Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 5753–5765 **5753**
DOI: 10.1021/ic100703h

Synthesis and Reactions of Ethynylferrocene-Derived Fluoro- and Chlorocyclotriphosphazenes

Karunesh Keshav, Nem Singh, and Anil J. Elias*

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India

Received April 12, 2010

The reactions of lithiated ethynylferrocene, FcC≡CLi (Fc = ferrocenyl), with fluoro- and chlorocyclotriphosphazenes, $N_3P_3X_6$ (X = F, Cl), resulted in the formation of stable mono-$FcC{\equiv}CP_3N_3X_5$ [X = F (**1**), Cl (**2**)] and geminal bis$[(FcC{\equiv}C)_2PN]$-$(X_2PN)_2$ [X=F (**3**), Cl (**4**)], ethynylferrocene-substituted cyclophosphazenes. The reactions of **1** and **2** with CpCo(COD) were found to differ in the nature of the sandwich compounds $(\eta^5\text{-Cp})Co\{\eta^4\text{-}C_4[Fc_2(N_3P_3X_5)_2]\}$ formed. While the fluorophosphazene-derived compound **1** yielded both *cis* and *trans* isomers of the cyclobutadiene complexes **5** and **6**, the chlorophosphazene-derived compound **2** was found to give only the *trans*-cyclophosphazene-disubstituted cyclobutadiene compound **7**. The reaction of **3** with CpCo(COD) was found to give the compound $(\eta^5\text{-Cp})Co\{\eta^4\text{-}C_4\text{-1,3-(Fc)}_2\text{-2,4-}[NP(C{\equiv}CFc)(NPF_2)_2]_2\}$ (**8**) having one of the alkyne units of the cyclophosphazene moiety of **3** remaining unreacted even after reaction with an excess of CpCo(COD). The first click reactions of ethynylferrocene-derived cyclophosphazenes have been carried out by reacting **1** and **4** with benzyl azide, resulting in novel mono- and disubstituted cyclophosphazene-derived 1,2,3-triazoles. The reaction of **1** with benzyl azide yielded two positional isomers of the 1,2,3-triazole, $(1\text{-PhCH}_2\text{, 4-Fc, 5-P}_3N_3F_5)C_2N_3$ (**9**), and $(1\text{-PhCH}_2\text{, 4-P}_3N_3F_5\text{, 5-Fc})C_2N_3$ (**10**), with the latter having a benzyl group in the vicinity of the ferrocene unit as the major product. A similar reaction of **4** with benzyl azide was found to yield five triazole-based products, with two, $[(1\text{-PhCH}_2\text{-4-FcC}_2N_3)(C{\equiv}CFc)PN](PNCl_2)_2$ (**11**) and $[(1\text{-PhCH}_2\text{-5-Fc-C}_2N_3)(C{\equiv}CFc)PN](PNCl_2)_2$ (**12**), having one unreacted alkyne unit in the molecule. Among the bis-triazole-derived chlorophosphazenes $[(1\text{-PhCH}_2\text{-4-Fc-C}_2N_3)_2PN]$-$(PNCl_2)_2$ (**13**), $[(1\text{-PhCH}_2\text{-4-Fc-C}_2N_3)(1\text{-PhCH}_2\text{-5-Fc-C}_2N_3)PN](PNCl_2)_2]$ (**14**), and $[(1\text{-PhCH}_2\text{-5-Fc-C}_2N_3)_2PN](PNCl_2)_2$ (**15**), the unsymmetrically disubstituted bis-triazole compound **14** was found to be the major product. The fluorophosphazene-derived triazole **10** was found to readily form a disubstituted square-planar complex *trans*-$[(1\text{-PhCH}_2\text{-4-P}_3N_3F_5\text{-5-Fc})C_2$-$N_3]_2PdCl_2$ (**16**) with $PdCl_2(PhCN)_2$. All of the new ferrocene- and cyclophosphazene-derived compounds except **8** and **12** have also been structurally characterized.

Introduction

The uniqueness of halogenated cyclophosphazenes among inorganic heterocycles stems from the fact that their reactive P−X bonds can be made to undergo a wide variety of substitution reactions, leading to derivatives with diverse application potential. The potential applications of cyclophosphazenes and their derivatives include their use as stable cores for preparing dendrimers, as precursors for phosphazene-based polymers, and as multidentate and multianionic ligands.[1] Among the known derivatives of cyclophosphazenes, those having P−N or P−O bonds dominate, with relatively lesser examples of P−C-bonded compounds.[2−7] While P−aryl-substituted

---

*To whom correspondence should be addressed. E-mail: eliasanil@gmail.com.

(1) (a) Chandrasekhar, V.; Thilagar, P.; Pandian, M. *Coord. Chem. Rev.* **2007**, *251*, 1045–1074. (b) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159–173. (c) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley: Hoboken, NJ, 2003; p 1. (d) Chandrasekhar, V. *Inorganic and Organometallic Polymers*; Springer-Verlag: Heidelberg, Germany, 2005; p 82. (e) Chandrasekhar, V.; Krishnan, V. In *Applicative Aspects of Cyclophosphazenes*; Gleria, M., De Jaeger, R., Eds.; Nova Science: New York, 2004; p 159.

(2) (a) Chandrasekhar, V.; Murugesapandian, B. *Acc. Chem. Res.* **2009**, *42*, 1047. (b) Chandrasekhar, V.; Andavan, G. T. S.; Azhakar, R.; Pandian, B. M. *Inorg. Chem.* **2008**, *47*, 1922–1944. (c) Chandrasekhar, V.; Thilagar, P.; Krishnan, V.; Bickley, J. F.; Steiner, A. *Cryst. Growth Des.* **2007**, *7*, 668–675. (d) Chandrasekhar, V.; Pandian, B. M.; Azhakar, R. *Inorg. Chem.* **2006**, *45*, 3510–3518. (e) Chandrasekhar, V.; Krishnan, V.; Steiner, A.; Bickley, J. F. *Inorg. Chem.* **2004**, *43*, 166–172.

(3) (a) Richards, P. I.; Bickley, J. F.; Boomishankar, R.; Steiner, A. *Chem. Commun.* **2008**, 1656–1658. (b) Benson, M. A.; Ledger, J.; Steiner, A. *Chem. Commun.* **2007**, 3823–3825. (c) Boomishankar, R.; Ledger, J.; Guilbaud, J. B.; Campbell, N. L.; Bacsa, J.; Bonar-Law, R.; Khimyak, Y. Z.; Steiner, A. *Chem. Commun.* **2007**, 5152–5154. (d) Benson, M. A.; Zacchini, S.; Boomishankar, R.; Chan, Y.; Steiner, A. *Inorg. Chem.* **2007**, *46*, 7097–7108. (e) Richards, P. I.; Boomishankar, R.; Steiner, A. *J. Organomet. Chem.* **2007**, *692*, 2773–2779. (f) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2005**, *44*, 275–281. (g) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2004**, *43*, 2810–2817.

(4) (a) Carriedo, G. A.; Crochet, P.; Alonso, F. J. G.; Gimeno, J.; Persa-Soto, A. *Eur. J. Inorg. Chem.* **2004**, *18*, 3668–3674. (b) Carriedo, G. A.; Garcia-Alonso, F. J.; Garcia-Alvarez, J. L.; Pappalardo, G. C.; Punzo, F.; Rossi, P. *Eur. J. Inorg. Chem.* **2003**, *13*, 2413–2418. (c) Carriedo, G. A.; Alonso, F. J.; Elipe, P. G.; Brillas, E.; Julia, L. *Org. Lett.* **2001**, *3*, 1625–1628. (d) Ainscough, E. W.; Brodie, A. M.; Davidson, R. J.; Moubaraki, B.; Murray, K. S.; Otter, C. A.; Waterland, M. R. *Inorg. Chem.* **2008**, *47*, 9182–9192. (e) Ainscough, E. W.; Brodie, A. M.; Derwahl, A.; Kirk, S.; Otter, C. A. *Inorg. Chem.* **2007**, *46*, 9841–9852.

(5) (a) Omotowa, B. A.; Phillips, B. S.; Zabinski, J. S.; Shreeve, J. M. *Inorg. Chem.* **2004**, *43*, 5466–5471. (b) Muralidharan, K.; Omotowa, B. A.; Twamley, B.; Piekarski, C.; Shreeve, J. M. *Chem. Commun.* **2005**, 5193–5195.

cyclophosphazenes are readily prepared by the Friedel−Crafts reaction, realizing derivatives with alkyl, alkenyl, or alkynyl groups is more difficult, often requiring organometallic reagents or the direct synthesis of cyclophosphazene from substituted phosphorus precursors.[8] The pioneering work by Allen and co-workers has shown that alkynyl derivatives of cyclophosphazenes, which are useful precursors for a host of new phosphazene-derived compounds, is accessible by the reaction of halocyclophosphazenes with organolithium reagents.[9] The known phosphazene-derived alkynes have so far been restricted to those having phenyl, *p*-tolyl, *n*-butylethynyl, and trimethylsilyl units, with most of them derived from $N_3P_3F_6$.[9a,10] We as well as others have shown the usefulness of arylethynyl derivatives of cyclophosphazenes in realizing novel cyclophosphazene-derived organoiron and organocobalt clusters as well as cobalt sandwich compounds and metallacycles.[11]

Ferrocene-derived alkynes are established structural motifs in synthetic organometallic chemistry and material science.[12] Functionalized ferrocenylalkynes have been utilized for the introduction of electroactivity on substrates especially oligomers, polymers, and dendrimers.[13,14] Their utility in making materials with nonlinear optical properties and in preparing nucleobase receptors is well documented.[15,16] Although few examples of ferrocene-derived cyclophosphazenes are known,[17] we have for the first time explored the possibility of introducing ferrocenylalkyne units on the phosphazene core and report herein the synthesis and structural characterization of the first examples of mono(ethynylferrocenyl)- and geminal bis(ethynylferrocenyl)-derived fluoro- and chlorocyclophosphazenes. The differences in reactivity of the ethynylferrocene-derived chloro- and fluorophosphazenes with the cobalt half-sandwich compound CpCo(COD) have been described. We also report the synthesis and structural studies of the first examples of cyclophosphazene-derived 1,2,3-triazoles prepared by click reactions of the new ethynylferrocene-derived fluoro- and chlorophosphazenes with benzyl azide. The usefulness of these cyclophosphazene-derived 1,2,3-triazoles as ligands has also been demonstrated by preparing a palladium complex of the triazole.

Results and Discussion

The reactions of lithiated ethynylferrocene with hexafluoro- and hexachlorocyclotriphosphazenes were found to proceed at −78 °C with the formation of mono(ethynylferrocenyl)- and geminal bis(ethynylferrocenyl)-derived fluoro- and chlorophosphazenes **1**−**4** (Schemes 1 and 2). The orange, air-stable compounds were purified easily by column chromatography. Interestingly, the reactions carried out in a 1:1 molar ratio resulted in the formation of both mono(ethynylferrocenyl) and geminal bis(ethynylferrocene) derivatives, with **1** being the major product in the case of $N_3P_3F_6$ and **4** being the major product in the case of $N_3P_3Cl_6$. Maximum yields of **1** and **2** were obtained in a 2:1 molar ratio reaction of $N_3P_3X_6$ and $FcC\equiv CLi$, while the geminal disubstituted derivatives **3** and **4** were obtained best from a 1:2 molar ratio of $N_3P_3X_6$ and $FcC\equiv CLi$. The reactions carried out with a view to realize more substitution on the phosphazene ring were found to result in decomposition products with traces of disubstituted derivatives. In general, compared to $N_3P_3F_6$, the reactions involving $N_3P_3Cl_6$ gave lesser yields of the alkyne derivatives, often giving unreacted $N_3P_3Cl_6$ as well as the dimer of ethynylferrocene as side products.

The reaction of **1** with CpCo(COD) in refluxing toluene was found to give CpCo-derived cyclobutadiene sandwich compounds of the type $(\eta^5\text{-Cp})Co[\eta^4\text{-}C_4(Fc)_2(N_3P_3F_5)_2]$ having both *cis*- and *trans*-substituted phosphazene-derived cyclobutadiene units. The *trans*-disubstituted compound **5** was the major product whose basic structural features were similar to those of $[\eta^5\text{-MeOC(O)Cp}]Co[\eta^4\text{-}C_4(Ph)_2(N_3P_3F_5)_2]$ reported earlier from the reactions of $[MeOC(O)Cp]Co(PPh_3)_2$ and $PhC\equiv CN_3P_3F_5$.[18] The minor *cis*-disubstituted cyclobutadiene compound **6** was a unique example of its kind, which has not

---

(6) (a) Asmafiliz, N.; Kílíç, Z.; Ozturk, A.; Hokelek, T.; Koc, L. Y.; Acik, L.; Kisa, O.; Albay, A.; Ustundag, Z.; Solak, A. O. *Inorg. Chem.* **2009**, *48*, 10102–10116. (b) Besli, S.; Coles, S. J.; Davies, D. B.; Erkovan, A. O.; Hursthouse, M. B.; Kilic, A. *Inorg. Chem.* **2008**, *47*, 5042–5044. (c) İlter, E. E.; Asmafiliz, N.; Kilic, Z.; Isiklan, M.; Hokelek, T.; Caylak, N.; Sahin, E. *Inorg. Chem.* **2007**, *46*, 9931–9944. (d) Bilge, S.; Demiriz, S.; Okumus, A.; Kilic, Z.; Tercan, B.; Hokelek, T.; Buyukgungor, O. *Inorg. Chem.* **2006**, *45*, 8755–8767. (e) Uslu, A.; Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthouse, M. B.; Kílíç, A.; Shaw, R. A. *Eur. J. Inorg. Chem.* **2005**, *6*, 1042–1047. (f) Coles, S. J.; Davies, D. B.; Eaton, R. J.; Hursthouse, M. B.; Kílíç, A.; Shaw, R. A.; Uslu, A. *Eur. J. Org. Chem.* **2004**, *9*, 1881–1886.

