A novel fluorene-containing κ^4-P_2N_2-tetradentate platinum(II) complex†

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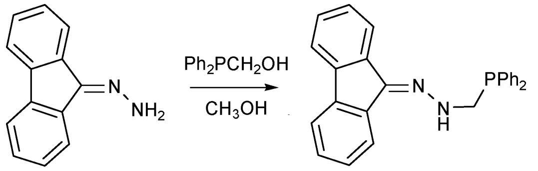
Received 18th September 2008, Accepted 6th November 2008
First published as an Advance Article on the web 17th November 2008
DOI: 10.1039/b816351k

Base induced *P*,*N*-chelation, C–C coupling and methylene C–H deprotonation affords an unusual fluorene containing square-planar Pt^{II} complex Pt(κ^4-P_2N_2-$Ph_2PCH{=}NN{-}CC_{12}H_8)_2$ which has been isolated and structurally characterised.

Acyclic tridentate and tetradentate ligands based on symmetric or nonsymmetric donor atom combinations (N, P, O, S) continue to attract much attention. Neutral or anionic tridentate and tetradentate ligand systems containing N/P donor sets are especially appealing for their diverse coordination modes and uses in metal based catalysis.[1,2] Furthermore chiral P_2N_2-ligands have successfully been employed in a range of asymmetric transformations using metal based catalysts.[2b,c,3,4] We recently described a readily synthesised $PNN'N''$-tetradentate ligand and its diverse bonding capabilities to a range of late transition-metals.[5]

Fluorene, diazofluorene or fluorenone groups have been used in organic synthesis[6] and for the preparation of metal complexes[7] including organometallic acetylides,[8] oligomers[9] and polymers.[10] However examples of monodentate or bidentate phosphine ligands bearing one or two fluorene groups are sparsely documented in the literature.[11] Herein we describe the synthesis and characterisation of a novel Pt^{II} coordinated P_2N_2-tetradentate ligand utilising a straightforward to prepare fluorene functionalised tertiary phosphine. A pivotal step in this transformation is the unusual C–C coupling or dimerisation reaction, a feature previously observed in carbodiimide,[12a] ketomalonate,[12b] 2-(arylazo)phenol,[12c] fulvene[12d] and phosphorus substituted alkene chemistry.[12e]

Reaction of Ph_2PCH_2OH and 9-fluorenone hydrazone, $H_2NN{=}CC_{12}H_8$, in CH_3OH gave the new tertiary phosphine



(1)

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$Ph_2PCH_2NHN{=}CC_{12}H_8$ **1** in excellent yield (93%) as a yellow solid which displayed the anticipated spectroscopic properties (eqn (1)). Oxidation of **1** with aq. H_2O_2 (27.5%) gave the phosphine oxide $Ph_2P(O)CH_2NHN{=}CC_{12}H_8$ **2** which has been structurally characterised (Fig. 1).‡ In the solid state **2** exists as a dimer pair with two molecules in the asymmetric unit.

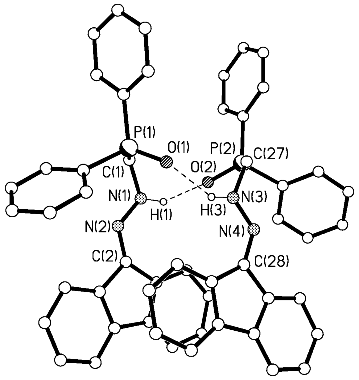

Fig. 1 Molecular structure of **2**. All C–H hydrogen atoms except those on N(1) and N(3) are omitted for clarity. Selected bond distances (Å) and angles (deg) (values in square brackets are for the second molecule): P(1)–O(1) 1.4929(13) [1.4914(13)]; O(1)–P(1)–C(1) 112.79(8) [113.28(8)], P(1)–C(1)–N(1) 112.64(12) [111.56(13)], C(1)–N(1)–N(2) 115.86(14) [116.55(15)], N(1)–N(2)–C(2) 122.30(15) [121.62(16)].

