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Introduction

Bi- and higher dentate P-donor ligands are ubiquitous in coordination chemistry, and their complexes have found a multitude of applications in, for example, catalysis, small molecule activations and the design of functional models of enzymes.¹ While numerous synthetic protocols have been developed to access multi-dentate P-donor ligand systems possessing varying steric and electronic properties, the identification of novel, facile, high yielding routes to such compounds is a perpetual goal of inorganic chemists. In this respect, we recently reported on the rapid and essentially quantitative syntheses of the tris(triazaphosphole)s, 1 and 2, via catalyst free "click" reactions between organotriazides and the phosphaalkynes, $P \equiv CR$ (R = Bu^t or Me).² The utility of one of these $(\mathbf{1}, \mathbf{R} = \mathbf{B}\mathbf{u}^t)$ as a tripodal P₃-ligand for the stabilisation of lowvalent platinum fragments was demonstrated in that report. One of the driving forces for the syntheses of 1 and 2 was the fact that although the compounds are essentially isostructural to previously reported tris(N-heterocyclic carbene) substituted

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The facile assembly of bis-, tris- and poly-(triazaphosphole) systems using "click" chemistry†

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Uncatalysed 1,3-dipolar cycloaddition reactions between two phosphaalkynes, $P \equiv CR$ ($R = Bu^t$ or Me), and a series of di-, tri- and poly-azido precursor compounds have given very high yields of a range of triazaphosphole substituted systems. These comprise the 1,1'-bis(triazaphosphole)ferrocenes, [Fe-{C₅H₄(N₃PCR)}₂], the tris(triazaphosphole)cyclohexane, *cis*-1,3,5-C₆H₉(N₃PCBu^t)₃, and the poly(allyltriazaphosphole)s, {C₃H₅(N₃PCR)}_∞. Electrochemical studies on the 1,1'-bis(triazaphosphole)ferrocenes reveal the compounds to undergo reversible 1-electron oxidation processes, at significantly more positive potentials than ferrocene itself. Attempts to chemically oxidise one 1,1'-bis(triazaphosphole)ferrocene with a silver salt, Ag[Al{OC(CF₃)₃}₄] were not successful, and led to the formation of a silver coordination complex, [{Fe[μ -C₅H₄(N₃PCBu^t)]₂(μ -Ag)}₂][Al{OC(CF₃)₃}₄]₂, thereby demonstrating the potential the reported triazaphosphole substituted systems possess as novel ligands in coordination chemistry.

> mesitylene and triethylamine,³ their electronic properties were predicted to be very different. While *N*-heterocyclic carbenes (NHCs) are generally accepted to be strong σ -donors and weak π -acceptors,⁴ compounds such as **1** and **2** which contain phosphaalkene moieties, RP=CR₂, are known to be weaker σ -donors and stronger π -acceptors.^{5,6} These attributes have led to the emergence of complexes of unsaturated P-donor ligands in many areas of homogeneous catalysis.⁶

> We wished to extend our preliminary study to the preparation of a range of new polyfunctional triazaphosphole containing compounds, thereby demonstrating the generality of the synthetic route that gave **1** and **2**. Considering our prior comparisons of spatially similar triazaphosphole and NHC containing compounds, in this study we chose to target both **1**,1'-bis(triazaphosphole)ferrocenes, and polymer supported poly(triazaphosphole)s, as the NHC analogues of these systems have been recently studied.^{7,8} In addition, the pursuit of further examples of tripodal P₃-ligands related to **1** and **2** was an objective of this work.



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 $[\]pm$ Electronic supplementary information (ESI) available: Crystal data, details of data collections and refinements for 3, 4, and $[Fe{C_5H_4(N_3PCBu'H)}_2][CF_3SO_3]_2$; ORTEP diagram for $[Fe{C_5H_4(N_3PCBu'H)}_2][CF_3SO_3]_2$; and cyclic voltammograms for 3 and 4. CCDC 925610–925612. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50505g

