The First Ligand-assisted Stereoselective Wittig Reactions. Synthesis and Crystal Structure of the 3-Palladaindan-1-one, [Pd{$C_6H[C(O)CH_2]$-6-$(OMe)_3$-2,3,4}$(Me_2NCH_2CH_2NMe_2)$]

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Reactions of [Pd(R^H)Cl(L–L)] [R^H = C_6H(CHO)-6-$(OMe)_3$-2,3,4] with Ph_3P=CHR (R = Ph or 2-pyridyl) gave mixtures of the isomeric compounds [Pd(*E*-R')Cl(L–L)] and [Pd(*Z*-R')Cl(L–L)] [R' = C_6H(CH=CHPh)-6-$(OMe)_3$-2,3,4 or C_6H{CH=CH(C_5H_5N-2)}-6-$(OMe)_3$-2,3,4] when L–L = 2,2'-bipyridine or only the corresponding *E* isomers when L–L = *N,N,N',N'*-tetramethylethylenediamine; however, the complex [Pd(R^{Me})Cl(tmeda)] [R^{Me} = C_6H{C(O)Me}-6-$(OMe)_3$-2,3,4] reacts with Ph_3P=CHPh to give [Pd{$C_6H[C(O)CH_2]$-6-$(OMe)_3$-2,3,4}(tmeda)].

Very few examples of *ortho*-alkenylaryl complexes are known. As far as we are aware, only one such palladium complex has been reported.[1] These compounds could be important in the fields of non-linear optics[2] or organometallic polymers.[3] Since the Wittig reaction constitutes one of the most important and useful synthetic routes to alkenes,[4] we have considered using this procedure for preparing *ortho*-alkenylaryl palladium complexes from the 6-formyl- and 6-acetyl-2,3,4-trimethoxyphenyl derivatives we have recently reported.[5–7] This Wittig reaction on a co-ordinated ligand has only been studied for a few cyclopentadienyl- or arene-iron, -chromium, -tungsten or -cobalt complexes.[2,3] We report here the first application of this synthetic approach to the preparation of alkenylaryl complexes. The 2,3,4-trimethoxy substitution of the aryl moiety is a feature of organic molecules of pharmaceutical interest.[8–10]

The reaction of [PdR^HCl(bipy)] **1a** [bipy = 2,2'-bipyridine; R^H = C_6H(CHO)-6-$(OMe)_3$-2,3,4][6] with the semistabilized ylide Ph_3Ph=CHPh¶ gives a mixture of the *E*- and *Z*-*ortho*-alkenylarylpalladium complexes [Pd(*E*-R^{Ph})Cl(bipy)] *E*-**2** [R^{Ph} = C_6H(CH=CHPh)-6-$(OMe)_3$-2,3,4] and [Pd(*Z*-R^{Ph})Cl(bipy)] *Z*-**2** (see Scheme 1) in ratios that vary with the nature of the solvent and the base [*E*:*Z* = 3:1 in diethyl ether with $LiBu^n$; 1:1 in dichloromethane with $KOBu^t$]. The reaction of **1a** with Ph_3P=$CH(C_5H_5N$-2)¶ in Et_2O affords a 4:1 mixture of [Pd(*E*-R^{py})Cl(bipy)] *E*-**3** [R^{py} = C_6H{CH=$CH(C_5H_5N$-2)}-6-$(OMe)_3$-2,3,4] and [Pd(*Z*-R^{py})Cl(bipy)] *Z*-**3** (see Scheme 1). We have been able to separate by crystallization and characterize the major isomers *E*-**2** and *E*-**3**‖ from these reactions. These results are similar to those of the above-mentioned Wittig reactions of cyclopentadienyl or arene complexes with ylides.[2,3] The dependence of the isomeric ratio on reaction conditions and on the nature of the solvent is also well known in organic Wittig reactions.[4]

In order to study the influence of the neutral ligand in these reactions, the compound [PdR^HCl(tmeda)] **1b** [tmeda = *N,N,N',N'*-tetramethylethylenediamine] was treated with Ph_3-P=CHPh giving selectively [Pd(*E*-R^{Ph})Cl(tmeda)] *E*-**4**‖ as the only isomer, using either $LiBu^n$ in Et_2O or $KOBu^t$ in CH_2Cl_2 (Scheme 1). Similarly, compound **1b** reacts with Ph_3P=$CH(C_5H_5N$-2) giving [Pd(*E*-R^{py})Cl(tmeda)] *E*-**5**‖ as the only isomer. It must be emphasized that the respective crude products obtained after removing the reaction solvent consist of $OPPh_3$ and *E*-**4** or *E*-**5**, and no signal attributable to *Z* isomers can be observed in the ^1H NMR spectra. In contrast, reactions of 3,4,5-trimethoxybenzaldehyde with Ph_3P=CHPh give mixtures of *E* and *Z* isomers similar to those found in reactions with **1a** (*E*:*Z* ratio = 45:55, CH_2Cl_2–$KOBu^t$; 2:1, Et_2O–$LiBu^n$).

