

Synthesis, Structure and Ligand-centred Reduction of an Orthometallated Complex of Palladium containing Two Phosphaalkene Groups

Abdelaziz Jouaiti, Michel Geoffroy,* Gustavo Terron and Gérald Bernardinelli

Department of Physical Chemistry and Laboratory of Crystallography, 30 Quai Ernest Ansermet, University of Geneva, 1211 Geneva, Switzerland

A novel ligand containing two phosphaalkene moieties has been synthesized, which forms a palladium(II) complex whose crystal structure has been determined and whose reduction has been shown, by EPR spectroscopy, to take place on the ligand rather than on the metal.

The chemistry of low-coordinate phosphorus compounds is currently a very active research field,¹ in particular, the nature of the bonding between phosphaalkene and transition metals is being intensively investigated and several complexes where

a metal is σ - or η^2 -coordinated to a single $-\text{P}=\text{C}<$ group have been reported.² Reduction of square-planar palladium(II) complexes is known to generate paramagnetic species in which the unpaired electron mainly lies in a $d_{x^2-y^2}$ metal orbital. This is the case, for example, of tetrakis(tetrahydropyrimidine-2(1*H*)-thione)³ or bis(dithioxolato) complexes.⁴ For a phosphaalkene ligand the π^* LUMO is expected to be relatively low lying and it seems plausible, for example, that reduction of a phosphaalkene Pd^{II} complex could generate a complex with the additional electron in a ligand-centred molecular orbital. In this context, we have undertaken the synthesis of a new ligand bearing two phosphaalkene moieties and able to complex a Pd^{2+} ion; we describe here the preparation of the ligand **1** and report the crystal structure of the corresponding cyclometallated Pd^{II} complex **2** whose reduction was studied by cyclic voltammetry and EPR spectroscopy.

The ligand **1** was synthesized by using the method of Yoshifuji *et al.*⁵ to generate the phosphaalkene groups: after addition of Bu^nLi to a solution of ArPH_2 ($\text{Ar} = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$), $\text{ClSiMe}_2\text{Bu}^t$ was added to the reaction mixture; a new lithiation was then followed by dropwise addition of a solution of isophthalaldehyde at room temperature. After

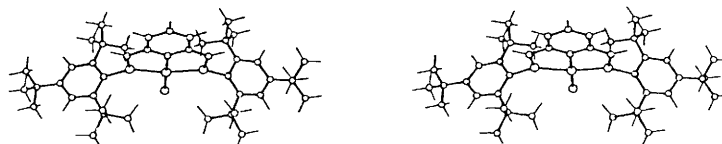
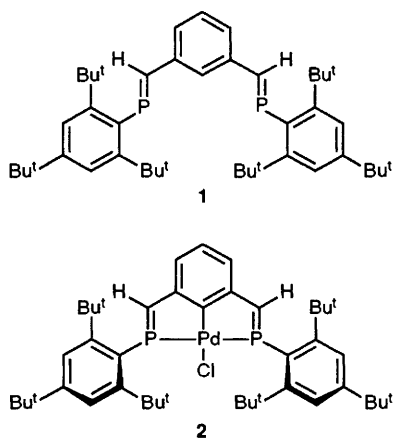


Fig. 1 Stereoscopic view of the Pd complex **2**

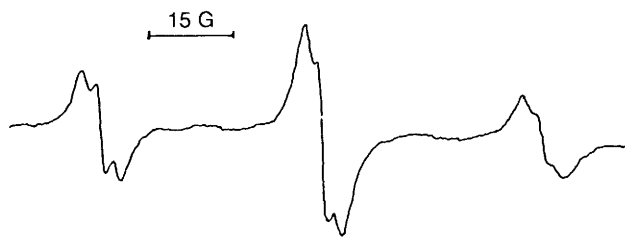


Fig. 2 EPR spectrum obtained by electrochemical reduction of the complex **2**

removal of the solvent and separation on a silica gel column with pentane as eluent the diphosphaalkene **1** was crystallized from benzene–MeCN (m.p. 150 °C) and characterized by ^1H , ^{31}P and ^{13}C NMR spectroscopy.

The complex **2** was obtained by addition, under an argon atmosphere, of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ to a solution of one equivalent of **1**. The resulting orange solution was stirred for 1 h and crystals of **2** were obtained by diffusion of benzene vapour into a solution of the complex in CH_2Cl_2 . The complex **2** (decomp. 181 °C) was characterized by NMR spectroscopy and X-ray crystallography.

The crystal structure† determination reveals a tridentate chelate structure (Fig. 1); the Pd^{II} centre is bound to both σ -phosphorus donors and an orthometallation of the phenyl ring is observed. The environment of the metal is square-planar and, except for the two phenyl rings which are oriented perpendicular to the molecular plane (86°), all the atoms of the complex are practically coplanar. Phosphine analogues of **2** (complexes for which the phosphalkene groups are replaced by phosphine moieties) have been synthesized,⁹ but, as far as we know, their crystal structure has not been reported. Nor has any crystal structure for a phosphalkene palladium complex. The bond lengths for **2** [Pd–Cl 2.348(4), Pd–P 2.274(3), Pd–C(8) 2.04(1) Å] are in good accordance with those previously measured for *trans*-chloro-2-(phenylazo)phenylbis(triethylphosphine)palladium(II)¹⁰ and the P=C bond length [1.63(1) Å] is similar to that reported for *cis*- $[\text{PtCl}_2(\text{PEt}_3)\{\text{P}(\text{mes})=\text{CPh}_2\}]$ (mes=2,4,6-Me₃C₆H₂).^{2c}