Results and discussion

Phosphaalkynes, P=CR, are well known to undergo uncatalysed 1,3-dipolar cycloaddition reactions with organoazides, R'N₃, to give 1,2,3,4-triazaphospholes, R'N₃PCR, in close to quantitative yields, and with complete regioselectivity.⁹ This reactivity is closely related to copper-catalysed Huisgen alkyneazide cycloadditions, and both reaction classes fulfil all of the requirements of "click" chemistry.¹⁰ In order to access the proposed targets of this study, the sterically hindered and unhindered phosphaalkynes, $P \equiv CR$ (R = Bu^t or Me), were reacted at ambient temperature with either 1,1'-diazidoferrocene, cis-1,3,5-triazidocyclohexane, or poly(allylazide) to give the triazaphosphole compounds, 3-7, in quantitative or near quantitative yields (Scheme 1). It is of note that the product from the reaction of P=CMe with triazidocyclohexane was not stable in solution and could not be isolated. Moreover, monitoring the progress of the other reactions using ³¹P NMR spectroscopy, revealed that the formation of 3-5 was complete within 30 min, whereas the formation of the triazaphosphole polymers, 6 and 7, required ca. 2 days to reach completion.

Compounds 3–7 are thermally very stable in the solid state, and the ferrocene and polymer based systems are indefinitely stable in the air. In contrast, the triazaphosphole substituted cyclohexane, **5**, is mildly air sensitive in the solid state. All of the molecular complexes exhibit single sharp resonances in their ³¹P{¹H} NMR spectra, which lie in a narrow range ($\delta = 173.6-179.1$ ppm), and are more than 200 ppm downfield from the signals for the phosphaalkyne starting materials.⁵ The positions of the signals are, however, fully consistent with what is expected for triazaphospholes^{2,9} and phosphaalkenes,⁵ based on prior studies. It is interesting that the solution state ³¹P{¹H} NMR spectra of the two polymers each display two broad signals (**6**: $\delta = 176.7$, 171.7 ppm; 7: $\delta = 179.0$,

174.1 ppm), with the higher field resonance being considerably less intense than the lower field resonance in both cases. It is believed this observation derives from the previously reported presence of some branching within the polymer backbone of the poly(allylazide) precursor.¹¹

The ¹H and ¹³C{¹H} NMR spectra of 3–5 are unexceptional and are consistent with their proposed structures. It is of note that the signals in the spectra for 5 are relatively sharp, which suggests it predominates as one isomeric form in solution. Based on steric considerations, this is most likely the chair form, as depicted in Scheme 1. In contrast, and not surprisingly, all the resonances in the ¹H NMR spectra for the polymers, **6** and **7**, are broad. Both polymers were subject to gel permeation chromatography which yielded average molecular weights of 2087 g mol⁻¹ for **6**, and 1948 g mol⁻¹ for **7**.

X-ray crystal structure analyses of the 1,1'-bis(triazaphosphole)ferrocenes, 3 and 4, were carried out, and the molecular structures of the compounds are depicted in Fig. 1 and 2 respectively. In both, the two cyclopentadienyl rings are eclipsed, though in the bulkier system, 3, the triazaphosphole rings are not eclipsed and do not appear to have any interaction with each other. In contrast, the triazaphosphole rings in 4 are almost perfectly eclipsed, and the distance between the two centroids of those heterocycles (3.58 Å, cf. Cpcent.- $Cp_{cent} = 3.30 \text{ Å}$) indicates a degree of intramolecular $\pi - \pi$ stacking. Indeed, previous computational studies have predicted significant aromatic character to 1,2,3,4-triazaphospholes,¹² which would account for the π -stacking behaviour in 4. Furthermore, the heterocycle and cyclopentadienyl rings on each side of 4 are close to co-planar (dihedral angle = 18.9° mean), which could allow for a degree of conjugation over each $C_5H_4(N_3PCMe)$ unit. Presumably similar π -stacking between



Scheme 1 (i) $Fe(C_5H_4N_3)_2$, toluene; (ii) $cis-1,3,5-C_6H_9(N_3)_3$, CH_2CI_2 ; (iii) $\{C_3H_5(N_3)\}_{oc}$, CH_2CI_2 .



Fig. 1 Molecular structure of 3 (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.6914(15), P(1)–C(11) 1.7168(19), N(1)–N(2) 1.348(2), N(1)–C(1) 1.428(2), N(2)–N(3) 1.307(2), N(3)–C(11) 1.355(2), N(4)–N(5) 1.347(2), N(4)–C(6) 1.424(2), N(5)–N(6) 1.306(2), N(6)–C(16) 1.358(2), P(2)–N(4) 1.6956(15), P(2)–C(16) 1.7144(18), N(1)–P(1)–C(11) 86.28(8), N(4)–P(2)–C(16) 86.41(8), N(3)–C(11)–P(1) 113.08(14), N(6)–C(16)–P(2) 112.95(13).



