

Isolation and Structural Characterisation of a Reactive Chiral Palladium(II) Complex Containing a ClO₄ Ligand

Soh-Kheang Loh, K. F. Mok and Pak-Hing Leung*

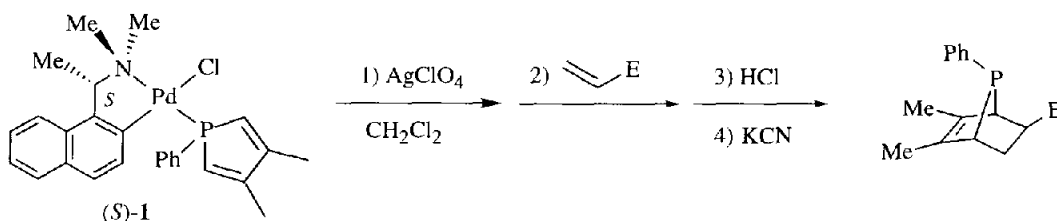
Department of Chemistry, National University of Singapore, Kent Ridge, Singapore, 0511

Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College, London, SW7 2AY, United Kingdom

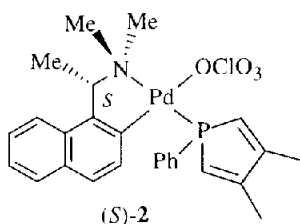
Abstract: The organopalladium(II) complex [Pd(OClO₃)(DMPP)]{(S)-CH₃CH(1-C₁₀H₆)NMe₂}] (where DMPP = 1-phenyl-3,4-dimethylphosphole) has been isolated. X-ray structural analysis of this reactive complex in the solid state revealed that the perchlorato ligand is bonded to Pd *via* one of its oxygen atoms and the DMPP is coordinated as a monodentate ligand *via* phosphorus. In non-coordinating solvents, conductivity measurements confirmed that the Pd–OClO₃ bond is retained.

DMPP is one of the most versatile ligands for transition metal ions. It commonly behaves in a monodentate fashion *via* phosphorus;¹ in the absence of a strong competing ligand, however, the diene component of the rigid 5-membered phosphole ring can also be involved in metal binding. Hence, DMPP has been commonly reported as a (μ-σ, η⁴) bridging ligand in dimeric complexes with Co, Fe, Mn, Mo and Rh.² In terms of chemical reactivity, Nelson and co-workers found that coordinated DMPP is capable of undergoing a [4+2] Diels-Alder reaction with dienophiles.³ Thus, a range of racemic P-chiral phosphine ligands with rigid norbornene skeletons have been synthesised. In contrast, free DMPP shows no reactivity towards such cycloaddition reactions. Recently, we have utilised the enantiomerically pure forms of **1** as the chiral promoters for the asymmetric Diels-Alder reactions between DMPP and dienophiles such as divinylsulfoxide,⁴ diphenylphosphine,^{5,6} *N,N*-dimethylacrylamide⁶ and divinylphenylphosphine,⁶ as illustrated in Scheme 1. Utilising this procedure, the P-chiral monodentate and bidentate phosphines were generated efficiently in their enantiomerically pure forms. Interestingly, in all these asymmetric processes the chloro ligand in **1** must be removed by AgClO₄ prior to reaction with dienophiles. We considered it important to investigate the intermediate complex that is formed immediately after this chloride abstraction, since it controls both the reactivity and the stereochemistry of the asymmetric [4+2] cycloaddition process. It should be noted, however, that this highly reactive species is not usually isolated as part of the normal synthetic route.



Scheme 1, E = Ph₂P, PhP(CH=CH₂), (CH₂=CH)₂SO, Me₂NCO

An intermediate complex was prepared by treating (*S*)-**1**⁴ with AgClO₄ in CH₂Cl₂. After the removal of AgCl and solvent, a yellow crystalline product was obtained from toluene and shown by single crystal X-ray analysis to be the complex (*S*)-**2**; 78% isolated yield; mp 190-192 °C, [α]_D +285 (*c* = 0.2, CH₂Cl₂).⁷ In theory, the chloride abstraction of (*S*)-**1** by AgClO₄ in CH₂Cl₂ vacates a coordination site on the palladium(II) template. Since coordination of perchlorate to palladium(II) is rare,⁸ we originally considered that the P-coordinated DMPP might utilise its diene ligating function to stabilise the coordinatively unsaturated intermediate complex. Accordingly, this species was expected to be either a monomeric cation with a chelating DMPP ligand or a dimeric cation with two DMPP bridges. With these structures in mind, we rationalised that the activation of the carbon-carbon double bonds in the subsequent asymmetric Diels-Alder reaction might be due to polarisation of electrons *via* phosphorus^{3,9} or coordinated carbons,¹⁰ or both. However, we were surprised to find that a CH₂Cl₂ solution of the complex was a non-electrolyte. This observation is in accord with perchlorate coordination in solution.



