Inorg. Chem. **2006**, *45*, 7835–7842

Inorganic Chemistry
Article

Synthesis and Characterization of Novel Fluorophosphazene-Derived Cobaltacyclopentadienyl Metallacycles: Reagents for Assembly of Aryl-Bridged Fluorophosphazenes

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Received May 26, 2006

Reaction of (β-phenylethynyl)pentafluorocyclotriphosphazene, $F_5P_3N_3C\equiv CPh$, with in situ generated η^5-(MeOC(O)C_5H_4)Co(PPh_3)$_2$ resulted in the formation of two isomers of cobaltacyclopentadienylmetallacycles, (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,5-bis(pentafluorocyclotriphosphazenyl)-3,4-diphenyl cobaltacyclopentadiene (**1**) and (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-2,4-bis(pentafluorocyclotriphosphazenyl)-3,5-diphenyl cobaltacyclopentadiene (**2**), along with the sandwich compound [η^5-carbomethoxycyclopentadienyl]-[η^4-1,3-bis(pentafluorocyclotriphosphazenyl)-2,4-diphenylcyclobutadiene]cobalt (**3**). Formation of cobaltacyclopentadienylmetallacycles or cyclobutadienylmetallocene having two fluorophosphazene units on vicinal carbon atoms of the rings was not observed in this reaction. Reaction of 1 with diphenylacetylene resulted in the formation of a novel aryl-bridged fluorophosphazene, 1,4-bis(pentafluorocyclotriphosphazenyl)–2,3,5,6-tetraphenyl benzene (**4**), and the conversion of cobaltametallacycle to the sandwich compound, [η^5-(MeOC(O)C_5H_4]Co(η^4-C_4Ph_4) (**5**). Reaction of 1 with phenylacetylene resulted in the formation of aryl-bridged fluorophosphazene, 1,4-bis(pentafluorophosphazenyl)–2,3,5,-triphenyl benzene (**6**). New compounds **1**–**4** were structurally characterized. In compound **1**, the two fluorophosphazene units were oriented in gauche form with respect to each other. However, in compounds **2** and **3**, they were eclipsed to each other, and in compound **4**, they were oriented anti to each other.

Introduction

Cyclic phosphazenes continue to attract considerable interest not only from the perspective of being precursors for phosphazene-based polymers [1] but also for a host of other applications. Recent reports indicate their potential as useful molecules for synthesizing ionic liquids and high-energy-density materials,[2] as highly stable cores for the design of dendrimers and air-stable inclusion adducts,[3] and as nodal ligands in coordination compounds and polymers.[4,5] The two well-known trimeric phosphazenes, $N_3P_3Cl_6$ and $N_3P_3F_6$, differ significantly in their stability, volatility, and reactivity,[6] and the latter has been the more favored molecule for making organometallic derivatives of phosphazenes because of lesser complexity in its reactions, resulting from the higher stability of the P−F bonds. Reported examples of organometallic fluorophosphazene compounds mostly include metallocenyl derivatives with $Cp-P_3N_3F_5$[7] or $Ph-P_3N_3F_5$[8] bonds, such

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(1) (a) Chandrasekhar, V. *Inorganic and Organometallic Polymers*; Springer-Verlag: Berlin, 2005; p 82. (b) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159−173. (c) Allcock, H. R, *Chemistry and Applications of Polyphosphazene*; Wiley-Interscience: Hoboken, NJ, 2003; p 1.

(2) (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**, *41*, 5193−5195.

(3) (a) Schneider, R.; Köllner, C.; Weber, I.; Togni, A. *Chem. Commun.* **1999**, 2415−2416. (b) Hertzsch, T.; Budde, F.; Weber, E.; Hulliger, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 2281−2284.

(4) (a) Rivals, F.; Steiner, A. *Eur. J. Inorg. Chem.* **2003**, *18*, 3309−3313. (b) Benson, M. A.; Steiner, A. *Chem. Commun.* **2005**, *40*, 5026−5028. (c) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2005**, *44*, 275−281. (d) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2004**, *43*, 2810−2817.

(5) (a) Chandrasekhar, V.; Pandian, B. M.; Azhakar, R. *Inorg. Chem.* **2006**, *45*, 3510−3518. (b) Chandrasekhar, V.; Nagendran, S. *Chem. Soc. Rev.* **2001**, *30*, 193−203. (c) Chandrasekhar, V.; Krishnan, V.; Steiner, A.; Bickley, J. F. *Inorg. Chem.* **2004**, *43*, 166−172. (d) Chandrasekhar, V.; Senthil-Andavan, G. T.; Nagendran, S.; Krishnan, V.; Azhakar, R.; Butcher, R. J. *Organometallics* **2003**, *22*, 976−986.

