Preparation of Cationic (*E*)-σ-Alkenyl Palladium Complexes having a P–O–N or a P–O–P Tridentate Ligand as a Stabilized Intermediate of Palladium-catalysed Stereoselective Addition of Methanol to Acetylenes; Characterisation, X-Ray Analysis and the Reaction Pathway

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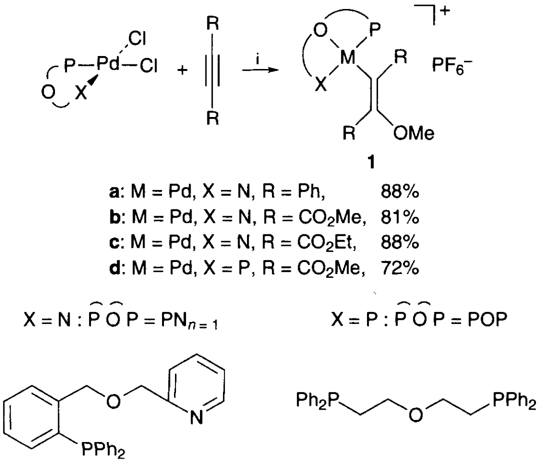
Cationic (*E*)-σ-alkenyl palladium complexes **1** having a P–O–N or a P–O–P tridentate ligand are prepared stereoselectively from *cis*-$PdCl_2(PN_{n=1})$ [PN = *o*-$Ph_2PC_6H_4CH_2O(CH_2)_n$-2-C_5H_4N-*P,N*] or *cis*-$PdCl_2$(POP) [POP = $Ph_2P(CH_2)_2O(CH_2)_2PPh_2$-*P,P*] and internal alkynes in the presence of $AgPF_6$ and MeOH; the X-ray crystal structure of **1c** is reported and a stepwise abstraction of chloride ligands for the formation of **1** is proposed.

In contrast to many examples of stereoselective synthesis of (*Z*)-σ-alkenyl palladium complexes by insertion of alkyne in to a palladium–Y bond (Y = H, alkyl or halide)[1] only a few concrete examples of stereoselective synthesis of (*E*)-σ-alkenyl palladium complexes by stereoselective addition of a nucleophile to an η^2-alkyne palladium complex are available.[2] The formation of such complexes has often been postulated as a reaction intermediate in the palladium catalysed oligomerisation of acetylene[3] or stereoselective addition of alcohol to acetylene.[4,5] (*E*)-Configuration of the σ-alkenyl group in these isolated complexes, however, was only postulated by NMR techniques.[2–4,6,7] Here, we describe the stereoselective formation of (*E*)-σ-alkenyl palladium complexes **1** from acetylene and methanol in the presence of cationic palladium complexes having potentially tridentate auxiliary ligands and to propose a possible reaction pathway for the formation of these σ-alkenyl complexes based on the isolated monocationic complex **2**.

We have recently designed and synthesized new PN hybrid ligands [PN = *o*-$Ph_2PC_6H_4CH_2O(CH_2)_n$-2-C_5H_4N-*P,N*, *n* = 1–3] and prepared their palladium(II) complexes.[8] In the course of our studies on the reactivity of $PdCl_2$(PN), we have found that in some cases the bidentate PN ligand served as a P–O–N tridentate ligand.[9] Reaction of *cis*-$PdCl_2(PN_{n=1})$ (0.17 mmol) with diphenylacetylene (0.42 mmol) in the presence of $AgPF_6$ (0.43 mmol) in CH_2Cl_2–methanol (10 ml, 200 : 1) afforded air-stable yellow powders, [Pd(PON){η^1-(*E*)-PhC=C(OMe)-Ph}][PF_6] **1a**, where PON represents the P–O–N tridentate $PN_{n=1}$ ligand, in 88% yield (Scheme 1). The elemental analysis and spectral data suggested the structure of **1a**.† Similar cationic (*E*)-σ-alkenyl palladium complexes were obtained in good yields from alkynes having electron-withdrawing groups such as DMAD (dimethylacetylene dicarboxylate) and DEAD (diethyl acetylenedicarboxylate), but an unactivated alkyne such as dodec-6-yne and a terminal alkyne such as methyl propynate did not give corresponding stable σ-alkenyl complexes from similar reactions.



