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Journal of Organometallic Chemistry 577 (1999) 316–322

Journal of Organometallic Chemistry

Synthesis and reactivity studies of Pd(II) complexes of the bulky $CH(SiMe_3)_2$ group. X ray structure of the indenyl derivative (η-Ind)Pd[$CH(SiMe_3)_2$](PMe_3)

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Received 8 June 1998

Abstract

The reaction of $PdCl_2$(cod) with Mg[$CH(SiMe_3)_2$]Cl and PMe_3 gives the dimeric species $\{Pd[CH(SiMe_3)_2](\mu\text{-}Cl)(PMe_3)\}_2$ (**2**), which, in the presence of PMe_3 and $Me_2PCH_2CH_2PMe_2$ (dmpe) affords the monomeric alkyls $Pd[CH(SiMe_3)_2]Cl(PMe_3)_2$ (**3**) and $Pd[CH(SiMe_3)_2]Cl$(dmpe) (**4**), respectively. Compound **3** is obtained as a mixture of *cis* and *trans* isomers, in a ratio that depends on the polarity of the solvent, as deduced from ^1H- and $^{31}P\{^1H\}$-NMR spectra. Some methatetical reactions are also reported. Spectroscopic and X-ray results obtained for the indenyl derivative (η-Ind)Pd[$CH(SiMe_3)_2$](PMe_3) (**7**) are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pd–alkyl complexes; Indenyl ligand; Dimeric species

1. Introduction

Organometallic palladium compounds play a very important role in a large variety of catalyzed organic reactions [1]. Recently we have reported on the effect of the bulky bis(trimethylsilyl)methyl group, $CH(SiMe_3)_2$, on the reactivity and structural characteristics of several Ni(II) compounds [2]. This bulky ligand exhibits considerable spatial demands and has attracted a great deal of attention due to its ability to stabilize metal complexes in low coordination numbers [3,4]. As a continuation of our studies on the reactivity of organotransition metal compounds that contain this bulky alkyl group, herein we report the synthesis and characterization of some related Pd(II) complexes. One of them, the complex (η-Ind)Pd[$CH(SiMe_3)_2$](PMe_3) constitutes a new example of an indenyl Pd(II) compound, and adds to the ever growing list of indenyl complexes of Group 10 metals [5]. Its characterization by X-ray diffraction methods has been accomplished and it is also reported.

2. Results and discussion

By following a procedure commonly used for the synthesis of other palladium alkyl complexes [6], namely the addition of one equivalent each of Mg[$CH(SiMe_3)_2$]Cl and PMe_3 to a cold suspension of $PdCl_2$(cod) (cod = 1,5-cyclooctadiene), the chloride-

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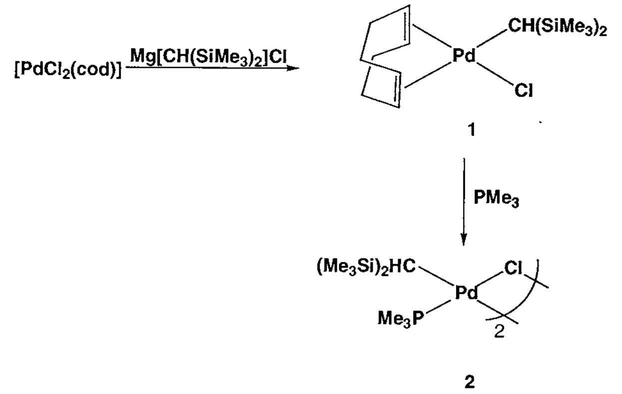
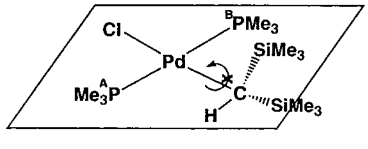
PII: S0022-328X(98)01100-0



Scheme 1.