(6) (a) Myer, C. N.; Allen, C. W. *Inorg. Chem.* **2002**, *41*, 60−66. (b) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119−135. (c) Muralidharan, K, Venugopalan, P.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 3176−3182. (d) Muralidharan, K.; Reddy, N. D.; Elias, A. J. *Inorg. Chem.* **2000**, *39*, 3988−3994.

10.1021/ic0609204 CCC: $33.50

as ferrocenyl or bisbenzene chromium derivatives, molecules with a direct metal−$P_3N_3F_5$ bond,[9] or those having a spacer between a cyclopentadienyl and phosphazene moiety.[10] Allen and co-workers have recently shown that pentafluorophosphazenyl-substituted acetylenes such as $F_5P_3N_3C{\equiv}CPh$ can be interesting reagents for the synthesis of novel fluorophosphazene-derived clusters by their reactions with metal carbonyls such as $Co_2(CO)_8$ and $Fe_2(CO)_9$.[11] In a related preliminary communication, they have also shown that reactions of the half-sandwich compound, $CpCo(CO)_2$, with $F_5P_3N_3C{\equiv}CPh$ results in a novel fluorophosphazene-substituted cyclobutadiene cobalt sandwich compound, along with a few other phosphazene-derived molecules.[12]

It has been observed that reactions of the half-sandwich compound $CpCo(CO)_2$ with disubstituted acetylenes differ significantly when compared to that of phosphine complex $CpCo(PPh_3)_2$.[13,14] Whereas the former, without exception, results in metallocenes with η^5-cyclopentadienyl-η^4-cyclobutadiene groups, the latter has also been found to form PPh_3 stabilized cobaltacyclopentadiene metallacycles, depending upon the reaction conditions and nature of substituents on the alkyne.[15,16] These cobaltametallocycles are potential precursors for making novel acetylene-trimerized aryl compounds as well as $[\eta^5\text{-Cp}]Co[\eta^4\text{-}R_4C_4]$ metallocenes.

Our interest in this chemistry stems from our previous work in the synthesis and transformations of bridged and ansa-substituted fluorinated phosphazenes with dialkoxy substituents.[6c,6d,10a] In our search for novel examples of bridged phosphazenes and ways to synthesize them, we were keen to explore the reactions of the half-sandwich compound η^5-$(MeOC(O)C_5H_4)Co(PPh_3)_2$ with fluorophosphazene-derived acetylenes to see the possibility of making bisfluorophosphazene-derived cobaltametallacycles. The facts that the bisphosphine complex η^5-$(MeOC(O)C_5H_4)Co(PPh_3)_2$, unlike the carbonyl complex, can be prepared in situ starting with the inexpensive $Co(PPh_3)_3Cl$ and that the ester moiety on the cyclopentadienyl group has the potential for further conversion to useful functional groups were added attractions in pursuing this reaction. Herein, we report the results of our studies on the reactions of $(MeOC(O)C_5H_4)Co(PPh_3)_2$ with $F_5P_3N_3C{\equiv}CPh$.

Experimental Section

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under a nitrogen atmosphere. Tetrahydrofuran, xylene, and toluene were freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere and used. Sodium salt of carbomethoxycyclopentadiene,[14] tris(triphenylphosphine)cobalt chloride,[17] and (β-phenylethynyl) pentafluorocyclotriphosphazene[12] were prepared according to literature procedures. Diphenyl acetylene, Dimethyl carbonate, and triphenylphosphine (Aldrich) were used as such.

Instrumentation. ^1H and $^{13}C\{^1H\}$ spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz, respectively. $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-400 NMR spectrometer at 161 and 376 MHz, respectively. 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 FAB mode using a JEOL SX 102/DA-6000 mass spectrometer.

X-ray Crystallography. Suitable crystals of compounds **1**−**4** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane solvent mixtures. X-ray diffraction studies of crystals mounted on a capillary were carried out on a BRUKER AXS SMART-APEX diffractometer equipped with CCD area detector ($K_\alpha = 0.71073$ Å, graphite monochromator).[18a] Frames were collected at $T =$ 298 K for compounds **1**, **3,** and **4** and at 100 K for compound **2** by ω, ϕ, and 2θ rotation with full quadrant data collection strategy (four domains each with 600 frames) at 10 s per frame with SAINT.[18b] The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[18b] Structure solution and refinement were carried out with the SHELXTL package by direct methods.[18c] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions, and a riding model was used for the refinement. Images were created with the program Diamond.[18d] For compound **1**, some of the observed intensi-

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(7) (a) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, *6*, 119−157. (b) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Suszko, P. R.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2337−2347. (c) Lavin, K. D.; Riding, G. H.; Parvez, M.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1986**, 117−118. (d) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R.; Parvez, M. *Organometallics* **1986**, *5*, 1626−1635.