(7) (a) Muralidharan, K.; Venugopalan, P.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 3176–3182. (b) Muralidharan, K.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 7535–7543. (c) Muralidharan, K.; Reddy, N. D.; Elias, A. J. *Inorg. Chem.* **2000**, *39*, 3988–3994.

(8) (a) Carter, K. R.; Calichman, M.; Allen, C. W. *Inorg. Chem.* **2009**, *48*, 7476–7481. (b) Allen, C. W. *J. Polym. Sci., Part C; Polym. Symp.* **1983**, *70*, 79–90. (c) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221. (d) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512. (e) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875–1878. (f) Wisian-Neilson, P.; Johnson, R. S.; Zhang, H.; Jung, J.-H.; Neilson, R. H.; Ji, J.; Watson, W. H.; Krawiec, M. *Inorg. Chem.* **2002**, *41*, 4775–4779.

(9) (a) Allen, C. W.; Desorcie, J. L.; Ramachandran, K. *J. Chem. Soc., Dalton Trans.* **1984**, 2843. (b) Bahadur, M.; Allen, C. W.; Geiger, W. E.; Bridges, A. *Can. J. Chem.* **2002**, *80*, 1393–1397. (c) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119–135.

(10) (a) Komuro, T.; Mori, K.; Tobita, H. *Heterocycles* **2009**, *77*, 1171–1183. (b) Allen, C. W.; Bahadur, M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *76*−*77*, 203–206.

(11) (a) Allen, C. W.; Bahadur, M. *J. Inorg. Organomet. Polym.* **1998**, *8*, 23–31. (b) Bahadur, M.; Allen, C. W.; Geiger, W. E.; Bridges, A. *Can. J. Chem.* **2002**, *80*, 1393–1397. (c) Kumar, M. S.; Gupta, R. P.; Elias, A. J. *Inorg. Chem.* **2008**, *47*, 3433–3441. (d) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256–2261.

(12) (a) Long, N. J.; Williams, K. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586. (b) Long, N. J. *Metallocenes*; Blackwell: London, U.K., 1995. (c) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: New York, 1995. (d) Stepnicka, P., Ed. *Ferrocenes: Ligands, Materials and Biomolecules*; Wiley: Chichester, U.K., 2008.

(13) (a) Plenio, H.; Hermann, H.; Sehring, A. *Chem.—Eur. J.* **2000**, *6*, 1820–1829. (b) Plenio, H.; Hermann, J.; Leukel, J. *Eur. J. Inorg. Chem.* **1998**, 2063–2069. (c) Schottenberger, H.; Buchmeiser, M. R. *Recent Res. Dev. Macromol. Res.* **1998**, *3*, 535. (d) Simionescu, C.; Lixandru, T.; Mazilu, I.; Tataru, L.; Ghivru, C. I. *Chem. Zvesti* **1974**, *28*, 810. (e) Vollmann, M.; Butenschoen, H. *C. R. Chim.* **2005**, *8*, 1282. (f) Rosenblum, M.; Brawn, N. M.; Ciappenelli, D.; Tancrede, J. *J. Organomet. Chem.* **1970**, *24*, 469–477.

(14) (a) Wang, A.; Ornelas, C.; Astruc, D.; Hapiort, P. *J. Am. Chem. Soc.* **2009**, *131*, 6652–6653. (b) Diallo, A. K.; Daran, J. C.; Varret, F.; Ruiz, J.; Astruc, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 3141–3145. (c) Orneals, C.; Salmon, L.; Ruiz, J.; Astruc, D. *Chem.—Eur. J.* **2008**, *14*, 50–64. (d) Ornelas, C.; Ruiz, J.; Cloutet, E.; Alves, S.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 872–877. (e) Diallo, A. K.; Orneals, C.; Salmon, L.; Ruiz, J.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644–8648. (f) Orneals, C.; Salmon, L.; Ruiz, J.; Astruc, D. *Chem. Commun.* **2007**, 4946–4948. (g) Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460.

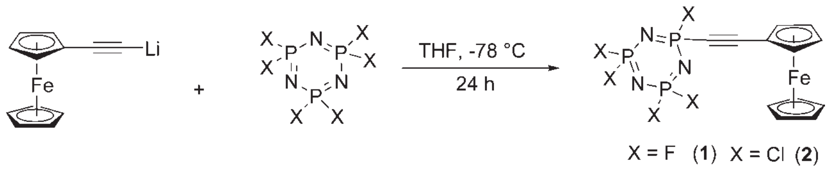
(15) (a) Di Bella, S. *Chem. Soc. Rev.* **2001**, *30*, 355. (b) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. In *Adv. Organomet. Chem.* **1998**, *42*, 291−362. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21–38.

(16) Inouye, M.; Itoh, M. S.; Nakazumi, H. *J. Org. Chem.* **1999**, *64*, 9393–9398.

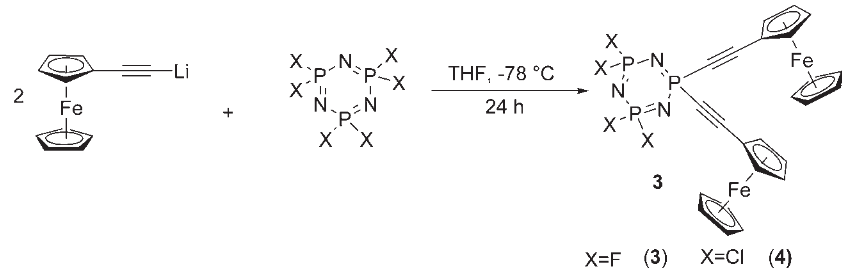
(17) (a) Chandrasekhar, V.; Andavan, G. T. S.; Nagendran, S.; Krishnan, V.; Azhakar, R.; Butcher, R. J. *Organometallics* **2003**, *22*, 976–986. (b) Nataro, C.; Myer, C. N.; Cleaver, W. M.; Allen, C. W. *J. Organomet. Chem.* **2001**, *637*−*639*, 284–290. (c) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119–157. (d) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R.; Parvez, M. *Organometallics* **1986**, *5*, 1626–1635. (e) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337–2347. (f) Herberhold, M.; Hofmann, A.; Milius, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1599–1608.

(18) Kumar, M. S.; Upreti, S.; Elias, A. J. *Inorg. Chem.* **2006**, *45*, 7835–7842.

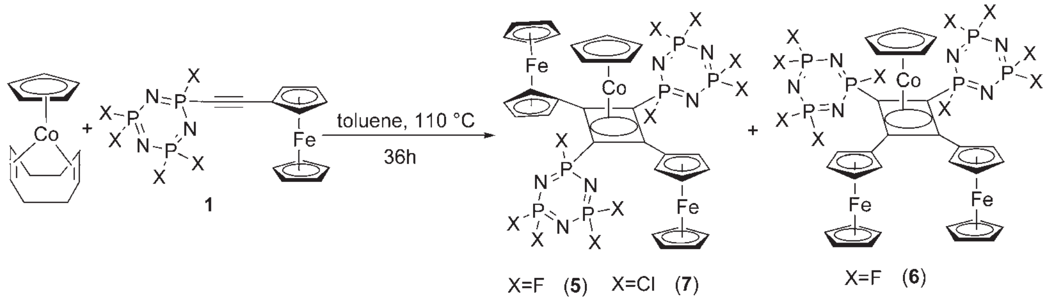
Scheme 1



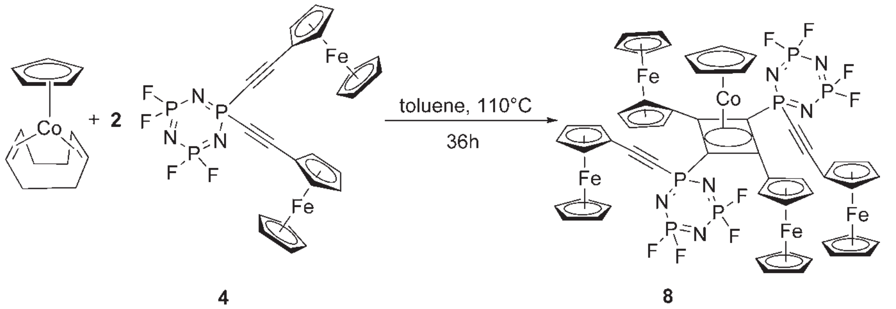
Scheme 2



Scheme 3



Scheme 4



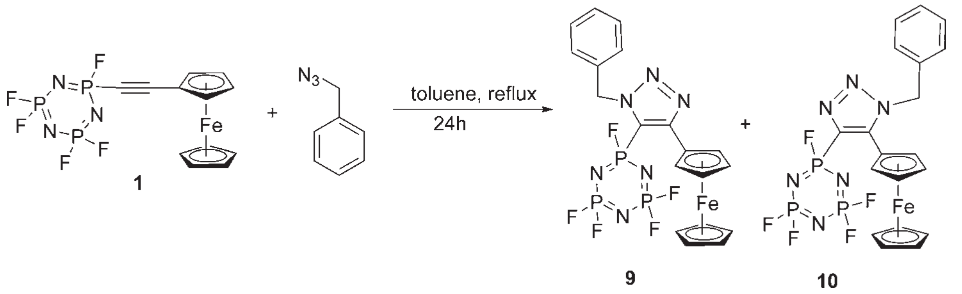
been observed to form in the reactions of $CpCo(PPh_3)_2$ or $CpCo(CO)_2$ with fluorophosphazene-derived phenylacetylene. In contrast, the reaction of **2** with CpCo(COD) resulted exclusively in the formation of the *trans*-disubstituted cyclobutadiene derivative $(\eta^5\text{-Cp})Co[\eta^4\text{-}C_4(Fc)_2(N_3P_3Cl_5)_2]$ (**7**; Scheme 3).

The reaction of geminal ethynylferrocene-disubstituted fluorophosphazene **4** with an excess of CpCo(COD) was found to result in $(\eta^5\text{-Cp})Co\{\eta^4\text{-}C_4\text{-}1,3\text{-}(Fc)_2\text{-}2,4\text{-}[NP(C{\equiv}CFc)(NPF_2)_2]_2\}$ (**8**), having two unreacted ethynylferrocene units on the fluorocyclophosphazene moieties (Scheme 4).

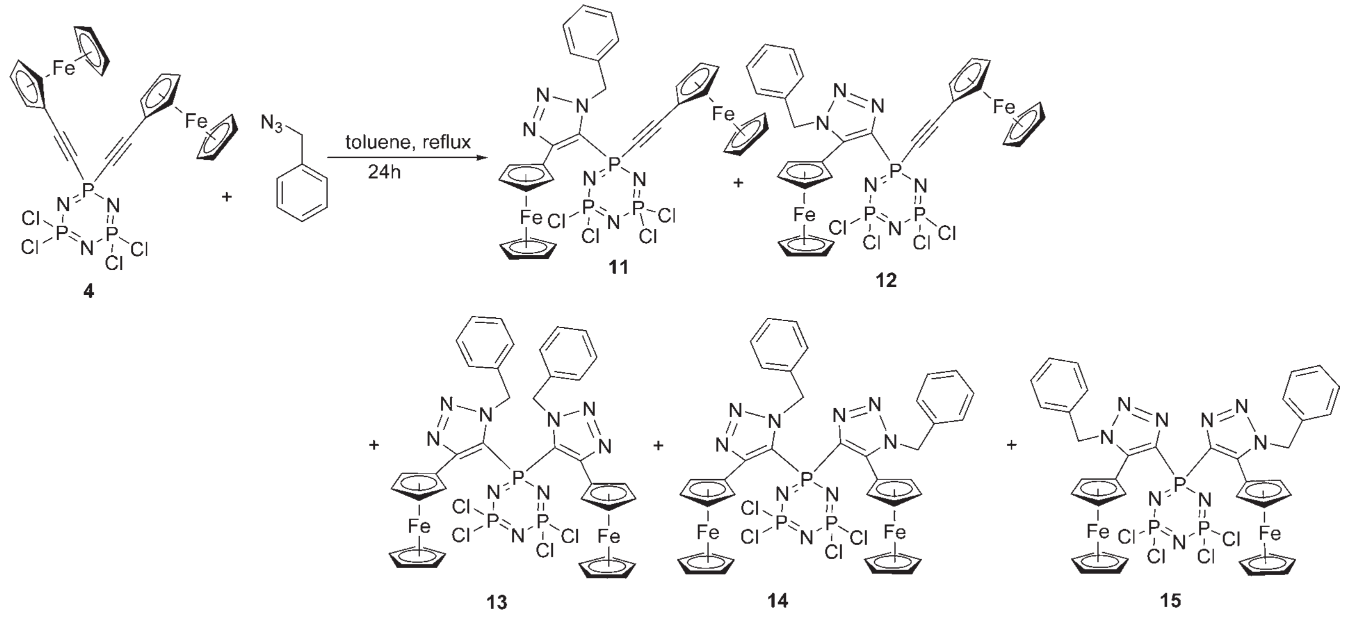
The Huisigen 3 + 2 cycloaddition reactions, commonly known as click reactions, involve the reaction of an azide with alkynes, resulting in the formation of substituted 1,2,3-triazoles. We were interested in observing the feasibility of such reactions of cyclophosphazene-derived alkynes and carried out the first click reactions of the fluoro- and chlorophosphazene-derived alkynes **1** and **4** with benzyl azide in refluxing toluene. The reaction of **1** with $PhCH_2N_3$ resulted in two positional isomers of the 1,2,3-triazoles $(1\text{-}PhCH_2, 4\text{-}Fc, 5\text{-}P_3N_3F_5)C_2N_3$ (**9**) and $(1\text{-}PhCH_2, 4\text{-}P_3N_3F_5, 5\text{-}Fc)C_2N_3$ (**10**) (Scheme 5). Compound **10**, having the benzyl group in the vicinity of ferrocenyl unit, was obtained as the major product.