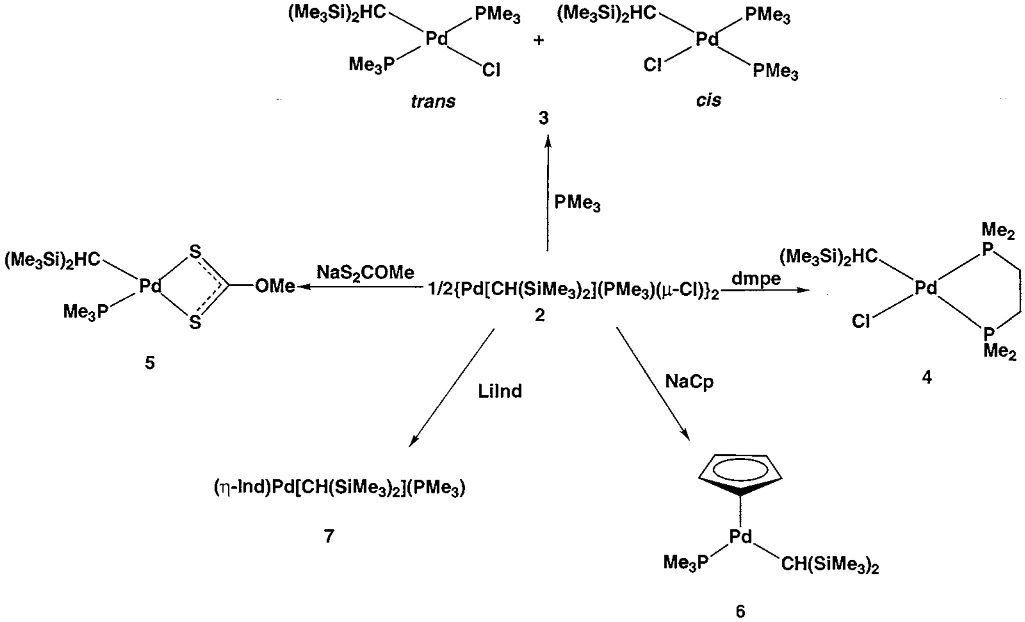
trans-3

Fig. 1. Restricted rotation around the Pd–CH$(SiMe_3)_2$ bond.

bridged dimer {Pd[CH$(SiMe_3)_2$](μ-Cl)(PMe_3)}$_2$ (**2**), can be obtained as yellow crystals, in ca. 55% yield (Scheme 1). Using a Pd:PMe_3 ratio lower than one produces in addition the monomeric, 1,5-cyclooctadiene complex Pd[CH$(SiMe_3)_2$]Cl(cod) (**1**). The spectroscopic and analytical data obtained for **1** are in excellent agreement with the proposed formulation and need no further comment (see Section 3). As for compound **2**, the integration of the ^{1}H-NMR signals due to the methyl groups of the phosphine and alkyl ligands (δ 0.95, $^2J_{HP} = 10.4$ Hz, and δ 0.48, respectively) reveals a PMe_3:CH$(SiMe_3)_2$ ratio of 1:1. This information, along with the microanalytical data and the reactivity studies to be discussed below, are in accord with the dimeric formulation advanced in Scheme 1.

A mixture of the *cis* and *trans* isomers of monomeric Pd[(CH$(SiMe_3)_2$]Cl$(PMe_3)_2$ (**3**) were cleanly obtained upon adding PMe_3 to solutions of **2** (Scheme 2). These isomeric species interchange readily, the ratio of the two isomers depends on the nature of the solvent. Thus, in polar solvents like acetone the *cis* isomer is almost exclusively observed, whereas in a non polar solvent, i.e. benzene, the *trans* species is clearly favoured (7:3 ratio in C_6D_6 at 25°C). This *cis–trans* isomerization is a well-known process in the chemistry of square-planar Pd(II) complexes [7]. The different ratio of the isomers found in solvents of different polarity has helped in their complete characterization. The ^{1}H-NMR spectrum of the *cis* isomer recorded in $CD_3C(O)CD_3$ shows two doublets which can be attributed to the methyl groups of the non-equivalent PMe_3 ligands (δ 1.42, d, $^2J_{HP} = 8.6$ Hz; δ 1.59, d, $^2J_{HP} = 10.2$ Hz), while the $^{13}C\{^1H\}$-NMR spectrum exhibits a characteristic doublet at δ 12.5 for the methyne –*C*H$(SiMe_3)_2$ carbon, with a large coupling constant to one of the phosphorus nuclei ($^2J_{CP} = 84$ Hz), that clearly indicates the presence of a PMe_3 ligand *trans* to the alkyl group. Finally, the AX spin system observed in the $^{31}P\{^1H\}$-NMR spectrum, characterized by a relatively small $^2J_{PP}$ coupling of 40 Hz, is also in agreement with the proposed *cis* geometry.

In C_6D_6 the $^{31}P\{^1H\}$-NMR spectrum shows, in addition to the two doublets of the AX system due to the *cis*



Scheme 2.

