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Synthesis and coordination chemistry of N-doped polyphenylenes

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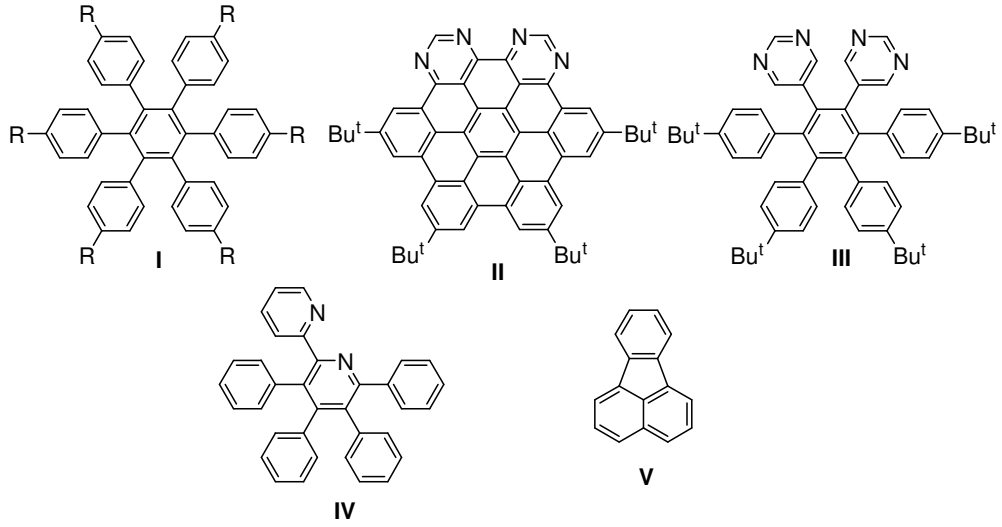
*The N-doped polyphenylene derivatives are expected to show interesting optical, electrochemical and structural properties. 8-Azafluoranthene ligands (**2a**) and (**2b**) were prepared by a Diels-Alder cycloaddition reaction between 2-cyanopyridine and the corresponding cyclopentadienone. Treatment of $[Mo(CO)_4(piperidine)_2]$ with ligands (**2**) gave the tetracarbonylmolybdenum(0) complexes $[Mo(CO)_4(\mathbf{2})]$ (**3**), in which the ligand is coordinated to the metal through both nitrogen donors. Treatment of (**2b**) with $[Pd(OAc)_2]$ gave the cyclometallated Pd(II) complex [Pd(OAc)(L)] (**4a**), in which L is an anionic terdentate-ligand. Treatment of (**2b**) with $[PdCl_2(NCPh)_2]$ gave the complex [PdCl(L)] (**4b**). The acetate group of (**4a**) can be easily replaced by halide ions to give [PdCl(L)] (**4b**), [PdBr(L)] (**4c**) and [PdI(L)] (**4d**), respectively. Treatment of (**4a**) with DMAP and PPh_3 in dichloromethane and the subsequent addition of NH_4PF_6 in methanol gave the corresponding salts $[Pd(DMAP)(L)]PF_6$ (**6a**) and $[Pd(PPh_3)(L)]PF_6$ (**6b**), respectively.*

Introduction

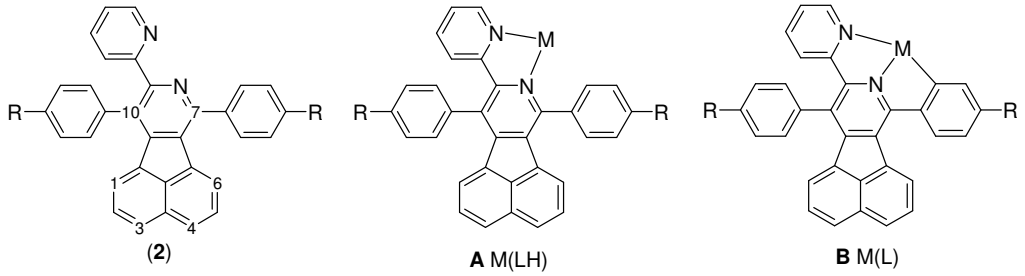
Polyphenylenes or hexaarylbenzene derivatives (**I**) are of considerable interest as they are the precursors for polycyclic aromatic hydrocarbons (Watson *et al* 2001). Introduction of heteroaromatic groups such as pyridyl and pyrimidyl into these systems opens the possibility for them to act as ligands. A few years ago we reported the synthesis of N-heterosuperbenzene (N-HSB) (**II**) by cyclodehydrogenation of the precursor (**III**) (Draper *et al* 2002). The N-doped graphene (**II**) and its transition metal complexes have shown interesting optical, electrochemical and structural properties (Draper *et al* 2004). Recently we reported the synthesis of a pyridyl-centred polyphenylene (**IV**) and its coordination chemistry, particularly with rhodium and palladium (Ollagnier *et al* 2008).

Figure 1 Some polyphenylene precursors and polycyclic aromatic hydrocarbons



Fluoranthene (**V**) is a fused ring system with three benzene rings linked to a central 5-membered ring. The presence of a fused 5-membered ring in the skeleton makes fluoranthene derivatives suitable for the preparation of curved molecules such as corannulene and semibuckminsterfullerene (Sygula & Rabidean, 1999). Fluoranthene derivatives can be cyclodehydrogenated to generate large aromatic sheets (Debad *et al* 1996 & Wehmeier *et al* 2001). In this paper we describe the synthesis of new ligands (**2a**) and (**2b**) based on 8-azafluoranthene, and their complexes with molybdenum(0) and palladium(II). (**2a**) and (**2b**) can be considered as bulky analogues of 6-phenyl-2,2'-bipyridine and they have the potential to coordinate to a metal centre in either bidentate or terdentate fashion *via* cyclometallation (see **A** and **B** in Figure 2).

Figure 2 Coordination modes of (**2**) to a metal centre M. R = H or Bu^t.



Methodology

All the experiments were carried out in an inert atmosphere (nitrogen or argon). Elemental analyses were carried out on a Carlo Erba 1006 automatic analyser. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. NMR spectra were recorded on a Bruker DPX 400 spectrometer (operating frequencies for ^{1}H and ^{13}C are 400.13 and 100.62 MHz, respectively) or Bruker Avance^{II} 600 spectrometer (operating frequencies for ^{1}H and ^{13}C are 600.13 and 150.9 MHz). ^{1}H and ^{13}C chemical shifts (δ) are in ppm with respect to TMS and coupling constants (J) are in Hz. Flash chromatography was carried out using silica gel as the stationary phase. Acenaphthenequinone was purchased from Aldrich. 7,9-Diphenyl-8H-cyclopenta[l] acenaphthylen-8-one (**1a**) was prepared according to a literature procedure (Wehmeier *et al* 2001).