Fig. 2 Molecular structure of **4** (25% thermal ellipsoids are shown; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.688(2), P(1)–C(11) 1.717(3), N(1)–N(2) 1.352(3), N(1)–C(1) 1.429(3), N(2)–N(3) 1.311(3), N(3)–C(11) 1.364(4), N(3)–C(11) 1.364(4), N(4)–N(5) 1.362(3), N(4)–C(6) 1.431(3), N(5)–N(6) 1.305(3), N(6)–C(13) 1.363(4), N(1)–P(1)–C(11) 86.35(13), N(4)–P(2)–C(13) 86.11(13), N(3)–C(11)–P(1) 113.1(2), N(6)–C(13)–P(2) 113.5(2).

the heterocycles of 3 does not occur due to their greater steric bulk. The intra-heterocycle geometries of 3 and 4 are very close to those reported for 1,² and again imply a degree of aromatic delocalisation over those rings. 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) bonds.⁵

Compounds 3 and 4 have the potential to act as bidentate ligands towards metal fragments, ML_n , or as bridging or linker ligands in 1-dimensional coordination polymers, [{Fe- $[\mu-C_5H_4(N_3PCR)]_2(\mu-ML_n)\}_{\infty}]$. If examples of the latter could be prepared, they could act as molecular wires, by allowing electron transfer between the redox active iron sites, the triazaphosphole coordinated metal fragment, and/or the C₅H₄(N₃PCR) rings themselves. In order to shed some light on the redox properties of 3 and 4, their electrochemistry was investigated. The cyclic voltammetric behaviour of the compounds at a glassy carbon electrode in dichloromethane solutions containing either $[Bu_4N][B(C_6F_5)_4]$ or $[Bu_4N][PF_6]$ as the supporting electrolyte is similar. Both compounds exhibit welldefined oxidation processes that have the same formal reversible potential $(E_{f(3,4)}^0 = 0.34 \text{ V} \nu s. \text{ Fc}^{0/+})$ to generate the cationic products 3^+ and 4^+ respectively. Scanning the potential to very positive and negative potentials did not produce evidence of any additional processes, thereby indicating that the ligand is electroinactive within the potential range available in dichloromethane (-2 V to +2 V). Thus, the process detected at 0.34 V is assigned to the metal based oxidation of Fe^{II} to Fe^{III} in the ferrocenyl moiety of both compounds.

Analysis of cyclic voltammetric data for 3 and 4 as a function of scan rate ($\nu = 0.1$ to 1 V s⁻¹) revealed that their oxidations correspond to chemically reversible, diffusioncontrolled, one-electron processes. The shape of the voltammograms (see ESI[†]) implies that the salts, [3⁺][PF₆⁻⁻] and [4⁺]-[PF₆⁻⁻], generated at the electrode surface are soluble and stable on the cyclic voltammetric time scale. The fact that the peak-to-peak separations ($\Delta E_{\rm p} = E_{\rm p}^{\rm ox} - E_{\rm p}^{\rm red}$) for both compounds are similar to that known for the reversible oxidation of ferrocene under the same experimental conditions ($\Delta E_{\rm p} =$ 70 mV at 0.1 V s⁻¹), confirms that the one-electron oxidation processes are electrochemically reversible (fast heterogeneous electron-transfer) at a glassy carbon electrode. The diffusion coefficients (*D*) of **3** and **4** were determined in CH₂Cl₂/0.1 M [NBu₄][PF₆] *via* application of the Randles–Sevcik equation. The values obtained were 4.25 × 10⁻⁶ and 5.85 × 10⁻⁶ cm² s⁻¹ respectively. These values are smaller than that obtained for ferrocene ($D = 1.67 \times 10^{-5}$ cm² s⁻¹) under similar conditions.¹³ This is consistent with the substitution at the Cp rings in the triazaphosphole-based ferrocene compounds, which results in higher molecular masses, and hence slower rates of diffusion.

The fact that the formal reversible potentials of **3** and **4** are identical $(E_{f(3,4)}^0 = 0.34 \text{ V } vs. \text{ Fc}^{0/+})$ implies that the redox couples are not very sensitive to substituent effects (*tert*-butyl *vs.* methyl) in the triazaphosphole rings. The positive shift in E_f^0 values compared to the [FeCp₂]^{0/+} couple is attributed to an electron-withdrawing effect of the triazaphosphole ligands, which results in an increase in the positive charge on the iron atom, thereby making its oxidation more difficult.