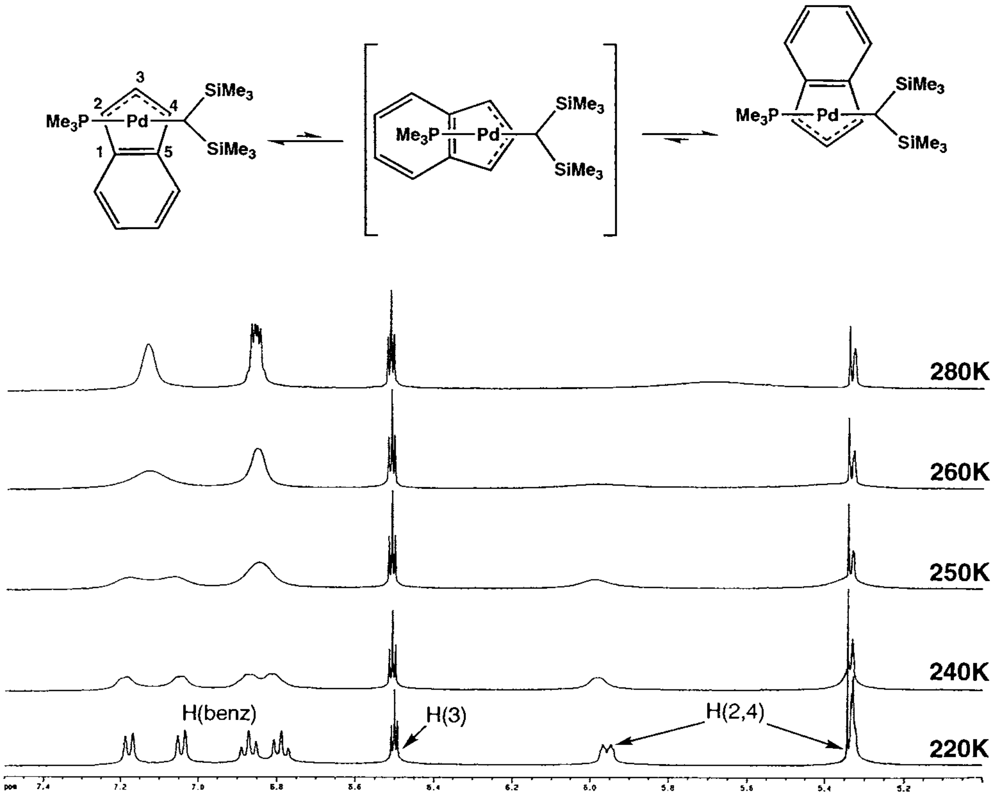


Fig. 2. Variable-temperature ^{1}H-NMR spectra (CD_2Cl_2, 400 MHz) of **7** and proposed mechanism for the observed fluxionality.

isomer, the signals characteristic of a strongly coupled AB spin system ($^2J_{PP} = 515$ Hz) which obviously corresponds to the *trans* isomer of complex **3**. The non equivalence of the phosphorus nuclei in the *trans* isomer can be attributed to a very high kinetic barrier, at least in the NMR time scale, for the rotation of the bulky $-CH(SiMe_3)_2$ group around the Pd–carbon bond (Fig. 1) [3d]. It is interesting to note the difference in the chemical shifts of the $\mathit{C}H(SiMe_3)_2$ carbon nucleus in both isomers (C_6D_6, δ 12.5, d, $^2J_{CP} = 84$ Hz for the *cis*, and δ -0.31, d, $^2J_{CP} = 4.5$ Hz for the *trans*) which may be due to the different *trans* influence of the phosphine and chloride ligands.

Addition of one equivalent of dmpe (dmpe = bis-(dimethylphosphino)ethane) to a solution of **2**, results in the formation of the new complex $Pd[CH(SiMe_3)_2]Cl(dmpe)$ (**4**) (Scheme 2). The NMR data for **4** are similar to those found for *cis*-**3** and do not merit additional comment.

A chelating ligand, such as the anionic methylxantate, affords the expected compound $Pd[CH(SiMe_3)_2](\eta^2\text{-}S_2COMe)(PMe_3)$ (**5**) (Scheme 2), for which a similar structure to that found for the Ni analogue is proposed on the basis of spectroscopic data [2b].

The reaction of **2** with NaCp leads to the formation of $(\eta^5\text{-}C_5H_5)Pd[CH(SiMe_3)_2](PMe_3)$ (**6**) (Scheme 2). ^{1}H- and $^{13}C\{^1H\}$-NMR studies are in accordance with the formulation of **6** as an 18-electron species with a η^5-Cp ligand [8]. However, the reaction of **2** with LiInd (Ind = indenyl ligand, C_9H_7) affords the complex $(\eta\text{-Ind})Pd[CH(SiMe_3)_2](PMe_3)$ (**7**), for which the hapticity of the indenyl ligand can not be unambiguously assigned (Scheme 2). NMR data are often valuable to assign the coordination mode of the indenyl ligand. At low temperature (-70°C) the NMR spectra recorded for **7** are similar to those found for Pd(II) allyl complexes [9]. Thus, in the $^{13}C\{^1H\}$-spectrum the carbon nuclei resonate at 77.1 [s, C(2); the numbering scheme

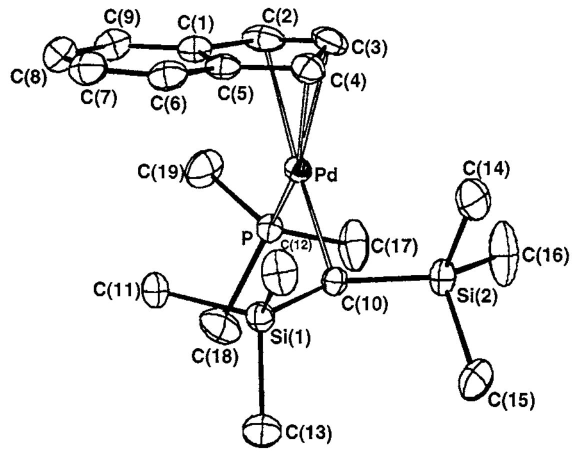


Fig. 3. Molecular structure and atom numbering scheme for compound **7**.

