Using "click" chemistry to access a new class of tripodal P₃-ligand containing P=C bonds[†]

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High yielding "click" reactions between phosphaalkynes and organo-triazides have afforded examples of tris(triazaphosphole)s, the utility of which as a new class of tripodal P_3 -ligand has been demonstrated with the preparation of an unusual diplatinum complex.

Tripodal ligand systems have been extensively used in the formation of complexes involving metals from across the periodic table.1 The enhanced chelate effect they have, relative to monoand bidentate ligands, allows them to robustly ligate metal centres, and often permits the stabilisation and isolation of unusual complex types and reactive intermediates. Consequently, metal complexes of tripodal ligands have found numerous applications in, for example, catalysis, enzyme mimicry and small molecule activation.1 Given their importance, the development of facile, high yielding synthetic routes to new tripodal ligand systems with variable steric and electronic properties has been an ongoing theme in inorganic and organometallic coordination chemistry. Perhaps most relevant to this study are neutral, sterically bulky tripodal tris(N-heterocyclic carbene) ligands, e.g. 1 and 2, the coordination chemistry of which is being developed by Meyer et al.² The utility of d-block metal complexes of such ligands for the activation of biologically relevant small molecules is currently emerging.²



It would be of considerable interest to develop tripodal ligand systems that have very similar steric profiles to tris(*N*-heterocyclic carbene)s, but different electronic properties. *N*-heterocyclic carbenes (NHCs) are well known to be very strong σ -donors, but they are generally poor π -acceptor ligands.³ If the NHC fragments of **1** and **2** could be replaced by weaker σ -donating/stronger π -accepting moieties, the coordinative properties of the resultant ligands would complement those of the tris(NHC)s, and could allow access to metal complexes with attractive catalytic characteristics. Compounds containing phosphaalkene fragments,

 $RP=CR_2$, are known to have these electronic attributes,^{4,5} which has led to their P-coordinated transition metal complexes finding widespread use in homogeneous catalysis.⁴ Here we report the near quantitative "click" synthesis and structural characterisation of several tris(triazaphosphole) compounds, which can be considered as phosphalkenic analogues of 1 and 2. The potential of one of these as a tridentate P-donor ligand is demonstrated with the preparation of two platinum complexes.

It is well known that phosphaalkynes, $P \equiv CR$, readily undergo uncatalysed 1,3-dipolar cycloaddition reactions with alkyl or aryl azides, R'N₃, to give 1,2,3,4-triazaphospholes, R'N₃PCR, with complete regioselectivity, and in close to quantitative yields.⁶ Such reactions are closely related to copper-catalysed Huisgen alkyne-azide cycloadditions, and like those reactions fulfil all the requirements of "click" chemistry.7 It seemed to us that phosphaalkyne/azide "click" reactions could be utilised to rapidly prepare multi-dentate P-donor triazaphosphole ligands in high yields. To the best of our knowledge the coordination chemistry of these heterocycles has never been explored.⁸ As a proof of concept, the reactions of the sterically hindered and unhindered phosphaalkynes, $P \equiv CR$ ($R = Bu^t$ or Me), with two triazides were explored (Scheme 1).9 All reactions were carried out at ambient temperature and were complete within two hours, affording excellent yields of the tris(triazaphosphole) compounds, 3-5. The very low solubility of the product from the reaction between $N(CH_2CH_2N_3)_3$ and $P \equiv CMe$ prevented its characterisation.



Scheme 1 Reagents and conditions: i, $1/3 C_6Me_3(CH_2N_3)_3-1,3,5$; ii, $1/3 N(CH_2CH_2N_3)_3$.

Compounds 3–5 are thermally very stable and solid samples of 3 are indefinitely stable in the air. In contrast, 4 and 5 slowly oxidise under aerobic conditions. The most diagnostic spectroscopic information for the compounds comes from their ³¹P{¹H} NMR spectra. Each exhibits a singlet resonance (3: δ 177.0 ppm; 4: δ 172.4 ppm; 5: δ 173.2 ppm) which is *ca*. 230 ppm downfield from the signal for the phosphaalkyne starting material,⁵ and is suggestive of the compounds possessing phosphaalkene fragments. Indeed, very similar chemical shifts have previously been reported for a variety of 1,2,3,4-triazaphospholes.⁶ The fact that

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only one resonance is seen in the spectrum of each compound indicates chemical equivalence of their heterocycles in solution.

