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Metal-template synthesis and co-ordination properties of a palladium complex containing a novel and stable imidazole-substituted phosphine C–P bidentate chelate

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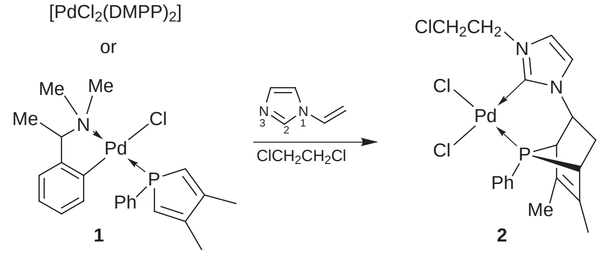
An organopalladium complex promoted Diels–Alder reaction between 1-phenyl-3,4-dimethylphosphole and 1-vinylimidazole gave a novel imidazole-substituted phosphanorbornene bidentate ligand which co-ordinated to the palladium template *via* the C^2 carbon atom of the imidazole group and the bridgehead phosphorus donor atom.

Transition-metal complexes containing imidazole and its derivatives play an important role in bioinorganic chemistry.[1] These compounds are frequently considered as models in the development of metal-based enzymes and proteins. In terms of co-ordination chemistry, imidazole may be considered as an ambidentate ligand. For instance, it has been well established that the imidazole unit co-ordinates to transition-metal ions, such as palladium(II) and platinum(II), predominantly *via* one of its nitrogen atoms. In some rare cases, however, the cyclic unit may also co-ordinate as a carbene or an amidine ligand *via* its C^2 carbon atom. This interesting mode of organometallic bonding has been observed in a small number of Cr^0, Fe^0, Ru^{II} and Ru^{III} complexes.[2] Apart from their biological interest, the availability of stable C-bound imidazole heavy-metal complexes is important for the study of the *trans* influence[3] and other related phenomena that are pertinent to the design and development of efficient support ligands for homogenous catalysis.[4] Indeed, it has been reported that palladium complexes containing C-bound imidazole ligands are efficient catalysts for cross-coupling reactions.[5] In general, however, palladium complexes containing monodentate ligands are kinetically labile. We believe that the development of a new class of stable C-bound imidazole complexes may significantly influence the design of catalysts in homogenous catalysis. Here we report the palladium-template synthesis of the first imidazole-substituted tertiary phosphine bidentate ligand in which the C^2 carbon of the imidazole unit is involved in metal chelation.

In the absence of the transition-metal ion, no Diels–Alder reaction was observed between 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-vinylimidazole. Upon co-ordination to palladium, however, DMPP is activated towards the [4 + 2] cycloaddition reaction. Thus, when $[PdCl_2(DMPP)_2]$ or the organopalladium complex **1**[6] was treated with the dienophile in 1,2-dichloroethane at 84 °C, the *exo*-cycloadduct **2** was obtained as the sole product (Scheme 1).† When the template complex **1** was used, the cycloaddition reaction was completed in 30 d. Interestingly, during the course of heating, the N^3 nitrogen of the imidazole unit underwent a parallel N-alkylation reaction with 1,2-dichloroethane and produced HCl as the side product.[7] The HCl thus generated led to further chemoselective cleavage of the orthometallated benzylamine ligand from the palladium template and thus facilitate the formation of the dichloro complex **2** as the final product.[6] The molecular structure and the co-ordination chemistry of **2** have been determined by X-ray structural analysis (Fig. 1).‡ The study reveals that the reaction of **1** with 1-vinylimidazole in 1,2-dichloroethane has resulted in the removal of the benzylamine chelate and the imidazole substituted *exo*-phosphanorbornene ligand created co-ordinates to palladium as a bidentate chelate *via* the bridgehead phosphorus atom and the C^2 carbon atom of the imidazole group. The palladium atom is in a slightly distorted square-planar geometry with the bond angles in the ranges 84.8(1)–94.8(2) and 167.0(1)–172.2(2)°. Due to the aromaticity of the imidazole ring, all C–C and C–N bonds [1.350(8)–1.383(6) Å] within the five-membered ring are noticeably shorter than the two attached C–N bonds [1.473(7)–1.453(7) Å]. The Pd(1)–C(11) distance of 1.993(5) Å is similar to the Pd–C bonds observed in other reported complexes containing the orthometallated benzylamine [2.004(11) Å] and naphthylamine units (2.006 Å) which experience a similar *trans* electronic influence from a chloro ligand.[8] The Pd(1)–P(1) distance of 2.207(1) Å is also within the normal range observed for this class of phosphanorbornene complex. The Pd···Cl(3) distance is 3.622(2) Å indicating that there is no interaction between the two heavy atoms.