Table 1
Selected bond distances (Å) and angles (°) with estimated S.D. in parentheses for complex **7**

Bond distances (Å)			
Pd–P	2.234(2)	C(1)–C(5)	1.433(7)
Pd–C(1)	2.724(5)	C(1)–C(9)	1.399(8)
Pd–C(2)	2.346(5)	C(2)–C(3)	1.401(9)
Pd–C(3)	2.217(5)	C(3)–C(4)	1.383(8)
Pd–C(4)	2.267(6)	C(4)–C(5)	1.448(8)
Pd–C(5)	2.659(5)	C(5)–C(6)	1.409(7)
Pd–C(10)	2.118(4)	C(6)–C(7)	1.386(9)
Si(1)–C(10)	1.862(5)	C(7)–C(8)	1.397(10)
Si(2)–C(10)	1.864(4)	C(8)–C(9)	1.369(8)
C(1)–C(2)	1.441(7)	ΔM–C	0.385(6)
Bond angles (°)			
P–Pd–C(1)	136.66(11)	C(1)–C(2)–C(3)	107.9(5)
P–Pd–C(2)	160.06(14)	C(2)–C(3)–C(4)	109.4(6)
P–Pd–C(3)	128.25(16)	C(3)–C(4)–C(5)	107.4(5)
P–Pd–C(4)	101.15(14)	C(1)–C(5)–C(4)	107.5(4)
P–Pd–C(5)	108.76(11)	C(1)–C(5)–C(6)	119.5(5)
P–Pd–C(10)	91.31(12)	C(4)–C(5)–C(6)	133.0(5)
C(2)–Pd–C(3)	35.6(2)	C(5)–C(6)–C(7)	119.1(5)
C(2)–Pd–C(4)	58.97(19)	C(6)–C(7)–C(8)	121.1(6)
C(3)–Pd–C(4)	35.9(2)	C(7)–C(8)–C(9)	120.5(6)
C(2)–C(1)–C(5)	106.2(4)	C(1)–C(9)–C(9)	120.5(5)
C(2)–C(1)–C(9)	134.6(5)	Si(1)–C(10)–Si(2)	120.7(2)
C(5)–C(1)–C(9)	119.2(4)	Fold angle	12.4(4)

used for the indenyl atoms appears in Fig. 2], 110.7 [d, $^2J_{CP} = 3$ Hz, C(3)] and 82.2 [d, $^2J_{CP} = 23$ Hz, C(4)].The magnitudes of the $^{31}P-^{13}C$ coupling constants observed for the carbon atoms C(2) and C(4) ($^3J_{CP} = 0$ and 23 Hz, respectively) are consistent with a coordination of the indenyl ligand that approaches η^3, in which C(2) and C(4) are, respectively *cisoid* and *transoid* with regard to the phosphorus atom. Baker and Tulip have proposed [10] that a very negative value (-20 to -40 ppm) of the $\Delta\delta$(C) parameter for the bridgehead carbons, defined as $\Delta\delta(C) = \delta[C(\eta\text{-indenyl})] - \delta[C\text{-(indenylsodium)}]$, may be taken as indicative of η^5-hapticity, whereas if $\Delta\delta(C) \gg 0$ the solution hapticity would be closed to η^3. For compound **7** this parameter amounts $+5$ ppm and it is therefore close to the range expected for trihapto coordination. However, and in view of the facility with which the indenyl ligand adapts itself to different electronic situations [5b,g,h], and of the low absolute value of $\Delta\delta$(C), it seems more reasonable to think of the coordination of the C_9H_7 ligand to the Pd(II) centre of **7** as intermediate between η^3 and η^5 (vide infra).

Table 2
Crystal data for complex **7**

Molecular formula	$PdSi_2PC_{19}H_{35}$
Formula weight	457.02
Wavelength (Mo–K$_\alpha$) (Å)	$\lambda = 0.71073$
Crystal system	Monoclinic
Space group	*Pc*
Unit cell dimensions	
a (Å)	10.074 (5)
b (Å)	12.533 (4)
c (Å)	9.393 (3)
β (°)	97.12 (3)
V (Å^3)	1176.8 (8)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.290
Absorption coefficient (cm^{-1})	9.57
F(000)	476
Crystal size (mm)	$0.32 \times 0.25 \times 0.18$
θ range for data collection (°)	3–30
Reflections collected	3609
Observed reflections [$I > 2\sigma(I)$]	3278
Parameters	213
Final R_1 indices [$I > 2\sigma(I)$]^a	0.0336, 0.0816
wR_2 indices (all data)^b	0.0375, 0.0834

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ $w = 1/[\sigma^2F_o^2 + (0.0545P)^2 + 0.000P]$ were $P = (F_o^2 + 2F_c^2)/3$.