Scheme 1 *Reagents and conditions*: i, excess $AgPF_6$, MeOH–CH_2Cl_2, room temp., 20 min

The structure of the σ-alkenyl palladium complex **1c** has been confirmed firmly by X-ray crystallography. Crystals suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$ and CCl_4. The ORTEP drawing of the cationic part of **1c** is presented in Fig. 1.‡ In this σ-alkenyl palladium complex the bidentate $PN_{n=1}$ ligand in *cis*-$PdCl_2(PN_{n=1})$ changed to a tridentate PON ligand. The diphenylphosphino group and the pyridyl group are mutually *trans* and the σ-alkenyl group situates at the *trans* position of the etheric oxygen of the PON ligand. The complex has a nearly square-planar geometry. The geometry of the C=C bond is in *E* configuration. The Pd···O(5) distance of 2.828(6) Å is shorter than the sum of the van der Waals radii[10] of palladium (1.60 Å) and oxygen (1.50 Å); thus, there should be a certain interaction between palladium and one of the carbomethoxy carbonyl groups.[2e]

The stereochemistry of the alkenyl moiety in **1a** was also determined to be (*E*)-configuration by preliminary X-ray analysis and that of **1b** was estimated by the similarity of the spectral data to those of **1c**. The structure is also supported by the fact that reaction of the σ-alkenyl palladium complexes with KCN in water–THF produced only dimethyl methoxyfumarate as the olefinic product.

Treatment of *cis*-$PdCl_2(PN_{n=1})$ with an equimolar amount of $AgPF_6$ in CH_2Cl_2 at 25 °C for 20 min afforded the cationic monochloropalladium complex [Pd(PON)Cl][PF_6] **2**§ as a yellow powder in 79% yield. The structure of **2** was fully characterised by spectroscopic methods and elemental analysis.

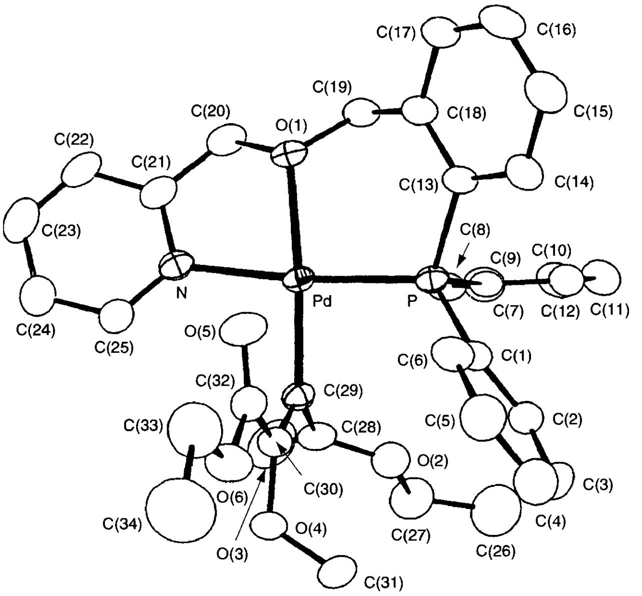
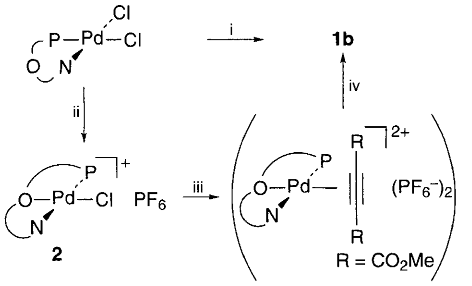


Fig. 1 Perspective view of the cationic part of **1c** showing the atom numbering. All hydrogen atoms have been omitted for clarity.