(8) (a) Riding, G. H.; Parvez, M.; Allcock, H. R. *Organometallics* **1986**, *5*, 2153−2154. (b) Allcock, H. R.; Dembek, A. A.; Bennet, J. L.; Manners, I.; Parvez, M. *Organometallics* **1991**, *10*, 1865−1874.

(9) (a) Allcock, H. R.; Wagner, L. J.; Levin, M. L. *J. Am. Chem. Soc.* **1983**, *195*, 1321−1327. (b) Allcock, H. R.; Greigger, P. P.; Wagner, L. J. *Inorg. Chem*. **1981**, *20*, 716−722. (c) Greigger, P. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1979**, *101*, 2492−2493.

(10) (a) Muralidharan, K.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 7535−7543. (b) Herberhold, M.; Hofmann, A.; Milius, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1599−1608. (c) Nataro, C.; Myer, C. N.; Cleaver, W. M.; Allen, C. W. *J. Organomet. Chem.* **2001**, *637*−*639*, 284−290.

(11) (a) Bahadur, M.; Allen, C. W.; Geiger, W. E.; Bridges, A. *Can. J. Chem*. **2002**, *80*, 1393−1397. (b) Allen, C. W. Bahadur, M. *J. Inorg. Organomet. Polym.* **1998**, *8*, 23−31.

(12) Allen, C. W.; Malik, P.; Bridges, A.; Desorcie, J.; Pellon, B. *Phosphorus*, *Sulfur Silicon Relat. Elem.* **1990**, *49*−*50*, 433−436.

(13) (a) Varela, J. A.; Saa, C. *Chem Rev*. **2003**, *103*, 3787−3801. (b) MacFarland, D. K.; Gorodetzer, R. *J. Chem. Educ*. **2005**, *82*, 109−110. (c) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888−3897. (d) Rausch, M.; D. *Pure Appl. Chem.* **1972**, *30*, 523−538.

(14) Stevens, A. M.; Richards, C. J. *Organometallics* **1999**, *18*, 1346−1348.

(15) Goswami, A.; Meier, C.-J.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem*. **2004**, *13*, 2635−2645. (b) Schaefer, C.; Gleiter.; Rominger, F. *Organometallics* **2004**, *23*, 2225−2227. (c) Laskoski, M.; Morton, J. G. M.; Smith, M. D.; Bunz, U. H. F. *Chem. Commun.* **2001**, *24*, 2590−2591.

(16) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma K.; Yamazaki, H. *J. Am. Chem. Soc*. **1983**, *105*, 1907−1912. (b) Yasafuku, K.; Yamazaki, H. *J. Organomet. Chem*. **1977**, *127*, 197−207. (c) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *132*, 157−167.

(17) Wakatsuki, Y.; Yamazaki, H. *Inorg. Synth*. **1989**, *26*, 189−200.

(18) (a) *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 1.2c; University of Bonn: Bonn, Germany, 1999.

ties were anomalously large because of contributions from overlapping reflections of another minor component. The imperfection in the crystal and room temperature data collection has possibly resulted in relatively high values of residual factors and standard uncertainties in compound **1**.

The ester group present in the cyclopentadienyl ring of **2** shows disorder, and O1, O2, C1, and C2 atoms occupied two crystallographically independent positions that could be located from the additional residual electron density observed in the difference map. The site occupancy factors were refined with the help of free variable PART instruction.[18c] Refinement of the site occupancy factors for the disordered atoms O1, O2, C1, and C2 gave the values 0.54 (2), 0.57(4), 0.56(3), and 0.57(5), respectively. These factors were thereafter fixed at 0.55. The occupancy factor of the other possible set of positions (O1D, O2D, C1D, and C2D) was 0.45. Hydrogen atoms were fixed to the terminal disordered carbon atoms C1 and C1D in idealized positions with site occupancy factors 0.55 and 0.45, respectively, and a riding model was used for the refinement.