The dynamic behaviour of **7** in solution has been studied by variable-temperature NMR spectroscopy. At -70°C (CD_2Cl_2) both the ^{1}H- and the $^{13}C\{^1H\}$-NMR spectra indicate that this complex possesses C_1 symmetry. Therefore, all the protons and carbon nuclei of the C_9H_7 ligand are anisochronous, as are also the two $SiMe_3$ groups (Fig. 2). At higher temperatures complex **7** attains C_s symmetry, probably as the result of rapid rotation of the indenyl ligand [11]. This fluxional process equilibrates the $SiMe_3$ groups whose resonances merge into a singlet above the coalescence temperature both in the ^{1}H- and $^{13}C\{^1H\}$-NMR spectra. Concomitantly, the resonances due to the C–H and C_q nuclei of the Ind rings coalesce in a pair-wise manner. $\Delta G^{\neq}$ calculated at the coalescence temperature (260 K) for the indenyl rotation is ca. 12.3 kcal mol^{-1} [12]. This value compares well with those reported for (Ind)Ni(PPh$_3$)Cl and (Ind)NiMe(PPh$_3$) (ca. 16.0 and 10.1 kcal mol^{-1}, respectively) [5h] and (1-Me–Ind)Rh(PMe$_3$)$_2$ (11.1 kcal mol^{-1}) [13].

The structure deduced for complex **7** from the solution spectroscopic studies is maintained in the solid state, as demonstrated by an X-ray diffraction study. A view of the molecule is shown in Fig. 3, together with the atomic labelling scheme [14]. Selected bond distances and angles are given in Table 1. The distances from palladium to the allylic carbons C(2), C(3) and C(4) (2.346(5), 2.217(5) and 2.267(6) Å, respectively) are significantly shorter than corresponding distances to the other two C atoms of the C_5 ring (C(1), 2.724(5); C(5), 2.659(5) Å). The Δ(M–C) value of 0.385(6) Å, which corresponds to the difference between the average metal–carbon bond distances to the two benzylic carbons and to the two quaternary carbons, is similar to those found in the cationic complexes [(η-Ind)Pd(tmeda)]CF$_3$SO$_3$ (Ind = 1-benzyl-2,3-diphenyl-5,6,7-trimethoxyindenyl or 1-benzyl-3-phenyl-5,6,7-trimethoxyindenyl, tmeda = *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine) [5g], where the hapticity of the indenyl ligands could not be assigned unambiguously. Similarly, the fold angle (dihedral angle between the plane defined by the three allylic carbons and that formed by the benzenoid carbons) has a value of 12.4(4)°, which is again intermediate between that corresponding to η^5-coordination (range 7.4–10°) and η^3-bonding (20–26°). Once again these data suggest an intermediate hapticity between η^3 and η^5. We would like to note, however, that the Pd–C(1) and Pd–C(5) bond lengths of 2.724(5) and 2.659(5) Å, respectively, appear to be too large for a significant interaction between the metal and these two carbon atom to exist [15]. Thus, whereas the indenyl coordination in complex **7** may not be described as purely η^3, the deviation toward η^5 is probably very small. Finally, the C–C distances within the pseudoallylic moiety of the five-membered ring average ca. 1.39 Å and are somewhat shorter than the other three (1.43 Å av.), whilst in the benzenoid moiety all C–C bond lengths appear equal (3σ criterium) within experimental error (Table 1).

3. Experimental details

3.1. General considerations

Microanalyses were performed by the Analytical Services of the University of Sevilla. IR spectra were obtained as Nujol mulls from Perkin Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker AMX-500, Bruker AMX-300 and Varian XL-200 spectrometers. Spectra are referenced to external $SiMe_4$ ($\delta = 0$ ppm) using the residual protio solvent peaks as internal standards (^{1}H-NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C-NMR experiments). $^{31}P\{^1H\}$-NMR shifts are referenced to external 85% H_3PO_4. Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen following conventional Schlenk techniques. All solvents were appropriately dried and degassed immediately prior to use. The compound $PdCl_2$(cod) [16] and PMe_3 [17] were prepared according to literature methods.

3.2. Synthesis of complexes

3.2.1. $\{Pd[CH(SiMe_3)_2](\mu\text{-}Cl)(PMe_3)\}_2$ (**2**)