In contrast to previous observations on phosphalkenes, which often show an irreversible reduction wave,^{1b} the compound **1** shows a reversible reduction at -1.91 V. The

cyclic voltammetric study of the complex **2** in tetrahydrofuran (THF) shows a reversible reduction at $E_{1/2} = -1.23$ V vs. standard calomel electrode (SCE); an irreversible reduction also occurs at -1.92 V vs. SCE. Electrolysis of a solution of **2** in an EPR cell at a potential corresponding to the first one-electron-reduction step produces a species with an intense EPR spectrum (Fig. 2). This spectrum is totally different from that obtained by electrochemical reduction of the pure ligand **1** (coupling with a single ^{31}P) and is characterized by a hyperfine interaction with two equivalent ^{31}P nuclei ($A_{\text{iso}} = 78$ G; and 1 G = 10^{-4} T) and a g value equal to 2.0044. An additional coupling with two equivalent protons ($A_{\text{iso}} = 3.5$ G) is also observed. The ^{31}P coupling indicates a strong spin delocalisation on the ligands [for comparison, the ^{31}P - A_{iso} value in $(\text{RP} = \text{PR})^-$ is 57 G] as does the closeness of the g -value to the free electron value. Furthermore, no hyperfine coupling with ^{105}Pd (natural abundance 22.2%, $I = 5/2$) is observed. These results are reminiscent of those reported for the one-electron-reduction products of tin(IV) chloride adducts of bis(dithiooxalato)palladium(II)¹¹ and suggest that the added electron occupies a ligand π antibonding orbital.

We thank the Swiss National Science Foundation for financial support.

Received, 27th June 1991; Com. 1103218F

References

- (a) R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; (b) W. W. Schoeller, J. Niemann, R. Thiele and W. Haug, *Chem. Ber.*, 1991, **124**, 417; (c) R. Appel, S. Korte, M. Halstenberg and F. Knoch, *Chem. Ber.*, 1982, **115**, 3610; (d) J. Hein, E. Niecke, M. F. Meidine, B. F. Trigo Passos and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1991, 41; (e) C. Thomson, *J. Chem. Soc., Chem. Commun.*, 1977, 322; (f) W. W. Schoeller and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1982, 569.
- (a) S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1983, 930; (b) H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1981, 199; (c) H. W. Kroto and J. F. Nixon, *ACS Symposium Series*, 1981, **171**, 383; (d) T. A. van der Knaap, F. Bickelhaupt, J. G. Kraaykamp, G. van Koten, J. P. C. Nernards, H. T. Edzes, W. S. Veeman, E. de Boer and E. J. Baerends, *Organometallics*, 1984, **3**, 1804.
- P. Arrizabalaga, G. Bernardinelli, M. Geoffroy, P. Castan and F. Dahan, *Chem. Phys. Lett.*, 1986, **124**, 549.
- W. Geiger, C. S. Allen, T. E. Mines and F. C. Senftleber, *Inorg. Chem.*, 1977, **16**, 2003.
- M. Yoshifuji, K. Toyota and N. Inamoto, *Tetrahedron Lett.*, 1985, **26**, 1727.
- P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, MULTAN, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, 1987, Universities of York, and Louvain-la Neuve.
- S. R. Hall and J. M. Stewart (ed.), *XTAL-3.0 User's Manual*, Universities of Western Australia and Maryland, 1990.
- International Tables for X-Ray Crystallography*, vol. IV, Kynoch Press, Birmingham, 1974.
- (a) C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020; (b) H. Rimml and L. M. Venanzi, *J. Organomet. Chem.*, 1983, **259**, C6; (c) H. Rimml and L. M. Venanzi, *J. Organomet. Chem.*, 1984, **260**, C52.
- D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2250.
- (a) D. Coucouvanis, N. C. Baenziger and S. M. Johnson, *J. Am. Chem. Soc.*, 1973, **95**, 3875; (b) G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1982, **21**, 3565.

† Crystal data and structure refinement for compound **2**. Cell parameters and reflection intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). $\text{Pd}(\text{C}_{44}\text{H}_{63}\text{P}_2\text{Cl})(\text{C}_6\text{H}_6)_2$, $M = 952.0$, orthorhombic, space group *Pbcn*, $a = 17.067(3)$, $b = 18.838(3)$, $c = 16.427(2)$ Å, $V = 5281(1)$ Å³, $Z = 4$, $D_m = 1.20$ Mg m⁻³, $D_c = 1.20$ Mg m⁻³, $\mu = 0.489$ mm⁻¹, $F(000) = 2016$. Data collection: $\sin \theta/\lambda < 0.53$, $h = 0-18$; $k = 0-19$, $l = 0-17$; ω - 2θ scans, absorption corrections: $A_{\text{min}}^* = 1.063$, $A_{\text{max}}^* = 1.067$. Of the 3261 measured reflections, 1995 were considered as observed [$|F_0| > 4\sigma(F_0)$] and used in structure refinement. The measurement of two reference reflections showed no significant deviation. The structure was solved by direct methods (MULTAN-87)⁶ and refined by least-squares analysis with the XTAL-3.0 program.⁷ Atomic scattering factors and anomalous-dispersion terms are taken from ref. 8. All coordinates of the H atoms were calculated. The maximum and minimum residual electron densities in the final ΔF map were 1.50 and -1.20 eÅ⁻³ respectively. Final R factors: $R = 0.082$, $R_w = 0.046$ [$w = 1/\sigma^2(F_0)$]. The Pd complex is located at a special position with atoms Pd, Cl, C(8) and C(11) in position 4c. The benzene molecule is ordered and located in general positions. Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.