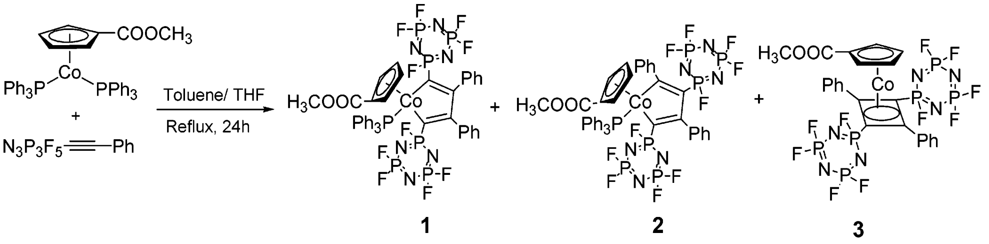
Preparation of 1−3. A solution of (β-phenylethynyl)pentafluorocyclotriphosphazene (2.00 g, 6.04 mmol) and $(PPh_3)_3CoCl$ (2.67 g, 3.00 mmol) in 35 mL of toluene was added to a stirred solution of a sodium salt of carbomethoxy cyclopentadiene (0.44 g, 3.00 mmol) in 10 mL of THF. The mixture was stirred at room temperature for 15 min before being refluxed for 24 h. Afterward, all solvents were removed under vacuum; the resulting crude product was chromatographed on a silica gel column and eluted with hexane to remove triphenylphosphine and triphenylphosphine oxide as the first and second fractions. The third fraction, which came out of the column at 2% ethyl acetate in hexane, was found to be (η^5-$MeOC(O)C_5H_4$)Co[1,3-$(N_3P_3F_5)_2$-2,4-$(C_6H_5)_2$] (**3**). Yield: 0.07 g, 15%. Mp: 84 °C. IR (ν, cm^{-1}): 1720s (C═O), 1267vs (P═N), 1062w, 1014w, 950s (P−F), 866s (P−F), 823s (P−F). ^{1}H NMR ($CDCl_3$): δ 3.37 [s, 3H, $COOCH_3$], 5.20 [s, 2H, CpH], 5.73 [s, 2H, CpH], 7.34−7.43 [m, 6H, PhH), 7.49−7.51 [m, 4H, −PhH].^{13}C{^{1}H} NMR: δ 51.98 [CH_3], 84.71, 86.92 [C_4 ring C], 87.83, 98.30, 99.27 [CpC], 125.22, 128.21, 129.15, 133.83 [PhC], 167.24 [-C═O]. ^{31}P{^{1}H} NMR: δ 9.90 [tm, $^1J_{P-F}$ = 921 Hz, −PF_2], 32.44 [tm, $^1J_{P-F}$ = 980 Hz, −PF(C)]. ^{19}F{^{1}H} NMR: δ −69.21 [dm, 4F, $^1J_{P-F}$ = 930 Hz, PF_2], −70.70 [dm, 4F, $^1J_{P-F}$ = 924 Hz, PF_2] −47.89 [d, 2F, $^1J_{P-F}$ = 970 Hz, PF(C)]. MS (FAB) [*m*/*e* (species)]: 843 [M]$^+$, 812 [M − CH_3O]$^+$, 181 [$COOCH_3CpCo$]$^+$. Anal. Calcd for $C_{25}H_{27}CoF_{10}N_6O_2P_6$: C, 34.19; H, 3.10; N, 9.57. Found: C, 34.13; H, 3.05; N, 9.50.

Compound (η^5-$MeOC(O)C_5H_4$)(PPh_3)Co[2,5-$(N_3P_3F_5)_2$-3,4-$(C_6H_5)_2$] (**1**) came as the fourth fraction, using 2.5% ethyl acetate in hexane as the eluant. Yield: 0.34 g, 11%. Mp: 198−200 °C. IR (ν, cm^{-1}): 1725s (C═O), 1269vs (P═N), 1091w, 1001w, 928s (P−F), 825s (P−F). ^{1}H NMR: δ 3.27 [s, 3H, $COOCH_3$], 5.31 [s, 2H, CpH], 5.7 [s, 2H, CpH], 6.73−6.80 [m, 4H, C_4Co ring Ph H], 7.39−7.41 [m, 6H, C_4Co ring Ph H], 7.48−7.57 [m, 15H, PPh_3 H]. ^{13}C{^{1}H} NMR: δ 52.47 [CH_3], 85.13, 86.82 [C_4Co ring C], 90.11, 93.75, 93.89 [CpC], 126.72, 126.94, 127.39, 127.83 127.95, 129.45, 134.52, 130.03, 134.52, 141.17 [PhC], 170 [C═O]. ^{31}P{^{1}H} NMR: δ 6.72 [tm, $^1J_{P-F}$ = 935 Hz, PF_2], 37.33 [dm, $^1J_{P-F}$ = 946 Hz, PF(C)], 51.16 [s, PPh_3]. ^{19}F{^{1}H} NMR: δ −73.12 [dm, 4F, $^1J_{P-F}$ = 940 Hz, PF_2], −67.45 [dm, 4F, $^1J_{P-F}$ = 940 Hz, PF_2], −41.35 [dt, 2F, $^1J_{P-F}$ = 950 Hz, PF(C)]. MS (FAB) [*m*/*e* (species)]: 1105 [M]$^+$, 1104 [M − 1]$^+$, 844 [(**3**) + 1]$^+$, 812 [M − CH_3O]$^+$, 263 [PPh_3^+ + 1], 181 [$COOCH_3CpCo$]$^+$. Anal. Calcd for $C_{42}H_{35}CoF_{10}N_6O_2P_7$: C, 44.98; H, 3.15; N, 7.49. Found: C, 44.90; H, 3.17; N, 7.43.