X-Ray crystallographic experiments were carried out on 3 and 4 and their molecular structures are depicted in Fig. 1.1 These represent the first structural characterisations of 1,2,3,4triazaphospholes and reveal significant differences between the compounds. Compound 3 is effectively isostructural with 1 in that it displays an asymmetric arrangement of its three heterocycles with respect to the mesitvlene linker. This is at odds with the NMR spectroscopic data for the compound and implies that in solution there is free rotation of the heterocycles about the methylene carbon centres. In contrast, the heterocycles of the less hindered compound, 4, all lie on the same side of the mesitylene plane, and their P-lone pairs are all directed inwards. As a result, the compound appears "pre-organised" to act as a tridentate ligand. The bond lengths within the 1,2,3,4-triazaphosphole fragments of both compounds show that there is a significant degree of aromatic delocalisation within the planar six π -electron heterocyclic systems. Of most note are their P-C distances (ca. 1.72 Å) which lie between the normal values for localised double (ca. 1.66 Å) and single (ca. 1.87 Å) bonded interactions.⁵ Previous computational studies have predicted significant aromaticity within 1,2,3,4triazaphospholes.¹⁰



Fig. 1 Molecular structures of (a) **3** and (b) **4** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **4**: P(1)–N(1) 1.698(2), P(1)–C(5) 1.723(3), N(1)–N(2) 1.340(3), N(2)–N(3) 1.311(3), N(3)–C(5) 1.353(3); N(1)–P(1)–C(5) 86.30(12). Symmetry operations: '-y + 1, x - y + 1, z; "-x + y, -x + 1, z.

In order to demonstrate the ligating properties of **3**, it was reacted with one equivalent of $[Pt(norbornen)_3]$ at -80 °C in an attempt to prepare the tridentate platinum(0) complex **6** (Scheme 2). It was thought that the very large "coordination cavity" expected for this ligand (*cf.* **1**¹¹) would lead to weakly ligated Pt centres, thus making the generated complex amenable to use in homogeneous catalysis.¹² The ³¹P{¹H} NMR spectrum of the pale yellow reaction mixture at 0 °C exhibited a singlet at



Scheme 2 Reagents and conditions: i, $Pt(norbornene)_3$; ii, 2 $Pt(norbornene)_3$.

 δ 180.0 ppm with ¹⁹⁵Pt satellites having a ¹J_{PtP} coupling constant of 6070 Hz. This value is large and is not indicative of weak Pt–P bonding in **6**. Indeed, the coupling constant is considerably greater than expected for related phosphine complexes, *e.g.* [Pt⁰(PAr₃)₃].¹³ Upon warming the reaction mixture to 20 °C, it rapidly took on a deep red colour and its ³¹P{¹H} NMR spectrum showed the development of several new products (at the expense of **6**), one of which was later identified by X-ray crystallography (*vide infra*) to be the unusual bimetallic species, **7**. Because of the apparent instability of **6** in solution at ambient temperature, efforts to isolate and fully characterise the material were not successful. Similarly, no identifiable products could be isolated from the reactions of **4** or **5** with [Pt(norbornene)₃].

As compound 7 is thermally stable, it was rationally synthesised in a 74% yield by treating 3 with two equivalents of [Pt(norbornene)₃]. Likewise, treating an *in situ* generated solution of **6** with one equivalent of $[Pt(norbornene)_3]$ led to a comparable yield of 7, suggesting that 6 is an intermediate in its formation. The ${}^{31}P{}^{1}H$ NMR spectrum of the deep red compound exhibits a doublet resonance for its two chemically equivalent P-centres (δ 138.8 ppm, ² J_{PP} = 82 Hz) that has two sets of platinum satellites with similar ${}^{1}J_{PP}$ couplings (2936 Hz and 2902 Hz). Both of these couplings are considerably lower than that in 6, which is in line with the bridging ligating mode of the P-centres. In contrast, the platinum satellites about the triplet signal corresponding to the unique P-centre (δ 179.9 ppm), display J_{PP} couplings (${}^{1}J_{PP}$ = 8310 Hz; ${}^{2}J_{PtP} = 106$ Hz) which differ by nearly two orders of magnitude. The one bond coupling is significantly greater than that for 6, as might be expected, given the apparent weakness of the interactions of the other two P-centres with the P₃-coordinated Pt centre. All of the aforementioned J_{PtP} couplings are reflected in the ¹⁹⁵Pt NMR spectrum of 7, which displays two signals at high field (Pt(1): δ –4702 ppm; Pt(2): δ –5165 ppm). The observation of ¹⁹⁵Pt satellites flanking each of these signals allowed the assignment of the ${}^{1}J_{PtPt}$ coupling constant for the complex as 3342 Hz. While it is known that it is difficult to correlate ${}^{1}J_{PtPt}$ couplings with Pt-Pt bond distances and strengths,¹⁴ the magnitude of the coupling in 7 appears consistent with a strong interaction between the metal centres.