The reaction of the geminal bis(ethynylferrocene)-substituted chlorophosphazene **4** with benzyl azide gave five products having triazole units that were carefully separated, purified, and structurally characterized (Scheme 6). Compounds **11** and **12** were positional isomers of the triazole having one of the ethynylferrocene units remaining intact. Compounds **13**–**15** were two triazole units, with **13** having benzyl and ferrocenyl units symmetrically substituted in the 1 and 4 positions of the triazole and **15** having the same groups symmetrically substituted at the 1 and 5 positions of the triazole. Compound **14**, which was the major product among the bis-triazole compounds, was found to be unsymmetrically

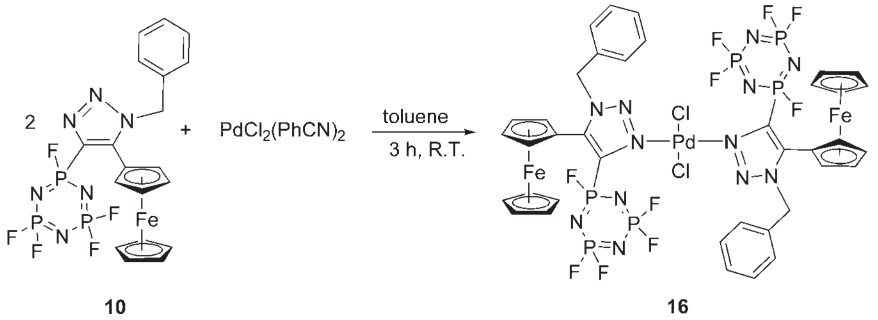
Scheme 5



Scheme 6



Scheme 7



substituted ,with one triazole ring having 1,4 and the other 1,5 substitution of the benzyl and ferrocenyl groups.

The utility of substituted phosphazenes, especially as multidentate ligands in coordination chemistry, is well documented.[1a,b] We were keen to explore the possibility of using the phosphazene- and ferrocene-derived 1,2,3-triazoles as ligands in coordination chemistry. A 2:1 molar reaction of the fluorophosphazene-derived triazole **10** with $PdCl_2(PhCN)_2$ resulted in the exclusive formation of a square-planar palladium complex, *trans*-$[(1\text{-}PhCH_2\text{-}4\text{-}P_3N_3F_5\text{-}5\text{-}Fc)C_2N_3]_2PdCl_2$ (**16**; Scheme 7).

Spectral Studies of Compounds 1–16. Compounds **1–16** have been characterized by IR, NMR (^1H, ^{13}C, ^{31}P, and ^{19}F), and mass spectral studies. The ^1H NMR chemical shifts for the unsubstituted cyclopentadienyl units of compounds **1–4** were found to be in the range of 4.23–4.32 ppm, whereas the α protons of the substituted cyclopentadienyl were located downfield in the range of 4.57–4.68 ppm. The cyclopentadiene ring attached to the cobalt metal center in compounds **5–8** gave a singlet in the range of 4.85–5.08 ppm. Both CH_2 groups, which were attached to the triazole ring, gave two different signals at 5.96 and 6.10 ppm in **14** because of different chemical environments, which was in contrast to **13** and **15**, which gave single peaks for these CH_2 groups at 5.80 and 5.94 ppm, respectively.

The ^{31}P NMR chemical shifts of the ethynylferrocene-substituted phosphorus atom of the cyclophosphazene rings were found to undergo significant changes on derivatization of the alkynes. While the chemical shift of the ethynylferrocene-bound PF unit of **1** was observed at 3.79 ppm (J_{PF} = 920 Hz), δ values of the *trans* and *cis*-cyclobutadiene-disubstituted cobalt sandwich compounds **5** and **6**, derived from **1**, were observed at 35.48 and 37.55 ppm, respectively. The chemical shift of the same phosphorus atom in the analogous *trans*-fluorophosphazene-disubstituted compound (η^5-$CH_3OC(O)C_5H_4$)Co{$\eta^4$$C_4$[1,3-($N_3P_3F_5$)$_2$-2,4-(Ph)$_2$]}[18] was observed at 32.44 ppm. Similar changes in the ^{31}P NMR chemical shifts were also observed for the phosphazene-derived triazoles as well. The two positional isomers **9** and **10** of the fluorophosphazene-derived 1,2,3-triazole gave resonances for the triazole-bound P−F units at 20.08 and 24.70 ppm, respectively. Upon formation of the square-planar palladium complex **16**, the ^{31}P NMR δ value of the triazole-bound P−F unit of **10** was found to shift from 24.70 to 20.65 ppm. The ^{31}P NMR δ value of the dialkyne-bound phosphorus atom of **3** was observed at −24.83 ppm, while for its partially CpCo cyclobutadiene-derived derivative **8**, it was found to shift to 0.65 ppm. In contrast, only minimal changes in the range of 6.63−7.91 ppm were observed in the ^{31}P NMR chemical shifts of the PF_2 units of all fluorophosphazene-derived compounds in the present study.

Similar shifts in the ^{31}P NMR δ values were also observed for the chlorophosphazene-derived alkynes and their derivatives. The chemical shift of the P(Cl)(C≡CFc) unit of the mono-substituted chlorophosphazene-derived alkyne **2**, upon conversion to the CpCo cyclobutadiene-derived sandwich compound **7**, was found to shift from −5.28 to +27.41 ppm. The P(C≡CFc)$_2$ unit of compound **4**, which showed a resonance at −33.18 ppm, underwent a considerable downfield shift after the formation of triazoles. The mixed triazole- and alkyne-substituted compounds **11** and **12** resonated at a higher field in comparison to compounds **13**−**15** because of the shielding nature of the ethynyl units. Triazole-substituted phosphorus atoms in compounds **13**−**15** resonated at −6.67, −1.80, and +0.94 ppm, respectively. The triazole-substituted phosphorus atom in compound **13** resonated slightly upfield in comparison to those of **14** and **15** because of its proximity to the electron-rich sp^3-hybridized nitrogen atoms.

^{13}C NMR analysis of the ethynylferrocene-derived chloro- and fluorophosphazenes **1**−**4** indicated the presence of one of the alkyne carbon atoms in the range of 104−107 ppm and the other carbon in the range of 79−83 ppm, which agreed with the reported ^{13}C NMR value of (FcC≡C)$_2$PhP=Se,[19a] where chemical shifts were reported at 106.3 and 79.5 ppm. Cyclobutadiene ring carbon atoms of the cobalt sandwich compounds **5**−**8** resonated in the range of 83.50−86.00 ppm, which agrees well with the ^{13}C NMR δ values reported for the C_4 ring of (η^5-$CH_3OC(O)C_5H_4$)Co{η^4-C_4-[1,3-($N_3P_3F_5$)$_2$-2,4-(Ph)$_2$]}.[18] The ^{13}C NMR δ values of the ring carbon atoms of the five-membered triazole rings of compounds **9**−**16** were observed in the expected range of 141.70−155.55 ppm.

The $\nu_{C\equiv C}$ stretching frequency for compounds **1**− **4**, **8**, **11**, and **12** were found to be in the range of 2152−2176 cm^{-1}. This corresponds to the $\nu_{C\equiv C}$ stretching frequency reported in the case of ethynylferrocenyl compounds (FcC≡C)$_2$PhP=Se, (FcC≡C)$_3$P=Se,[19a] and N_3P_3[C≡C-(*p*-Tol)]$_2$$Cl_4$,[10a] where it was observed in the range of 2148−2179 cm^{-1}. The $\nu_{N=N}$ stretching frequencies for all triazole-containing compounds were found to be between 1545 and 1552 cm^{-1} and were comparable to those observed for other reported 1,2,3- triazole heterocycles.[20]

The ^{19}F NMR spectra of compounds **1**, **3**, **5**, **6**, **8**−**10**, and **16** gave signals between −64.43 and −69.63 ppm for PF_2 groups and between 42.05 and 48.08 ppm for the PF(C) moiety. This chemical shift is consistent with previously reported ethynyl-derived fluorophosphazene-[9a] and fluorophosphazene-substituted metallocenes and metallacycles.[18] ^{19}F NMR spectra of compounds **1**, **5**, **6**, **8**−**10**, and **16** showed two sets of doublet of multiplets at different chemical shifts for the PF_2 groups ($^1J_{P-F}$ ∼ 750−970 Hz) because of the diastereotopic nature of the fluorine atoms of the $N_3P_3F_5$ units.

Electrochemical Studies. The redox properties of the ferrocenyl units of some of the new compounds were studied by cyclic voltammetry using 0.1 M *tert*-butylammonium perchlorate in dichloromethane as the supporting electrolyte with a scan rate of 50−100 mV. The potential of the Fc/Fc$^+$ couple under experimental conditions was 0.10 V (80 mV) vs Ag/Ag$^+$. The cyclic voltammograms of **1**−**4** exhibited only one reversible redox wave, despite having the presence of two ferrocene units in **3** and **4**, indicating that both of these ferrocene units are in the same chemical environment, an observation supported by X-ray crystallography. Similar electrochemical behaviors were reported in the cases of (FcC≡C)$_2$PhP and (FcC≡C)$_3$P.[21] Compounds **5**−**7** having two ferrocenyl units in the molecule indicated the presence of two redox waves in their cyclic voltammograms in the half-wave potential range of $E_{1/2}$ = 0.21−0.44 V. The nature of these cyclic voltammograms was found to be similar as that of the previously reported (η^5-Cp)Co{η^4-[C_4(C_5H_5)$_2$-(Fc)$_2$]}.[22] In the case of the chlorophosphazene-derived compound **7**, the separation between the two redox peaks (at 0.24 and 0.38 V) was found to be more noticeable in comparison to the fluorophosphazene-derived compounds **5** and **6**. The monoferrocenyl compounds **9** and **10** showed reversible redox waves with $E_{1/2}$ at 0.28 and 0.46 V, respectively. The diferrocenyl compounds **8**, **11**, and **14** showed two separate oxidation waves having chemical reversibility ($E_{1/2}$ = 0.23 and 0.43 V for **8**; $E_{1/2}$ = 0.25 and 0.44 V for **11**; $E_{1/2}$=0.23 and 0.46 V for **14**). Oxidation waves at $E_{1/2}$ = 0.43 and 0.44 V in the case of **8** and **11** were due to the ethynylferrocene units. Compound **14** showed two different redox peaks due to the different chemical environments around the two ferrocene units, while observation of a single peak in the case of **13** and **15** indicated similar chemical environments around both of the ferrocene units, which was substantiated from single-crystal X-ray structural analysis. The palladium complex **16** showed a reversible oxidation wave for the ferrocene units at $E_{1/2}$ = 0.54 V, slightly higher than the parent triazole **10** because of the decreased electron density at the ferrocene moieties, caused by complexation of the triazole ring nitrogen atom with the palladium center.

---

(19) (a) Jakob, A.; Milde, B.; Ecorchard, P.; Schreiner, C.; Lang, H. *J. Organomet. Chem.* **2008**, *693*, 3821–3830. (b) Jakob, A.; Ecorchard, P.; Linseis, M.; Winter, R. F.; Lang, H. *J. Organomet. Chem.* **2009**, *694*, 655–666.

(20) Kamalraj, V. R.; Senthil, S.; Kannan, P. *J. Mol. Struct.* **2008**, *892*, 210–215.

(21) Baumgartner, T.; Fiege, M.; Pontzen, F.; Muller, R. A. *Organometallics* **2006**, *25*, 5657–5664.

(22) Kotz, J.; Neyhart, G.; Vining, W. J.; Rausch, M. D. *Organometallics* **1983**, *2*, 79–82.

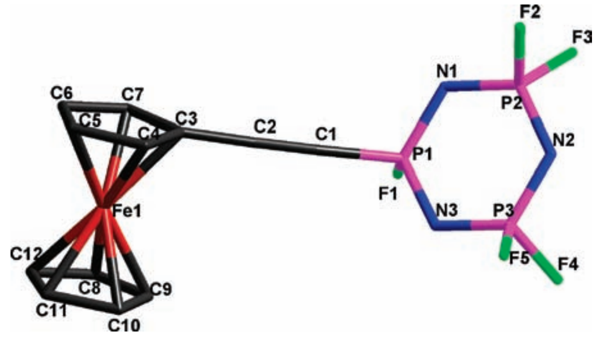


Figure 1. Molecular structure of compound **1** (hydrogen atoms have been omitted for clarity).

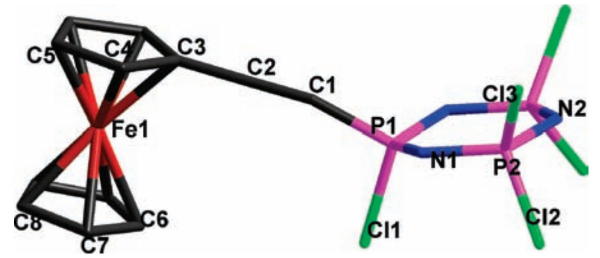


Figure 2. Molecular structure of compound **2** (hydrogen atoms have been omitted for clarity).

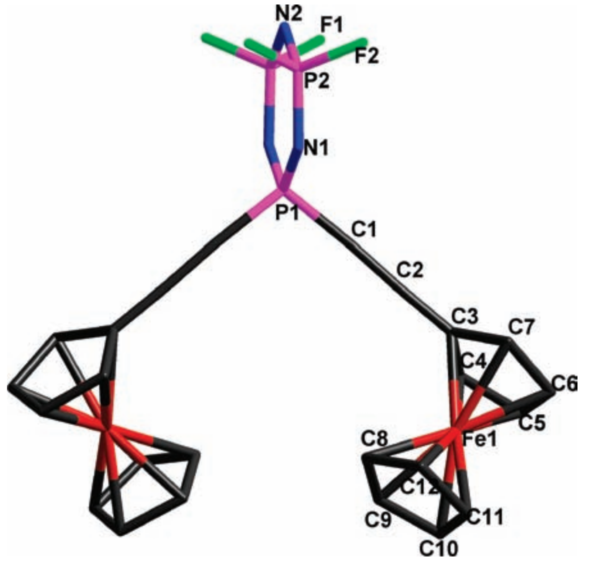


Figure 3. Molecular structure of compound **3** (hydrogen atoms have been omitted for clarity).

