**SHORT PAPER**

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# Three new spirocyclic palladium(0) complexes containing diphosphines derived from *N,N′*-substituted ethylenediamines[†]

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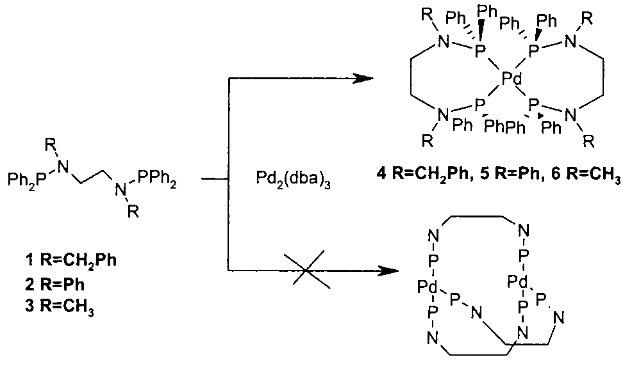
The reactions of $Ph_2PN(R)CH_2CH_2N(R)PPh_2$ (LL) (**1** R=$CH_2Ph$, **2** R=Ph, **3** R=$CH_3$) with $[Pd_2(dba)_3]$ (dba=dibenzylidene acetone) in $CH_2Cl_2$ yield mononuclear complexes of the type $[Pd(\eta^2\text{-}LL)_2]$ in good yield.

**Keywords:** spirocyclic palladium (0) complexes

Palladium complexes in their zero-valent state are found to be very valuable catalysts in organic synthesis.[1] Tertiary phosphines are excellent ligands to stabilise the metals in their low valent states.[2-4] Although, several bis(phosphine) bound palladium(0) complexes and bis-chelated palladium(II) cationic complexes are known; bis-chelated palladium(0) derivatives of the type $[Pd(\eta^2\text{-}LL)_2]$ [LL=bis(phosphine)] are rare. This may be due to the thermal sensitivity[5] of such complexes which on warming readily decompose to give metallic palladium and the free ligands. As a part of our study on platinum metal chemistry of phosphorus based ligands,[6-8] we report here the synthesis and characterisation of moderately air stable spirocyclic palladium(0) complexes containing diphosphines with an *N,N′*-substituted ethylenediamine framework. The new complexes have been characterised by mass, elemental analysis, IR and NMR ($^1H$ and $^{31}P$) spectroscopic data.

The reactions of $[Pd_2(dba)_3]$[9] with bis(phosphine)s **1–3** in benzene at room temperature afford the complexes **4–6** in 74–80% yield (Scheme 1). These complexes are moderately stable to air in solid state and in non-chlorinated organic solvents. In chlorinated organic solvents such as dichloromethane they readily decompose to give black metallic palladium. Although these complexes were analytically pure; attempts to grow suitable single crystals for X-ray studies have been unsuccessful. However, the chemical compositions of **4–6** are established by elemental analysis, mass and NMR spectroscopic data.

The $^{31}P\{^1H\}$ NMR spectra of complexes **4–6** exhibit single resonances at 30.6, 24.8 and 30.7 ppm respectively indicating the symmetric nature of the molecules. $^1H$ NMR data are quite consistent with the proposed structure of the complexes (see Experimental). Similar reactions of a diphosphazane ligand with a P–N–P framework have afforded novel dinuclear complexes of the type $[Pd_2(\mu\text{-}LL)_3]$ (LL=$X_2PN(R)PX_2$) containing three bridging ligands.[10] However, in the present investigation only mononuclear complexes were obtained as revealed by mass spectral data. The mass spectral data clearly indicate the mass corresponding to complexes containing two chelated diphosphine ligands. Analogous palladium(0) complex such as $[Pd(PPh_3)_4]$ have been extensively used as catalysts in organic synthesis. The three complexes obtained in the present investigation are moderately stable to air and can be easily synthesised and the application of these novel zerovalent palladium complexes in organic synthesis is under active investigation in our laboratory.



Scheme 1

## Experimental

$[Pd_2(dba)_3].CHCl_3$ (0.048 mmol) was dissolved in benzene (10 ml) in a 100 ml Schlenk apparatus under dinitrogen. $(Ph_2PN(R)CH_2)_2$ (**1** R=$CH_2Ph$, **2** R=Ph, **3** R=$CH_3$) (0.0193 mmol) in benzene (15 ml) was added dropwise with stirring. The mixture was stirred for 30 min. The dark violet solution turned orange red; stirring was continued for 2h. Solvent was evaporated under reduced pressure and the orange coloured product was extracted with hot hexane to remove dba. The product was crystallised from a 1:2 mixture of benzene and hexane to give analytically pure samples of **4–6**. **4**, (0.078g, 80%); m.p. 144–146°C; $^1H$ NMR ($CDCl_3$): $\delta$ 7.00–7.91 (m, 60H, phenyl), $\delta$ 3.82 (dd, 8H, $-CH_2C_6H_5$), $\delta$ 3.08 (dd, 8H, $CH_2CH_2$); HRMS: Mol. Wt. 1323.8; Found: C, 71.79; H, 5.63; N, 4.12%. $C_{80}H_{76}N_4P_4Pd$ requires C, 72.58; H, 5.78; N, 4.23%. **5**, yield (0.069g, 74%); m.p. 178–180°C (dec.); $^1H$ NMR ($CDCl_3$): $\delta$ 6.08–8.04 (m, 60H, phenyl), $\delta$ 3.53 (dd, 8H, $CH_2CH_2$); Found: C, 72.53; H, 5.32; N, 4.29%. $C_{76}H_{68}N_4P_4Pd$ requires C, 72.00; H, 5.40; N, 4.42%. **6**, yield (0.060g, 79%); m.p. 150–152°C (dec.); $^1H$ NMR ($CDCl_3$): $\delta$ 7.39–7.89 (m, 40H, phenyl), 2.83 (d, 12H,$-CH_3$), $\delta$ 3.53 (dd, 8H, $CH_2CH_2$); Found: C, 65.78 H, 5.75, N, 5.37%. $C_{56}H_{60}N_4P_4Pd$ requires C, 65.98; H, 5.93; N, 5.49%.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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