These are linked through intermolecular N–H···O H-bonding [N(1)···O(2) 2.813(2), H(1)···O(2) 2.02(2) Å, N(1)–H(1)···O(2) 150(2)°; N(3)···O(1) 2.798(2), H(3)···O(1) 2.04(2) Å, N(3)–H(3)···O(1) 147(2)°]. The P(1)–C(1)/P(2)–C(27) [1.8336(19), 1.8347(19)], C(1)–N(1)/C(27)–N(3) [1.445(2), 1.441(2)] and N(2)–C(2)/N(4)–C(28) [1.297(2), 1.303(2)] distances are all as anticipated whereas the N(1)–N(2)/N(3)–N(4) distances are rather short [1.334(2), 1.330(2)][13,14] suggesting some possible π-electron delocalisation.

The yellow dichloroplatinum(II) complex **3** was prepared by reaction of $PtCl_2$(cod) with two equiv. of **1** in dichloromethane. Confirmation of the *cis* stereochemistry was ascertained by $^{31}P\{^1H\}$ NMR and FT – IR spectroscopy. The molecular structure of **3** was elucidated by a single crystal X-ray study (Fig. 2).† The molecule lies on a two-fold axis. Upon coordination the P(1)–C(1), C(1)–N(1), N(1)–N(2) and N(2)–C(2) bond lengths are similar to those of **2** (*vide infra* for notable comparisons with **4**). There is also an intramolecular N–H···Cl H-bond [N(1)···Cl(1) 3.206(2), H(1)···Cl(1) 2.62(3) Å, N(1)–H(1)···Cl(1) 128(3)°].

Since the amine proton in **3** is acidic we reasoned deprotonation with base should promote *P*,*N*-coordination of the *cis* coordinated ligands.[1b,c] Treatment of **3** with ^{t}BuOK gave **4** and was obtained in 64% yield as a dark orange solid following isolation from CH_3OH (Eqn. (2)). In the $^{31}P\{^1H\}$ NMR spectrum of **4** a new downfield phosphorus resonance at δ(P) 55.3 ppm ($^1J_{PtP}$ 3300 Hz) was observed indicating both phosphorus donor atoms are within five-membered chelate rings. Interestingly the ^1H NMR spectrum (298 K) showed, in addition to broad signals in the aromatic region attributed to the fluorene and phenyl hydrogens, a new doublet [δ(H) 5.75 ppm, $^2J_{PH}$ 32 Hz. *c.f.* 4.65 ppm for **3**] consistent with

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† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic data and additional X-ray figures. CCDC reference numbers 702768–702770. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b816351k

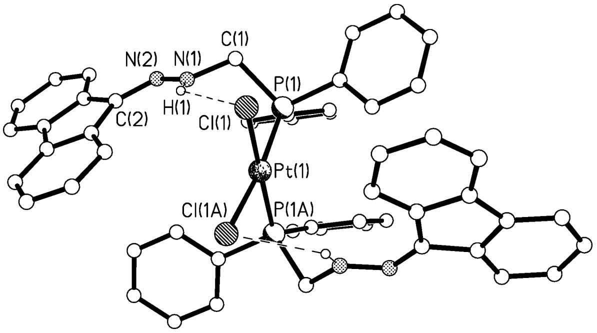
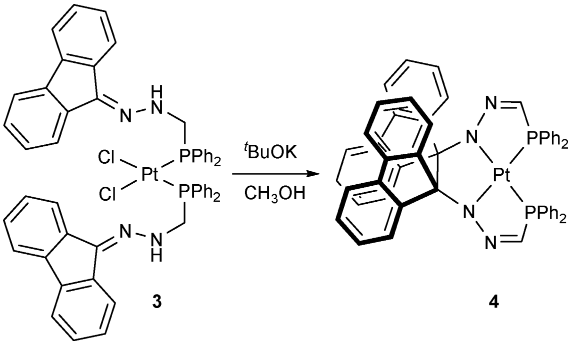