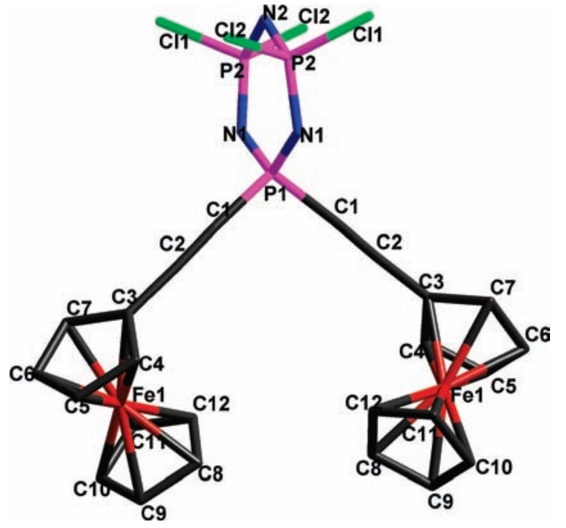


Figure 4. Molecular structure of compound **4** (hydrogen atoms have been omitted for clarity).

X-ray Crystal Structures of Compounds 1−4. The crystal structures of compounds **1**−**4** are given in Figures 1−4. The fluorophosphazene ring was found to be in an almost planar geometry in **1** and **3** because the phosphorus atoms bearing the ethynylferrocene groups do not deviate significantly from the mean plane defined by the other four atoms of the phosphazene ring. In contrast, the N_3P_3 ring of the chlorophosphazene-derived alkyne **2** was clearly in a chair conformation, with P(1) and N(2) deviating from the mean plane defined by the other four ring atoms by +0.204(1) and −0.123(5) Å, respectively. In compound **4**, the N_3P_3 ring was found to be in a twist-boat form, which is in contrast to the chair configuration reported for geminal bis(*p*-tolylethynyl)tetrachlorocyclotriphosphazene.[10a] In compounds **1**−**4**, the P−N bond distances involving the ethynylferrocene-substituted phosphorus atoms were found to be in the range of 1.568(6)−1.595(4) Å, which were longer than the other P−N bonds for both chloro- and fluoro-substituted cyclophosphazene units in **1**−**4** [1.530(4)−1.574(3) Å]. Similarly, N(1)−P(1)−N(1) angles in **2**−**4** and the N(1)−P(1)−N(3) angle in **1** (mean value 116.13°) were found to be narrower than the other N−P−N angles of compounds **1**−**4**. These variations were found to be more noticeable in the geminal bis(ethynylferrocenyl)-derived cyclophosphazenes **3** and **4** and can be attributed to the greater electron donation by the two alkynyl groups to the phosphorus atom. Similar variations were observed in the crystal structures of several mono- and diorgano-substituted cyclotriphosphazenes.[10a,23] The P−C bond distances in compounds **1**−**4** were in the range of 1.705(8)−1.726(3) Å, and the C≡C triple bond distances in **1**−**4** were between 1.189(7) and 1.194(10) Å. These distances were similar to those found in phosphorus-based ferrocenylalkynes $(FcC{\equiv}C)_3P{=}O$ and $(FcC{\equiv}C)_3P{=}Se$.[19a] The ethynyl units show deviation from linearity with P(1)−C(1)−C(2) angles of 178.6(7)° (**1**), 166.7(5)° (**2**), 176.5(5)° (**3**), and 176.7(3)° (**4**). A similar deviation from linearity in the range 167.9(2)−175.6(3)° has been reported for $(FcC{\equiv}C)_3P$, $(FcC{\equiv}C)_3P{=}O$, and $(FcC{\equiv}C)_3P{=}Se$.[19] In contrast, the C(1)−C(2)−C(3) angles for **1**−**4** were found to be almost linear [177.3(8)°, 179.5(4)°, 177.8(6)°, and 177.9(4)°, respectively]. These bond angles were found to vary in the range 176.4(3)−180.0(3)° for $(FcC{\equiv}C)_3P$ and $(FcC{\equiv}C)_3P{=}Se$.[19a]

X-ray Crystal Structures of Compounds 5−7. The crystal structures of compounds **5**−**7** are given in Figures 5−7. The structure of **6** given in Figure 6 shows the occurrence of two different molecules (A and B) within the asymmetric unit. In compound **5**, the two pentafluorophosphazene units bound to the cyclobutadiene ring were *trans* to each other. The phosphazene units were gauche to each other in **5**−**7**. For compounds **5**−**7**, mean planes containing the two phosphazene

---

[23] (a) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434–2446. (b) Allcock, H. R.; Brennan, D. J.; Dunn, B. J.; Parvez, M. *Inorg. Chem.* **1988**, *27*, 3226–3233. (c) Mani, N. V.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1965**, *19*, 693–698.

units intersect each other at angles of 35.4(1)°, 73.6(1)° [71.9(1)°], and 74.5(1)°, respectively. The mean plane of the phosphazene units makes angles of 42.4(1)° and 58.1(1)° in **5**, 40.6(2)° [41.5(2)°] and 74.7(2)° [76.0(2)°] in **6**, and 41.2(2)° and 33.6(2)° in **7**, with the mean plane passing through the cyclobutadiene ring. In **5** and **7**, the two ferrocene units were *cis* with respect to the cyclobutadiene ring of the cobalt sandwich unit, which was in contrast to compound **6**, where the two ferrocene units were found to be oriented nearly perpendicular to each other, with the substituted Cp rings making an angle of 74.2(3)° [72.1(3)°] between them. Mean planes passing through the substituted cyclopentadiene rings of the ferrocene units of **5** and **7** make relatively small angles [9.8(3) −22.1(3)°] with the mean plane passing through the cyclobutadiene unit. In contrast, these angles were found to be 20.6(3)° [16.7(3)°] and 55.7(3)° [56.7(4)°] for **6**. Porous molecular materials attract lot of attention because of their extensive application in heterogeneous catalysis. The crystal structure of compound **7** features voids that can possibly accommodate small molecules (Figure 8). These voids are a result of the weak C−H···π(Cp) and

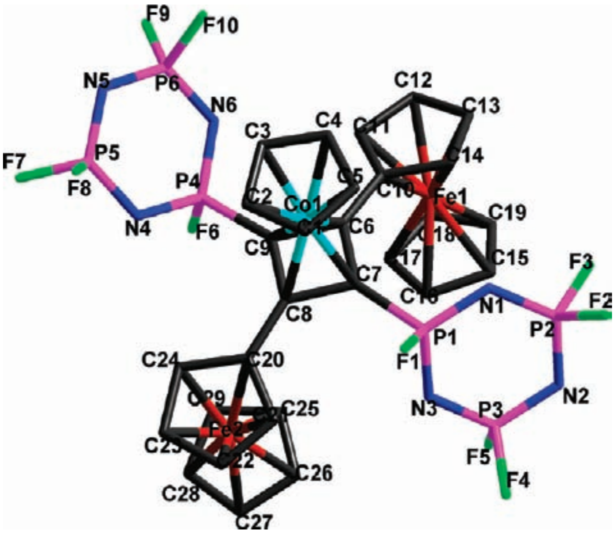


Figure 5. Molecular structure of compound **5** (hydrogen atoms have been omitted for clarity).

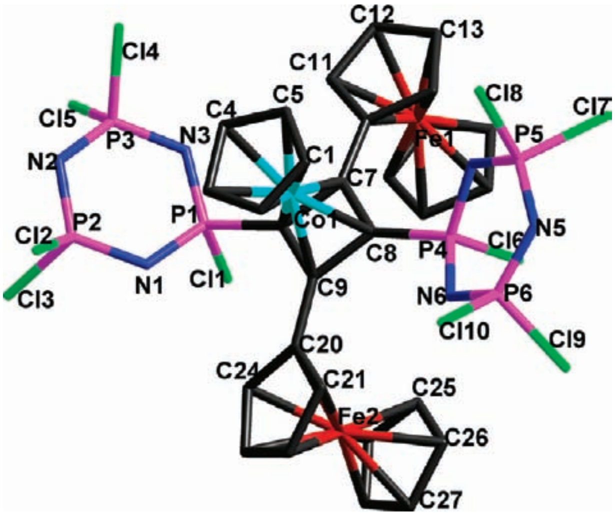


Figure 7. Molecular structure of compound **7** (hydrogen atoms and the solvent molecule have been omitted for clarity).

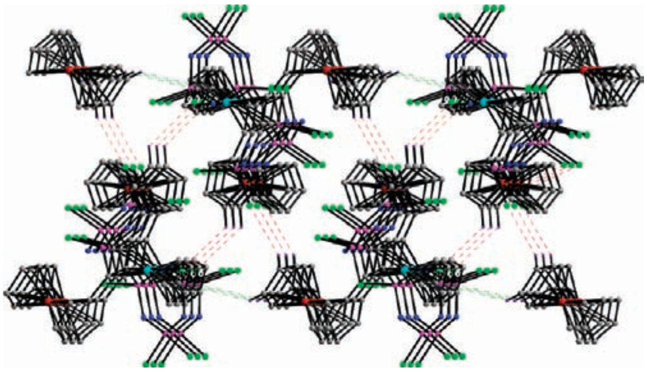


Figure 8. Crystal packing diagram of compound **7** showing voids and weak interactions (hydrogen atoms that are not involved in intermolecular interactions have been omitted for clarity).

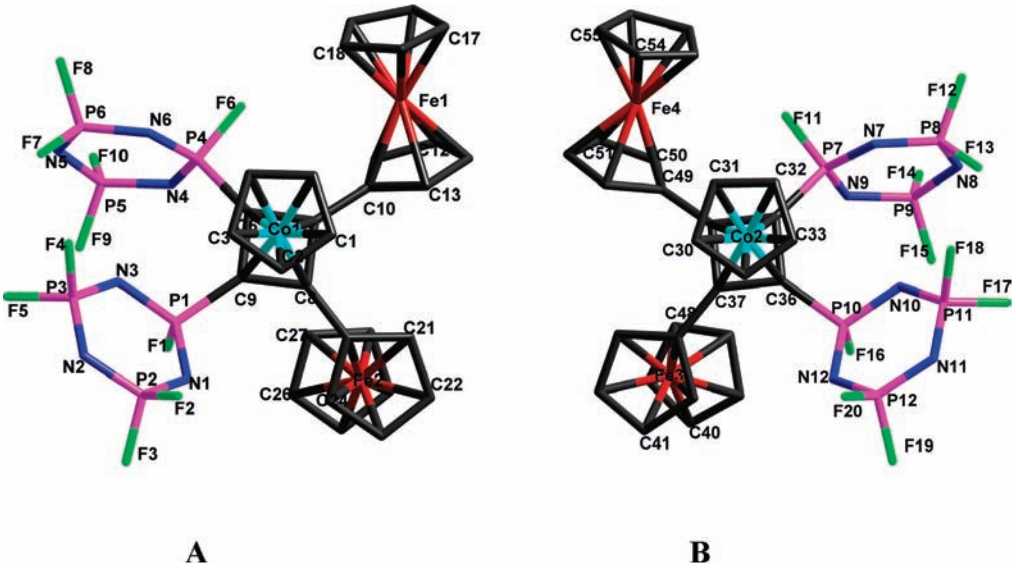


Figure 6. Molecular structure of compound **6** (hydrogen atoms have been omitted for clarity).

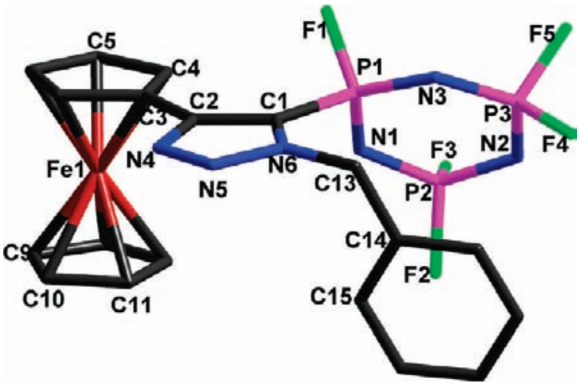


Figure 9. Molecular structure of compound **9** (hydrogen atoms have been omitted for clarity).

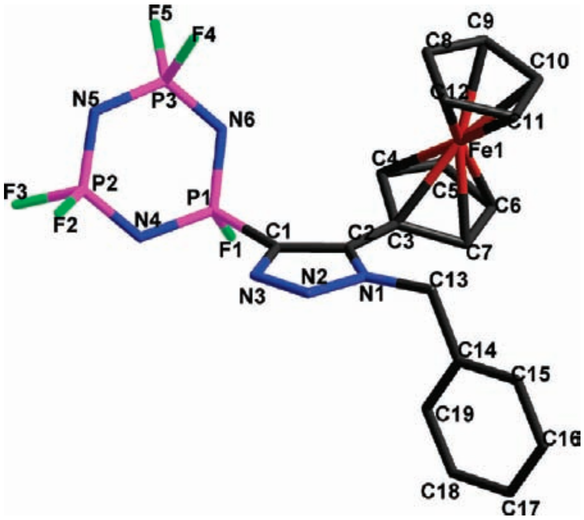


Figure 10. Molecular structure of compound **10** (hydrogen atoms have been omitted for clarity).

P−Cl···H interactions found between the cyclopentadienyl rings and the cyclophosphazenyl units.