To a cooled (-50°C) stirred suspension of $PdCl_2$(cod) (1.71 g, 6 mmol) in Et_2O (80 ml), a solution of $Mg[CH(SiMe_3)_2]Cl$ in Et_2O (10 ml, 0.6 M, 6 mmol) was added. The mixture was stirred at low temperature for 1 h, during which time the colour became dark green. After stirring for a further hour at 0°C, PMe_3 (0.6 ml, 6 mmol) was added and the stirring continued at this temperature for a further 30 min period. The solvent was evaporated under reduced pressure and the residue extracted with a mixture (140 ml) of petroleum ether:Et_2O (50:90). The suspension obtained was filtered through a bed of celite and the solution concentrated under vacuo and cooled to -30°C to yield pale yellow crystals of compound **2** (1.24 g, 55%). Anal. Calc. for $C_{20}H_{56}Si_4P_2Cl_2Pd_2$: C, 31.8; H, 7.5. Found: C, 31.7; H, 7.5. ^{1}H-NMR (C_6D_6, 25°C) δ 0.15 [d, $^3J_{HP} =$ 9.5 Hz, 1H, $CH(SiMe_3)_2$], 0.48 (s, 18H, 2 $SiMe_3$), 0.95 (d, $^2J_{HP} = 10.4$ Hz, 9H, PMe_3); $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C) δ 4.7 ($SiMe_3$), 13.8 [$CH(SiMe_3)_2$], 15.9 (d, $^1J_{CP} =$ 34 Hz, PMe_3); $^{31}P\{^1H\}$-NMR (C_6D_6) δ -0.3.

In some of the preparations of complex **2** employing the above procedure, particularly when less than one equivalent of PMe_3 was used, the intermediate species $Pd[CH(SiMe_3)_2]Cl$(cod) (**1**) was isolated as a by-product of the reaction. Anal. Calc. for $C_{15}H_{31}Si_2ClPd$: C, 44.0; H, 7.6. Found: C, 43.9; H, 7.8. ^{1}H-NMR (C_6D_6, 25°C) δ 0.48 (s, 18H, 2 $SiMe_3$), δ 0.91 [1H, $CH(SiMe_3)_2$], 1.5–2.0 [m, 8H, 4 CH_2(cod)], 4.50 and 5.71 [m, 2H each, 4 CH(cod)]; $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C): δ 4.0 ($SiMe_3$), 33.5 [$CH(SiMe_3)_2$], 27.2 and 30.5 [CH_2(cod)], 101.9 and 123.4 [CH(cod)].

3.2.2. $Pd[CH(SiMe_3)_2]Cl(PMe_3)_2$ (**3**)

In total 0.11 g (0.15 mmol) of the dimer **2** was dissolved in Et_2O (30 ml) and the resulting yellow solution cooled to -30°C. A THF solution of PMe_3 (0.3 ml, 1 M, 0.3 mmol) was added via syringe and the reaction mixture became instantaneously colourless. After stirring for 30 min the solvent was removed under reduced pressure and the product extracted into a mixture of petroleum ether:Et_2O (20 ml, 1:1). Crystallization at -30°C afforded white crystals of **3** in quantitative yield. Anal. Calc. for $C_{13}H_{37}Si_2P_2ClPd$: C, 34.4; H, 8.2. Found: C, 34.4; H, 8.5. NMR data for the *cis* isomer: ^{1}H-NMR ($CD_3C(O)CD_3$, 25°C) δ 0.07 (s, 18H, 2 $SiMe_3$), 1.42 (d, $^2J_{HP} = 8.6$ Hz, 9H, PMe_3), 1.59 (d, $^2J_{HP} = 10.2$ Hz, 9H, PMe_3); $^{13}C\{^1H\}$-NMR ($CD_3C(O)CD_3$, 25°C) δ 1.8 ($SiMe_3$), 12.5 [d, $^2J_{CP} = 84$ Hz, $CH(SiMe_3)_2$], 11.2 (d, $^1J_{CP} = 22$ Hz, PMe_3), 14.4 (dd, $^1J_{CP} = 33$, $^3J_{CP} = 5$ Hz, PMe_3); $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$, 25°C) δ -5.2 and -21.5 (d, $^2J_{PP} = 40$ Hz). NMR data for the *trans* isomer: ^{1}H-NMR (C_6D_6, 25°C) δ 0.22 (s, 18H, 2 $SiMe_3$), 1.15 (dd, $^2J_{HP} = 9.1$, $^4J_{HP} = 2.2$ Hz, 9H, PMe_3), 1.30 (dd, $^2J_{HP} = 8.7$, $^4J_{HP} =$ 2.4 Hz, 9H, PMe_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C) δ -0.31 [d, $^2J_{CP} = 4.5$ Hz, $CH(SiMe_3)_2$], 4.8 ($SiMe_3$), 14.2 (d, $^1J_{CP} = 27$ Hz, PMe_3), 16.1 (dd, $^1J_{CP} = 25$, $^3J_{CP} = 3$ Hz, PMe_3); $^{31}P\{^1H\}$-NMR (C_6D_6, 25°C) δ -11.3 and -19.1 (d, $^2J_{PP} = 515$ Hz).