In consequence, the different behaviours observed for **1b** and **1a** are due to the different nature of their N-donor ligands, which exert a dramatic *modulating* effect on the observed stereoselectivity. To the best of our knowledge, such an effect has not previously been observed. It has been reported that sterically hindered aldehydes give a significant increase in the *Z*-alkene;[4] therefore, the moderate increase in the *E* isomer that results in reactions of Ph_3P=CHPh with **1a**, compared to those with 3,4,5-trimethoxybenzaldehyde, could be due to an electronic effect that opposes the expected increase of the *Z* isomer, caused by replacement of an *ortho*-hydrogen atom by the more sterically demanding {PdCl(bipy)} moiety. This electronic effect must be considerably greater for the {PdCl(tmeda)} moiety to explain the stereoselective formation of *E*-**4** and *E*-**5**.

The acetylaryl complex [Pd(R^{Me})Cl(tmeda)] **1c**[7] [R^{Me} = C_6H{C(O)Me}-6-$(OMe)_3$-2,3,4] reacts differently with

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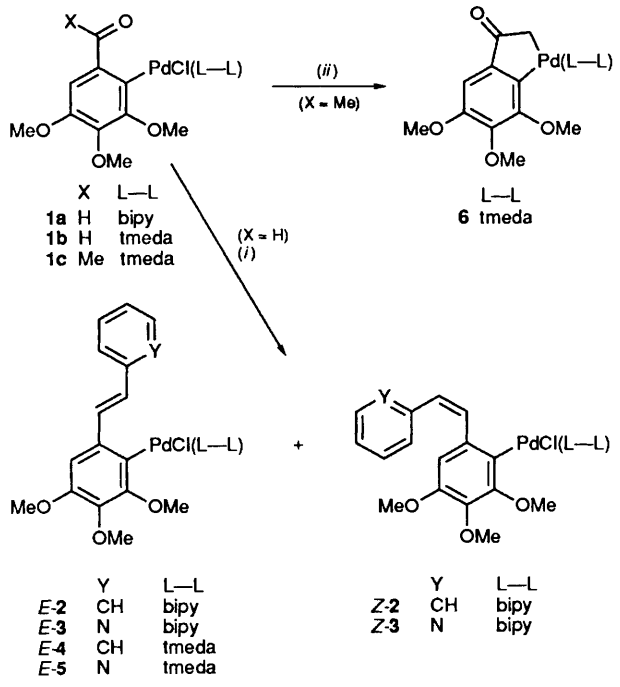
¶ The ylides Ph_3P=CHPh and Ph_3P=$CH(C_5H_5N$-2) were prepared *in situ* by reaction of the corresponding phosphonium chlorides with $LiBu^n$ in Et_2O, or $KOBu^t$ in CH_2Cl_2 and were not isolated.

‖ Satisfactory elemental analyses were obtained for all complexes. Spectroscopic data are in agreement with the proposed structures.



Scheme 1 (*i*) + $Ph_3P{=}CH(C_5H_4X)$ − $Ph_3P{=}O$, Et_2O, 20 h, yield: *E*-**2** + *Z*-**2**, 83%; isolated *E*-**2**, 14%; *E*-**3** + *Z*-**3**, 79%; isolated *E*-**3**, 19%; isolated *E*-**4**, 65%; isolated *E*-**5**, 43%. (*ii*) + NaOMe − NaCl − MeOH, MeOH, 5 min, yield: 87%

$Ph_3P{=}CHPh$ giving $[\overline{Pd\{C_6H[C(O)CH_2]}\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}\text{-}(tmeda)]$ **6**, *i.e.*, the complex resulting from deprotonation of the acetyl group instead of the Wittig product (see Scheme 1). Complex **6** is, however, best obtained by treating **1c** with NaOMe. This is the first reported 3-metallaindan-1-one.

The crystal structure of *E*-**4** (see Fig. 1) shows that the alkenyl group has the postulated *E* configuration.* The metal atom shows the expected square-planar co-ordination (mean deviation of five atoms 0.04 Å); the aryl group bonded to Pd is almost perpendicular (79°) to the co-ordination plane. The Pd–N bond distances are significantly different, showing the greater *trans* influence of the aryl group compared to the chloro ligand; Pd–C, Pd–Cl and C=C bond distances are normal.[12] Surprisingly, both Pd–C bond distances in complex **6** (see Fig. 2) † are significantly longer than in complex *E*-**4**. The greater *trans* influence of the methylene than the aryl group is shown by the longer Pd–N(2) bond compared to Pd–N(1).