7,9-Bis(4-tert-butylphenyl)-8H-cyclopenta[l]acenaphthylen-8-one (1b)

Acenaphthenequinone (400 mg, 2.19 mmol), 1,3-bis(4-*tert*-butylphenyl)propan-2-one (700 mg, 2.2 mmol) and NaOH (100 mg) were stirred at room temperature in MeOH (50 mL) for 24 h. The resulting black precipitate (**1b**) was filtered, washed with MeOH and dried in a vacuum. Yield (960 mg, 94%). An analytical sample was crystallised from CH_2Cl_2/MeOH. Found: C, 88.69; H, 6.79, calcd. (%) for $C_{35}H_{32}O{\cdot}0.1CH_2Cl_2$: C, 88.28; H, 6.80. IR (neat) cm^{-1}: 2958, 1701, 1473, 1360, 1271, 1130, 840, 825 and 773. ^{1}H-NMR (400 MHz,

$CDCl_3$): 8.12 (d, 2H, ^{3}J(HH) 7.0 Hz, H^3), 7.88 (d, 2H, ^{3}J(HH) 8.0, Hz, H^1), 7.80 (d, 4H, ^{3}J(HH) 8.0 Hz, H^4), 7.61 (app. t, 2H, ^{3}J(HH) 7.5 Hz, H^2), 7.57 (d, 4H, ^{3}J(HH) 8.0 Hz, H^5) and 1.42 (s, 18H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 202.0 (1C, C=O), 128.3 (2C, C^4), 127.9 (1C, C^2), 127.0 (1C, C^1), 125.1 (2C, C^5), 121.1 (C_{quat}), 120.4 (1C, C^3), 34.4 (CMe$_3$) and 30.9 (C*Me*$_3$).

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7,10-Diphenyl-9-(2-pyridyl)-8-azafluoranthene (2a)

7,9-Diphenyl-8H-cyclopenta[l]acenaphthylen-8-one (600 mg, 1.68 mmol) and 2-cyano pyridine (1.1 g, 11.6 mmol) were refluxed under nitrogen for 48 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using MeOH/ CH_2Cl_2 gave (**2a**) as a pale yellow crystalline solid. Yield (180 mg, 25%). Found: C, 87.30; H, 4.62; N, 6.23, calcd. (%) for $C_{32}H_{20}N_2.0{\cdot}1CH_2Cl_2$: C, 87.35; H, 4.58; N, 6.35. IR (neat) cm^{-1}: 3006, 1586, 1546, 1475, 1422, 1402, 1276, 1261, 828, 766, 749 and 704. ESI-MS (acetone, m/z): found: 433.1697, calcd. 433.1705, for $C_{32}H_{21}N_2$, $[M+1]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.52 (br, m, 1H, ^{3}J(HH) 5.0 Hz, H^{10}), 7.95 (m, 2H, H$^{4'}$), 7.91 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1), 7.87 (d, 1H, ^{3}J(HH) 8.0 Hz, H$^{1'}$), 7.63-7.55 (m, 5H, H$^{3'}$, H$^{5'}$, H$^{6'}$ and H^8), 7.52-7.49 (m, 2H, H$^{2'}$ and H^7), 7.46-7.40 (m, 6H, H^2, H^4, H^5 and H^6), 7.12 (m, 1H, ^{3}J(HH) 5.0, 7.5 Hz, ^{4}J(HH) 1.5 Hz, H^9) and 7.00 (d, 1H, ^{3}J(HH) 7.0, Hz, H^3). ^{13}C-NMR (100 MHz, $CDCl_3$): 148.4 (1C, C^{10}), 135.2 (1C, C^8), 129.6 (2C, C^4), 128.8 (2C, C$^{4'}$), 128.5 (1C, C^1), 128.3 (1C, C$^{6'}$), 128.2 (2C, C$^{5'}$), 128.1 (2C, C^5), 127.5 (1C, C^6), 127.3 (1C, C$^{2'}$), 127.2 (1C, C^2), 127.0 (1C, C$^{1'}$), 124.9 (1C, C^3), 124.6 (1C, C^7), 123.4 (1C, C$^{3'}$) and 121.6 (1C, C^9).

7,10-Di(4-tert-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (2b) (LH)

Bis(4-*tert*-butylphenyl)-8H-cyclopenta[l]acenaphthylen-8-one (700 mg, 1.49 mmol) and 2-cyanopyridine (2.0 g) were refluxed under nitrogen for 60 h. The resulting brownish red solution was allowed to cool. Chromatography on silica using MeOH and CH_2Cl_2 gave (**2b**) as a pale yellow crystalline solid. Yield (310 mg, 38%). Found: C, 88.69; H, 6.79, calcd. (%) for $C_{35}H_{32}O{\cdot}0.1CH_2Cl_2$: C, 88.28; H, 6.80. IR (neat) cm^{-1}: 2958, 1701, 1473, 1360, 1271, 1130, 840, 825 and 773. ESI-MS (acetone, m/z): found: 545.2953, calcd. 545.2957, for $C_{40}H_{37}N_2$, $[M+1]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.52 (br, m, 1H, ^{3}J(HH) 4.0 Hz, H^{10}), 7.91 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1), 7.90 (d, 2H, ^{3}J(HH) 8.5 Hz, H$^{4'}$), 7.87 (d, 1H, ^{3}J(HH) 8.0 Hz, H$^{1'}$), 7.72 (d, 1H, ^{3}J(HH) 7.0 Hz, H$^{3'}$), 7.61 (d, 2H, ^{3}J(HH) 8.5 Hz, H$^{5'}$), 7.55-7.51 (m, 2H, H$^{2'}$ and H^8), 7.47-7.44 (m, 3H, ^{3}J(HH)

8.5 Hz, H^5 and H^2), 7.43 (d, 1H, ^3J(HH) 8.0 Hz, H^7), 7.35 (d, 2H, ^3J(HH) 8.5 Hz, H^4), 7.12 (m, 1H, H^9), 7.02 (d, 1H, ^3J(HH) 7.0, Hz, H^3), 1.45 (s, 9H, CMe_3) and 1.41 (s, 9H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ in ppm): 148.3 (1C, C^{10}), 134.9 (1C, C^8), 129.2 (2C, C^4), 128.4 (2C, $C^{4'}$), 128.3 (1C, C^1), 127.5 (1C, $C^{2'}$), 127.3 (1C, C^2), 126.9 (1C, $C^{1'}$), 125.0 (2C, $C^{5'}$), 124.9 (2C, C^5), 124.8 (1C, C^3), 124.6 (1C, C^7), 123.4 (1C, $C^{3'}$), 121.5 (1C, C^9), 34.4 (1C, *C*Me_3), 34.2 (1C, *C*Me_3) and 31.0 (6C, C*Me*$_3$).