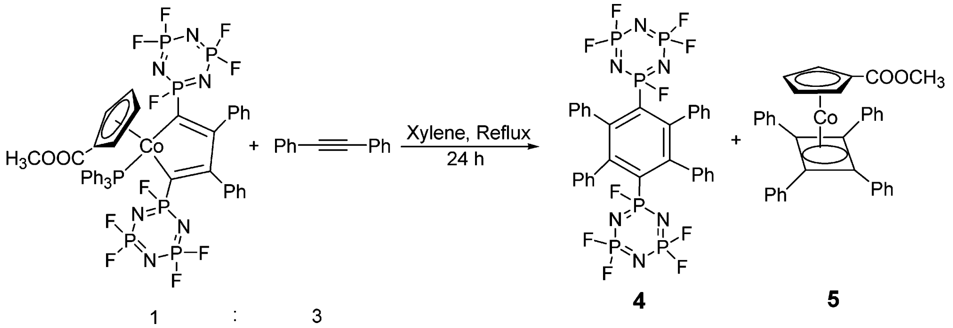
The fifth fraction, which came out of the column at 3% ethyl acetate in hexane, was analyzed and identified as (η^5-$MeOC(O)C_5H_4$)(PPh_3)Co[2,5-$(N_3P_3F_5)_2$-3,4-$(C_6H_5)_2$] (**2**). Yield: 0.16 g, 20%. Mp: 150−152 °C. IR (ν, cm^{-1}): 1717s (C═O), 1252vs (P═N), 1089w, 1000w, 936s (P−F), 851s (P−F), 825s (P−F). ^{1}H NMR: δ 3.57 [s, 3H, $COOCH_3$], 4.65 [s, 1H, CpH], 5.09 [s, 1H, CpH], 5.27 [s, 1H, CpH], 5.52 [s, 1H, CpH], 6.53−6.55 [m, 2H, C_4Co ring Ph H], 7.09−7.26 [m, 8H, C_4Co ring Ph H], 7.27−8.06 [m, 15H, PPh_3 H]. ^{13}C{^{1}H} NMR: δ 53.15 [CH_3], 85.06, 86.91 [C_4Co ring C], 92.84, 98.73, 99.73 [CpC], 127.32, 127.41, 128.23, 128.32, 128.62, 128.72, 129.03, 130.80, 131.21, 134.27 [PhC], 166.04 [-C═O]. ^{31}P{^{1}H} NMR: δ 7.36 [tm, $^1J_{P-F}$ = 910 Hz, PF_2], 19.09 [dm, $^1J_{P-F}$ = 1002 Hz, PF(C)], 35.81 [dm, $^1J_{P-F}$ = 945 Hz, PF(C)], 43.81 [s, PPh_3]. ^{19}F{^{1}H} NMR: δ −72.99 [dm, 4F, $^1J_{P-F}$ = 899 Hz, PF_2], −69.25 to −65.07 [m, 4F, $^1J_{P-F}$ = 915 Hz, PF_2], −53.24 [dt, 1F, $^1J_{P-F}$ = 1000 Hz, PF(C)], −40.67 [dt, 1F, $^1J_{P-F}$ = 939 Hz, PF(C)]. MS (FAB) [*m*/*e* (species)]: 1105 [M]$^+$, 1104 [M − 1]$^+$, 843 [**3**]$^+$, 812 [M − CH_3O]$^+$, 263 [PPh_3^+ + 1], 181 [$COOCH_3CpCo$]$^+$. Anal. Calcd for $C_{42}H_{35}CoF_{10}N_6O_2P_7$: C, 44.98; H, 3.15; N, 7.49. Found: C, 44.93; H, 3.10; N, 7.41.