An X-ray crystallographic study was carried out on 7 and its molecular structure is depicted in Fig. 2. This shows it to be a bimetallic species with one platinum centre, Pt(1), coordinated by the three P-centres of the ligand, while the other, Pt(2), is ligated by the two bridging P-centres and has an η^2 -interaction with a molecule of norbornene. The terminal Pt(1)-P(1) distance (2.183(3) Å) is at the short end of the known range (2.114-2.514 Å), mean 2.285 Å¹⁵), which is in line with the very large ${}^{1}J_{PtPt}$ coupling associated with it. In contrast, the four $Pt\text{--}P_{\text{bridging}}$ distances are at the higher end of the known range. There is no significant Pt-arene interaction in the compound (Pt(1)-arene centroid: 3.125 Å). If the platinum centres of 7 are considered as having closed shell 5d¹⁰ electronic configurations, it is difficult to reconcile the short Pt-Pt distance (2.6218(8) Å) in the compound, which is in the normal range for Pt^I-Pt^I bonds.^{15,16} That said, unsupported, albeit longer, Pt⁰-Pt⁰ interactions have been crystallographically characterised (e.g. 2.765(1) Å in [(DBPP)PtPt(DBPP)] (DBPP = $(Bu_{2}^{t}PCH_{2})_{2}CH_{2})^{17}$, and are thought to arise from mixing of filled Pt d-orbitals with low lying empty p-orbitals.¹⁸ Moreover, Pt-Pt interactions of a similar length to that in 7 are common in formally



Fig. 2 Molecular structure of 7 (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Pt(1)-P(1) 2.183(3), Pt(1)-P(2) 2.358(4), Pt(1)-P(3) 2.359(3), Pt(1)-Pt(2) 2.6218(8), P(1)-N(1) 1.654(12), P(1)-C(13) 1.710(13), N(1)-N(2) 1.349(14), N(2)-N(3) 1.328(15), N(3)-C(13) 1.345(17), Pt(2)-P(2) 2.302(4), Pt(2)-P(3) 2.304(4), P(2)-C(18) 1.702(14), P(2)-N(4) 1.706(11), N(4)-N(5) 1.376(15), N(5)-N(6) 1.291(16), N(6)-C(18) 1.336(16); P(1)-Pt(1)-P(2) 126.01(13), P(1)-Pt(1)-P(3) 124.65(13), P(2)-Pt(1)-P(3) 108.94(12), Pt(2)-P(2)-Pt(1) 68.47(10), Pt(2)-P(3)-Pt(1) 68.42(10), N(1)-P(1)-C(13) 88.0(6), C(18)-P(2)-N(4) 87.2(6), N(7)-P(3)-C(23) 85.4(7).

platinum(0) triangular clusters, [{(L)Pt(μ -L)}₃](L = CO, isonitrile *etc.*).¹⁵ Another very unusual structural feature of **7** is the fact that two of its triazaphosphole ligands bridge the Pt–Pt interaction. As a result, the P-centres of these ligands have distorted tetrahedral geometries, as opposed to the trigonal planar geometry of P(1). Despite these differences, the intra-ring geometries of the three effectively planar heterocycles are similar to each other, and to that in the free ligand, **3**. At this stage we cannot be certain what the nature of the bonding within the Pt₂(μ -P) fragments of **7** is, but it is of note that this bridging mode is comparable to that exhibited by the phosphabenzene ligand, PC₃Ph₃-2,4,6 (TPPB), in the palladium(0) trimer, [{(Et₃P)Pd(μ -TPPB)}₃].¹⁹ In that case, computational studies suggested that both σ - and low lying π -orbitals at phosphorus are involved in bridging its short Pd–Pd bonds.

In summary, high yield "click" chemistry has been used to prepare several examples of tris(triazaphosphole)s which are spatially similar to previously reported tris(NHC) ligands. The utility of these as a new class of tripodal P₃-ligand has been demonstrated with the preparation of an unusual diplatinum complex. Studies are under way to systematically investigate the curious electronic and ligating properties of tris(triazaphosphole)s.