Oxidative bulk electrolyses undertaken inside a glovebox, at 20 °C, for (1-3 mM) solutions of 3 confirmed the one-electron stoichiometry ($n = 1.0 \pm 0.05$ F/eq.). However, steady-state voltammograms obtained with a Pt-microelectrode before and after bulk electrolyses (see ESI⁺), revealed that when 2 mM of 3 was exhaustively electrolysed at $E_{appl} = 0.6$ V vs. $[FeCp_2]^{0/+}$ in CH₂Cl₂/[Bu₄N][PF₆] only 70% of **3**⁺ was generated, assuming equal diffusion coefficients for 3 and 3⁺. As the electrolysis proceeded, the solution changed colour from yellow to deep green. Reductive back electrolysis, in which the initially generated cation, 3^+ , was reduced back to the neutral starting material, 3, was carried out at $E_{appl} = 0.2$ V. The total charge passed was equivalent to 0.5 F/eq. and the solution colour became deep orange. Cyclic and near steady-state linear sweep voltammograms recorded after complete reductive electrolysis were consistent with the regeneration of approximately 55% of 3, along with other products. One side product gave rise to a reversible process at the same potential as that for the $[FeCp_2]^{0/+}$ couple, thus indicating the formation of ferrocene. A second side product was observed at more positive potentials $(E_{\rm f}^0 = 0.6 \text{ V})$ than $3^{0/+}$, and is probably derived from the triazaphosphole fragment. The combined exhaustive oxidation/ reduction results demonstrate that 3⁺ slowly decomposes on time scales of ~30 min or longer.

In an attempt to chemically oxidise 3 to 3^+ , it was treated with a dichloromethane solution of Ag[Al{OC(CF₃)₃}₄]. However, instead of forming a ferrocenium salt, the reaction yielded the dimeric cationic coordination complex, [{Fe-[μ -C₅H₄(N₃PCBu^t)]₂(μ -Ag)}₂][Al{OC(CF₃)₃}₄]₂ 8 (Scheme 2). This was confirmed by an X-ray crystal structural analysis of the salt, though the poor quality of that crystal structure precludes its inclusion here. With that said, it is clear from this structure that the silver centres are coordinated by N-atoms adjacent to the intracyclic C-centres of two heterocycles. The absence of

Scheme 2 (i) Ag[Al{OC(CF₃)₃}, dichloromethane.

any discernible ^{107/109}Ag satellites in the ³¹P NMR spectrum of 8, provides further evidence for this. It might be thought that compound 3 could not be oxidised by the silver salt because it is more resistant to oxidation than ferrocene, as detailed above. However, it has been reported that the redox potential of Ag^+ in dichloromethane is +0.65 V (vs. Fc),¹⁴ and therefore the oxidation should proceed, on the basis of the electrochemical results for 3. One possibility as to why it doesn't is the fact that Ag⁺ is coordinated by the triazaphosphole arms of 3, which could impart a barrier to its oxidation. In another attempt to oxidise 3, it was treated with a dichloromethane solution of $Ag[CF_3SO_3]$. This gave a mixture of products from which a few crystals of the protonated form of 3, viz. [Fe- $\{C_5H_4(N_3PCBu^tH)\}_2$ [[CF₃SO₃]₂, were recovered. Although no spectroscopic data could be obtained for this compound because of its very low yield, its structure was confirmed by X-ray crystallography (see ESI⁺). In an effort to intentionally prepare the compound in higher yield by the reaction of 3 with triflic acid, only a complex mixture of unidentified products was obtained.

Conclusion

In summary, regioselective, uncatalysed 1,3-dipolar cycloaddition reactions between two phosphaalkynes and a series of di-, tri- and poly-azido precursor compounds have given rise to very high yields of a range of triazaphosphole substituted systems, which have potential for use as polydentate ligands towards transition metal fragments. Electrochemical studies on two 1,1'-bis(triazaphosphole) substituted ferrocenes have shown that these compounds undergo diffusion controlled, reversible one-electron oxidation processes, and that the compounds are significantly more difficult to oxidise than ferrocene itself. Attempts to chemically oxidise one 1,1'-bis-(triazaphosphole)ferrocene with a silver salt were not successful, and instead led to the formation of a dimeric silver coordination complex.