Preparation of 4. A solution of **1** (0.29 g, 0.26 mmol) and diphenyl acetylene (0.14 g, 0.78 mmol) in 20 mL of xylene was refluxed for 24 h. During the course of the reaction, the color of the solution changed from dark red to brown. After completion of the reaction, the solvent was evaporated off by applying a vacuum, and the crude product mixture was chromatographed through a silica gel column using a ethyl acetate/hexane mixture as the eluant. With pure hexane as eluant, PPh_3 was removed; at 2% ethyl acetate in hexane, a colorless compound came out. All solvents were removed from the fraction by a vacuum. The compound crystallized by slow cooling of a saturated solution in ethyl acetate and was characterized as [{1,4-$(N_3P_3F_5)_2$-2,3,5,6-$(C_6H_5)_4$}C_6] (**4**). Yield: 0.12 g, 54%. Mp: 215−220 °C. IR (ν, cm^{-1}): 1256 vs (P═N), 1077 w, 1014 w, 935 s (P−F), 859 s (P−F), and 828 s (P−F) ^{1}H NMR: δ 6.97−6.99 [m, 8H, PhH], 7.08−7.15 [m, 12H, PhH].^{13}C{^{1}H} NMR: δ 127.40 [*m*-PhC], 127.64 [p-PhC], 130.41 [*o*-PhC], 137.56 [ipso-PhC], 142.86 [PhC], 146.70 [PhC]. ^{31}P{^{1}H} NMR: δ 6.96 [tm, J_{P-F} = 911 Hz, −PF_2], 31.24 [dm, J_{P-F} =1004 Hz, −PF(C)]. ^{19}F{^{1}H} NMR: δ −73.12 [dm, 4F, J_{P-F} = 913 Hz, −PF_2], −66.45 [dm, 4F, J_{P-F} = 913 Hz, −PF_2], −45.15 [d, 2F, J_{P-F} = 1003 Hz, −PF(C)]. MS (FAB) [*m*/*e* (species)]: 840 [M]$^+$; Anal. Calcd for $C_{30}H_{20}F_{10}N_6P_6$: C, 42.88; H, 2.40; N, 10.00. Found: C, 42.83; H, 2.35; N, 9.94. The second fraction, which came out at 5% ethyl acetate in

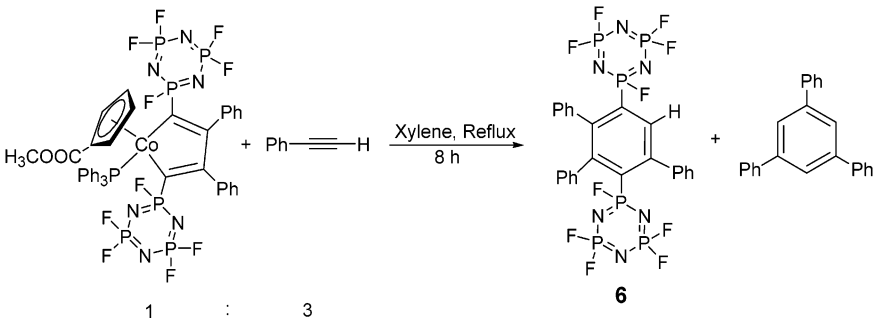
Scheme 1



Scheme 2



Scheme 3



hexane, was crystallized and identified as [η^5-(MeOC(O)-C_5H_4]Co(η^4-C_4Ph_4) (**5**). Melting point, ^{1}H NMR, and IR spectral data of this compound were found to agree well with the reported values for the same (yield: 0.12 g, 25%).[14]

Preparation of 6. A solution of **1** (0.16 g, 0.14 mmol) and phenylacetylene (0.04 g, 0.42 mmol) in 20 mL of xylene was refluxed for 8 h. After completion of the reaction, the solvent was evaporated by applying vacuum, and the crude product was chromatographed on a silica gel column using an ethyl acetate/hexane mixture as the eluant. Compound [{1,4-($N_3P_3F_5$)$_2$-2,3,5-(C_6H_5)$_3$}C_6] (**6**) came out, along with PPh_3, while using pure hexane as the eluant and was purified further by fractional crystallization. Yield: 0.06 g, 54%. Mp: 65 °C. IR (ν, cm^{-1}): 2924m (Ar C−H), 1267vs (P=N), 1071w, 1017w, 930w (P−F), 834s (P−F). ^{1}H NMR: δ 6.59−8.45 (m, ArH). ^{13}C{^{1}H} NMR: δ 121.93, 122.30, 126.07, 127.62, 128.30, 128.52, 129.21, 129.41, 130.40, 132.45, 138.94, 141.33 [PhC]. ^{31}P{^{1}H} NMR: δ 7.42 [tm, $^1J_{P-F} = 941$ Hz, −PF_2], 31.02 [dm, $^1J_{P-F} = 1000$, −PF(C)], 29.53 [dm, $^1J_{P-F} = 1003$ Hz, −PF(C)]. ^{19}F{^{1}H} NMR δ −73.00 [dm, 4F, $^1J_{P-F} = 939$, −PF_2], −67.25 [dm, 4F, $^1J_{P-F} = 940$ Hz, −PF_2], −58.16 [d, 1F, $^1J_{P-F} = 1005$ Hz, −PF(C)], −47.64 [d, 1F, $^1J_{P-F} = 997$ Hz, −PF(C)]. MS (FAB) [*m/e* (species)]: 765 [M + 1]$^+$. Anal. Calcd for $C_{24}H_{16}N_6P_6F_{10}$: C, 37.72; H, 2.11; N, 11.00. Found: C, 37.67; H, 2.08; N, 10.92. On increasing the polarity of the solvent mixture to 2% ethyl acetate in hexane, a colorless compound was isolated that was identified as 1,3,5-triphenylbenzene.[19]

