DALTON COMMUNICATION

Reactivity of chiral diiminodiphosphine ligands towards $PdCl_2(PhCN)_2$: synthesis and crystal structures of two unexpected dinuclear palladium(II) complexes

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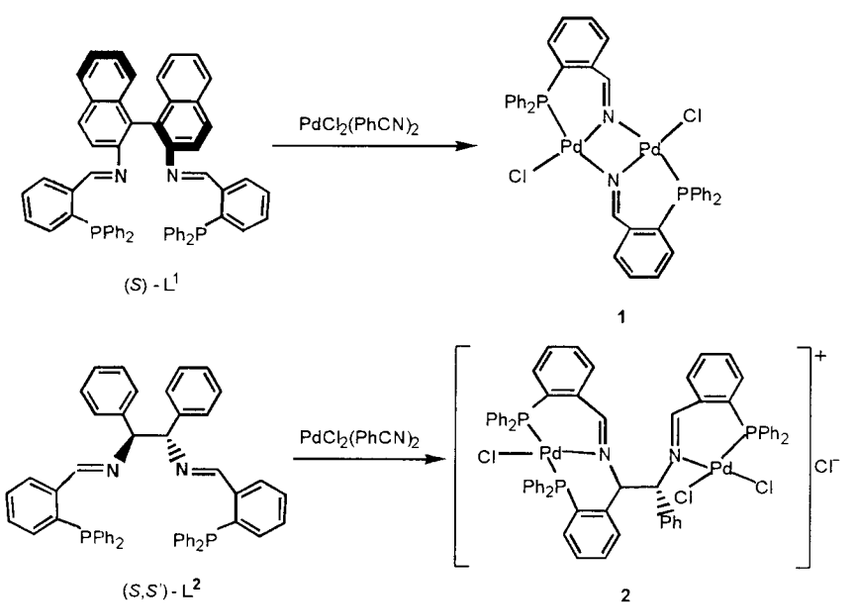
The interaction of $PdCl_2(PhCN)_2$ with (*S*)-*N*,*N*′-bis[2-(diphenylphosphino)benzylidene]-2,2′-diimino-1,1′-binaphthylene (*S*)-L^1 and (*S*,*S*′)-*N*,*N*′-bis[2-(diphenylphosphino)-benzylidene**]-1,2-diimino-1,2-diphenylethane (*S*,*S*′)-L^2 gave the dimeric complex $\{PdCl[2\text{-}(Ph_2P)C_6H_4CH{=}N]\}_2$ 1 and the dinuclear complex $\{cis\text{-}PdCl_2[2\text{-}(Ph_2P)C_6H_4CH{=}NCH(Ph)CH(C_6H_4PPh_2\text{-}2){=}NC_6H_4(PPh_2)\text{-}2]PdCl\}Cl$ 2, respectively, whose structures were ascertained by X-ray crystallography.**

Transition metal complexes with chiral diamino-, diimino- and diamido-diphosphine ligands have been shown to be effective catalysts for asymmetric hydrogen transfer reactions,[1] epoxidation[2] and allylic alkylation,[3] respectively. Thus, the synthesis of chiral diamino-, diimino- and diamido-diphosphine ligands and their application as auxiliaries for the preparation of chiral catalysts have aroused considerable recent interest. We have investigated the preparation and chemistry of diamino-, diimino- and diamido-diphosphine ligands[4] and reported the synthesis of *N*,*N*′-bis[2-(diphenylphosphino)benzylidene]-2,2′-diimino-1,1′-binaphthylene (L^1) and its Cu(I) and Ag(I) complexes.[5] Here we describe unexpected results of the reactions of $PdCl_2(PhCN)_2$ with (*S*)-L^1 and (*S*,*S*′)-*N*,*N*′-bis[2-(diphenylphosphino)benzylidene]-1,2-diimino-1,2-diphenylethane (*S*,*S*′)-L^2 (Scheme 1).