The X-ray analysis¹¹ of **2** reveals the presence of two crystallographically independent molecules, each having an *S* configuration at the C(2) centre (the methyl group being axial¹²) and essentially identical conformations—Figure 1. The palladium is coordinated to the nitrogen and the *ortho* carbon atom of the bidentate naphthylamine ligand, the phosphorus of the DMPP group and an oxygen atom of a perchlorate anion in a distorted square planar geometry. In common with all recorded X-ray structures of phosphorus complexes derived from the chelating naphthylamine moiety, the soft donor atom occupies the position *trans* to the NMe₂ group.¹³ The central palladium atom and the four donor atoms forming the inner coordination sphere are planar to within 0.08 Å in both cases, with the N(1)–Pd–C(4) angle contracted to *ca.* 81° due to the bite size of the naphthylamine ligand. The O–Pd–P angle is slightly enlarged at *ca.* 93°. The Pd–aryl, –P and –N distances, 1.977(4) [1.981(4)], 2.246(1) [2.247(1)] and 2.143(3) [2.138(4)] Å respectively—values in square brackets refer to the second independent molecule—are unexceptional. The Pd–O distance, 2.203(3) [2.202(3)] Å, is very similar to that previously reported for a Pd–OH₂¹⁴ (2.20 Å) but significantly shorter than in the only other reported structure containing a perchlorate coordinated to a palladium centre,⁸ [Pd(az)(OCIO₃)(SPPH₃)] (2.22 Å)—which also has a 1,4-*C,N* ligand with the coordinated carbon atom part of an aromatic ring and *trans* to the perchlorate. A feature of both of these Pd–OCIO₃ complexes is a noticeable lengthening of the Cl–O bond involving the coordinated oxygen atom relative to the other three. In [Pd(az)(OCIO₃)(SPPH₃)] the Cl–O (coordinated) distance is 1.472 Å, whilst the other Cl–O distances are in the range 1.359(12) to 1.455(7) Å, though the shortening of some of these may be artificial and a reflection of the disorder present in this group in this structure. In (*S*)-**2**, however, the perchlorate anion is ordered and the three non-coordinated Cl–O distances lie within a much narrower range—1.411(4) to 1.430(4) Å (for the two independent molecules)—and are still all significantly shorter than that to the coordinated oxygen atom 1.474(3) [1.471(3)] Å. Inspection of the pattern of

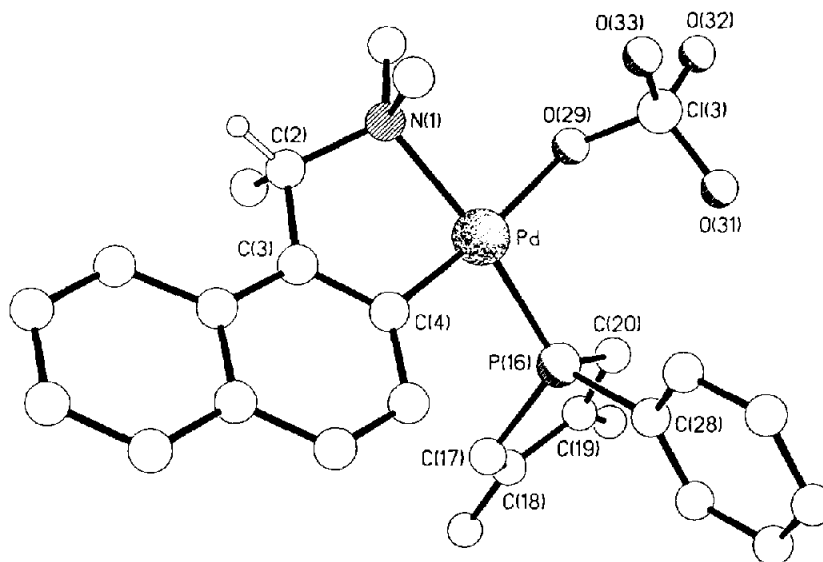


Figure 1. Molecular structure and labelling scheme for (*S*)-**2**.

bonding within the phosphole ring reveals a marked bond ordering with the C(17)–C(18) and C(19)–C(20) bonds exhibiting significant double bond character. An analysis of the packing of the two independent molecules in the crystal reveals a marked absence of any dominant π – π , C–H \cdots π or C–H \cdots O interactions.

It is important to note that palladium(II) is a typical "soft" metal ion. Thus with the diene normally being considered as a soft ligand and the perchlorate as hard, the adoption of the rare perchlorato-Pd bonding rather than the relatively common diene-Pd coordination in (*S*)-**2** is clearly attributed to the strong *trans*-withdrawing effect from the metalated naphthalene carbon and the steric repulsion from the *cis*-NMe₂ group. Since DMPP is not connected to Pd *via* any Pd–C bond, either in the solid state or in solution, it is clear that the activation of the phosphole C=C double bonds in our system is solely due to the electronic polarisation of the phosphole ring through the P–Pd bond. On the other hand, the weak perchlorato ligand in (*S*)-**2** stabilises the reactive intermediate and also offers a readily available site for the incoming dienophile so that the dienophile and DMPP can be coordinated simultaneously on the chiral palladium template during the course of the cycloaddition reaction. We are currently investigating the origins of the stereoselectivity in these palladium(II) promoted reactions.