Results and Discussion

Reaction of (β-phenylethynyl)pentafluorocyclotriphosphazene with in situ generated (η^5-(MeOC(O)C_5H_4)Co(PPh_3)$_2$ resulted in three new compounds, **1**−**3** (Scheme 1). Compounds **1** and **2** are two isomers of fluorophosphazene-derived cobaltacyclopentadiene metallacycles, and compound **3** is a metallocene with a η^4-cyclobutadiene unit with trans arrangement of two fluorophosphazene units. It is of interest to note that although the *cis*-fluorophosphazene-substituted cyclobutadienylmetallocene or the metallacycle having both phosphazenyl units on vicinal carbons, (η^5-carbomethoxycyclopentadienyl)(triphenylphosphine)-3,4-bis(pentafluorocyclotriphosphazenyl)-2,5-diphenyl cobaltacyclopentadiene, can be expected as products, they were not isolated from these reactions. The reactions of (β-phenylethynyl)pentafluorocyclotriphosphazene, sodium carbomethoxycyclopentadiene, and tris(triphenylphosphine)cobalt chloride were carried out in two different molar ratios, namely 1.5:1:1 and 2:1:1.

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[19] Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566−1567.

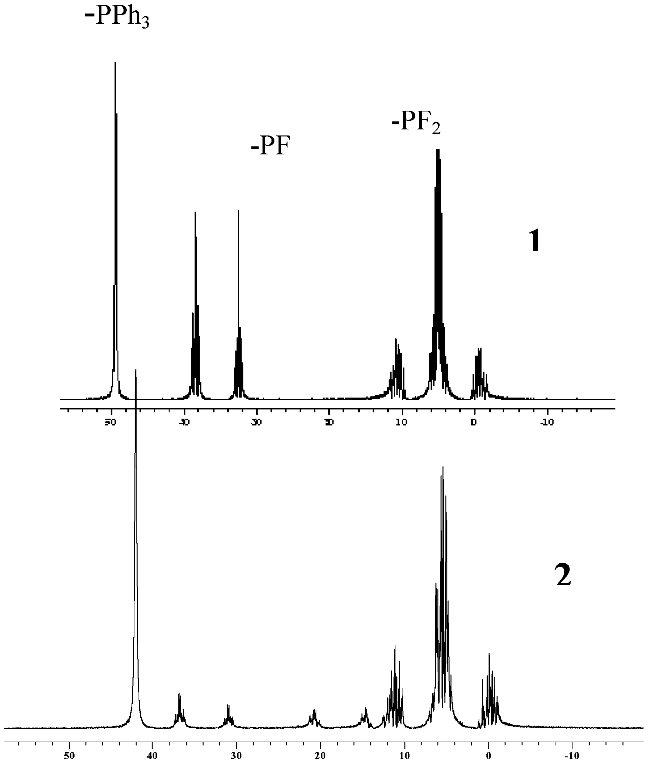

Figure 1. ^{31}P NMR spectra of compounds **1** and **2**.

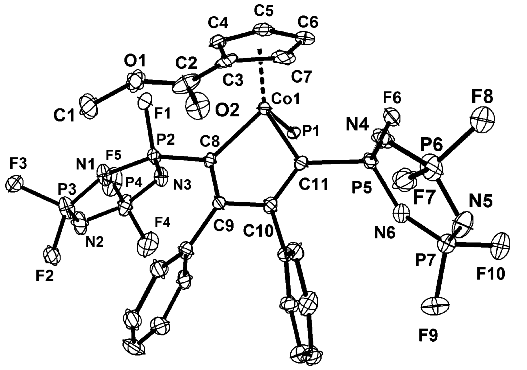

Figure 2. Thermal ellipsoid view of compound **1** with 30% probability factor (hydrogen atoms and the phenyl groups attached to the triphenylphosphine moiety have been omitted for clarity).