Fig. 2 Molecular structure of **3**. The disordered diethyl ether solvent molecule and all C–H hydrogen atoms except those on N(1) are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(1)–P(1) 2.2420(6), Pt(1)–Cl(1) 2.3603(6), P(1)–C(1) 1.871(3), C(1)–N(1) 1.451(4), N(1)–N(2) 1.332(3), N(2)–C(2) 1.305(4); P(1)–Pt(1)–P(1A) 101.61(3), P(1)–Pt(1)–Cl(1) 85.36(2), P(1)–Pt(1)–Cl(1A) 172.04(2), Cl(1)–Pt(1)–Cl(1A) 87.95(3), Pt(1)–P(1)–C(1) 107.80(9), P(1)–C(1)–N(1) 110.94(19), C(1)–N(1)–N(2) 119.4(2), N(1)–N(2)–C(2) 119.1(2).

the presence of two =C*H*PPh$_2$ hydrogens (by integration). The ^{13}C{^{1}H} NMR spectrum of **4** revealed the absence of a fluorene N=C resonance suggesting loss of double bond character.



(2)

An X-ray crystallographic study† shows the unprecedented formation of a *P*$_2$*N*$_2$-coordinated ligand at a square-planar Pt^{II} centre in **4** (Fig. 3). The coordination sphere about Pt(1) comprises two *cis* Pt–P–C–N–N five-membered chelate rings and a third Pt–N–C–C–N metallocyclic ring formed by carbon carbon coupling [C(2)–C(28) 1.597(6) Å][12c,15] between both fluorene groups from each *cis* chelated *P*,*N*-tertiary phosphine. The Pt^{II} centre lies 0.0375 Å out of the P(1)/N(2)/N(4)/P(2) coordination plane. Within each Pt–P–C–N–N ring it is clear that a change in hybridisation (sp^3 to sp^2) about C(1) and C(27) has occurred as indicated by the significant contraction of the C–N bond lengths [1.299(5), 1.309(5) Å] and enlarged P–C–N bond angles [119.3(3), 118.9(3)°].[1b,c] The N(1)–N(2) [1.345(5) Å] and N(3)–N(4) [1.332(4) Å] bond lengths remain similar to those of **2** and **3** and suggest some π-electron delocalisation may exist in the C(1)–N(1)–N(2)/C(27)–N(3)–N(4) backbones. However the N(2)–C(2)/N(4)–C(28) distances [1.477(5), 1.473(5) Å] are considerably longer than found in **2** and **3** implying these should formally be viewed as single bonds. Each Pt–P–C–N–N ring can be described as near planar [N(1) deviates by ±0.0560 Å from the Pt(1)–P(1)–C(1)–N(1)–N(2) plane; N(4) deviates by ±0.0694 Å from the Pt(1)–P(2)–C(27)–N(3)–N(4) plane]. The average torsion angle [C(3)–C(2)–C(28)–C(29), C(14)–C(2)–C(28)–C(40)] between the two fluorene groups is *ca.* 50° indicating significant twisting presumably to minimise steric interactions between these planar aromatic rings. The X-ray structure of **4** is unique and represents the first crystallographic example of a complex bearing a MP$_2$C$_4$N$_4$ metallacyclic ring.[16]