X-ray Crystal Structures of Compounds 9−11 and 13−15. The crystal structures of compounds **9**−**11** and **13**−**15** are given in Figures 9−14. The C=C bond distances of triazole rings vary in these compounds in the range from 1.380(5) to 1.393(8) Å, and the N=N bond distances of the triazole unit vary in the range of 1.296(5)−1.323(5) Å, which agree with analogous distances for the reported structure of monoferrocenyltriazole.[24] For the isomeric monotriazolyl compounds **9** and **10**, the bond distances and angles of the triazole ring were found to be almost identical, but the orientations of $P_3N_3F_5$ and the substituted cyclopentadiene ring of ferrocene with respect to the triazole ring were different. The angles between the mean plane of the triazole and the Cp rings to which they are attached were found to be 6.1(2)° for **9** and 22.4(2)° for **10**, whereas the angles between the mean plane of the triazole and the $P_3N_3F_5$ ring were found to be 59.2(1)° and 69.2(2)°, respectively.

The C≡C bond distance for compound **11** was found to be 1.196(1) Å, which is comparable to that of the related compound $(FcC{\equiv}C)P(Ph)_2$.[19a] The angle P(1)−C(20)−C(21) was found to be 165.0(5)° in **11**, which corresponds

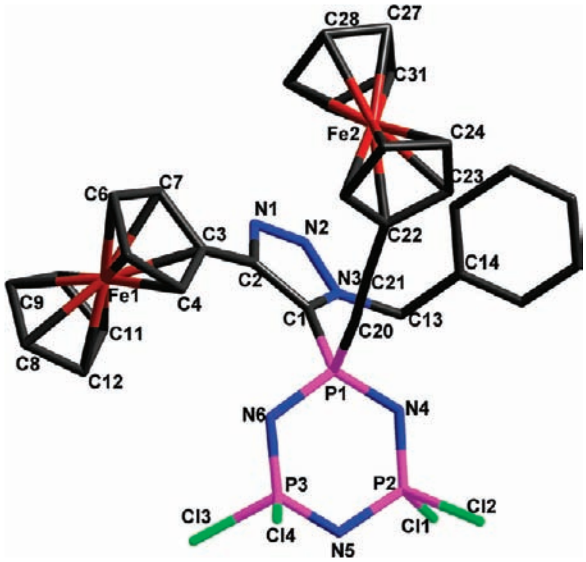


Figure 11. Molecular structure of compound **11** (hydrogen atoms have been omitted for clarity).

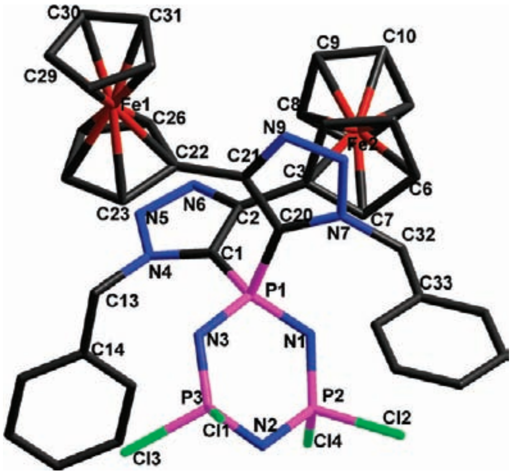


Figure 12. Molecular structure of compound **13** (hydrogen atoms and the solvent molecule have been omitted for clarity).

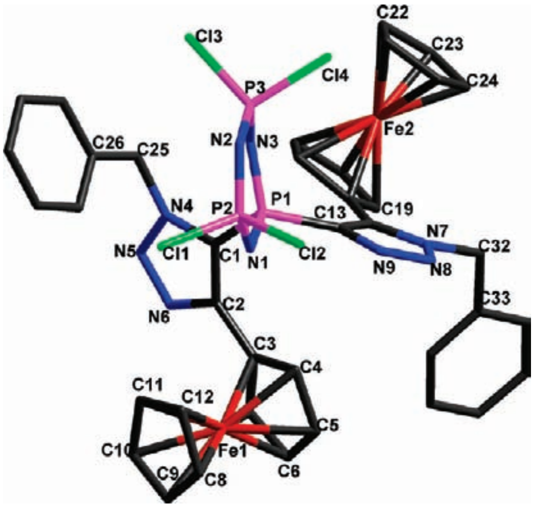


Figure 13. Molecular structure of compound **14** (hydrogen atoms have been omitted for clarity).

---

(24) Badèche, S.; Daran, J. C.; Ruiz, J.; Astruc, D. *Inorg. Chem.* **2008**, *47*, 4903–4908.

very well [165.1(13)°] to similar angles in the ferrocene-derived alkyne−phosphine complex $[(\mathrm{FcC{\equiv}C})_3\mathrm{P}]_2\mathrm{PdCl}_2$.[19a] The mean plane passing through the triazole ring makes angles of 12.3(2)° and 49.3(2)° with the substituted cyclopentadienyl unit of ferrocene and the phosphazene ring, respectively.

The angles between the mean planes passing through the two triazole rings were found to be in the range of 67.6(1)−73.0(1)°. The angles between the mean plane of the $\mathrm{P_3N_3Cl_4}$ unit and the two geminal triazole rings were found to be 58.0(1)° and 60.5(1)° in **13**, 70.6(1)° and 60.0(1)° in **14**, and 77.0(1)° in **15**. The angles between the triazole and the Cp ring with which it is attached were found to be 71.5(1)° and 73.8(1)° in **13**, 20.5(1)° and 10.5(1)° in **14**, and 43.5(1)° in **15**. In the structure of **13**, a solvated ethyl acetate molecule was also found in the crystal lattice.

The angles between the mean plane of the triazole ring and the plane defined by ring atoms of $\mathrm{P_3N_3F_5}$ were found to be 59.2(1)° in **9** and 69.2(2)° in **10**. Analogous angles for the chlorophosphazene-derived triazoles were found to be 49.3(1)° in **11**, 60.4(1)° and 57.9(1)° in **13**, 70.6(1)° and 59.9(1)° in **14**, and 77.0(1)° in **15**.

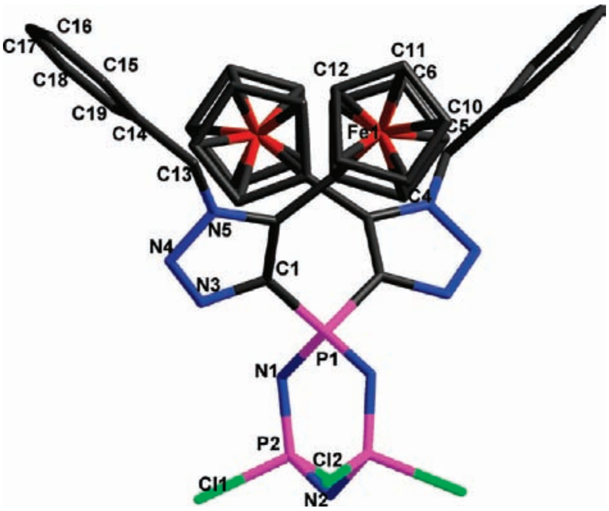


Figure 14. Molecular structure of compound **15** (hydrogen atoms have been omitted for clarity).

X-ray Crystal Structure of Compound 16. The crystal structure of compound **16** is given in Figure 15. In **16**, two molecules of the fluorophosphazene-derived triazole **10** form a square-planar complex, with the triazole rings oriented *trans* to each other. Interestingly, the nitrogen atom that was at the β position with respect to the electron-withdrawing fluorophosphazene unit readily takes part in coordination. Coordination to palladium through the N(6) atom of the triazole did not affect significantly the geometry of the triazole ring, but there was a change in the orientation of $\mathrm{P_3N_3F_5}$ and the ferrocene units with respect to the triazole ring. Pd−N(6) and Pd−Cl(1) were found to be 2.020(3) and 2.288(2) Å, which were similar to analogous distances in a recently reported monoferrocenyltriazole complex.[24] The dihedral angle between the mean plane of the triazole ring and the Cp connected to it changed from 22.4(2)° to 38.2(2)° after forming the palladium complex. In addition, the dihedral angle between the triazole and $\mathrm{P_3N_3F_5}$ changed to 58.8(1)° from 69.2(2)° of the triazole. The dihedral angle between the triazole ring and the palladium square plane was found to be 55.9(2)°. Two solvated molecules of chloroform were also found to be present in the crystal lattice.

Conclusion

The first examples of mono(ethynylferrocene)- and geminal bis(ethynylferrocene)-derived fluoro- and chlorophosphazenes have been synthesized and structurally characterized. The reactions of these alkynes with CpCo(COD) were found to show interesting differences, with the fluorophosphazene-derived alkyne $\mathrm{FcC{\equiv}CP_3N_3F_5}$ yielding both *cis* and *trans* isomers of the cyclobutadienecobalt complexes of the type $(\eta^5\text{-Cp})\mathrm{Co}\{\eta^4\text{-C}_4[\mathrm{Fc}_2(\mathrm{N_3P_3F_5})_2]\}$ and the chlorophosphazene analogue, $\mathrm{FcC{\equiv}CP_3N_3Cl_5}$, giving exclusively the *trans*-cyclobutadiene-substituted product. The reaction of the geminal bis(ethynylferrocene)-derived fluorophosphazene

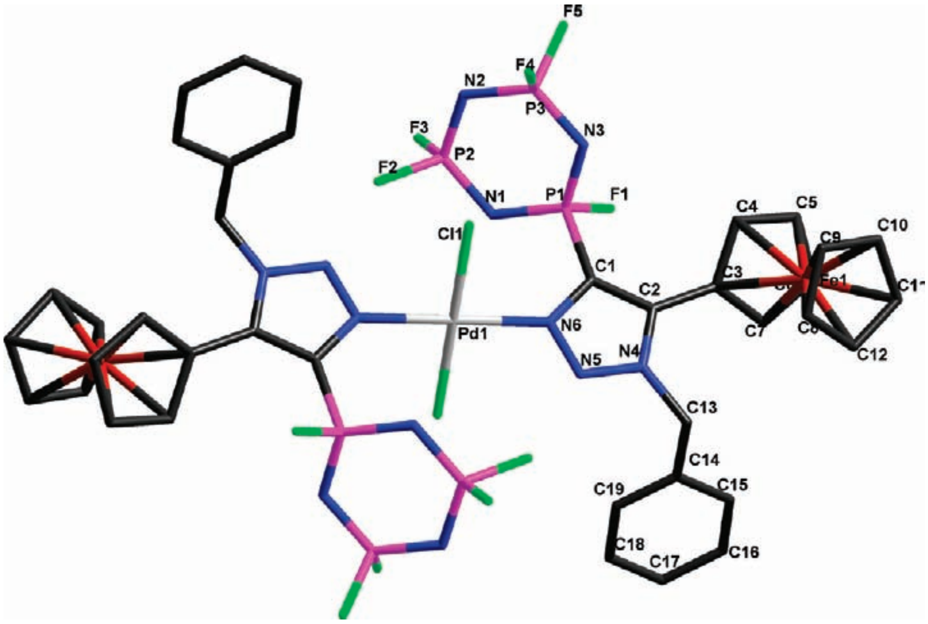


Figure 15. Molecular structure of compound **16** (hydrogen atoms and solvent molecules have been omitted for clarity).

Table 1. X-ray Crystallographic Data for Compounds **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{12}H_9F_5FeN_3P_3$	$C_{12}H_9Cl_5FeN_3P_3$	$C_{24}H_{18}F_4Fe_2N_3P_3$	$C_{24}H_{18}Cl_4Fe_2N_3P_3$
fw	438.98	521.23	629.02	694.82
space group	*Pca*21	*P*21/*m*	*C*2/*c*	*C*2/*c*
a (Å)	20.224(4)	8.1060(13)	15.469(4)	15.993(3)
b (Å)	10.136(2)	9.3159(15)	19.649(4)	20.501(3)
c (Å)	7.9972(17)	13.322(2)	10.899(3)	11.1149(17)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	105.453(2)	130.422(3)	130.846(2)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	1693.4(6)	969.6(3)	2522.0(10)	2756.9(7)
Z	4	2	4	4
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	1.779	1.785	1.657	1.674
μ (mm^{-1})	1.264	1.715	1.390	1.635
θ range	1.96−25.00	2.61−25.00	2.02−23.50	1.95−25.50
R1^a, wR2^b [$I > 2\sigma(I)$]	0.0623, 0.1335	0.0395, 0.1037	0.0558, 0.1246	0.0383, 0.0897

^{a}R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b}wR $= \{[\sum(|F_o|^2|F_c|^2)^2]\}^{1/2}$.

Table 2. X-ray Crystallographic Data for Compounds **5**−**7**, **9**, and **10**

	5	**6**	**7**	**9**	**10**
empirical formula	$C_{29}H_{23}CoF_{10}Fe_2N_6P_6$	$C_{29}H_{23}CoF_{10}Fe_2N_6P_6$	$C_{29}H_{23}CoCl_{10}Fe_2N_6P_6,C_3$	$C_{19}H_{16}F_5FeN_6P_3$	$C_{19}H_{16}F_5FeN_6P_3$
fw	1001.98	1001.98	1202.52	572.14	572.14
space group	*P*21/*n*	$P\bar{1}$	*P*21/*c*	$P\bar{1}$	*P*21/*c*
a (Å)	11.758(2)	13.050(2)	7.3106(11)	7.532(3)	15.181(2)
b (Å)	16.499(3)	13.242(2)	22.024(3)	11.945(4)	8.5883(13)
c (Å)	18.172(4)	21.410(3)	19.681(3)	14.564(5)	18.934(3)
α (deg)	90.00	106.769(3)	90.00	108.477(5)	90.00
β (deg)	94.498(3)	95.080(3)	94.876(3)	98.823(6)	109.710(3)
γ (deg)	90.00	90.957(3)	90.00	103.195(6)	90.00
V (Å^3)	3514.4(12)	3524.7(10)	3157.2(8)	1173.3(7)	2324.0(6)
Z	4	4	4	2	4
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	1.894	1.888	1.776	1.620	1.635
μ (mm^{-1})	1.642	1.638	0.943	0.907	0.916
θ range	1.67−24.00	1.57−25.50	1.65−25.50	1.52−25.50	1.42−25.00
R1^a, wR2^b [$I > 2\sigma(I)$]	0.0345, 0.0812	0.0844, 0.1830	0.0630, 0.1764	0.0521, 0.1340	0.0756, 0.1507

^{a}R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b}wR $= \{[\sum(|F_o|^2|F_c|^2)^2]\}^{1/2}$.