3.2.3. $Pd[CH(SiMe_3)_2]Cl$(dmpe) (**4**)

To a cold (-30°C) solution of complex **2** (0.26 g, 0.34 mmol) in Et_2O (30 ml) a solution of 1,2-bis-

(dimethylphosphine)ethane (dmpe) in THF (0.7 ml, 1 M, 0.7 mmol) was added. The reaction mixture became colourless. The cooling bath was then removed and the stirring continued for 2 h. The solvent was evaporated in vacuo and the resulting residue extracted into a mixture of 10 ml of heptane and 4 ml of THF. After concentration and cooling at −30°C, complex **4** was isolated as white crystals (0.28 g, 90%). Anal. Calc. for $C_{13}H_{35}Si_2P_2ClPd$: C, 34.6; H, 7.8. Found: C, 34.6; H, 7.6. ^{1}H-NMR ($CD_3C(O)CD_3$, 25°C) δ 0.08 (s, 18H, 2 $SiMe_3$), 0.16 [dd, $^3J_{HP} = 11.2$ and 10.3 Hz, 1H, C*H*($SiMe_3$)$_2$], 1.47 (d, $^2J_{HP} = 10.3$ Hz, 6H, PMe_2), 1.69 (d, $^2J_{HP} = 10.4$ Hz, 6H, PMe_2), 1.70–2.25 (m, 4H, 2 PCH_2); $^{13}C\{^1H\}$-NMR ($CD_3C(O)CD_3$, 25°C) δ 5.7 ($SiMe_3$), 5.8 ($SiMe_3$), 10.3 [d, $^3J_{CP} = 86$ Hz, *C*H($SiMe_3$)$_2$], 11.4 (d, $^1J_{CP} = 22$ Hz, PMe_2), 14.7 (d, $^1J_{CP} = 31$ Hz, PMe_2), 24.6 (dd, $^1J_{CP} = 27$, $^3J_{CP} = 10$ Hz, PCH_2), 31.6 (dd, $^1J_{CP} = 35$, $^3J_{CP} = 24$ Hz, PCH_2); $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$, 25°C) δ 40.5 and 47.3 (d, $^2J_{PP} = 17$ Hz).

3.2.4. *Pd[CH(SiMe$_3$)$_2$](S$_2$COMe)(PMe$_3$)* (**5**)

To a solution of complex **2** (0.27 g, 0.36 mmol) in Et_2O (30 ml) at −50°C was added a slurry of KS_2COMe in THF (30 ml). The reaction mixture was allowed to warm slowly at room temperature (r.t.) and stirred for 4 h. The mixture was evaporated to dryness and extraction into petroleum ether (30 ml), followed by concentration and crystallization at −30°C, resulted in the deposition of yellow needles of **5**. Yield: 0.19 g (60%). Anal. Calc. for $C_{12}H_{31}Si_2PS_2OPd$: C, 32.1; H, 7.0. Found: C, 32.3; H, 6.9. ^{1}H-NMR ($CD_3C(O)CD_3$, 25°C) δ 0.09 (s, 18H, 2 $SiMe_3$) 0.19 [d, $^3J_{HP} = 11.9$ Hz, 1H, C*H*($SiMe_3$)$_2$], 1.53 (d, $^2J_{HP} = 10.5$ Hz, 9H, PMe_3), 4.17 (s, 3H, COMe); $^{13}C\{^1H\}$-NMR ($CD_3C(O)CD_3$, 25°C) δ 4.7 ($SiMe_3$), 8.5 [br, *C*H($SiMe_3$)$_2$], 15.9 (d, $^1J_{CP} = 36$ Hz, PMe_3), 58.1 (CO*Me*), the *C*OMe resonance was not observed; $^{31}P\{^1H\}$-NMR ($CD_3C(O)CD_3$) δ 1.3.

3.2.5. *CpPd[CH(SiMe$_3$)$_2$](PMe$_3$)* (**6**)

A solution of compound **2** (0.11 g, 0.15 mmol) in Et_2O (10 ml) was cooled at −30°C and then treated with a solution of NaCp in THF (0.8 ml, 0.37 M, 0.30 mmol). The cooling bath was then removed and the solution became of an intense red colour and the precipitation of NaCl was evident. After stirring for 30 min at r.t., the solvent was stripped off in vacuum to obtain a red solid. Dissolution in light petroleum (10 ml) was followed by filtration and crystallization at −30°C to afford **6** as red crystals (0.10 g, 82%). Anal. Calc. for $C_{15}H_{33}Si_2PPd$: C, 44.3; H, 8.2. Found: C, 43.7; H, 8.2. ^{1}H-NMR (C_6D_6, 25°C) δ −1.27 [d, $^3J_{HP} = 10.3$ Hz, 1H, C*H*($SiMe_3$)$_2$], 0.29 (s, 18H, 2 $SiMe_3$), 0.78 (d, $^2J_{HP} = 10.3$ Hz, 9H, PMe_3), 5.75 (d, $^3J_{HP} = 1.6$ Hz, 5H, Cp); $^{13}C\{^1H\}$-NMR (C_6D_6, 25°C) δ −8.6 [d, $^2J_{CP} = 5$ Hz, *C*H($SiMe_3$)$_2$], 4.7 ($SiMe_3$), 19.9 (d, $^1J_{CP} = 36$ Hz, PMe_3), 97.0 (Cp); $^{31}P\{^1H\}$-NMR (C_6D_6) δ −4.5.