[Mo(CO)$_4$(2a)] (3a)

A solution containing (**2a**) (20 mg, 0.046 mmol) and [Mo(CO)$_4$(piperidine)$_2$] (17 mg, 0.046 mmol) in CH_2Cl_2 (1.5 mL) was stirred at room temperature for 30 min. The resulting dark brown solution was concentrated to a low volume (*ca.* 0.5 mL); the addition of methanol gave (**3a**) as black crystals (29 mg, 97%). Found: C, 57.99; H, 3.02; N, 3.62, calcd. (%) for $C_{36}H_{20}N_2O_4Mo \cdot 1.5CH_2Cl_2$: C, 58.70; H, 3.01; N, 3.64. IR (neat, ν, cm^{-1}): 2005, 1863, 1823, 1420, 1408, 828, 766 and 700. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.24 (br, d, 1H, ^3J(HH) 5.5 Hz, H^{10}), 7.98 (d, 1H, ^3J(HH) 8.0 Hz, H^1 or $H^{1'}$), 7.91 (d, 1H, ^3J(HH) 8.5 Hz, H^1 or $H^{1'}$), 7.75-7.71 (m, 6H, Ph), 7.67-7.65 (m, 2H, Ph), 7.59-7.57 (m, 2H, Ph), 7.48-7.44 (m, 2H, H^2 and $H^{2'}$), 7.41 (m, 1H, ^3J(HH) 7.5 Hz, ^4J(HH) 1.5 Hz, H^8), 7.23 (d, 1H, ^3J(HH) 8.5 Hz, H^7), 7.16 (m, 1H, ^3J(HH) 5.5 Hz, ^4J(HH) 1.5 Hz, H^9), 6.79 (d, 1H, ^3J(HH) 7.5 Hz, H^3 or $H^{3'}$) and 6.66 (d, 1H, ^3J(HH) 7.0 Hz, H^3 or $H^{3'}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 225.7 (1C, C≡O), 217.1 (1C, C≡O), 204.6 (2C, C≡O), 152.5 (1C, C^{10}), 134.9 (1C, C^8), 130.0 (1C, Ph), 129.7 (1C, C^1 or $C^{1'}$), 129.4 (2C, Ph), 129.1 (1C, Ph), 129.0 (2C, Ph), 128.9 (2C, Ph), 128.4 (2C, Ph), 128.2 (1C, C^1 or $C^{1'}$), 127.9 (1C, C^2 or $C^{2'}$), 127.6 (1C, C^2 or $C^{2'}$), 126.9 (1C, C^7), 126.3 (1C, C^3 or $C^{3'}$), 125.4 (1C, C^3 or $C^{3'}$) and 122.9 (1C, C^9).

[Mo(CO)$_4$(2b)] (3b)

A solution containing (**2b**) (20 mg, 0.036 mmol) and [Mo(CO)$_4$(piperidine)$_2$] (13.8 mg, 0.036 mmol) in CH_2Cl_2 (2 mL) was stirred at 20 °C for 30 min. The resulting dark brown solution was concentrated to a low volume (*ca.* 0.5 mL), then MeOH was added to give (**3b**) as black crystals (23 mg, 83%). Found: C, 69.87; H, 4.81; N, 3.65, calcd. (%) for $C_{44}H_{36}N_2O_4Mo$: C, 70.21; H, 4.82; N, 3.72. IR (neat, ν, cm^{-1}): 2963, 2001, 1872, 1829, 1815, 1422, 1118, 828 and 779. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.23 (br, d, 1H, ^3J(HH) 4.5 Hz, H^{10}), 7.97 (d, 1H, ^3J(HH) 8.0 Hz, H^1 or $H^{1'}$), 7.90 (d, 1H, ^3J(HH) 8.0 Hz, H^1 or $H^{1'}$), 7.73 (d, 2H, ^3J(HH) 8.5 Hz, H^5 or $H^{5'}$), 7.71 (d, 2H, ^3J(HH) 8.5 Hz, H^5 or $H^{5'}$), 7.58 (d, 2H, ^3J(HH) 8.5 Hz, H^4 or $H^{4'}$), 7.47 (d, 2H, ^3J(HH) 8.5 Hz, H^4 or $H^{4'}$), 7.48-7.44 (m, 2H, H^2 and $H^{2'}$), 7.36 (m, 1H, ^3J(HH) 8.5 Hz,

^{4}J(HH) 1.5 Hz, H^8), 7.20 (d, 1H, ^{3}J(HH) 8.0 Hz, H^7), 7.13 (br, m, 1H, H^9), 6.81 (d, 1H, ^{3}J(HH) 7.5 Hz, H^3 or H$^{3'}$), 6.72 (d, 1H, ^{3}J(HH) 7.0 Hz, H^3 or H$^{3'}$), 1.52 (s, 9H, CMe$_3$) and 1.51 (s, 9H, CMe$_3$). ^{13}C-NMR: 225.8 (1C, C≡O), 216.6 (1C, C≡O), 204.8 (2C, C≡O), 152.4 (1C, C^{10}), 134.7 (1C, C^8), 129.7 (1C, C^1 or C$^{1'}$), 128.6 (Ar), 128.0 (1C, C^1 or C$^{1'}$), 127.9 (Ar and C^2 or C$^{2'}$), 127.5(1C, C^2 or C$^{2'}$), 126.8 (1C, C^7), 126.8 (Ar), 126.3 (1C, C^3 or C$^{3'}$), 125.7 (Ar), 125.4 (1C, C^3 or C$^{3'}$), 122.7 (1C, C^9), 34.61 (1C, *C*Me$_3$), 34.58 (1C, *C*Me$_3$), 31.1 (3C,C*Me*$_3$) and 31.0 (3C, C*Me*$_3$).

[Pd(OAc)(L)] (4a)

A solution containing (**2b**) (40 mg, 0.073 mmol) and [Pd(OAc)$_2$] (16.5 mg, 0.073 mmol) in CH_2Cl_2 (4 mL) was refluxed for 3 h. The solution was concentrated to a low volume (*ca.* 1 mL) then diethyl ether was added to give (**4a**) as a yellow solid (49 mg, 94%). Found: C, 69.33; H, 5.13; N 3.69, calcd. (%) for $C_{42}H_{38}N_2O_2Pd{\cdot}0.2CH_2Cl_2$: C, 69.79; H, 5.33; N 3.86. IR (neat, ν, cm^{-1}): 2962, 1619 (C=O), 1584, 1420, 1368, 1319, 1266, 824, 781 and 669. ESI-MS (acetone, m/z): found: 649.1848, calcd. 649.1835 for $C_{40}H_{35}N_2Pd$, [M-OAc]$^+$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 8.81 (d, 1H, ^{3}J(HH) 7.0 Hz, H$^{3'}$), 8.61 (br, d, 1H, ^{3}J(HH) 5.0 Hz, H^{10}), 8.21 (d, 1H, ^{3}J(HH) 8.0 Hz, H^{13}), 8.02 (d, 1H, ^{3}J(HH) 7.5 Hz, H$^{1'}$), 8.02 (d, 1H, ^{3}J(HH) 7.5 Hz, H^1), 7.77 (t, 1H, ^{3}J(HH) 7.5 Hz, H$^{2'}$), 7.74 (d, 2H, ^{3}J(HH) 8.0 Hz, H^5), 7.47 (d, 1H, ^{4}J(HH) 1.5 Hz, H^{11}), 7.47 (m, 1H, ^{4}J(HH) 1.5 Hz, H^8, overlaps with H^{11}), 7.40 (m, 1H, H^2, overlaps with H^4), 7.40 (d, 2H, ^{3}J(HH) 8.0 Hz, H^4), 7.35 (m, 1H, H^9), 7.26 (dd, 1H, ^{3}J(HH) 8.0 Hz, ^{4}J(HH) 1.5 Hz, H^{12}), 6.83 (d, 1H, ^{3}J(HH) 8.5 Hz, H^7), 6.46 (d, 1H, ^{3}J(HH) 7.0 Hz, H^3), 1.53 (s, 9H, CMe$_3$) and 1.43 (s, 9H, CMe$_3$). ^{13}C-NMR: 177.5 (C=O), 160.4 (C$_{quat}$, PdC), 149.8 (1C, C^{10}), 137.6 (1C, C^8), 129.9 (1C, C^{11}), 129.6 (1C, C$^{1'}$), 128.4 (1C, C^1), 128.2 (2C, C^4), 127.6 (1C, C^2), 127.5 (1C, C$^{2'}$), 127.1 (2C, C^5), 126.2 (1C, C^{13}), 125.6 (1C, C^3), 125.6 (1C, C$^{3'}$), 125.3 (1C, C^7), 125.1 (1C, C^9),120.9 (1C, C^{12}), 34.71 (*C*Me$_3$), 34.65 (*C*Me$_3$), 31.0 (C*Me*$_3$), 30.8 (C*Me*$_3$) and 23.8 (C(=O)*Me*).