Experimental section

General considerations

Synthetic studies. All manipulations were carried out using standard Schlenk and glove box techniques under an

atmosphere of high purity dinitrogen. THF, toluene and hexane were distilled over molten potassium, diethyl ether was distilled over a Na/K alloy, while dichloromethane and fluorobenzene were distilled over CaH2. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were carried out at the Science Centre, London Metropolitan University, or Campbell Microanalytical, Otago. Reproducible microanalyses could not be obtained for the polymer products. IR spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates. ¹H, ¹³C $\{^{1}H\}$, ³¹P $\{^{1}H\}$ and ¹⁹F NMR spectra were recorded on either Bruker DPX300 or AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used, external H_3PO_4 (85% solution in D_2O), or external CFCl₃. UV/vis spectra were acquired using a Cary 1E spectrometer. Gel permeation chromatography studies were carried out using a Tosoh ecosystems 8310 instrument. $P \equiv CBu^t$ was synthesised by a variation of Becker's original method,¹⁵ viz. the [Li{N- $(SiMe_3)_2$ catalysed elimination of hexamethyldisiloxane from a tetraglyme solution of $(Me_3Si)P=C(Bu^t)(OSiMe_3)$.¹⁶ $P \equiv CMe$,¹⁷ 1,1'-diazidoferrocene,¹⁸ cis-1,3,5-triazidocyclohexane,¹⁹ and poly(allylazide)¹¹ were prepared by literature procedures, $Ag[Al{OC(CF_3)_3}_4]$ was kindly supplied by Prof. Ingo Krossing (Freiburg University), while all other reagents were used as received.

Electrochemical studies. All measurements were performed inside a Vacuum Atmospheres glovebox connected to a BAS100B computer-controlled electrochemical work station at 293 \pm 2 K in CH₂Cl₂ containing either 0.1 M [Bu₄N][PF₆] or 0.05 M $[Bu_4N][B(C_6F_5)_4]$ as the supporting electrolyte. A standard three-electrode cell equipped with a 1.5 mm diameter glassy carbon (Cypress) disk working electrode, a platinum mesh counter electrode, and a silver wire coated with AgCl as reference electrode, was used for voltammetric experiments. For bulk electrolysis experiments, large platinum gauze and platinum mesh baskets were used as the working electrode and counter electrode, respectively. The reference electrode was the same as that employed in the voltammetric studies. All reported potentials are in V versus the ferrocene/ferrocenium [FeCp₂]^{0/+} redox couple. This was achieved by addition of ferrocene as an internal standard at the end of each experiment, measurement of the reversible potential of [FeCp₂]^{0/+} couple vs. Ag/Ag⁺ by cyclic voltammetry, followed by conversion to $[FeCp_2]^{0/+}$ scale.

Preparation of $[Fe\{C_5H_4(N_3PCBu^t)\}_2]$ 3. Neat $P \equiv CBu^t$ (0.288 cm³, 1.75 mmol) was added to a solution of 1,1'-diazidoferrocene (0.20 g, 0.77 mmol) in toluene (15 cm³) at 20 °C. The resultant dark orange solution was allowed to stir at ambient temperatures for 2 h, whereupon volatiles were removed *in vacuo* and the crude product extracted into hexane (10 cm³). The extract was filtered, and the filtrate placed at -30 °C overnight to yield orange crystals of 3 (0.34 g, 96%). M.p. 125–127 °C (decomp.); ¹H NMR (300 MHz, C₆D₆, 298 K): $\delta = 1.42$ (s, 18H, CH₃), 3.77 (m, 4H, Cp–H), 4.64 (m, 4H, Cp–H); ¹³C NMR (75 MHz, C₆D₆, 300 K): δ = 31.4 (d, ³*J*_{PC} = 7.9 Hz, C(*C*H₃)₃), 35.3 (d, ²*J*_{PC} = 15.6 Hz, *C*(*C*H₃)₃), 65.6 (Cp–*C*), 69.1 (Cp–*C*), 99.3 (d, ²*J*_{PC} = 14 Hz, *C*(N₃CP)), 197.8 (d, ¹*J*_{PC} = 130.0 Hz, P=*C*); ³¹P{¹H} NMR (121 MHz, C₆D₆, 300 K): δ = 173.6; IR ν /cm⁻¹ (Nujol): 1633w, 1377s, 1260s, 1218w, 1092s, 1019s, 876w, 800s; UV-vis, toluene solution (ε , L mol⁻¹ cm⁻¹): λ _{max} = 288 nm (1328), 368 nm (1395), 446 nm (520); MS (EI/70 eV), *m*/*z* (%): 468.3 (M⁺, 27); anal. calc. for C₂₀H₂₆FeN₆P₂ C 51.30%, H 5.60%, N 17.95%; found C 51.11%, H 5.58%, N 17.82%.