Acknowledgement The work was supported by the National University of Singapore (Research Grant No. RP 920606) and we thank the EPSRC for the diffractometer.

References and Notes

1. MacDougall, J.; Nelson, J. H.; Mathey, F.; Mayerle, J. J. *Inorg. Chem.* **1980**, *19*, 709.
2. Kessler, J. M.; Nelson, J. H.; Fischer, J.; Cian, A. D.; Bearden, W. H.; Fujii, N. *Inorg. Chem.* **1994**, *33*, 4319 and references cited therein.

3. Rahn, J. A.; Holt, M. S.; O'Neil-Johnson, M.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 1316 and references cited therein. Ji, H. L.; Nelson, J. H.; Cian, A. D.; Fischer, J.; Solujic, L.; Milosavljevic, E. B. *Organometallics* **1992**, *11*, 1840. Wilson, W. L.; Rahn, J. A.; Alcock, N. W.; Fischer, J.; Frederick, J. H.; Nelson, J. H. *Inorg. Chem.* **1994**, *33*, 109.
4. Siah, S. Y.; Leung, P. H.; Mok, K. F. *J. Chem. Soc., Chem Comm.* **1995**, 1174.
5. Aw, B. H.; Leung, P. H. *Tetrahedron Asymmetry* **1994**, *5*, 1160.
6. Aw, B. H.; Loh, S. K.; Mok, K. F.; Seah, S. Y.; Vanniasingham, S.; White, A. J. P.; Williams, D. J.; Leung, P. H. results to be published.
7. **Caution!** (*S*)-**2** is a potentially explosive compound and should be handled carefully. When in contact with a naked flame, a small crystal of the complex produced an explosive flash. Key data: ^1H NMR (300 MHz, CDCl_3) δ 1.87 (3H, d, $^3J_{\text{HH}} = 6.4$ Hz, *CHMe*), 2.10 (3H, s, *C=CMe*), 2.14 (3H, s, *C=CMe*), 2.83 (3H, d, $^4J_{\text{PH}} = 3.4$ Hz, *NMe*), 2.88 (3H, d, $^4J_{\text{PH}} = 1.5$ Hz, *NMe*), 4.30 (1H, qn, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.1$ Hz, *CHMe*), 6.23 (1H, s, *C=CH*), 6.34 (1H, s, *C=CH*), 6.75-7.91 (11H, m aromatics); ^{31}P NMR (CDCl_3) 35.32 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_4\text{ClPPd}$: C, 52.72; H, 4.93; N, 2.36. Found: C, 52.72; H, 5.05; N, 2.32.
8. Fornies, J.; Navarro, R.; Sicilia V.; Tomas, M. *Inorg. Chim. Acta* **1990**, *168*, 201. A search of the CCDC data base - release of Oct. 1995 revealed only this one example.
9. Mathey, F. *Chem. Rev.* **1988**, *88*, 429.
10. Pruchnik, F. P.; Duraj, S. A. *Organometallic Chemistry of the Transition Elements*; Plenum Press: New York-London, 1990, Chap 6.
11. Crystal data for (*S*)-**2**: $\text{C}_{26}\text{H}_{29}\text{NO}_4\text{ClPPd}$, $M = 592.3$, triclinic, $a = 9.911(1)$, $b = 11.263(1)$, $c = 12.579(2)$ Å, $\alpha = 89.62(1)$, $\beta = 85.10(1)$, $\gamma = 72.11(1)^\circ$, $V = 1331.0(2)$ Å³, space group *P1*, $Z = 2$ (two crystallographically independent molecules), $D_c = 1.48$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 8.9$ cm⁻¹, $F(000) = 604$. A yellow block of dimensions 0.50 x 0.50 x 0.35 mm was used. 6470 Independent reflections were measured on a Siemens P4/PC diffractometer with Mo- $K\alpha$ radiation (graphite monochromator) using ω -scans. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 with absorption corrected data to give $R_1 = 0.026$, $wR_2 = 0.067$ for 6195 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 55^\circ$] and 590 parameters. The *S* configuration at C(2) in the naphthylamine ligand, though known from the starting material, was also determined unambiguously *via* i) Flack parameter, $x^+ = -0.02(4)$, $x^- = +1.02(4)$ and ii) by an *R*-factor test, $wR_2^+ = 0.068$, $wR_2^- = 0.073$.
12. The distinctive axial/equatorial geometry for the C(2) H and methyl substituents is a consequence of the puckered geometry of the PdC_3N ring, the nitrogen atom lying *ca.* 0.75 Å out of the Pd, C(2), C(3), C(4) plane. The axial rather than equatorial geometry observed for the methyl substituent is probably due to the steric congestion that would otherwise be present between the proximal naphthyl C-H moiety and the methyl group.¹⁵
13. Alcock, N. W.; Hulmes, D. I.; Brown, J. M. *J. Chem. Soc., Chem Comm.* **1995**, 395. Leung, P. H.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1406 and references cited therein. Chooi, S. Y. M.; Hor, T. S. A.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494.
14. Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.*, **1978**, 1490.
15. Chooi, S. Y. M.; Tan, M. K.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1994**, *33*, 3096.

(Received in UK 25 October 1995)