[PdCl(L)] (4b)

A solution containing the ligand (**2b**) (20 mg, 0.037 mmol) and [$PdCl_2$(NCPh)$_2$] (14mg, 0.037 mmol) in CH_2Cl_2 (2 mL) was refluxed for 45 min to give a yellow precipitate. The solution was concentrated to a low volume and the yellow precipitate (**4b)** was filtered and washed with methanol, (22 mg, 88%). Found: C, 69.62; H, 5.12; N 3.88, calcd. (%) for $C_{40}H_{35}N_2ClPd$: C, 70.07; H, 5.15; N 4.09. IR (neat, ν, cm^{-1}): 2949, 1546, 1582, 1422, 826 and 772. ESI-MS (MeCN, m/z): found: 649.1855; calcd. 649.1835 for $C_{40}H_{35}N_2Pd$, [M-Cl]$^+$. ^{1}H-NMR (400 MHz,

$CDCl_3$): 9.06 (br, m, 1H, H^{10}), 8.83 (d, 1H, ^3J(HH) 7.5 Hz, $H^{3'}$), 8.24 (d, 1H, ^3J(HH) 8.0 Hz, H^{13}), 8.05 (d, 1H, ^4J(HH) 2.0 Hz, H^{11}), 8.04 (d, 1H, ^3J(HH) 8.0 Hz, $H^{1'}$), 8.02 (d, 1H, ^3J(HH) 7.5 Hz, H^1), 7.78 (t, 1H, ^3J(HH) 7.5 Hz, $H^{2'}$), 7.76 (d, 2H, ^3J(HH) 8.0 Hz, H^5), 7.51 (dt, 1H, ^3J(HH) 8.0 Hz, ^4J(HH) 1.5 Hz, H^8), 7.44 (d, 2H, ^3J(HH) 8.0 Hz, H^4), 7.39 (m, 2H, H^2 & H^9), 7.26 (dd, 1H, ^3J(HH) 8.0 Hz, ^4J(HH) 2.0 Hz, H^{12}), 6.84 (d, 1H, ^3J(HH) 8.5 Hz, H^7), 6.48 (d, 1H, ^3J(HH) 7.5 Hz, H^3), 1.54 (s, 9H, CMe_3) and 1.45 (s, 9H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 150.0 (1C, C^{10}), 133.8 (1C, C^{11}), 138.1 (1C, C^8), 130.1 (1C, C^1), 128.9 (1C, $C^{1'}$), 128.8 (2C, C^4), 128.1 (1C, C^2), 128.1 (1C, $C^{2'}$), 127.6 (2C, C^5), 126.3 (1C, C^{13}), 126.7 (1C, C^3), 126.2 (1C, $C^{3'}$), 125.6 (1C, C^7), 125.4 (1C, C^9) and 121.2 (1C, C^{12}).

[PdCl(L)] (4b) *from* ***(4a)***

A solution of NH_4Cl (6 mg, 0.112 mmol) in methanol (1 mL) was added to a suspension of (**4a**) (15 mg, 0.021 mmol) in acetone (4 mL) and dichloromethane (1 mL). The reaction mixture was stirred at room temperature for 15 h; the solvent was then removed and the product extracted into dichloromethane. The combined extract was concentrated and methanol was added to give the required product (**4b)** as a yellow solid, (12 mg, 83%).

[PdBr(L)] (4c) *from* ***(4a)***

A solution of NaBr (11 mg, 0.109 mmol) in methanol (1 mL) was added to a suspension of (**4a**) (13 mg, 0.0183 mmol) in acetone (4 mL) and dichloromethane (1 mL). The reaction mixture was stirred at room temperature for 24 h; the solvent was then removed and the residue was extracted with dichloromethane. The combined extract was concentrated and methanol was added to give the required product (**4c)** as a yellow solid, (11 mg, 83%). Found: C, 65.55; H, 4.80; N 3.57, calcd. (%) for $C_{40}H_{35}N_2BrPd$: C, 65.81; H, 4.83; N 3.84. IR (neat, ν, cm^{-1}): 2960, 1582, 1545, 1421, 1276, 1261, 824, 765 and 750. ESI-MS (acetonitrile, m/z): found: 649.1823; calcd. 649.1835 for $C_{40}H_{35}N_2Pd$, $[M\text{-}Br]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 9.21 (dd, 1H, ^3J(HH) 5.0 Hz, ^4J(HH) 2.0 Hz, H^{10}), 8.81 (d, 1H, ^3J(HH) 7.0 Hz, $H^{3'}$), 8.28 (d, 1H, ^4J(HH) 2.0 Hz, H^{11}), 8.23 (d, 1H, ^3J(HH) 8.0 Hz, H^{13}), 8.03 (d, 1H, ^3J(HH) 8.0 Hz, $H^{1'}$), 8.01 (d, 1H, ^3J(HH) 8.0 Hz, H^1), 7.78 (t, 1H, ^3J(HH) 8.0 Hz, $H^{2'}$), 7.76 (d, 2H, ^3J(HH) 8.5 Hz, H^5), 7.49 (dt, 1H, ^3J(HH) 8.0 Hz, ^4J(HH) 1.5 Hz, H^8), 7.43 (d, 2H, ^3J(HH) 8.5 Hz, H^4), 7.42 (m, 1H, H^2 overlap with H^4), 7.35 (m, 1H, ^3J(HH) 5.0 Hz, ^4J(HH) 1.5 Hz, H^9), 7.25 (dd, 1H, ^3J(HH) 8.5 Hz, ^4J(HH) 2.0 Hz, H^{12}), 6.85 (d, 1H, ^3J(HH) 8.5 Hz, H^7), 6.48 (d, 1H, ^3J(HH) 7.5 Hz, H^3), 1.54 (s, 9H, CMe_3) and 1.44 (s,

9H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$): 151.1 (1C, C^{10}), 136.4 (1C, C^{11}), 137.9 (1C, C^8), 130.1 (1C, C^1), 129.0 (1C, $C^{1'}$), 128.8 (2C, C^4), 128.0 (1C, C^2), 128.1 (1C, $C^{2'}$), 127.6 (2C, C^5), 126.4 (1C, C^{13}), 126.7 (1C, C^3), 126.2 (1C, $C^{3'}$), 125.7 (1C, C^7), 125.6 (1C, C^9) and 121.0 (1C, C^{12}).

[PdBr(L)] (4c) *from* ***(4b)***

A solution of NaBr (11 mg, 0.109 mmol) in methanol (1 mL) was added to a suspension of (**4b**) (13 mg, 0.0189 mmol) in acetone (4 mL) and CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature for 20 h; the solvent was then removed and the residue was extracted with dichloromethane. The combined extract was concentrated and methanol was added to give the required product (**4c)** as a yellow solid, (13 mg, 94%).