Preparation of $[Fe_1C_5H_4(N_3PCMe)]_2$ 4. A solution of P=CMe in diethyl ether (0.345 mmol in 1 cm³) was added to a solution of 1,1'-diazidoferrocene (0.036 g, 0.13 mmol) in toluene (2 cm³) at 20 °C. The resultant dark orange solution was allowed to stir at ambient temperatures for 30 min, whereupon volatiles were removed in vacuo and the crude product extracted into diethyl ether (3 cm³). The extract was filtered, and the filtrate placed at -30 °C overnight to yield orange crystals of 4 (0.05 g, 99%). M.p. 131-133 °C (decomp.); ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 2.89 (d, 6H, ³J_{PH} = 11.7 Hz, CH₃), 3.73 (m, 4H, Cp-H), 4.68 (m, 4H, Cp-H); ¹³C NMR (75 MHz, C_6D_6 , 300 K): $\delta = 14.4$ (d, ${}^{2}J_{PC} = 24.8$ Hz), 64.5 (d, ${}^{3}J_{PC} = 5.4$ Hz, Cp-*C*), 65.6 (Cp-*C*), 99.3 (d, ${}^{2}J_{PC}$ = 20.0 Hz, *C*(N₃CP)), 179.4 (d, ${}^{1}J_{PC} = 125.2 \text{ Hz}, P = C); {}^{31}P{}^{1}H} \text{ NMR (121 MHz, C_6D_6, 300 K)}:$ δ = 173.7; IR v/cm⁻¹ (Nujol): 1789m, 1261w, 1096m, 1020m, 836m, 799m; UV-vis, toluene solution (ε , L mol⁻¹ cm⁻¹): λ_{max} = 286 nm (1304), 368 nm (1676), 446 nm (2026); MS (EI/70 eV), m/z (%): 384.2 (M⁺, 100); anal. calc. for C₁₄H₁₄FeN₆P₂ C 43.78%, H 3.67%, N 21.88%; found C 43.56%, H 3.61%, N 21.67%.

Preparation of cis-1,3,5- $C_6H_9(N_3PCBu^t)_3$ 5. Neat P=CBu^t (0.50 cm³, 3.0 mmol) was added to a solution of *cis*-1,3,5-triazidohexane (0.20 g, 0.80 mmol) in dichloromethane-THF $(50:50 \text{ v/v}, 20 \text{ cm}^3)$ at 20 °C. The reaction solution stirred for 4 h before all volatiles were removed in vacuo. The colourless residue was extracted into a toluene-hexane mixture and stored at -30 °C to yield colourless needle-like crystals of 5 (0.38 g, 93%). M.p. 224-227 °C (decomp.); ¹H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.45 (s, 27H, $C(CH_3)_3$), 2.74 (m, 3H, CH_2), 3.02 (m, 3H, CH_2), 5.18 (m, 3H, Cy-CH); ¹³C{¹H} NMR (75 MHz, CDCl₃, 298 K): δ = 31.6 (C(CH₃)₃), 35.6 (d, ²J_{PC} = 16.2 Hz, $C(CH_3)_3$, 43.3 (CH_2), 58.7 (d, ${}^2J_{PC}$ = 12.0 Hz, CH), 199.4 (d, ${}^{1}J_{PC} = 108.1 \text{ Hz}, P = C$; ${}^{31}P{}^{1}H$ NMR (121 MHz, CDCl₃, 298 K): δ 179.1; IR ν /cm⁻¹ (Nujol): 1655w, 1205m, 1181m, 1125s, 1058s, 893m, 800m; MS (EI/70 eV), m/z (%): 507.5 (M⁺, 54); anal. calc. for C21H36N9P3 C 49.70%, H 7.15%, N 24.84%; found C 49.01%, H 7.00%, N 24.52%.