Unlike the reactions with Cu(I) and Ag(I), which gave the mononuclear tetrahedral complex $[(CuL^1)(BF_4)]$ or $[(AgL^1)(BF_4)]$,[5] (*S*)-L^1 reacted with $PdCl_2(PhCN)_2$ *via* elimination of the binaphthylene backbone to give the unexpected dimeric species $\{PdCl[2\text{-}(Ph_2P)C_6H_4CH{=}N]\}_2$ **1** in good yield (70%).† The structure of compound **1** was established by X-ray crystallography (Fig. 1).‡ Structural analysis revealed that (*S*)-L^1 has undergone cleavage at the binaphthylene C–N bonds to form two $[2\text{-}(Ph_2P)C_6H_4CH{=}N]^-$ units. The dimer is centrosymmetric with the palladium atoms adopting a slightly distorted square planar geometry. The $[2\text{-}(Ph_2P)C_6H_4CH{=}N]^-$ moiety behaves as a chelating ligand with P(1) and N(1) coordinated to Pd(1) forming a six-membered ring and as a bridging ligand with N(1) bonded unsymmetrically to two palladium centres. The nitrogen atom acts as a four-electron donor forming a σ-bond with Pd(1) [Pd(1)–N(1), 1.990(5) Å] and a dative bond with Pd(1*) [Pd(1*)–N(1), 2.105(6) Å]. The Pd(1*)–N(1) distance is comparable to the Pd–N distances [2.086(6), 2.164(6) Å] of $(PdL^3)Cl_2$ (L^3 = *N*,*N*′-bis[2-(diphenylphosphino)benzylidene]-2,2′diimino-1,1′-biphenylene).[6] Within the cleaved diimino-phosphino ligand, the N(1)–C(1) distance of 1.236(8) Å is in agreement with the C=N bond distance. The Pd(1), N(1), Pd(1*) and N(1*) atoms form a parallelogram with N(1)–Pd(1)–N(1*) and Pd(1)–N(1)–Pd(1*) angles being 79.9(2) and 100.1(2)°, respectively. The result is in contrast to the reaction of the analogous L^3 ligand with $PdCl_2(MeCN)_2$, which gives the mononuclear square planar complex $(PdL^3)Cl_2$.[6] This may be due to the fact that the biphenylene backbone is more flexible than the binaphthylene, and can thus accommodate a Pd(II)



Scheme 1

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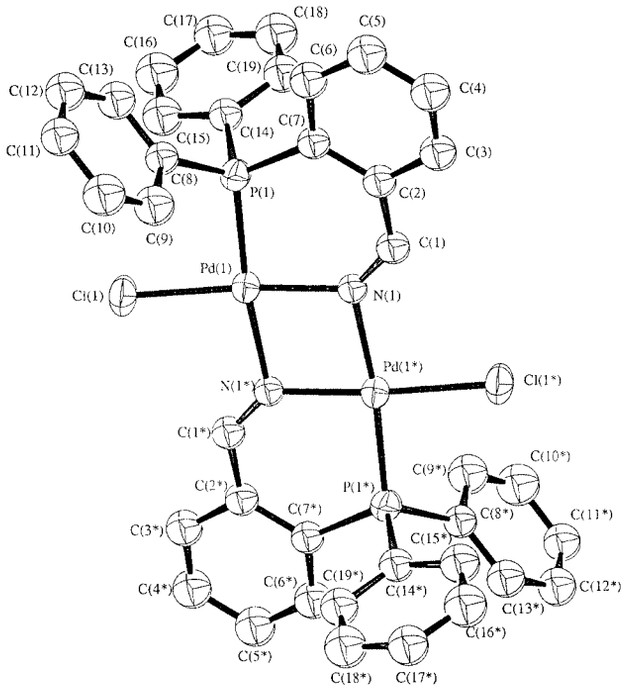

Fig. 1 A perspective drawing of compound **1**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.217(2), Pd(1)–Cl(1) 2.322(2), Pd(1)–N(1) 1.990(5), Pd(1)–N(1*) 2.105(6), N(1)–C(1) 1.236(8); P(1)–Pd(1)–N(1) 93.7(2), P(1)–Pd(1)–N(1*) 173.1(1), P(1)–Pd(1)–Cl(1) 91.46(7), Cl(1)–Pd(1)–N(1) 174.8(2), Cl(1)–Pd(1)–N(1*) 94.9(2), N(1)–Pd(1)–N(1*) 79.9(2), Pd(1)–N(1)–Pd(1*) 100.1(2), N(1)–C(1)–C(2) 132.1(6).