[PdI(L)] (4d)

To a suspension of (**4a**) (15 mg, 0.021 mmol) in acetone (4 mL) and CH_2Cl_2 (1 mL) was added NaI (16 mg, 0.105 mmol). The reaction mixture was stirred at room temperature for 20 h; the solvent was then removed and the residue extracted with CH_2Cl_2. The combined extract was concentrated and added methanol to give the required product (**4d)** as a yellow solid, (15 mg, 91%). Found: C, 61.46; H, 4.53; N 3.34, calcd. (%) for $C_{40}H_{35}N_2IPd$: C, 61.83; H, 4.54; N 3.61. IR (neat, ν, cm^{-1}): 2960, 1584, 1547, 1420, 824 and 771. ESI-MS (acetonitrile, m/z): found: 649.1865; calcd. 649.1835 for $C_{40}H_{35}N_2Pd$, $[M\text{-}I]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 9.45 (dd, 1H, ^{3}J(HH) 5.0 Hz, ^{4}J(HH) 1.0 Hz, H^{10}), 8.80 (d, 1H, ^{3}J(HH) 7.0 Hz, $H^{3'}$), 8.65 (d, 1H, ^{4}J(HH) 2.0 Hz, H^{11}), 8.23 (d, 1H, ^{3}J(HH) 8.0 Hz, H^{13}), 8.04 (d, 1H, ^{3}J(HH) 8.0 Hz, $H^{1'}$), 8.02 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1), 7.76 (t, 1H, ^{3}J(HH) 8.0 Hz, $H^{2'}$), 7.75 (d, 2H, ^{3}J(HH) 8.5 Hz, H^5), 7.48 (dt, 1H, ^{3}J(HH) 8.0 Hz, ^{4}J(HH) 1.5 Hz, H^8), 7.42 (d, 2H, ^{3}J(HH) 8.5 Hz, H^4), 7.42 (m, 1H, H^2, overlap with H^4), 7.33 (m, 1H, ^{3}J(HH) 7.5 Hz, ^{4}J(HH) 1.0 Hz, H^9), 7.23 (dd, 1H, ^{3}J(HH) 8.0 Hz, ^{4}J(HH) 2.0 Hz, H^{12}), 6.88 (d, 1H, ^{3}J(HH) 8.0 Hz, H^7), 6.48 (d, 1H, ^{3}J(HH) 7.0 Hz, H^3), 1.54 (s, 9H, CMe_3) and 1.43 (s, 9H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ in ppm): 153.4 (1C, C^{10}), 141.4 (1C, C^{11}), 137.5 (1C, C^8), 130.1 (1C, C^1), 129.0 (1C, $C^{1'}$), 128.8 (2C, C^4), 128.1 (1C, C^2), 128.1 (1C, $C^{2'}$), 127.6 (2C, C^5), 126.7 (1C, C^{13}), 126.7 (1C, C^3), 126.1 (1C, $C^{3'}$), 125.9 (1C, C^7), 125.8 (1C, C^9) and 120.6 (1C, C^{12}).

[(η³-methallyl)Pd(2b)]PF₆ (5)

The ligand (**2b**) (20 mg, 0.037 mmol) and $[(\eta^3\text{-metallyl})Pd(\mu\text{-Cl})]_2$ (7.2 mg, 0.018 mmol) were dissolved in dichloromethane (1 mL). After

15 min, a solution of NH_4PF_6 (12 mg, 0.073 mmol) in methanol (1 mL) was added. The solution was concentrated to yield the required product (**5**) as a yellow solid (26 mg, 81%). Found: C, 61.31; H, 5.02; N 3.18, calcd. (%) for $C_{44}H_{43}N_2PF_6Pd{\cdot}0.2CH_2Cl_2$: C, 61.14; H, 5.04; N 3.22. IR (neat, ν, cm^{-1}): 2959, 1610, 1559, 1476, 1460, 1420, 1275, 1267, 1116 and 829. ESI-MS (acetone, m/z): found: 705.2438; calcd. 705.2461 for $C_{44}H_{43}N_2Pd$, $[M\text{-}PF_6]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 8.92 (br, d, 1H, ^{3}J(HH) 4.5 Hz, H^{10}), 8.06 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1 or H$^{1'}$), 7.99 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1 or H$^{1'}$), 7.78-7.76 (m, 6H, H^5, H$^{4'}$ and H$^{5'}$), 7.62-7.54 (m, 4H, H^2, H$^{2'}$, H^8 and H^9), 7.52 (d, 2H, ^{3}J(HH) 8.0 Hz, H^4), 7.18 (d, 2H, ^{3}J(HH) 7.0 Hz, H^3 and H$^{3'}$), 6.89 (d, 1H, ^{3}J(HH) 7.0 Hz, H^7), 3.99 (br, 1H, allyl-H), 3.30 (br, 1H, allyl-H), 2.48 (br, 1H, allyl-H), 2.01 (s, 3H, Me), 1.85 (br, 1H, allyl-H), 1.51 (s, 9H, CMe_3) and 1.53 (s, 9H, CMe_3). ^{13}C-NMR (100 MHz, $CDCl_3$, δ in ppm): 153.9 (1C, C^{10}), 138.1 (1C, C^8), 130.6 (1C, C^1 or C$^{1'}$), 129.3 (C_{quat}), 129.1 (1C, C^1 or C$^{1'}$), 128.9 (Ar), 128.4 (Ar), 128.1 (C^2 or C$^{2'}$), 127.9 (1C, C^2 or C$^{2'}$), 127.5 (1C, C^7), 127.1 (Ar), 126.2 (1C, C^3 or C$^{3'}$), 125.7 (Ar), 125.5 (1C, C^3 or C$^{3'}$), 125.4 (1C, C^9), 34.8 (1C, *C*Me$_3$), 34.7 (1C, *C*Me$_3$), 31.0 (3C,C*Me*$_3$), 31.0 (3C, C*Me*$_3$) and 22.1 (1C, Me).

[Pd(DMAP)(L)]PF$_6$ (6a)