Preparation of $\{C_3H_5(N_3PCBu^t)\}_{\infty}$ 6. Neat P=CBu^t (0.10 cm³, 0.6 mmol) was added to a solution of poly(allylazide) (0.010 g, 0.1 mmol monomer equivalents) in dichloromethane (5 cm³) at 20 °C. The resultant solution was stirred for 3 days. All volatiles were subsequently removed *in vacuo*, and the brown residue washed with 2 cm³ of hexane to give a pale brown solid (0.011 g, 66%); ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.40 (br., C(CH₃)₃), 0.80–2.40 (br., CH and CH₂), 4.50–5.00 (br., CH₂(N₃PCR)); ³¹P{¹H} NMR (121 MHz, CDCl₃, 298 K): δ =

176.7, 171.7; IR ν/cm^{-1} (Nujol): 1708m, 1380s, 1279s, 1091m, 800m; GPC (DMF, 298 K): $M_{w(Av)} = 2087 \text{ g mol}^{-1}$.

Preparation of $\{C_3H_5(N_3PCMe)\}_{\infty}$ 7. A solution of P≡CMe in diethyl ether (2 cm³, 0.6 mmol) was added to a solution of poly(allylazide) (0.010 g, 0.1 mmol monomer equivalents) in dichloromethane (2.5 cm³) at 20 °C. The resultant solution was stirred for 3 days. All volatiles were subsequently removed *in vacuo*, and the brown residue washed with 2 cm³ of hexane to give a pale brown solid (0.017 g, 100%); ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 1.32 (br., *CH*₃), 0.82–2.45 (br., *CH* and *CH*₂), 4.40–4.95 (br., *CH*₂(N₃PCR)); ³¹P{¹H} NMR (121 MHz, CDCl₃, 298 K): δ 179.0, 174.1; IR ν /cm⁻¹ (Nujol): 1600w, 1377s, 1261m, 1093m, 1021m, 800m; GPC (DMF, 298 K): $M_{w(Av)}$ = 1948 g mol⁻¹.

Preparation of $[{Fe[\mu-C_5H_4(N_3PCBu^t)]_2(\mu-Ag)}_2][Al{OC(CF_3)_3}_4]_2$ 8. A solution of $Ag[Al{OC(CF_3)_3}_4]$ (0.12 g, 0.11 mmol) in dichloromethane (5 cm^3) was added to a solution of 3 (0.05 g, 0.11 mmol) in dichloromethane (5 cm³) at 20 °C. The resultant solution was stirred for 2 h, all volatiles removed in vacuo, and the residue extracted into fluorobenzene (2 cm³). Layering the extract with hexane afforded red crystalline plates of 8 (0.13 g, 75%); M.p. 221-226 °C (decomp.); ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 2.22 (s, 36H, C(CH₃)₃), 4.12 (m, 8H, Cp-H), 4.74 (m, 8H, Cp-H); ¹³C NMR (75 MHz, C₆D₆, 300 K): δ = 28.3 (d, ³J_{PC} = 8.2 Hz, $C(CH_3)_3$, 36.1 (d, ${}^2J_{PC}$ = 16.2 Hz, $C(CH_3)_3$), 65.2 (Cp–*C*), 69.1 (Cp–C), 106.2 (d, ${}^{2}J_{PC}$ = 14 Hz, C(N₃CP)), 212.2 (d, ${}^{1}J_{PC}$ = 129.0 Hz, P=C); ³¹P NMR (121 MHz, C₆D₆, 300 K): δ = 163.8; ¹⁹F NMR (377 MHz, CD₂Cl₂, 298 K): $\delta = -75.7$ (s); IR ν/cm^{-1} (Nujol): 1718w, 1377s, 1261w, 1090m, 1020m, 800m; MS (EI 70 eV), m/z (%): 1152.2 ({Fe[μ -C₅H₄(N₃PCBu^t)]₂(μ -Ag)}₂⁺, 15), 468.3 (Fe{ $C_5H_4(N_3PCBu^t)$ }₂⁺, 100).

X-Ray crystallography

Crystals of **3**, **4**, and $[Fe{C_5H_4(N_3PCBu^tH)}_2][CF_3SO_3]_2$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using an Enraf Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 by full matrix least squares $(SHELX97)^{20}$ using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures, except the N–H protons of $[Fe-{C_5H_4(N_3PCBu^tH)}_2][CF_3SO_3]_2$, the positional and thermal parameters of which were freely refined. Crystal data, details of data collections and refinement are given in Table S1 in the ESI.[†]

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