Scheme 2 *Reagents and conditions*: i, DMAD; MeOH–CH_2Cl_2, excess $AgPF_6$, room temp., 20 min; ii, 1 equiv. $AgPF_6$, CH_2Cl_2; iii, DMAD, 1 equiv. $AgPF_6$; iv, MeOH

In this monocationic complex **2** the initial bidentate $PN_{n=1}$ ligand changed also to a tridentate PON ligand by coordination of the etheric oxygen. This monochloro palladium complex **2** reacted smoothly with DMAD in the presence of 1 equivalent of $AgPF_6$ and methanol in CH_2Cl_2 to give the σ-alkenyl complex **1b** in 73% yield. The most plausible reaction pathway for the formation of the σ-alkenyl complexes is shown in Scheme 2. Two chloride ligands of *cis*-$PdCl_2(PN_{n=1})$ are abstracted stepwise by Ag^+ and after removal of one of the chloride anions the $PN_{n=1}$ ligand occupied the three coordination sites of the palladium to produce the monochloro complex **2**. The next step is abstraction of the remaining chloride ligand and concomitant coordination of an acetylenic compound and the subsequent nucleophilic attack of MeOH to the coordinated acetylene leads to the formation of the (*E*)-σ-alkenyl complex **1**.

For the isolation of the cationic σ-alkenyl palladium complex, it seems that the presence of a tridentate ligand is essential. Using a POP tridentate ligand, $Ph_2P(CH_2)_2O(CH_2)_2PPh_2$, a similar σ-alkenyl palladium complex **1d** could also be prepared from an analogous reaction, but bidentate ligands such as $Ph_2P(CH_2)_5PPh_2$ and $PN_{n=3}$ did not give similar complexes. When the $PN_{n=3}$ ligand acts as a tridentate ligand towards a single metal centre, it should form a five- and seven-membered chelate coordination. The ring strain produced may prevent the $PN_{n=3}$ ligand from acting as a PON tridentate ligand.

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Footnotes

† All new compounds gave satisfactory analytical values. Selected data for **1a**: mp. 173.0–174.0 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 3.24 (s, 3 H), 4.58 (d, *J* 11.5 Hz, 1 H), 4.87 (dd, *J* 11.5, 1.2 Hz, 1 H), 5.40 (d, *J* 14.1 Hz, 1 H), 5.48 (d, *J* 14.1 Hz, 1 H), 6.33 (d, *J* 7.2 Hz, 2 H), 6.72–7.24 (m, 13 H), 7.30–7.72 (m, 10 H), 7.87 (d, *J* 7.7 Hz, 1 H), 8.71 (dt, *J* 1.5, 7.7 Hz, 1 H), 8.82–8.92 (m, 1 H, 6-*H* of C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −143.8 (spt, *J* 712.0 Hz, 1P, $\mathit{P}F_6$), 23.4 (s, 1P, $Ph_2\mathit{P}$). MS (FAB) of the cationic part: *m*/*z* 697, 698, 700 (M^+). IR (Nujol): 1603, 1570, 1290, 1215, 1100, 1060, 1040, 840, 770, 745, 695, 555, 530, 520 cm^{-1}.