Table 3. X-ray Crystallographic Data for Compounds **11** and **13**−**16**

	11	**13**	**14**	**15**	**16**
empirical formula	$C_{31}H_{25}\ Cl_4Fe_2N_6P_3$	$C_{38}\ H_{32}Cl_4Fe_2N_9P_3$, $C_4H_8O_2$	$C_{38}\ H_{32}Cl_4Fe_2N_9P_3$	$C_{38}H_{32}Cl_4Fe_2N_9P_3$	$C_{38}H_{32}Cl_2Fe_{10}Fe_2$-$N_{12}P_6Pd$, 2(CHCl$_3$)
fw	827.98	1049.24	961.14	961.14	1560.31
space group	*P*21/*n*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	$P\bar{1}$
a (Å)	15.187(4)	12.1626(14)	9.1867(16)	21.634(2)	11.2154(12)
b (Å)	12.902(3)	12.9545(15)	10.7009(19)	16.0644(18)	11.6282(12)
c (Å)	17.846(4)	15.2079(18)	20.921(4)	13.7657(15)	12.7845(13)
α (deg)	90.00	84.723(2)	90.512(3)	90.00	115.258(2)
β (deg)	101.052(4)	83.885(2)	95.073(3)	124.220(2)	97.712(2)
γ (deg)	90.00	76.853(2)	95.919(3)	90.00	94.298(2)
V (Å^3)	3431.9(14)	2314.4(5)	2037.4(6)	3955.9(7)	1477.9(3)
Z	4	2	2	4	1
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm^3)	1.602	1.506	1.567	1.614	1.753
μ (mm^{-1})	1.330	1.009	1.134	1.168	1.384
θ range	1.62−25.00	1.62−25.50	2.46−25.50	1.70−25.49	1.79−25.50
R1^a, wR2^b [$I > 2\sigma(I)$]	0.0763, 0.1627	0.0525, 0.1432	0.0618, 0.1364	0.0359, 0.0861	0.0562, 0.1415

^{a}R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b}wR2 $= \{[\sum(|F_o|^2|F_c|^2)^2]\}^{1/2}$.

[(FcC≡C)$_2$PN](F$_2$PN)$_2$ with an excess of CpCo(COD) gave only the partial cycloadded product, with one of the alkyne units remaining unreacted. Both the mono- and bis(ethynylferrocene)-derived fluoro- and chlorocyclophosphazenes underwent click reactions with benzyl azide, yielding the first example of phosphazene-derived mono- and geminal bis-1,2,3-triazoles that were structurally characterized. The usefulness of the triazole-derived cyclophosphazenes as novel nitrogen-based ligands was demonstrated by preparing a *trans*-disubstituted square-planar complex of the fluorophosphazene-derived triazole (1-$PhCH_2$, 4-$P_3N_3F_5$, 5-Fc)C_2N_3 with palladium dichloride.

Experimental Section

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under a nitrogen atmosphere. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere and used. CpCo(COD),[25] ethynylferrocene,[26] hexafluorocyclotriphosphazene,[27] and benzyl azide,[28] were prepared according to literature procedures. $PdCl_2(PhCN)_2$, $N_3P_3Cl_6$, and *n*-BuLi (1.6 M in hexanes) were procured from Aldrich and used as such.

Instrumentation. The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 121.48, and 282.37 MHz, respectively, using $CDCl_3$ as the solvent. IR spectra in the range 4000−250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded in the fast-atom-bombardment mode using a JEOL SX 102/DA-6000 mass spectrometer and in the time-of-flight mass spectrometry mode (HRMS) using an AB Sciex spectrometer (model 1011273/A).

X-ray Crystallography. Suitable crystals of compounds **1**−**7**, **9**−**11**, **13**−**15**, and **16** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane and chloroform/hexane solvent mixtures, respectively. The single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.710 73 Å) sealed tube. All crystal structures were solved by direct methods. The program *SAINT* (version 6.22) was used for integration of the intensity of reflections and scaling. The program *SADABS* was used for absorption correction. The crystal structures were solved and refined using the *SHELXTL* (version 6.12) package.[29] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Crystallographic data and data collection parameters for compounds **1**−**4** are given in Table 1, those for **5**−**7**, **9**, and **10** in Table 2, and those for **11**, **13**, and **14**−**16** in Table 3.

Preparation of $FcC{\equiv}CP_3N_3F_5$. A solution of ethynylferrocene (0.85 g, 4.04 mmol) in 20 mL of anhydrous THF was placed in an oven-dried, two-neck, round-bottomed flask and was cooled to −78 °C. To this was added dropwise a solution of *n*-BuLi (2.45 mL, 4.04 mmol, 1.6 M). The reaction mixture was brought to room temperature, stirred for 3 h, and cooled again to −78 °C. A solution of $N_3P_3F_6$ (2.02 g, 8.08 mmol) in 5 mL of THF was cooled to −78 °C, and the cooled lithiated ethynylferrocene solution was added slowly to the solution of $N_3P_3F_6$. The mixture was stirred at room temperature for 24 h. Afterward, all solvents were evaporated off and the crude product was purified by chromatography over silica gel. The compound obtained as orange-red crystals upon elution with ethyl acetate/hexane (2%), followed by slow evaporation, was characterized as $FcC{\equiv}CP_3N_3F_5$ (**1**). Yield: 1.42 g (80%). Mp: 72−74 °C. IR (ν, cm^{-1}): 2180 s (C≡C), 1261 vs (P═N), 946 s and 831 and 787 s (P−F). ^1H NMR: δ 4.32 [s, 5H, Cp], 4.42 (m, 2H, −CH), 4.68 (m, 2H, −CH). $^{13}C\{^1H\}$ NMR: δ 57.54 (d, *J*(C,P) = 7 Hz, Cp_1), 70.66 (s, Cp), 70.98 (s, $Cp_{2/5}$), 72.95 (s, $Cp_{3/4}$), 82.16 (s, C≡C), 106.20 [d, *J*(C,P) = 63 Hz, C≡C]. $^{31}P\{^1H\}$ NMR: δ 3.79 [d, J_{P-F} = 920 Hz, −PF(C≡CFc)], 7.52 [t, J_{P-F} = 837 Hz, $-PF_2$]. $^{19}F\{^1H\}$ NMR: δ −69.06 (dm, 2F, J_{P-F} = 835 Hz, $-PF_2$), −67.61 (dm, 2F, J_{P-F} = 844 Hz, $-PF_2$), −43.25 [dm, 1F, J_{P-F} = 917 Hz, −PF(C≡CFc)]. MS (ESI) [*m*/*e* (species)]: 439.90 $[M + 1]^+$. Anal. Calcd for $C_{12}H_9F_5N_3P_3$: C, 32.83; H, 2.07; N, 9.57. Found: C, 33.09; H, 2.20; N, 9.44. $E_{1/2}$ = 0.52 V vs ferrocene, reversible.

Preparation of $FcC{\equiv}CP_3N_3Cl_5$. Following a synthetic procedure similar to that outlined for $FcC{\equiv}CP_3N_3F_5$, ethynylferrocene (0.50 g, 2.38 mmol) was reacted with $N_3P_3Cl_6$ (1.60 g, 4.60 mmol) at −78 °C. Afterward, all of the solvents were evaporated off, and the crude product was purified through a silica gel column. The first and second fractions that were obtained with hexane were identified as unreacted hexachlorocyclotriphosphazene and ethynylferrocene (0.20 g), respectively. The compound obtained upon elution with ethyl acetate/hexane (2%), followed by slow evaporation as orange-red crystals, was characterized as $FcC{\equiv}CP_3N_3Cl_5$ (**2**). Yield: 0.20 g (20%). Mp: 120−122 °C. IR (ν, cm^{-1}): 2154 m (C≡C), 1198 vs (P═N), 605 m (P═N), 523 m (P−Cl). ^1H NMR: 4.32 (s, 5H, CpH), 4.42 (m, 2H, −CH), 4.68 (m, 2H, −CH). $^{13}C\{^1H\}$ NMR: δ 57.76 (d, Cp_1), 70.67 (s, Cp), 71.07 (s, $Cp_{2/5}$), 73.01 (s, $Cp_{3/4}$), 81.06 (s, C≡C), 106.42 [d, *J*(C,P) = 65 Hz, C≡C]. $^{31}P\{^1H\}$ NMR: δ −5.28 [t, *J* = 47 Hz, −PCl(C≡C−Fc)], 20.01 (d, *J* = 46 Hz, $-PCl_2$). MS (ESI) [*m*/*e* (species)]: 517.80 $[M - 1]^+$. Anal. Calcd for $C_{12}H_9Cl_5FeN_3P_3$: C, 27.65; H, 1.74; N, 8.06. Found: C, 28.24; H, 1.79; N, 7.87. $E_{1/2}$ = 0.50 V vs ferrocene, reversible.

Preparation of $[(FcC{\equiv}C)_2PN](F_2PN)_2$. Following a synthetic procedure similar to that outlined for $FcC{\equiv}CP_3N_3F_5$ except with a reverse mode of addition, ethynylferrocene (2.30 g, 10.95 mmol) was reacted with $N_3P_3F_6$ (1.36 g, 5.46 mmol) at −78 °C. The compound obtained as red crystals upon elution with ethyl acetate/hexane (2%), followed by slow evaporation, was characterized as $(FcC{\equiv}C)_2PN(F_2PN)_2$ (**3**). Yield: 2.34 g (68%). Mp: 126−128 °C. IR (ν, cm^{-1}): 2162 m (C≡C), 1252 vs (P═N), 929 s and 817 and 772 s (P−F). ^1H NMR: δ 4.23 (s, 10H, CpH), 4.29 (m, 4H, −CH), 4.57 (m, 4H, −CH). $^{13}C\{^1H\}$ NMR: δ 57.57 [d, *J*(C,P) = 6 Hz, Cp_1], 70.67 (s, Cp), 71.97 (s, $Cp_{2/5}$), 72.99 (s, $Cp_{3/4}$), 82.02 (s, C≡C), 104.02 [d, *J*(C,P) = 58 Hz, C≡C]. $^{31}P\{^1H\}$ NMR: δ −24.83 [t, *J* = 86 Hz, $-P(C{\equiv}C-Fc)_2$], 6.36 (t, J_{P-F} = 787 Hz, $-PF_2$). $^{19}F\{^1H\}$ NMR: δ −68.10 (dm, 4F, J_{P-F} = 768 Hz, $-PF_2$). MS (ESI) [*m*/*e* (species)]: 629.89 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{18}F_4Fe_2N_3P_3$: C, 45.83; H, 2.88; N, 6.68. Found: C, 45.87; H, 2.92; N, 6.65. $E_{1/2}$ = 0.45 V vs ferrocene, reversible.

Preparation of $[(FcC{\equiv}C)_2PN](Cl_2PN)_2$. Following a synthetic procedure similar to that outlined for $[(FcC{\equiv}C)_2PN](F_2PN)_2]$, ethynylferrocene (0.75 g, 3.57 mmol) was reacted with $N_3P_3Cl_6$ (0.61 g, 1.78 mmol) at −78 °C. Afterward, all solvents were evaporated off and the crude product was purified through a silica gel column. The first fraction that was obtained with hexane was identified as unreacted ethynylferrocene (0.11 g). The compound obtained as red crystals upon elution with ethyl acetate/hexane (4%), followed by slow evaporation, was characterized as $[(FcC{\equiv}C)_2PN](Cl_2PN)_2$ (**4**). Yield: 0.34 g (27%). Mp: 196 °C. IR (ν, cm^{-1}): 2163 m (C≡C), 1211 vs (P═N), 581 m (P═N), 523 m (P−Cl). ^1H NMR: δ 4.30 (s, 10H, CpH), 4.36 (s, 4H, −CH), 4.65 (s, 4H, −CH). $^{13}C\{^1H\}$ NMR: δ 59.21 [d, *J*(C, P) = 6 Hz, C≡C, Cp_1], 70.52 (s, Cp), 70.58 (s, $Cp_{2/5}$), 72.73 (s, $Cp_{3/4}$), 80.08 (s, C≡C), 104.30 [d, *J*(C,P) = 56 Hz, C≡C]. $^{31}P\{^1H\}$ NMR: δ −33.18 [t, *J* = 43 Hz, $-P(C{\equiv}C)_2$], 18.71 [d, *J* = 43 Hz, $-PCl_2$]. Anal. Calcd for $C_{24}H_{18}Cl_4Fe_2N_3P_3$: C, 41.49; H, 2.61; N, 6.05. Found: C, 41.61; H, 2.65; N, 6.07. $E_{1/2}$ = 0.44 V vs ferrocene, reversible.

Preparation of Isomers of $(\eta^5\text{-}Cp)Co[\eta^4\text{-}C_4(N_3P_3F_5)_2(Fc)_2]$. Compound **1** (0.35 g, 0.79 mmol) was dissolved in 35 mL of toluene, and CpCo(COD) (0.10 g, 0.43 mmol) in 5 mL of toluene was added with constant stirring. The mixture was refluxed at 110 °C for 36 h. Afterward, all solvents were removed under

---

[25] Wakatsuki, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2715–2716.

[26] Polin, J.; Schottenberger, H. *Org. Synth.* **1996**, *73*, 262.

[27] Paddock., N. L.; Patmore, D. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1029–1031.

[28] Ritschel, J.; Sasse, F.; Maier, M. E. *Eur. J. Org. Chem.* **2007**, *1*, 78–87.