To a suspension of (**4a**) (14 mg, 0.0197 mmol) in CH_2Cl_2 (2 mL) was added 4-dimethylaminopyridine (DMAP) (10 mg, 0.082 mmol) followed by NH_4PF_6 (12 mg, 0.073 mmol) in methanol (1 mL). After 15 min, the resulting pale yellow solution was concentrated to give (**6a**) as a yellow solid, (16 mg, 89%). Found: C, 60.29; H, 4.82; N 5.90, calcd. (%) for $C_{47}H_{45}N_4PF_6Pd{\cdot}0.25CH_2Cl_2$: C, 60.47; H, 4.89; N 5.98. IR (neat, ν, cm^{-1}): 2948, 1618, 1541, 1422, 1392, 1275, 1261, 1224, 835, 750 and 764. ESI-MS (acetone, m/z): found: 771.2663; calcd. 771.2679 for $C_{47}H_{45}N_4Pd$, $[M\text{-}PF_6]^+$. ^{1}H-NMR (600 MHz, $CDCl_3$, δ in ppm): 8.81 (d, 1H, ^{3}J(HH) 7.5 Hz, H$^{3'}$), 8.40 (d, 2H, ^{3}J(HH) 7.0 Hz, H^2 of DMAP), 8.35 (d, 1H, ^{3}J(HH) 8.0 Hz, H^{13}), 8.09 (d, 1H, ^{3}J(HH) 8.0 Hz, H$^{1'}$), 8.06 (d, 1H, ^{3}J(HH) 8.0 Hz, H^1), 8.04 (br, d, 1H, ^{3}J(HH) 6.5 Hz, H^{10}, overlaps with H^4), 7.82 (t, 1H, ^{3}J(HH) 8.0 Hz, H$^{2'}$), 7.79 (d, 2H, ^{3}J(HH) 8.5 Hz, H^5), 7.65 (m, 1H, ^{3}J(HH) 6.5 Hz, H^9), 7.59 (m, 1H, ^{3}J(HH) 8.0 Hz, ^{4}J(HH) 1.5 Hz, H^8), 7.42 (m, 1H, ^{3}J(HH) 8.0 Hz, H^2 overlaps with H^4), 7.43 (d, 2H, ^{3}J(HH) 8.5 Hz, H^4), 7.34 (dd, 1H, ^{3}J(HH) 8.5 Hz, ^{4}J(HH) 2.0 Hz, H^{12}), 6.92 (d, 1H, ^{3}J(HH) 8.5 Hz, H^7), 6.84 (d, 2H, ^{3}J(HH) 7.0 Hz, H^3 of DMAP), 6.82 (d, 1H, ^{4}J(HH) 2.0 Hz, H^{11}), 6.53 (d, 1H, ^{3}J(HH) 7.0 Hz, H^3), 3.23 (s, 6H, NMe_2),1.55 (s, 9H, CMe_3) and 1.32 (s, 9H, CMe_3). ^{13}C-NMR (150.9 MHz, $CDCl_3$, δ in ppm): 150.4 (1C, C^{10}), 139.3 (1C, C^8), 131.1 (1C, C^{11}), 130.6 (1C, C^1), 129.4 (1C, C$^{1'}$), 128.6 (2C, C^4), 128.3

(1C, C^{2}), 128.1 (1C, $C^{2'}$), 127.8 (2C, C^{5}), 127.7 (1C, C^{9}), 127.4 (1C, C^{7}), 127.3 (1C, C^{3}), 126.9 (1C, C^{13}), 126.2 (1C, $C^{3'}$) and 122.1 (1C, C^{12}).

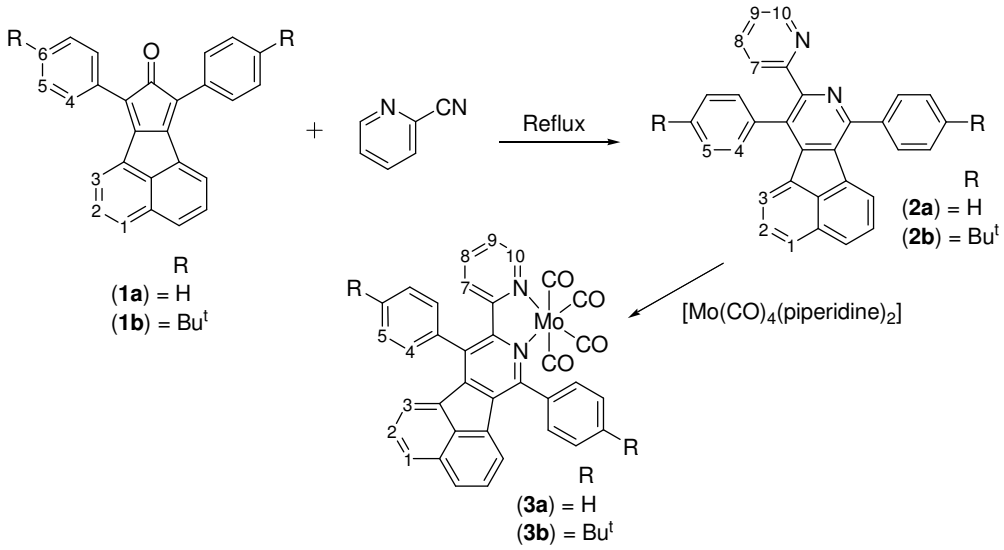
[Pd(PPh_3)(L)]PF_6 (6b)

To a solution of (**4a**) (15 mg, 0.021 mmol) in CH_2Cl_2 (3 mL) was added PPh_3 (7 mg, 0.026 mmol) followed by NH_4PF_6 (12 mg, 0.073 mmol) in methanol (1 mL). After 30 min, the resulting pale yellow solution was concentrated to give (**6b**) as a yellow solid (19 mg, 85%). Found: C, 62.25; H, 4.73; N 2.46, calcd. (%) for $C_{58}H_{50}N_2P_2F_6Pd$: C, 65.88; H, 4.77; N 2.65. IR (neat, ν, cm^{-1}): 2966, 1584, 1419, 1276, 1261, 834, 765 and 750. ESI-MS (acetone, m/z): found: 911.2779; calcd. 911.2746 for $C_{58}H_{50}N_2PPd$, $[M\text{-}PF_6]^+$: ^{31}P-NMR (161 MHz, $CDCl_3$, δ in ppm): 42.4 (s, PPh_3) and -143.2 (septet, PF_6^-). ^{1}H-NMR (600 MHz, $CDCl_3$, δ in ppm): 8.89 (d, 1H, ^{3}J(HH) 7.0 Hz, $H^{3'}$), 8.35 (d, 1H, ^{3}J(HH) 8.0 Hz, H^{13}), 8.13 (d, 1H, ^{3}J(HH) 8.0 Hz, $H^{1'}$), 8.10 (d, 1H, ^{3}J(HH) 8.0 Hz, H^{1}), 7.88-7.84 (m, 6H, Ph and $H^{2'}$), 7.79 (d, 2H, ^{3}J(HH) 8.5 Hz, H^{5}), 7.64 -7.54 (m, 11H, Ph and H^{8}), 7.49 (t, 1H, ^{3}J(HH) 8.0 Hz, H^{2}), 7.46 (d, 2H, ^{3}J(HH) 8.5 Hz, H^{4}), 7.25 (dd, 1H, ^{3}J(HH) 8.0 Hz, ^{4}J(HH) 2.0 Hz, H^{12}), 7.05 (m, 2H, H^{7} and H^{9}), 6.75 (dd, 1H, ^{4}J(PH) 6.0 Hz, ^{4}J(HH) 2.0 Hz, H^{11}), 6.63 (br, d, 1H, ^{3}J(HH) 6.5 Hz, H^{10}), 6.57 (d, 1H, ^{3}J(HH) 7.0 Hz, H^{3}), 1.53 (s, 9H, CMe_3) and 0.82 (s, 9H, CMe_3). ^{13}C-NMR (150.9 MHz, $CDCl_3$, δ in ppm): 150.8 (1C, C^{10}), 139.7 (1C, C^{8}), 137.2 (1C, C^{11}), 130.9 (1C, C^{1}), 129.8 (1C, $C^{1'}$), 128.6 (2C, C^{4}), 128.5 (1C, C^{2}), 128.1 (1C, $C^{2'}$), 127.9 (2C, C^{5}), 127.7 (1C, C^{13}), 127.7 (1C, C^{3}), 127.1 (1C, C^{7}), 126.3 (1C, $C^{3'}$), 126.3 (1C, C^{9}), 121.9 (1C, C^{12}), 31.0 (3C,CMe_3), and 30.1 (3C, CMe_3).

