Marín, M. Paneque, M.L. Poveda, Organometallics 6 (1987) 1757.
[33] L.E. Crascall, J.L. Spencer, J. Chem. Soc., Dalton Trans. (1992) 3445.
[34] Y. Becker, J.K. Stille, J. Am. Chem. Soc. 90 (1978) 845.
[35] R. van Asselt, E.E.C.G. Gielens, R.E. Rülke, K. Vrieze, C.J. Elsevier, J. Am. Chem. Soc. 116 (1994) 977.
[36] Y. Becker, J.K. Stille, J. Am. Chem. Soc. 90 (1978) 838.
[37] E. Carmona, M. Paneque, M.L. Poveda, Polyhedron 8 (1989) 285.
[38] G.P.C.M. Dekker, A. Buijs, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, W.J.J. Smeets, A.L. Spek, Y.F. Wang, C.H. Stam, Organometallics 11 (1992) 1937.
[39] G.K. Anderson, R.J. Cross, J. Chem. Soc., Dalton Trans. (1979) 1246.
[40] J M. Brown, N.A. Cooley, Organometallics 9 (1990) 353.
[41] J. Cámpora, S.A. Hudson, E. Carmona, Organometallics 14 (1995) 2151.
[42] E. Carmona, P. Palma, M. Paneque, M.L. Poveda, Organometallics 9 (1990) 583.
[43] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[44] P.K. Byers, A.J. Canty, R.T. Honeyman, Adv. Organomet. Chem. 34 (1992) 1.
[45] A.J. Canty, H. Jin, A.S. Roberts, B.W. Skelton, P.R. Traill, A.H. White, Organometallics 14 (1995) 199.
[46] E. Gutiérrez, S.A. Hudson, A. Monge, M.C. Nicasio, M. Paneque, E. Carmona, J. Chem. Soc., Dalton Trans. (1992) 2651.
[47] S. Trofimenko, Adv. Inorg. Chem. Ser. 150 (1976) 289.
[48] D.L. Reger, M.F. Huff, A.L. Rheingold, B.S. Haggerty, J. Am. Chem. Soc. 114 (1992) 579.
[49] P.K. Byers, A.J. Canty, R.T. Honeyman, A.A. Watson, J. Organomet. Chem. 385 (1990) 429.
[50] G. Minghetti, M.A. Cinellu, A.L. Bandini, G. Banditelli, F. Demartin, M. Manassero, J. Organomet. Chem. 315 (1986) 387.
[51] D.L. Reger, S.J. Knox, M.F. Huff, A.L. Rheingold, B.S. Haggerty, Inorg. Chem. 30 (1991) 1754.
[52] E. Gutiérrez, S.A. Hudson, A. Monge, M.C. Nicasio, M. Paneque, C. Ruiz, J. Organomet. Chem., in press.
[53] C.K. Johnson, ORTEP II, Oak Ridge National Laboratory, TN, 1971.
[54] A.J. Canty, N.J. Minchin, L.M. Engelhardt, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1986) 645.
[55] M. Parra-Hake, M.F. Rettig, R.M. Wing, J.C. Woolcock, Organometallics 1 (1982) 1478.
[56] L. Benchekroun, P. Herpin, M. Julia, L. Saussine, J. Organomet. Chem. 128 (1977) 275.
[57] K. Miki, Y. Kay, N. Yasuoka, N. Kasai, J. Organomet. Chem. 135 (1977) 53.
[58] M. Horike, Y. Kay, N. Yasuoka, N. Kasai, J. Organomet. Chem. 86 (1975) 269.
[59] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288.
[60] S. Trofimenko, Inorg. Synth. 12 (1970) 99.
[61] International Tables for X-Ray Crystallography, Vol. 4, Kynoch, Birmingham, 1974, pp. 72–98.
[62] N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158.
[63] J.M. Stewart, X-RAY 80 System, Computer Science Center, Universtiy of Maryland, College Park, MD, 1985.