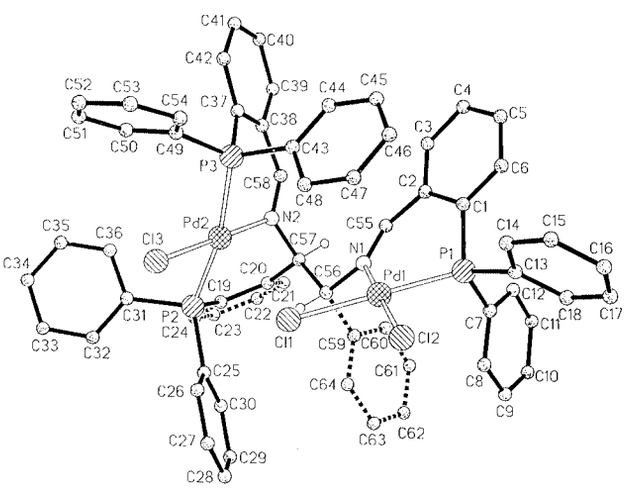

Fig. 2 A perspective drawing of the cation of compound **2**. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.216(2), Pd(1)–N(1) 2.079(4), Pd(1)–Cl(1) 2.346(2), Pd(1)–Cl(2) 2.280(2), Pd(2)–P(2) 2.340(1), Pd(2)–P(3) 2.304(1), Pd(2)–N(2) 2.059(4), Pd(2)–Cl(3) 2.298(2), N(1)–C(55) 1.272(6), N(1)–C(56) 1.528(6), N(2)–C(57) 1.500(6), N(2)–C(58) 1.271(6); N(1)–Pd(1)–P(1), 88.3(1), N(1)–Pd(1)–Cl(1) 92.8(1), N(1)–Pd(1)–Cl(2) 176.0(1), P(1)–Pd(1)–Cl(1) 178.59(5), P(1)–Pd(1)–Cl(2) 90.09(6), Cl(1)–Pd(1)–Cl(2) 88.87(6), N(2)–Pd(2)–Cl(3) 178.8(1), N(2)–Pd(2)–P(2) 91.61(11), N(2)–Pd(2)–P(3) 89.1(1), P(2)–Pd(2)–P(3) 166.68(5), P(2)–Pd(2)–Cl(3) 87.55(6), P(3)–Pd(2)–Cl(3) 91.52(5).

cation to form a square planar complex. These results suggest that the binaphthylene ligand, L^1, when behaving as a tetradentate chelating ligand, is sterically more rigid than the corresponding biphenylene ligand and prefers to form a tetrahedral complex.

The interaction of (*S*,*S*′)-L^2 with $PdCl_2(PhCN)_2$ in refluxing tetrahydrofuran gave a dinuclear complex {*cis*-$PdCl_2$[2-(Ph_2P)-C_6H_4CH=NCH(Ph)CH($C_6H_4PPh_2$-2)=NC_6H_4(PPh_2)-2]PdCl}-{Cl} **2**,† whose structure was established by X-ray crystallography (Fig. 2).‡ The structure analysis revealed that an *ortho* proton of one of the phenyl rings on the ethane backbone had been activated and replaced by a diphenylphosphino group. The resulting pentadentate ligand, with two imino and three phosphino donor groups, behaves as a bridging ligand and coordinates unsymmetrically to two different palladium centres in the complex cation. Both palladium atoms adopt a slightly distorted square planar geometry with the Pd(1) atom coordinated to an imino, a phosphino and two chloro groups having a *cis*-$PdCl_2$ arrangement; and the Pd(2) atom to an imino, a chloro and two phosphino groups having a *trans*-PdP_2 arrangement. The Pd–P [Pd(1)–P(1) 2.216(2), Pd(2)–P(2) 2.340(1), Pd(2)–P(3) 2.304(1) Å] and Pd–N distances [Pd(1)–N(1) 2.079(4), Pd(2)–N(2) 2.059(4) Å] are comparable to those of (PdL^3)Cl_2 [Pd–P 2.243(2), 2.262(2); Pd–N 2.086(6), 2.164(6) Å]. The N(1)–C(55) and N(2)–C(58) distances are 1.272(6) and 1.271(6) Å, respectively, and in agreement with the C=N bond distance. The ^{31}P NMR data, which are consistent with its solid-state structure show two doublets and a singlet at δ −2.9 (d, J_{PP} = 484), 23.1 (d, J_{PP} = 484 Hz) and 31.8 (s) for P(1), P(3) and P(2), respectively.

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Notes and references

† Synthetic procedures for compound **1**: A solution of (*S*)-L^1 (0.08 g, 0.1 mmol) in tetrahydrofuran was added dropwise to a solution of $PdCl_2(PhCN)_2$ (0.04 g, 0.1 mmol) in tetrahydrofuran (25 cm^3) at room temperature over a period of 15 minutes, during which a yellow precipitate was obtained. After stirring at room temperature for an additional 5 h, the precipitate was filtered, washed with diethyl ether (2 × 20 cm^3) and recrystallized from a chloroform–diethyl ether solution to give pale yellow crystals, which were filtered and dried *in vacuo*. Yield: 0.04 g, 70%; mp 221–222 °C. NMR ($CDCl_3$): ^{31}P, δ 27.5 (s); ^1H, δ 8.88 (d, 2H, J_{PH} = 9.7 Hz, -N=CH-), 6.80–7.75 (m, 28H, phenyl). IR (in KBr): $\nu_{C=N}$, 1621 cm^{-1}. Found (calc. for $C_{38}H_{30}Pd_2Cl_2N_2P_2\cdot 2CHCl_3$): C, 43.3 (43.7); H, 2.9 (2.9); N, 2.3 (2.6)%.