Results and Discussion

Ligands and molybdenum complexes

The ligands (**2a**) and (**2b**) were prepared by a Diels-Alder cycloaddition reaction between 2-cyanopyridine and the corresponding cyclopentadienone (**1a**) and (**1b**), respectively (Scheme 1). Characterising data for the ligands and other metal complexes are given in the experimental section. Spectroscopic data are discussed later.



Scheme 1 Synthesis of ligands (**2**) and molybdenum complexes (**3**), and atom labelling used for the assignment of NMR data.

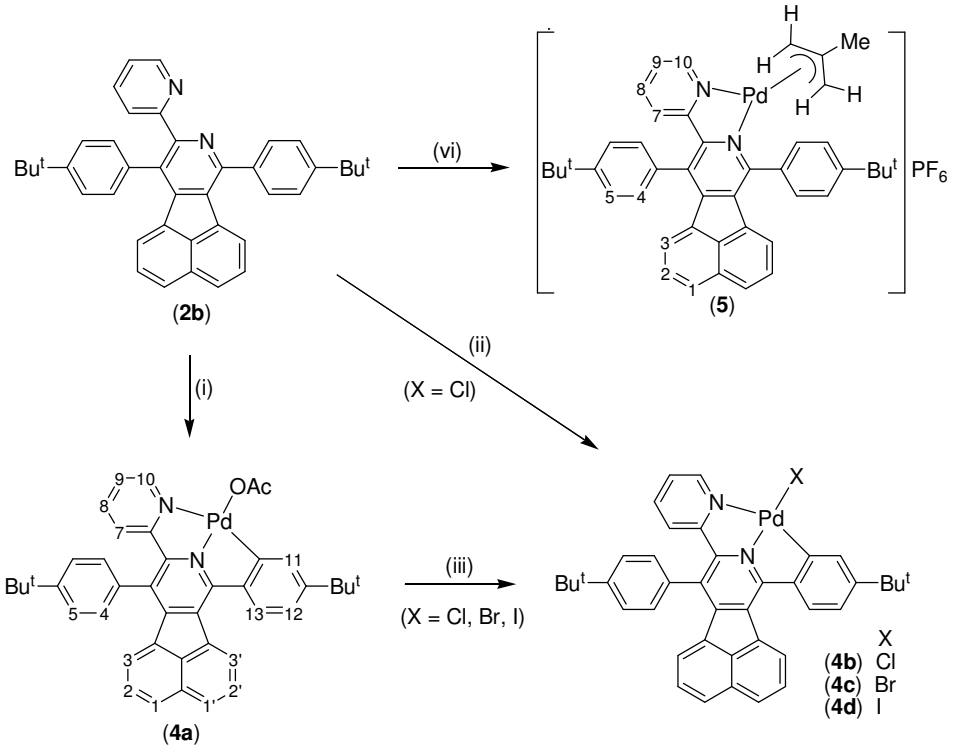
First we studied the coordination chemistry of these two ligands with zerovalent molybdenum centres stabilised by carbonyl ligands. Replacement of the two labile piperidine molecules of $[Mo(CO)_4(piperidine)_2]$ (Darensbourg & Kump, 1978) with ligands (**2**) gave the tetracarbonylmolybdenum complexes of the type $[Mo(CO)_4(\mathbf{2})]$ (**3**) in which the ligand is coordinated to the metal through both nitrogen donors.

Palladium complexes

The coordination chemistry of the ligand (**2b**) with palladium(II) centres was investigated as similar ligand systems are known to undergo cyclometallation *via* C-H bond activation (Ollagnier *et al* 2008).

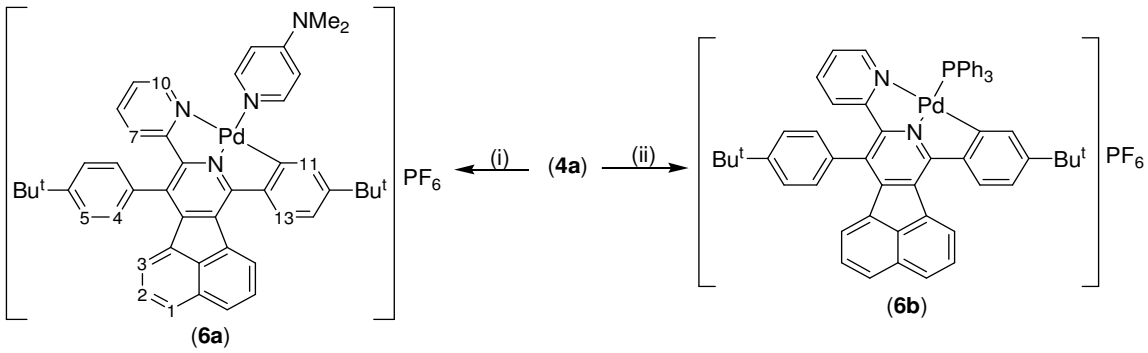
We decided to use the ligand (**2b**) (LH) with *tert*-butyl groups at the *para*-positions due to easy identification of the cyclometallated complexes by NMR spectroscopy and to increase the solubility of the resulting palladium complexes. Treatment of (**2b**) with $[Pd(OAc)_2]$ in refluxing dichloromethane resulted in the formation of the cyclometallated palladium(II) complex [Pd(OAc)(L)] (**4a**) as a yellow solid in 94% yield (Scheme 2). Treatment of (**2b**) with $[PdCl_2(NCPh)_2]$ in refluxing dichloromethane resulted in the formation of the palladium(II) complex [PdCl(L)] (**4b**) as a yellow solid in 88% yield.

We studied the substitution reactions of (**4a**) and (**4b**) with monoanionic ligands such as halides. The acetate group of (**4a**) can be easily replaced by halide ions to give [PdCl(L)] (**4b**), [PdBr(L)] (**4c**) and [PdI(L)] (**4d**) respectively. Treatment of (**2b**) with 0.5 equivalent of [(η^3-methallyl)Pd(μ-Cl)]$_2$ in dichloromethane and subsequent addition of NH_4PF_6 in methanol resulted in the formation of the N-N chelate complex (**5**) as a yellow solid in 81% yield.



Scheme 2 (i) [Pd(OAc)$_2$]; (ii) [PdCl$_2$(NCPh)$_2$]; (iii) NH_4Cl or NaBr or NaI; (vi) [(η^3-methallyl)Pd(μ-Cl)]$_2$.

We also studied the substitution reactions of (**4a**) with neutral ligands such as 4-dimethylaminopyridine (DMAP) and triphenylphosphine (Scheme 3).



Scheme 3 (i) 4-Dimethylaminopyridine/NH_4PF_6;
(ii) triphenylphosphine/NH_4PF_6.

Treatment of (**4a**) with DMAP in dichloromethane and subsequent addition of NH_4PF_6 in methanol resulted in the formation of the salt (**6a**) as a yellow solid in 89% yield. The analogous phosphine complex (**6b**) was prepared similarly in 85% yield.