Interestingly, when $[PdCl_2(DMPP)_2]$ was used for the Diels–Alder reaction, a much lower reaction rate was observed. The ^{31}P NMR studies indicated that 80% of $[PdCl_2(DMPP)_2]$



Scheme 1

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† Preparation of complex **2**. A solution of the organopalladium complex **1** (0.46 g, 0.97 mmol) in 1,2-dichloroethane (40 cm^3) was treated with silver perchlorate (0.2 g, 0.97 mmol) in water (1 cm^3) for 30 min. The resulting mixture was filtered through a layer of Celite to remove silver chloride and the organic layer was dried over anhydrous $MgSO_4$. The dried solution was treated with 1-vinylimidazole (0.37 g, 3.87 mmol) and the reaction mixture was then stirred at 84 °C for 30 d. The solution was washed with water (50 cm^3) and then dried over $MgSO_4$. The solvent was removed under reduced pressure to give a yellow residue. Upon crystallization from acetonitrile–diethyl ether, the dichloro complex **2** was obtained as yellow prisms (0.21 g, 40%), m.p. 256–258 °C (decomp.). ^{31}P NMR ($CDCl_3$): δ 105.3 (s).

‡ Crystal data for **2**: $C_{19}H_{22}Cl_3N_2PPd$, $M = 522.11$, orthorhombic, space group $Pna2_1$, $a = 14.9398(1)$, $b = 16.5294(1)$, $c = 8.6207(1)$ Å, $U = 2128.85(3)$ Å^3, $Z = 4$, $D_c = 1.629$ g cm^{-3}, $T = 293$ K, μ(Mo-Kα) = 13.29 cm^{-1}, $F(000) = 1048$, $R1 = 0.0408$, $wR2 = 0.0885$ for 4214 independent observed reflections [$I > 2\sigma(I)$, $1.84 \leqslant 2\theta \leqslant 29.31°$] and 236 parameters. The Flack parameter was refined to −0.02(4). CCDC reference number 186/1018.

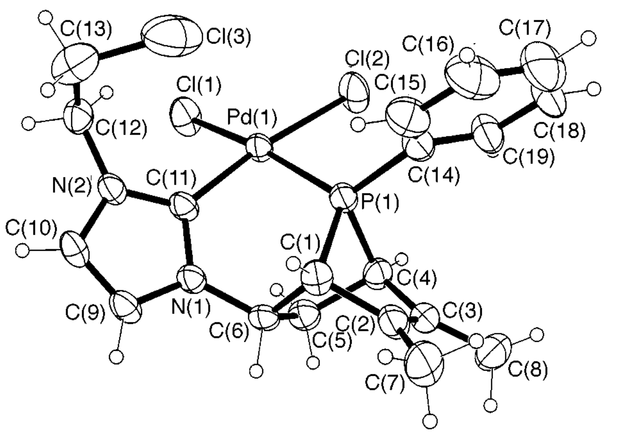

Fig. 1 Molecular structure and co-ordination chemistry of complex **2**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.207(1), Pd(1)–C(11) 1.993(5), Pd(1)–Cl(1) 2.391(2), Pd(1)–Cl(2) 2.358(2), P(1)–C(1) 1.859(6), P(1)–C(4) 1.842(5), N(1)–C(6) 1.473(7), N(1)–C(11) 1.375(7), N(1)–C(9) 1.383(6), C(9)–C(10) 1.350(8), C(10)–N(2) 1.381(7), N(2)–C(11) 1.357(7), N(2)–C(12) 1.453(7), C(13)–Cl(3) 1.781(9); P(1)–Pd–Cl(1) 167.0(1), P(1)–Pd–Cl(2) 84.8(1), P(1)–Pd–C(11) 87.8(2), C(11)–Pd–Cl(1) 94.8(2), C(11)–Pd–Cl(2) 172.2(2), Cl(1)–Pd–Cl(2) 92.0(1), C(1)–P(1)–C(4) 81.8(3), C(6)–N(1)–C(11) 124.0(4), N(1)–C(9)–C(10) 106.3, C(9)–C(10)–N(2) 107.7(4), C(10)–N(2)–C(11) 110.7(4), N(2)–C(11)–N(1) 104.4(4)

remains unchanged after the complex was treated with 1-vinylimidazole for 30 d under similar reaction conditions. Nevertheless, a small quantity of **2** was observed in the ^{31}P NMR spectra of the reaction mixture. Clearly, the co-ordinated cyclic diene in the template complex **1** receives a higher degree of activation as compared with its counterparts in $[PdCl_2(DMPP)_2]$. We are currently investigating the optical resolution and the catalytical properties of transition-metal complexes containing the imidazole-substituted phosphine ligand.

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