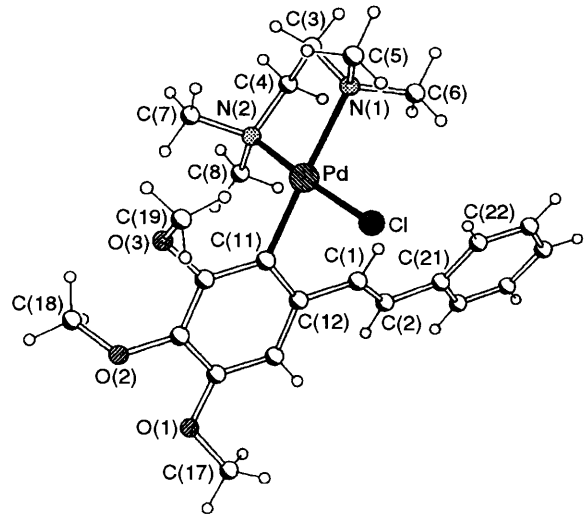


Fig. 1 Crystal structure of *E*-**4**. Selected bond distances (Å) and angles (°): Pd–C(11) 1.999(2), Pd–N(1) 2.169(2), Pd–N(2) 2.085(2), Pd–Cl 2.3220(7), C(1)–C(12) 1.470(3), C(1)–C(2) 1.325(3), C(2)–C(21) 1.468(3); N(2)–Pd–N(1) 84.23(8), C(11)–Pd–Cl 90.00(6), C(11)–Pd–N(2) 92.92(8), N(1)–Pd–Cl 92.78(6)

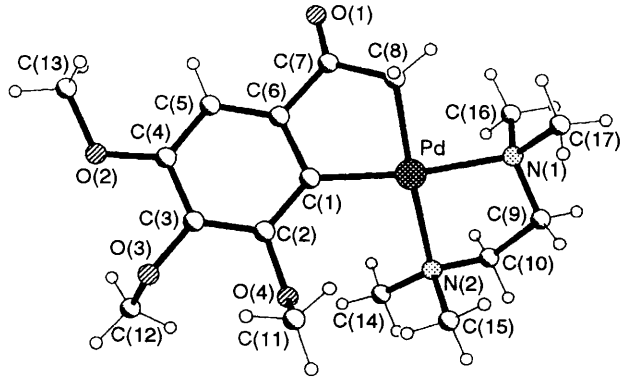


Fig. 2 Crystal structure of **6**. Selected bond distances (Å) and angles (°): Pd–C(1) 2.035(2), Pd–C(2), 2.045(2), Pd–N(1) 2.165(2), Pd–N(2) 2.195(2), C(7)–O(1) 1.226(3); N(2)–Pd–N(1) 82.83(7), C(1)–Pd–C(8) 79.90(8), C(8)–Pd–N(1) 93.45(8), C(1)–Pd–N(2) 103.61(7)

Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (PB92-0982-C) and the Fonds der Chemischen Industrie for financial support and the Human Capital and Mobility research program of the Commission of the European Communities for a research training fellowship to R. B. (contract No. ERBCHBGCT920143). D. B. is grateful to Ministerio de Educación y Ciencia (Spain) for a grant.

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* $C_{23}H_{33}ClN_2O_3Pd$, monoclinic, $P2_1/c$, a = 7.736(2), b = 14.389(3), c = 21.134(5) Å, β = 92.58(2)°, U = 2350.2 Å^3, Z = 4, D_c = 1.490 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 0.9 mm^{-1}. An orange tablet 0.8 × 0.6 × 0.3 mm was mounted on a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low-temperature device. A total of 4574 intensities was recorded at 143 K to $2\theta_{max}$ 50°. After absorption corrections (ψ scans), 4153 unique reflections were used for all calculations. Structure refinement[11] on F^2 to $wR(F^2)$ 0.058, conventional $R(F)$ 0.024 for 278 parameters (S 1.09; max. $\Delta\rho$ 0.34 e Å^{-3}). † $C_{17}H_{28}N_2O_4Pd$, monoclinic, $P2_1/n$, a = 10.8570(14), b = 11.3205(10), c = 15.2970(14) Å, β = 95.933(8)°, U = 1870.0 Å^3, Z = 4, D_c = 1.530 Mg m^{-3}, μ = 1.0 mm^{-1}. Yellow prism, 0.7 × 0.35 × 0.3 mm, Siemens P4 diffractometer with LT-2 low-temperature device, 3472 intensities at 173 K, 3271 unique; $wR(F^2)$ 0.047, $R(F)$ 0.019 for 224 parameters (S 1.05; max. $\Delta\rho$ 0.35 e Å^{-3}). Other details as for *E*-**4**. Atomic coordinates, thermal parameters and bond lengths and angles for both structures have been deposited at the Fachinformationszentrum Karlsruhe [reference numbers CSD 401888 (*E*-**4**), 404026 (**6**)]. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

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Received 12*th June* 1995; *Communication* 5/03790E