[29] *SMART: Bruker Molecular Analysis Research Tools*, version 5.618; Bruker Analytical X-ray Systems: Madison, WI, 2000. (b) Sheldrick, G. M. *SAINT-NT*, version 6.04; Bruker Analytical X-ray Systems: Madison, WI, 2001. (c) Sheldrick, G. M. *SHELXTL-NT*, version 6.10; Bruker Analytical X-ray Systems: Madison, WI, 2000. (d) Klaus, B. *DIAMOND*, version 2.1c; University of Bonn: Bonn, Germany, 1999.

vacuum, and the resulting crude product was purified through a silica gel column using an ethyl acetate/hexane mixture as the eluent. The fraction that was obtained with an ethyl acetate−hexane (2%) mixture upon evaporation yielded the compound (η^5-Cp)Co[η^4-$\mathrm{C_4}$-1,3-(Fc)$_2$-2,4-($\mathrm{N_3P_3F_5}$)$_2$] (**5**). Yield: 0.16 g (41%). Mp: 194−196 °C. IR (ν, cm^{-1}): 1268 vs (P═N), 1011 w (P═N), 942 s, 829 s (P−F). ^{1}H NMR: δ 4.24 (s, 10H, FeCp), 4.40 (s, 4H, −CH), 4.76 (s, 4H, −CH), 4.93 (s, 5H, CoCp). ^{13}C{^{1}H} NMR: δ 69.06 (s, Cp$_1$), 69.10 (s, Cp$_{2/5}$), 69.91 (s, Cp), 74.77 (s, Cp$_{3/4}$), 83.28 (s, CoCp), 85.81, 85.94 ($\mathrm{C_4}$ ring C). ^{31}P{^{1}H} NMR: δ 7.64 (tm, $J_{\mathrm{P-F}}$ = 891 Hz, −PF$_2$), 35.48 [dm, $J_{\mathrm{P-F}}$ = 939 Hz, −PF(C)]. ^{19}F{^{1}H} NMR: δ −68.99 (dm, 4F, $J_{\mathrm{P-F}}$ = 880 Hz, −PF$_2$), −65.55 (dm, 4F, $J_{\mathrm{P-F}}$ = 897 Hz, −PF$_2$), −42.05 [d, 2F, $J_{\mathrm{P-F}}$ = 960 Hz, −PF(C)]. HRMS. Calcd for $\mathrm{C_{29}H_{23}CoF_{10}Fe_2N_6P_6}$: exact mass, 1001.8281; measured mass, 1001.8271. Anal. Calcd for $\mathrm{C_{29}H_{23}CoF_{10}Fe_2N_6P_6}$: C, 34.76; H, 2.31; N, 8.39. Found C, 34.81; H, 2.29; N, 8.37. $E_{1/2}$ = 0.30 and 0.42 V vs ferrocene, reversible.

Further elution using an ethyl acetate/hexane (4%) mixture gave a more polar compound that was characterized as (η^5-Cp)Co[η^4-$\mathrm{C_4}$-1,2-(Fc)$_2$-3,4-($\mathrm{N_3P_3F_5}$)$_2$] (**6**). Yield: 0.03 g (8%). Mp: 144−146 °C. IR (ν, cm^{-1}): 1270 vs (P═N), 1022 m (P═N), 940 m, 828 s (P−F). ^{1}H NMR: δ 4.39 (s, 10H, FeCp), 4.50−4.60 (m, 4H, −CH), 4.84−4.94 (m, 4H, −CH), 5.08 (s, 5H, CoCp). ^{13}C{^{1}H} NMR: δ 68.85 (s, Cp$_1$), 68.95 (s, Cp$_{2/5}$), 69.19 (s, Cp$_{3/4}$), 69.52 (s, Cp$_1$), 69.57 (s, Cp$_{2/5}$), 69.69 (s, Cp$_{3/4}$), 69.84 (s, Cp), 85.16, 85.55 ($\mathrm{C_4}$ ring C). ^{31}P{^{1}H} NMR: δ 7.07 (tm, $J_{\mathrm{P-F}}$ = 858 Hz, −PF$_2$), 37.55 [dm, $J_{\mathrm{P-F}}$ = 1002 Hz, −PF(C)]. ^{19}F{^{1}H} NMR: δ −69.36 (dm, 4F, $J_{\mathrm{P-F}}$ = 860 Hz, −PF$_2$), −66.78 (dm, 4F, $J_{\mathrm{P-F}}$ = 884 Hz, −PF$_2$), −42.79 [d, 2F, $J_{\mathrm{P-F}}$ = 967 Hz, −PF(C)]. Anal. Calcd for $\mathrm{C_{29}H_{23}CoF_{10}Fe_2N_6P_6}$: C, 34.76; H, 2.31; N, 8.39. Found C, 34.75; H, 2.31; N, 8.42. $E_{1/2}$ = 0.26 and 0.37 V vs ferrocene, reversible.

Preparation of (η^5-Cp)Co[η^4-$\mathrm{C_4}$-1,3-(Fc)$_2$-2,4-($\mathrm{N_3P_3Cl_5}$)$_2$]. Following a synthetic procedure similar to that outlined for (η^5-Cp)Co[η^4-$\mathrm{C_4}$(Fc)$_2$($\mathrm{N_3P_3F_5}$)$_2$], compound **2** (0.21 g, 0.40 mmol) was reacted with CpCo(COD) (0.05 g, 0.21 mmol) in toluene under reflux conditions for 36 h. Afterward, all solvents were removed under vacuum, and the resulting crude product was purified through a silica gel column using an ethyl acetate/hexane (4%) mixture as the eluent. The compound formed was characterized as (η^5-Cp)Co[η^4-$\mathrm{C_4}$-1,3-(Fc)$_2$-2,4-($\mathrm{N_3P_3Cl_5}$)$_2$] (**7**). Yield: 0.10 g (42%). Mp: 240 °C (dec). IR (ν, cm^{-1}): 1269 vs (P═N), 942 m, 830 s. ^{1}H NMR: δ 4.28 (s, 10H, FeCp), 4.40 (s, 4H, −CH), 4.87 (s, 5H, CoCp), 5.29 (s, 4H, −CH). ^{13}C{^{1}H} NMR: δ 69.79 (s, Cp$_1$), 69.93 (s, Cp), 70.42 (s, CoCp), 70.67 (s, Cp$_{2/5}$), 75.01 (s, Cp$_{3/4}$), 83.50, 85.50 ($\mathrm{C_4}$ ring C). ^{31}P{^{1}H} NMR: δ 18.89 (m, −PCl$_2$), 27.41 [m, −PCl(C)]. Anal. Calcd for $\mathrm{C_{29}H_{23}CoCl_{10}Fe_2N_6P_6}$: C, 29.86; H, 1.99; N, 7.20. Found: C, 29.84; H, 1.95; N, 7.29. $E_{1/2}$ = 0.20 and 0.33 V vs ferrocene, reversible.

Preparation of (η^5-Cp)Co-{η^4-$\mathrm{C_4}$-1,3-(Fc)$_2$-2,4-[NP(C≡CFc)-($\mathrm{NPF_2}$)$_2$]$_2$}. Following a synthetic procedure similar to that outlined for (η^5-Cp)Co[η^4-$\mathrm{C_4}$(Fc)$_2$ ($\mathrm{N_3P_3F_5}$)$_2$], compound **3** (0.21 g, 0.33 mmol) was reacted with CpCo(COD) (0.15 g, 0.65 mmol) in toluene under reflux conditions for 36 h. Afterward, all solvents were removed under vacuum, and the resulting crude product was purified through a silica gel column using an ethyl acetate/hexane (1%) mixture as the eluent. The red fraction that was obtained using an ethyl acetate/hexane (2%) mixture in evaporation gave a solid that was identified as (η^5-Cp)Co{η^4-$\mathrm{C_4}$-1,3-(Fc)$_2$-2,4-[NP-(C≡CFc)($\mathrm{NPF_2}$)$_2$]$_2$} (**8**). Yield: 0.05 g (22%) Mp: 242−244 °C. IR (ν, cm^{-1}): 2162 m (C≡C), 1253 vs (P═N), 922 m, 814 m, and 776 w (P−F), 747 w. ^{1}H NMR: δ 4.20−4.35 (m, 28H, FeCpH), 4.55−4.63 (m, 4H, −CH), 4.85 (s, 5H, −CoCp), 5.20−5.30 (m, 4H, −CH). ^{13}C{^{1}H} NMR: δ 60.05 (m, C≡C, Cp$_1$), 69.40 (s, Cp$_1$), 69.85 (s, Cp), 70.42 (s, Cp), 70.60 (s, Cp$_{2/5}$), 72.57 (s, Cp$_{3/4}$), 80.55 (s, C≡C), 83.00 (s, CoCp), 83.79, 86.00 ($\mathrm{C_4}$ ring C), 104.14 [d, J(C,P) = 46.79 Hz, C≡C]. ^{31}P{^{1}H} NMR: 0.65 [t, −PC(C≡CFc)], 6.57 (t, $J_{\mathrm{P-F}}$ = 886 Hz, −PF$_2$). ^{19}F{^{1}H} NMR: δ −69.40 (dm, 4F, $J_{\mathrm{P-F}}$ = 875 Hz, −PF$_2$), −65.40 (dm, 4F, $J_{\mathrm{P-F}}$ = 903 Hz, −PF$_2$). HRMS. Calcd for $\mathrm{C_{53}H_{41}CoF_8Fe_4N_6P_6}$: exact mass, 1381.8420; measured mass, 1381.8421. Anal. Calcd for $\mathrm{C_{53}H_{41}CoF_8Fe_4N_6P_6}$: C, 46.06; H, 2.99; N, 6.08. Found C, 46.10; H, 2.98; N, 6.04. $E_{1/2}$ = 0.23 V (Fc attached to the cyclobutadiene ring), $E_{1/2}$ = 0.43 V (−C≡CFc) vs ferrocene, reversible. Further elution indicated the presence of traces of two more colored species that could not be separated and characterized.

General Procedure for the Click Reactions. The ferrocenylethynyl derivatives of cyclophosphazenes **1** and **4** were dissolved in 25 mL of toluene, and benzyl azide was added with constant stirring. The resulting reaction mixture was refluxed for 24 h. Afterward, all of the solvents were evaporated off under vacuum, and the crude product was purified by chromatography using silica gel.

Preparation of Isomers of [($\mathrm{FcC_2N_3(C_6H_5CH_2)P_3N_3F_5}$]. The reaction between benzyl azide (0.18 g, 1.35 mmol) and (ethynylferrocenyl)pentafluorocyclotriphosphazene (**1**; 0.45 g, 1.02 mmol) was carried out. Chromatography of the reaction mixture using ethyl acetate/hexane (2%), followed by slow evaporation, gave (1-PhCH$_2$, 4-Fc, 5-$\mathrm{P_3N_3F_5}$)$\mathrm{C_2N_3}$ (**9**) as orange-red crystals. Yield: 0.02 g (3%). Mp: 80−82 °C. IR (ν, cm^{-1}): 1552 w (N═N), 1269 vs (P═N), 957 m, 838 m (P−F). ^{1}H NMR: δ 4.17 (s, 5H, CpH), 4.41 (s, 2H, −CH), 4.96 (s, 2H, −CH), 5.94 (s, 2H, −CH$_2$), 7.01−7.04 (m, 2H, Ar−H), 7.34−7.36 (m, 3H, Ar−H). ^{13}C{^{1}H} NMR: δ 54.27 (s, −CH$_2$), 69.37 [d, J(C,P) = 2 Hz, Cp$_1$], 69.72 (s, Cp$_{2/5}$), 69.91 (s, Cp), 72.84 (s, Cp$_{3/4}$), 126.09 (s, *m*-Ph), 128.50(s, *p*-Ph), 129.08 (s, *o*-Ph), 134.74 (s, *ipso*-Ph), 155.24, 155.55 (triazole C). ^{31}P{^{1}H} NMR: δ 6.63 (tm, $J_{\mathrm{P-F}}$ = 928 Hz, −PF$_2$), 20.08 [dm, $J_{\mathrm{P-F}}$ = 994 Hz, −PF($\mathrm{C_2N_3}$)]. ^{19}F{^{1}H} NMR: δ −69.63 (dm, 2F, $J_{\mathrm{P-F}}$ = 943 Hz, −PF$_2$), −65.40 (dm, 2F, $J_{\mathrm{P-F}}$ = 906 Hz, −PF$_2$), −44.00 [d, 1F, $J_{\mathrm{P-F}}$ = 964 Hz, −PF(C)]. MS (ESI) [*m*/*e* (species)]: 572.97 [M + 1]$^+$. Anal. Calcd for $\mathrm{C_{19}H_{16}F_5FeN_6P_3}$: C, 39.89; H, 2.82; N, 14.69. Found: C, 39.79; H, 2.86; N, 14.74. $E_{1/2}$ = 0.28 V vs ferrocene, reversible. Upon further elution using ethyl acetate/hexane (4%), a second fraction obtained upon slow evaporation gave (1-PhCH$_2$, 4-$\mathrm{P_3N_3F_5}$, 5-Fc)$\mathrm{C_2N_3}$ (**10**) as orange-red crystals. Yield: 0.24 g (41%). Mp: 142−144 °C. IR (ν, cm^{-1}): 1551 w (N═N), 1270 vs (P═N), 956 m, 837 m (P−F). ^{1}H NMR: δ 4.20 (s, 5H, CpH), 4.50 (s, 2H, −CH), 4.67 (s, 2H, −CH), 6.07 (s, 2H, −CH$_2$), 7.16−7.18 (m, 2H, Ar−H), 7.41−7.43 (m, 3H, Ar−H). ^{13}C{^{1}H} NMR: δ 52.27 (s, −CH$_2$), 67.83 (s, Cp$_1$), 69.35 (s, Cp$_{2/5}$), 69.84 (s, Cp), 70.73 (s, Cp$_{3/4}$), 126.17 (s, *m*-Ph), 128.46 (s, *p*-Ph), 129.33 (s, *o*-Ph), 134.91 (s, *ipso*-Ph), 143.39, 143.89 (triazole C). ^{31}P{^{1}H} NMR: δ 7.20 (tm, $J_{\mathrm{P-F}}$ = 899 Hz, −PF$_2$), 24.70 [dm, $J_{\mathrm{P-F}}$ = 959 Hz, −PF($\mathrm{C_2N_3}$)]. ^{19}F{^{1}H} NMR: δ −66.78 (dm, 2F, $J_{\mathrm{P-F}}$ = 906 Hz, −PF$_2$), −68.63 (dm, 2F, $J_{\mathrm{P-F}}$ = 911 Hz, −PF$_2$), −52.53 [d, 1F, $J_{\mathrm{P-F}}$ = 957 Hz, −PF(C)]. MS (ESI) [*m*/*e* (species)]: 572.92 [M + 1]$^+$. Anal. Calcd for $\mathrm{C_{19}H_{16}F_5FeN_6P_3}$: C, 39.89; H, 2.82; N, 14.69. Found: C, 39.91; H, 2.95; N, 14.32. $E_{1/2}$ = 0.46 V vs ferrocene, reversible.