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Notes and references

[‡] *Crystal data* for 3: C₂₇H₄₂N₉P₃, *M* = 585.61, orthorhombic, space group *Pbca*, *a* = 19.543(4) Å, *b* = 10.510(2) Å, *c* = 30.197(6) Å, *V* = 6202(2) Å³, *Z* = 8, *D_c* = 1.254 g cm⁻³, *F*(000) = 2496, μ(Mo-Kα) = 0.225 mm⁻¹, 123(2) K, 6767 unique reflections [*R*(int) 0.0199], *R* (on *F*) 0.0375, w*R* (on *F*²) 0.1076 (all data); 4: C₁₈H₂₄N₉P₃, *M* = 459.37, hexagonal, space group *R*3, *a* = *b* = 17.456(3) Å, *c* = 12.415(3) Å, *V* = 3276.2(9) Å³, *Z* = 6, *D_c* = 1.397 g cm⁻³, *F*(000) = 1440, μ(Mo-Kα) = 0.298 mm⁻¹, 123(2) K, 1586 unique reflections [*R*(int) 0.0548], *R* (on *F*) 0.0492, w*R* (on *F*²) 0.1311 (all data); 7·(toluene): C₄₁H₅₈N₉P₃Pt₂, *M* = 1160.05, monoclinic, space group *P*2₁/*n*, *a* = 16.300(3) Å, *b* = 10.424(2) Å, *c* = 28.869(6) Å, *β* = 92.59(3)°, *V* = 4900.5(17) Å³, *Z* = 4, *D_c* = 1.572 g cm⁻³, *F*(000) = 2272, μ(Mo-Kα) = 5.837 mm⁻¹, 123(2) K, 8596 unique reflections [*R*(int) 0.0934], *R* (on *F*) 0.0653, w*R* (on *F*²) 0.1800 (all data).

- See for example (a) S. Trofimenko, Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999; (b) R. R. Schrock, Acc. Chem. Res., 1997, **30**, 9; (c) T. A. Betley and J. C. Peters, Inorg. Chem., 2003, **42**, 5074; (d) H. A. Mayer and W. C. Kaska, Chem. Rev., 1994, **94**, 1239.
- 2 (a) K. Meyer and S. C. Bart, Adv. Inorg. Chem., 2008, 60, 1; (b) C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon and K. Meyer, Angew. Chem., Int. Ed., 2008, 47, 2681.
- 3 (a) F. E. Hahn and M. C. Jahnke, Angew. Chem., Int. Ed., 2008, 47, 3122; (b) W. A. Herrmann, Angew. Chem., Int. Ed., 2002, 41, 1290.
- 4 P. Le Floch, Coord. Chem. Rev., 2006, 250, 627.
- 5 K. B. Dillon, F. Mathey and J. F. Nixon, in *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.
- 6 W. Rösch, T. Facklam and M. Regitz, Tetrahedron, 1987, 43, 3247.
- 7 H. C. Kolb, M. G. Finn and K. B. Sharpless, Angew. Chem., Int. Ed., 2001, 40, 2004.
- 8 N. B. Several, examples of P-coordinated 1,2,4,3-triazaphosphole complexes have been reported. See for example J. G. Kraaijkamp, G. van Koten, K. Vrieze, D. M. Grove, E. A. Klop, A. L. Spek and A. Schmidpeter, J. Organomet. Chem., 1983, 256, 375.
- 9 N. B. Several, bis- and tris(triazaphosphole) substituted cyanopyridine compounds have been reported. See for example S. V. Chapyshev, U. Bergstrasser and M. Regitz, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 252.
- 10 L. Nyulászi, T. Veszprémi, J. Réffy, B. Burkhardt and M. Regitz, J. Am. Chem. Soc., 1992, 114, 9080.
- 11 H. Nakai, Y. Tang, P. Gantzel and K. Meyer, *Chem. Commun.*, 2003, 24.
- 12 M. L. Clarke, Polyhedron, 2001, 20, 151.
- 13 C. J. Cobley and P. G. Pringle, Inorg. Chim. Acta, 1997, 265, 107.
- 14 J. Autschbach, C. D. Inga and T. Ziegler, J. Am. Chem. Soc., 2003, 125, 1028.
- 15 As determined from a survey of the Cambridge Crystallographic Database, February, 2010.
- 16 P. Leoni, G. Chiaradonna, M. Pasquali and F. Marchetti, *Inorg. Chem.*, 1999, 38, 253.
- 17 T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers and S. Otsuka, J. Am. Chem. Soc., 1978, 100, 2063.
- 18 (a) A. Dedieu and R. Hoffmann, J. Am. Chem. Soc., 1978, 100, 2074; (b) P. Pyykkö, Chem. Rev., 1997, 97, 597.
- 19 M. T. Reetz, E. Bohres, R. Goddard, M. C. Holthausen and W. Thiel, *Chem.-Eur. J.*, 1999, 5, 2101.