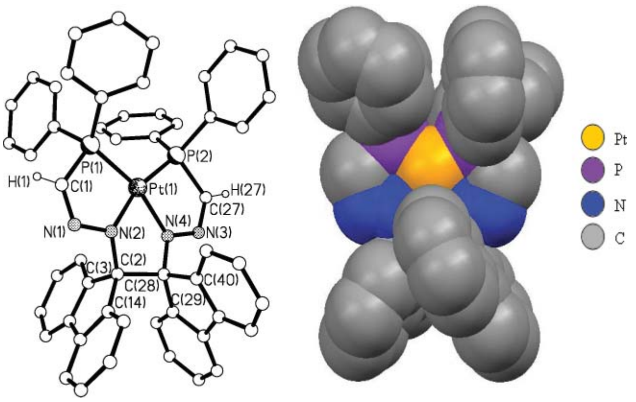


Fig. 3 (a) Ball and stick model of **4**. All C–H hydrogen atoms except those on C(1) and C(27) and the toluene solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(1)–P(1) 2.2341(11), Pt(1)–P(2) 2.2436(11), Pt(1)–N(2) 2.007(3), Pt(1)–N(4) 2.007(3), P(1)–C(1) 1.820(5), C(1)–N(1) 1.299(5), N(1)–N(2) 1.345(5), N(2)–C(2) 1.477(5), C(2)–C(28) 1.597(6), C(28)–N(4) 1.473(5), N(4)–N(3) 1.332(4), N(3)–C(27) 1.309(5), C(27)–P(2) 1.820(5); P(1)–Pt(1)–P(2) 112.31(4), N(2)–Pt(1)–N(4) 81.68(13), Pt(1)–P(1)–C(1) 97.43(15), P(1)–C(1)–N(1) 119.3(3), C(1)–N(1)–N(2) 116.7(4), N(1)–N(2)–C(2) 116.5(3), N(2)–C(2)–C(28) 105.2(3), C(2)–C(28)–N(4) 104.9(3), C(28)–N(4)–N(3) 117.6(3), N(4)–N(3)–C(27) 116.5(4), N(3)–C(27)–P(2) 118.9(3), C(27)–P(2)–Pt(1) 97.61(15). (b) Space filling view of **4** showing the twisted orientation of the two fluorene groups.

In conclusion, we have shown that in one-step a coordinated *P*-monodentate phosphine bearing a fluorene auxillary group can undergo sequential *P*,*N*-chelation, C–C coupling and methylene C–H deprotonation to give a remarkable *P*$_2$*N*$_2$-tetradentate ligand. Further studies are now underway to probe the generality of this reaction and investigate the mechanistic pathway associated with this transformation. These results will be published in due course.

Acknowledgements

We would like to thank the EPSRC and Loughborough University for funding (AJL). Johnson and Matthey are gratefully acknowledged for the generous loan of precious metal salts.

Notes and references

‡ *Crystal data:* For **2**, C$_{26}$H$_{21}$N$_2$OP: M_r = 408.42, triclinic, space group $P\bar{1}$, a = 12.6349(7), b = 13.7094(8), c = 13.7679(8), α = 71.744(2), β = 84.887(2), γ = 71.011(2)°, V = 2141.3(2) Å^3, T = 150(2) K, Z = 4, μ(Mo-K$_\alpha$) = 0.148 mm^{-1}, 9889 independent reflections measured, d_{calc} = 1.267 g cm^{-3}, $R1$ = 0.0446 (for 7137 data with $I > 2\sigma(I)$), $wR2$ = 0.1181 (all data) and 547 refined parameters. CCDC reference number 702768. For **3**·Et$_2$O, C$_{52}$H$_{42}$Cl$_2$N$_4$PPt·C$_4$H$_{10}$O: M_r = 1124.94, monoclinic, space group $I2/a$, a = 20.0646(8), b = 10.7880(4), c = 23.7050(9), β = 111.046(2), V = 4788.8(3) Å^3, T = 150(2) K, Z = 4, μ(Mo-K$_\alpha$) = 3.154 mm^{-1}, 5835 independent reflections measured, d_{calc} = 1.560 g cm^{-3}, $R1$ = 0.0208 (for 4567 data with $I > 2\sigma(I)$), $wR2$ = 0.0471 (all data), and 313 refined parameters. CCDC reference number 702769. For **4**·C$_7$H$_8$, C$_{52}$H$_{38}$N$_4$P$_2$Pt·C$_7$H$_8$: M_r = 1068.03, monoclinic, space group $P2_1/n$, a = 12.0681(6), b = 15.7231(8), c = 25.0731(13), β = 98.648(2), V = 4703.5(4) Å^3, T = 150(2) K, Z = 4, μ(Mo-K$_\alpha$) = 3.096 mm^{-1}, 10772

independent reflections measured, $d_{calc} = 1.508$ g cm^{-3}, $R1 = 0.0374$ (for 7718 data with $I > 2\sigma(I)$), $wR2 = 0.0732$ (all data), and 596 refined parameters. CCDC reference number 702770.

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