‡ *Crystal data* for **1c**: $C_{34}H_{35}F_6NO_6P_2Pd\cdot PF_6\cdot CHCl_3$, M_r = 955.39, triclinic, space group $P\bar{1}$, a = 13.024(1), b = 15.305(1), c = 12.015(1) Å, α = 113.034(8), β = 110.614(8), γ = 93.870(9)°, V = 2003.4(4) Å^3, Z = 2, λ = 1.54178 Å, μ(Cu-Kα) = 71.24 cm^{-1}, T = 293(1) K, 6261 reflections measured, 5955 unique reflections, no. of observations [$(F_o) > 3.0\sigma(F_o)$] 4844, non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed contributions [C–H(sp^2) = 0.95 Å, C–H(sp^3) = 1.08 Å, and U_{iso} = 0.0682 Å^2]. 487 parameters, R = 0.0662, R_w = 0.0581, $w = 1/\sigma^2(F_o)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ **2**: mp 132.0–137.5 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 5.08 (br s, 1 H), 5.09 (br s, 1 H), 5.71 (br s, 2 H), 6.85–6.96 (m, 1 H), 7.46–7.84 (m, 15 H), 8.02 (dt, *J* 1.5, 7.8 Hz, 1 H), 8.75–8.81 (m, 1 H, 6 *H* of C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −143.4 (spt, *J* 712.7 Hz, 1P, $\mathit{P}F_6$), 26.4 (s, 1P, $Ph_2\mathit{P}$). MS (FAB) of the cationic part: *m*/*z* 523, 524, 526 (M^+). IR (Nujol): 1610, 1570, 1290, 1210, 1100, 1030, 1010, 980, 840, 758, 690, 556, 538, 520, 370 cm^{-1}.

References

1 P. M. Maitlis, P. Espinet and M. J. H. Russell, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982; vol. 6, 38. 9; Y. Tohda, K. Sonogashira and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1975, 54; H. C. Clark, C. R. Milne and C. S. Wong, *J. Organomet. Chem.*, 1977, **136**, 265; T. Yasuda, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2888; H. C. Clark and C. R. Milne, *J. Organomet. Chem.*, 1978, **161**, 51.

2 (*a*) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2557; (*b*) M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, 1972, **94**, 1532; (*c*) M. H. Chisholm and H. C. Clark, *Acc. Chem. Res.*, 1973, **6**, 202; (*d*) D. L. Reger, S. A. Klaeren and L. Lebioda, *Oganometallics*, 1986, **5**, 1072; (*e*) A. Albinati, P. S. Pregosin and R. Rüedi, *Helv. Chim. Acta*, 1985, **68**, 2046.

3 P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic, New York, 1971, vol. 2, pp. 47–58; *Acc. Chem. Res.*, 1976, **9**, 93; T. R. Jack, C. J. May and J. Powell, *J. Am. Chem. Soc.*, 1977, **99**, 4707.

4 A. Avshu, R. D. O'Sullivan and A. W. Parkins, *J. Chem. Soc., Dalton Trans.*, 1983, 1619.

5 Y. Kataoka, O. Matsumoto, M. Ohashi, Y. Yamagata and K. Tani, *Chem. Lett.*, 1994, 1283.

6 Concrete examples for *trans* addition of a nucleophile to the coordinated alkyne to produce (*E*)-σ-alkenyl complexes have been indicated for molybdenum and iron complexes: D. L. Reger, K. A. Belmore, E. Mintz, N. G. Charles, E. A. H. Griffith and E. L. Amma, *Organometallics*, 1983, **2**, 101; D. L. Reger, K. A. Belmore, E. Mintz and P. J. McElligott, *Organometallics*, 1984, **3**, 134; D. L. Reger, S. A. Klaeren and L. Lebioda, *Organometallics*, 1986, **5**, 1072.

7 The X-ray crystal structure of an (*E*)-σ-alkenyl platinum complex has been reported, see; F. Canziani, L. Garlaschelli and M. C. Malatesea, *J. Organomet. Chem.*, 1978, **146**, 179.

8 M. Yabuta, S. Nakamura, T. Yamagata and K. Tani, *Chem. Lett.*, 1993, 323; K. Tani, M. Yabuta, S. Nakamura and T. Yamagata, *J. Chem. Soc., Dalton Trans.*, 1993, 2781.

9 K. Tani, S. Nakamura, T. Yamagata and Y. Kataoka, *Inorg. Chem.*, 1993, **32**, 5398.

10 J. E. Huheey, *Inorganic Chemistry*, 3rd edn., Harper & Row, New York, 1983, pp. 258–259.