For compound **2**: A solution of (*S*,*S*′)-L^2 (0.11 g, 0.14 mmol) and $PdCl_2(PhCN)_2$ (0.05 g, 0.14 mmol) in tetrahydrofuran (25 cm^3) was refluxed for 8 h to give a yellow precipitate. The precipitate was filtered, washed with tetrahydrofuran and recrystallized from a mixture of DMF–methanol–diethyl ether to give yellow crystals, which were filtered and dried *in vacuo*. Yield: 0.07 g, 35%; mp 211–214 °C. ^{31}P NMR ($CDCl_3$): δ −2.9 (d, J_{PP} = 484), 23.1 (d, J_{PP} = 484 Hz), 31.8 (s). IR (in KBr): $\nu_{C=N}$, 1668vs, 1630s cm^{-1}. MS (FAB, +ve) *m*/*z*: 1257 [(M − 2Cl) for ^{106}Pd and ^{35}Cl]. Found (calc. for $C_{64}H_{51}Pd_2Cl_4N_2P_3\cdot C_3H_7NO\cdot 2CH_3OH$): C, 57.5 (57.9); H, 4.8 (4.6); N, 3.0 (2.9)%.

‡ Crystal data for **1**: $C_{38}H_{30}Pd_2Cl_2N_2P_2$, yellow plate, 0.03 × 0.24 × 0.25 mm, M = 860.32, monoclinic, $P2_1/n$ (no. 14), a = 9.889(1), b = 17.607(2), c = 10.282(1) Å, β = 107.90(1)°, V = 1703.6(3) $Å^3$, Z = 2, T = 298 K, μ(Mo-K_α) = 13.38 cm^{-1}, 16020 reflections measured, 2685 unique, final R = 0.047, Rw = 0.036 (based on F) for 1755 [$I > 1.5\sigma(I)$] observed reflections. For **2**·CH_3OH: $C_{64}H_{51}Pd_2Cl_4N_2P_3\cdot CH_3OH$, yellow prism, 0.16 × 0.16 × 0.40 mm, M = 1327.62, triclinic, $P\bar{1}$ (no. 2), a = 12.574(1), b = 13.636(1), c = 20.058(1) Å, α = 80.03(1), β = 75.67(1), γ = 81.04(1)°, V = 3258.8(4) $Å^3$, Z = 2, T = 293 K, μ(Mo-K_α) = 8.29 cm^{-1}, 9163 reflections measured, final R_1 = 0.061 for 7937 [$I > 2.0\ \sigma(I)$] observed reflections, wR_2 = 0.164 (based on F^2) for 9163 unique reflections. CCDC reference number 186/1913. See http://www.rsc.org/suppdata/dt/b0/b001245i/ for crystallographic files in .cif format.

1 J. X. Gao, T. Ikariya and R. Noyori, *Organometallics*, 1996, **15**, 1087.
2 R. M. Stoop and A. Mezzetti, *Green Chem.*, 1999, 39.
3 (*a*) B. M. Trost, *Acc. Chem. Res.*, 1996, **29**, 355; (*b*) C. P. Butts, J. Crosby, G. C. Lloyd-Jones and S. C. Stephen, *Chem. Commun.*, 1999, 1707 and refs. therein.
4 (*a*) J. X. Gao, H. L. Wan, W. K. Wong, M. C. Tse and W. T. Wong, *Polyhedron*, 1996, **15**, 1241; (*b*) W. K. Wong, T. W. Chik, X. Feng and T. C. W. Mak, *Polyhedron*, 1996, **15**, 3905; (*c*) W. K. Wong, T. W. Chik, K. N. Hui, I. Williams, X. Feng, T. C. W. Mak and C. M. Che, *Polyhedron*, 1996, **15**, 4447.
5 (*a*) W. K. Wong, J. X. Gao, W. T. Wong and C. M. Che, *Polyhedron*, 1993, **12**, 2063; (*b*) W. K. Wong, J. X. Gao, W. T. Wong, W. C. Cheng and C. M. Che, *J. Organomet. Chem.*, 1994, **471**, 277.
6 A. G. J. Ligtenbarg, E. K. van den Beuken, A. Meetsma, N. Veldman, W. J. J. Smeets, A. L. Spek and B. L. Feringa, *J. Chem. Soc., Dalton Trans.*, 1998, 263.