3.2.6. *(η^3-C$_9$H$_7$)Pd[CH(SiMe$_3$)$_2$](PMe$_3$)* (**7**)

This complex was prepared by a method analogous to that described above for **6**. The dimer **2** (0.18 g, 0.24 mmol) was dissolved in Et_2O (30 ml) and reacted at −30°C with a solution of LiInd (Ind = C_9H_7) (0.48 mmol) prepared in situ by treatment of a solution of indene in Et_2O with $LiBu^n$. Subsequent work-up as above furnished **7** as orange crystals. Yield: 0.15 g (70%). Anal. Calc. for $C_{19}H_{35}Si_2PPd$: C, 49.9; H, 7.7. Found: C, 49.9; H, 7.5. ^{1}H-NMR (CD_2Cl_2, 25°C) δ −1.12 [d, $^3J_{HP} = 11$ Hz, 1H, C*H*($SiMe_3$)$_2$], −0.12 (s, 18H, 2 $SiMe_3$), 1.33 (d, $^2J_{HP} = 10$ Hz, 9H, PMe_3), 5.69 [br s, 2H, CH(2,4)], 6.52 [t, $^3J_{HH} = 3.1$ Hz, 1H, CH(3)], 6.86 [m, 2H, CH(benz)], 7.13 [br m, 2H, CH(benz)]; $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25°C) δ −3.1 (d, $^2J_{CP} = 6$ Hz, *C*H($SiMe_3$)$_2$), 4.4 ($SiMe_3$), 18.3 (d, $^1J_{CP} = 29$ Hz, PMe_3), 80.2 [br, CH(2,4)], 110.8 [CH(3)], 117.6, 122.6 [CH(benz)], 135.8 [s, C(1,5)]; $^{31}P\{^1H\}$-NMR (CD_2Cl_2) δ −11.4. ^{1}H-NMR (CD_2Cl_2, −70°C) δ −1.28 [d, $^3J_{HP} = 11$ Hz, 1H, C*H*($SiMe_3$)$_2$], −0.36 (s, 9H, $SiMe_3$), −0.08 (s, 9H, $SiMe_3$), 1.27 (d, $^2J_{HP} = 10$ Hz, 9H, PMe_3), 5.33 [br m, 1H, CH(2)], 5.92 [br m, CH(4)], 6.49 [t, $^3J_{HH} = 3.0$ Hz, 1H, CH(3)], 6.77 [t, 1H, $^3J_{HH} = 7.4$ Hz, CH(benz)], 6.86 [t, $^3J_{HH} = 7.4$ Hz, 1H, CH(benz)], 7.03 [d, $^3J_{HH} = 7.4$ Hz, 1H, CH(benz)], 7.16 [d, $^3J_{HH} = 7.4$ Hz, 1H, CH(benz)]; $^{13}C\{^1H\}$-NMR (CD_2Cl_2, −70°C): δ −3.0 [d, $^2J_{CP} = 6$ Hz, *C*H($SiMe_3$)$_2$], 3.3 ($SiMe_3$), 4.6 ($SiMe_3$), 18.6 (d, $^1J_{CP} = 29$ Hz, PMe_3), 77.1 [CH(2)], 82.2 [d, $^3J_{CP} = 23$ Hz, CH(4)], 110.7 [d, $^3J_{CP} = 3$ Hz, CH(3)], 115.6, 118.3, 121.4, 122.6 [CH(benz)], 134.9 [d, $^3J_{CP} = 4$ Hz, CH(5)], 135.3 [CH(1)].

3.3. *Crystal structure determination of complex* **7**

Crystallographic data are summarized in Table 2. The intensity data were collected at r.t. (293 K) on a Philips PW 1100 single-crystal diffractometer using the graphite-monochromated Mo–K$_\alpha$ radiation and the $\theta/2\theta$ scan technique. Final unit cell parameters were obtained from a least-squares refinement using 24 reflections. In total 3609 reflections, were measured (with θ in the range of 3–30°) and included in the structural refinement. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycle of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2 + (0.0545P)^2]$ were $P = (F_o^2 + 2F_c^2)/3$ was used. The refinement converged at $wR_2 = 0.0834$ for all data and 213 parameters [$R_1 = 0.0336$ for 3278 reflections with $I > 2\sigma(I)$]. The maximum peak in the final difference Fourier map was 0.870 e Å^{-3}.

All calculations were carried out on the CNRDIF computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELXS-96 and SHELXL-96 systems of crystallographic computer programs [18].

Atomic coordinates for this structure have been deposited with the Cambridge Crystallography 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 Ministerio de Educación y Ciencia (F.M. Alías and T.R. Belderrain) for research fellowships. We also thank M.L. Poveda for his help and suggestions.

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