Preparation of Isomers of [(FcC≡C)($\mathrm{FcC_2N_3C_6H_5CH_2}$)-PN]($\mathrm{Cl_2PN}$)$_2$ and [($\mathrm{FcC_2N_3C_6H_5CH_2}$)$_2$PN]($\mathrm{Cl_2PN}$)$_2$. The reaction between benzyl azide (0.20 g, 1.50 mmol) and *gem*-ethynylferrocenyltetrachlorophosphazene (**4**; 0.42 g, 0.60 mmol) was carried out using the general procedure given for click reactions. The first fraction that was obtained using an ethyl acetate/hexane mixture (1%) was evaporated to give [1-(PhCH$_2$)-4-$\mathrm{FcC_2N_3}$(C≡CFc)PN-($\mathrm{NPCl_2}$)$_2$] (**11**). Yield: 0.12 g (24%). Mp: 155−157 °C. IR (ν, cm^{-1}): 2152 m (C≡C), 1545 w (N═N), 1214 vs (P═N), 519 m (P−Cl). ^{1}H NMR: δ 4.23 (s, 5H, CpH), 4.30 (s, 5H, CpH), 4.41−4.42 (m, 2H, −CH), 4.50 (m, 4H, −CH), 5.35−5.37 (m, 2H, −CH), 6.20 (s, 2H, −CH$_2$), 7.25−7.39 (m, 2H, Ar−H), 7.44−7.55 (m, 3H, Ar−H). ^{13}C{^{1}H} NMR: δ 53.80 (s, −CH$_2$), 58.62 [d, J(C,P) = 6 Hz, Cp$_1$], (69.35 (s, Cp$_1$), 69.86 (s, Cp), 70.24 (s, Cp$_1$), 70.42 (s, Cp), 70.59 (s, Cp$_{2/5}$), 72.61 (s, Cp$_{3/4}$), 80.37 (s, C≡C), 106.77 [d, J(C,P) = 51 Hz, C≡C], 127.03 (s, *m*-Ph), 128.00 (s, *p*-Ph), 128.70 (s, *o*-Ph), 135.72 (s, *ipso*-Ph), 153.54, 153.83 (triazole C). ^{31}P{^{1}H} NMR: δ −20.10 [t, J = 35 Hz, −P(C≡C)($\mathrm{C_2N_3}$)], 18.32 (d, J = 34 Hz, −PCl$_2$). MS (ESI) [*m*/*e* (species)]: 826.84 [M + 1]$^+$. Anal. Calcd for $\mathrm{C_{31}H_{25}Cl_4Fe_2N_6P_3}$: C, 44.97; H, 3.04; N, 10.15. Found: C, 44.89, H, 3.01, N, 10.23. $E_{1/2} = 0.25$ V (Fc attached to the triazole ring). $E_{1/2} = 0.44$ V (Fc attached to the ethynyl unit) vs ferrocene, reversible. Elution with ethyl acetate/hexane (2%) gave a second fraction that upon evaporation gave a yellow compound that was identified as [1-(PhCH$_2$)-5-FcC$_2$N$_3$(C≡CFc)PN(NPCl$_2$)$_2$] (**12**). Yield: 0.01 g (2.0%). Mp: 162−164 °C. IR (ν, cm^{-1}): 2161 m (C≡C), 1549 w (N═N), 1209 vs (P═N), 517 w (P−Cl). ^{1}H NMR: δ 4.13 (s, 5H, CpH), 4.24 (s, 5H, CpH), 4.26−4.27 (m, 2H, CpH), 4.45−4.51 (m, 4H, CpH), 4.83−4.88 (m, 2H, CpH), 7.14−7.19 (m, 2H, Ar−H), 7.30−7.43 (m, 3H, Ar−H). ^{31}P{^{1}H} NMR: δ −14.44 [t, J = 31 Hz, −P(C≡C)(C$_2$N$_3$)], 19.26 (d, J = 31 Hz, −PCl$_2$). HRMS. Calcd for $C_{31}H_{26}Cl_4Fe_2N_6P_3$: exact mass, 826.8885; measured mass, 826.8884. Anal. Calcd for $C_{31}H_{25}Cl_4Fe_2N_6P_3$: C, 44.97; H, 3.04; N, 10.15. Found: C, 44.99; H, 3.04; N, 10.11. Further elution with ethyl acetate/hexane (3%) gave a third fraction that upon evaporation gave light-yellow crystals that were identified as [1-(PhCH$_2$)-4-Fc-C$_2$N$_3$]$_2$PN-(PNCl$_2$)$_2$ (**13**). Yield: 0.06 g (10%). Mp: 180 °C (dec). IR (ν, cm^{-1}): 1548 w (N═N), 1202 vs (P═N), 521 m (P−Cl). ^{1}H NMR: δ 4.05−4.15 (m, 2H, CpH), 4.20−4.30 (m, 12H, CpH), 4.40−4.50 (m, 4H, CpH), 5.80 (s, 4H, −CH$_2$), 7.05−7.15 (m, 4H, Ar−H), 7.27−7.40 (m, 6H, Ar−H). ^{13}C{^{1}H} NMR: δ 53.33 (s, −CH$_2$), 64.97 (s, Cp$_1$), 68.88 (s, Cp$_{2/5}$), 69.67 (s, Cp$_{3/4}$), 69.79 (s, Cp), 126.64 (s, *m*-Ph), 128.12 (s, *p*-Ph), 128.92 (s, *o*-Ph), 135.33 (s, *ipso*-Ph), 152.87, 153.17 (triazole C). ^{31}P{^{1}H} NMR: δ −6.67 [t, J = 28 Hz, −P(C$_2$N$_3$)$_2$], 19.56 (d, J = 28 Hz, −PCl$_2$). Anal. Calcd for $C_{42}H_{40}Cl_4Fe_2N_9O_2P_3$: C, 48.08; H, 3.84; N, 12.01. Found: C, 48.01; H, 3.79; N, 12.08. $E_{1/2} = 0.40$ V (Fc attached to the triazole ring), reversible. Further elution with ethyl acetate/hexane (5%) gave a fourth fraction that upon evaporation gave yellow crystals that were identified as [(1-PhCH$_2$)4-Fc-C$_2$N$_3$)(1-PhCH$_2$5-Fc-C$_2$N$_3$)PN(PNCl$_2$)$_2$] (**14**). Yield: 0.09 g (15%). Mp: 260 °C (dec). IR (ν, cm^{-1}): 1547 w (N═N), 1207 vs (P═N), 518 m (P−Cl). ^{1}H NMR: δ 4.04−4.19 (m, 16H, CpH), 4.63 (s, 2H, CpH), 5.96 (s, 2H, −CH$_2$), 6.10 (s, 2H, −CH$_2$), 6.90−7.00 (m, 2H, Ar−H), 7.20−7.45 (m, 8H, Ar−H). ^{13}C{^{1}H} NMR: δ 51.69 (s, −CH$_2$), 53.64 (s, −CH$_2$), 68.69 (s, Cp$_1$), 69.00 (s, Cp$_{2/5}$), 69.50 (s, Cp), 69.70 (s, Cp$_1$), 69.83 (s, Cp$_{2/5}$), 70.12 (s, Cp$_{3/4}$), 126.41 (s, *m*-Ph), 127.08 (s, *m*-Ph), 128.01 (s, *p*-Ph), 128.11 (s, *p*-Ph), 128.80 (s, *o*-Ph), 129.12 (s, *o*-Ph), 134.78 (s, *ipso*-Ph), 135.54 (s, *ipso*-Ph), 141.70, 142.14, 153.73, 154.02 (triazole C). ^{31}P{^{1}H} NMR: δ −1.80 [t, J = 25 Hz, −P(C$_2$N$_3$)$_2$], 19.24 (d, J = 25 Hz, −PCl$_2$). MS (ESI) [*m/e* (species)]: 959.80 [M + 1]$^+$. Anal. Calcd for $C_{38}H_{32}Cl_4Fe_2N_9P_3$: C, 47.49; H, 3.36; N, 13.12. Found: C, 47.51; H, 3.38; N, 13.18. $E_{1/2}$ = 0.23 and 0.46 V (Fc attached to the triazole ring), reversible. The final fraction that was obtained during elution using ethyl acetate/hexane (7%) gave a light-yellow compound that was identified as [1-(PhCH$_2$)-5-Fc-C$_2$N$_3$]$_2$PN-(PNCl$_2$)$_2$ (**15**). Yield: 0.03 g (5%). Mp: 204−206 °C (dec). IR (ν, cm^{-1}): 1552 w (N═N), 1213 s (P═N), 517 m (P−Cl). ^{1}H NMR: δ 4.11−4.18 (m, 14H, CpH), 4.40−4.46 (m, 4H, CpH), 5.94 (s, 2H, −CH$_2$), 6.81−6.91 (m, 4H, Ar−H), 7.24−7.40 (m, 6H, Ar−H). ^{13}C{^{1}H} NMR: δ 51.57 (s, −CH$_2$), 68.02 (s, Cp$_1$), 69.53 (s, Cp), 69.59 (s, Cp$_{2/5}$), 70.08 (s, Cp$_{3/4}$), 126.10 (s, *m*-Ph), 127.90 (s, *p*-Ph), 128.98 (s, *o*P-h), 135.11 (s, *ipso*-Ph), 142.02, 142.40 (triazole C). ^{31}P{^{1}H} NMR: δ 0.94 [t, J = 23 Hz, −P(C$_2$N$_3$)$_2$], 19.40 (d, J = 24 Hz, −PCl$_2$). Anal. Calcd for $C_{38}H_{32}Cl_4Fe_2N_9P_3$: C, 47.49; H, 3.36; N, 13.12. Found C, 47.46; H, 3.41; N, 13.05. $E_{1/2}$ = 0.44 V (Fc attached to the triazole ring), reversible.

Preparation of *trans*-[(1-PhCH$_2$-4-P$_3$N$_3$F$_5$-5-Fc)C$_2$N$_3$]$_2$PdCl$_2$. Compound **10** (0.12 g, 0.21 mmol) was dissolved in 40 mL of toluene, and then PdCl$_2$(PhCN)$_2$ (0.04 g, 0.10 mmol) dissolved in 5 mL of toluene was added with constant stirring. The solution was stirred at room temperature for 6 h. Afterward, all solvents were removed under vacuum, and the resulting crude product was washed twice with diethyl ether. Crystallization of the crude reaction product in a chloroform/hexane solvent mixture yielded orange-red crystals that were characterized as the palladium complex *trans*-[(1-PhCH$_2$-4-P$_3$N$_3$F$_5$-5-Fc)C$_2$N$_3$]$_2$PdCl$_2$ (**16**). Yield: 82%. Mp: 135−137 °C. IR (ν, cm^{-1}): 1551 m (N═N), 1274 vs (P═N), 518 w (P−F). ^{1}H NMR: δ 4.31 (s, 10H, CpH), 4.45−4.55 (m, 4H, −CH), 4.60−4.70 (s, 4H, −CH), 6.18 (s, 4H, −CH$_2$), 7.35−7.50 (m, 10H, Ar−H). ^{13}C{^{1}H} NMR: δ 53.11 (s, −CH$_2$), 67.26 (s, Cp$_1$), 69.91 (s, Cp$_{2/5}$), 70.06 (s, Cp), 70.93 (s, Cp$_{3/4}$), 126.63 (s, *m*-Ph), 128.80 (s, *p*-Ph), 129.50 (s, *o*P-h), 133.41 (s, *ipso*-Ph), 145.87, 146.29 (triazole C). ^{31}P{^{1}H} NMR: δ 7.91 (tm, J = 949 Hz, −PF$_2$), 20.65 [dm, J = 994 Hz, −PF(C$_2$N$_3$)]. ^{19}F{^{1}H} NMR: δ −69.52 (dm, 4F, J_{P-F} = 976 Hz, −PF$_2$), −64.43 (dm, 4F, J_{P-F} = 965 Hz, −PF$_2$), −48.08 [d, 2F, J_{P-F} = 948 Hz, −PF(C)]. $E_{1/2}$ = 0.54 V (Fc attached to the triazole ring) vs ferrocene, reversible.

Acknowledgment. The authors thank the Department of Science and Technology (DST), India, for financial assistance in the form of a research grant to A.J.E. (DST (SR/S1/IC-31/2007). We thank DST-FIST and IITD for funding of the single-crystal X-ray diffraction facility at IIT Delhi. The authors thank Prof. D. S. Pandey, Department of Chemistry, BHU, India, for help in recording the electrochemical data. Thanks are due to SAIF, CDRI, Lucknow, for providing analytical data. N.S. thanks UGC for a senior research fellowship.

Supporting Information Available: Tables of selected bond lengths and angles of compounds **1**−**7**, **9**−**11**, and **13**−**16** and crystallographic information files (CIF) for compounds **1**−**7**, **9**−**11**, and **13**−**16**. This material is available free of charge via the Internet at http://pubs.acs.org.