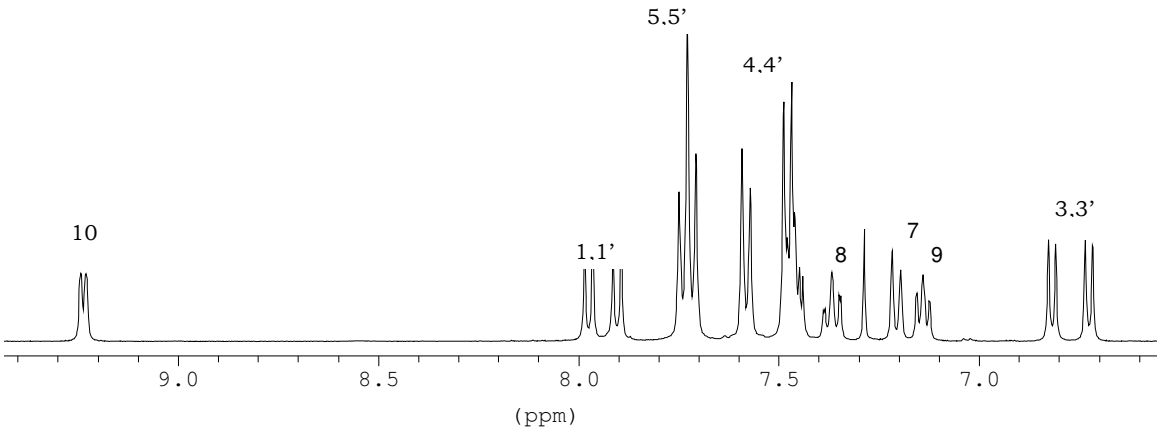
Spectroscopic characterisation

The compounds were fully characterized using IR, NMR, mass spectrometry and elemental analysis. For complexes (**4a**), (**4b**), (**4c**), (**4d**), (**5**), (**6a**) and (**6b**), the ESI-MS gave signals in agreement with the theoretically expected masses and isotopic distributions of $[M-OAc]^+$, $[M-halide]^+$ or $[M-PF_6]^+$. The ligands (**2a**) and (**2b**) gave an isotopic distribution of $[M+1]^+$. Molybdenum complexes did not yield ESI-MS spectra. The ^1H and ^{13}C NMR chemical shifts were assigned by performing H–H and C–H COSY and NOE experiments.

The ^1H and ^{13}C NMR data observed for the 2-pyridyl group of the ligands (**2a**) and (**2b**), (δ) 7.5 (H^7), 7.6 (H^8), 7.12 (H^9), 8.52 (H^{10}), 124.6 (C^7), 135 (C^8), 121.6 (C^9) and 148.4 (C^{10}) ppm, are in good agreement with the values reported in the literature (Ollagnier *et al* 2008 and Hii *et al*, 1995). The ^1H NMR spectrum of (**2b**) displays two sets of AB-patterns with $^3J(HH)$ = 8.5 Hz, consistent with the presence of two aryl groups.

The molybdenum complexes (**3a**) and (**3b**) were fully characterized. The IR spectrum of (**3a**) showed three IR bands at 2005, 1863 and 1823 cm^{-1} for the carbonyl ligands. The aromatic region of the ^1H NMR spectrum of (**3b**) is shown in Figure 3.

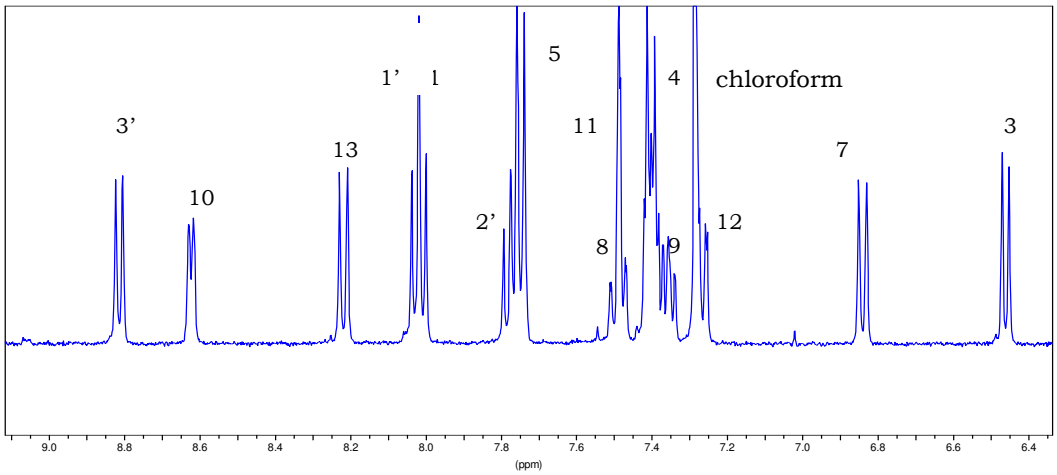
Figure 3 Aromatic region of the ^{1}H NMR spectrum of (**3b**) with the atom labelling used for the assignment of NMR data



In the ^{13}C NMR spectra of (**3a**) and (**3b**), the carbon resonances for the four carbonyl ligands appeared at 225, 217 and 205 ppm with the intensity ratio of (1:1:2). The signal at 205 ppm is assigned to the two axial carbonyl ligands. The proton resonance for H^{10} showed a downfield shift of 0.7 ppm upon coordination to molybdenum.

The cyclometallated palladium(II) complexes (**4a**) – (**4d**) are characterised by ^{1}H and ^{13}C NMR spectroscopy and they show similar chemical shifts except for H^{10} and H^{11}. (**4b**), (**4c**) and (**4d**) are less soluble in $CDCl_3$ than (**4a**), and this limited solubility hindered performing some of the NMR experiments. The aromatic region of the ^{1}H NMR spectrum of (**4a**) is shown in Figure 4. In the ^{1}H NMR spectrum of (**4a**), H^{11} appeared as a doublet at 7.47 ppm with a weak four bond coupling to H^{12}, $^{4}J(HH)$ = 1.5 Hz. The chemical shifts of H^{10} and H^{11} showed up field shifts when the halide is changed from chloride to iodide. The peak observed at 160.4 ppm in the ^{13}C NMR spectrum of (**4a**) is tentatively assigned to the orthometallated carbon. In the ^{1}H NMR spectrum of (**5**) the allyl protons appeared as broad peaks at 3.99, 3.30, 2.45 and 1.85 ppm and are similar to other allyl compounds reported (Ahmad *et al* 1996 & Ollagnier *et al* 2008).

Figure 4 Aromatic region of the ^{1}H NMR spectrum of (**4a**) with the atom labelling used for the assignment of NMR data



In the ^{1}H NMR spectrum of [Pd(DMAP)(L)]PF_6 (**6a**), H^{11} appeared as a doublet at 6.82 ppm with $^{4}J(HH)$ = 2.0 Hz whilst the aryl protons of DMAP gave a AB-pattern at 8.40 and 6.84 ppm with $^{3}J(HH)$ = 7.0 Hz. The phosphorus-31 resonance of (**6b**) was observed at 42.3 ppm. In the ^{1}H NMR spectrum, H^{11} was a doublet of doublet at 6.75 ppm with coupling to H^{10} and phosphorus, $^{4}J(PH)$ = 6.0 Hz.

Conclusion

We have prepared a novel ligand system based on fluoranthene which can act as a bidentate ligand through both N-donors and an anionic terdentate NNC-ligand.

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