Table 1. Selected Bond Lengths and Bond Angles of Compound **1**

Bond Lengths (Å)			
Co(1)−C(3)	2.074 (6)	Co(1)−C(5)	2.130(9)
Co(1)−P(1)	2.219(4)	Co(1)−C(11)	1.955(7)
Co(1)−C(8)	1.988(6)	P(2)−F(1)	1.775(8)
P(5)−C(11)	1.587(6)	P(2)−C(8)	1.552(6)
P(2)−N(3)	1.775(8)	P(2)−N(1)	1.584(7)
P(3)−N(2)	1.554(7)	P(3)−F(3)	1.530(6)
P(3)−F(2)	1.530(6)	P(3)−N(1)	1.553(7)
P(5)−F(6)	1.548(6)	P(5)−N(6)	1.591(6)
P(7)−F(9)	1.520(6)		
Bond Angles (deg)			
P(1)−Co(1)−C(8)	92.64 (17)	P(1)−Co(1)−C(11)	93.30(17)
C(10)−C(11)−P(5)	119.57(43)	C(9)−C(8)−P(2)	118.03(47)
N(3)−P(2)−N(1)	114.57(30)	P(3)−N(2)−P(4)	137.14(40)
N(6)−P(5)−N(4)	115.23(32)	P(6)−N(5)−P(7)	120.17(51)

Table 2. Selected Bond Lengths and Bond Angles of compound **2**

Bond Lengths (Å)			
Co(1)−C(3)	2.073(3)	Co(1)−C(5)	2.155(3)
Co(1)−P(1)	2.217(1)	Co(1)−C(11)	1.951(5)
Co(1)−C(8)	1.960 (3)	P(2)−C(8)	1.769(3)
P(5)−C(10)	1.786(2)	P(4)−N(2)	1.566(3)
P(3)−N(2)	1.567(2)	P(2)−N(1)	1.599(3)
P(4)−F(4)	1.538(2)	P(4)−F(5)	1.529(2)
P(3)−F(2)	1.536(2)	P(3)−F(3)	1.530(2)
P(5)−F(6)	1.549(2)	P(6)−F(7)	1.538(2)
P(7)−F(10)	1.524(2)	P(7)−F(9)	1.531(2)
Bond Angles (deg)			
P(1)−Co(1)−C(8)	95.43(15)	P(1)−Co(1)−C(11)	95.58(7)
C(11)−C(10)−P(5)	124.82(23)	C(9)−C(10)−P(5)	119.77(17)
N(1)−P(2)−N(3)	115.64(12)	P(3)−N(2)−P(4)	119.09(15)
N(6)−P(5)−N(4)	115.46(12)	P(7)−N(5)−P(6)	119.50(16)
F(7)−P(6)−F(8)	97.26(10)	F(6)−P(5)−C(10)	104.73(10)
F(9)−P(7)−F(10)	97.89(13)	F(1)−P(2)−C(8)	103.67(10)
F(2)−P(3)−F(3)	97.83(11)	F(4)−P(4)−F(5)	97.36(10)

Table 3. . Selected Bond Lengths and Bond Angles of Compound **3**

Bond Lengths (Å)			
Co(1)−C(3)	2.058 (5)	Co(1)−C(5)	2.053 (5)
Co(1)−C(11)	1.958 (5)	Co(1)−C(8)	1.968 (5)
P(4)−C(10)	1.744 (10)	P(1)−C(8)	1.734 (4)
C(2)−O(1)	1.334(7)	C(2)−O(2)	1.202(7)
P(1)−N(1)	1.581(4)	P(2)−N(1)	1.548(4)
P(1)−N(3)	1.583(4)	P(3)−F(4)	1.517(4)
P(5)−N(5)	1.561(4)	P(5)−F(7)	1.518(4)
P(5)−N(4)	1.544(4)	P(4)−N(6)	1.577(4)
P(4)−F(6)	1.537(3)		
Bond Angles (deg)			
C(12)−C(9)−C(8)	135.34 (36)	C(9)−C(8)−P(1)	141.68 (31)
C(9)−C(10)−P(4)	141.95 (31)	N(1)−P(1)−N(3)	115.62(20)
F(1)−P(1)−C(8)	104.20(18)	C(10)−P(4)−F(6)	104.40(17)
C(18)−C(11)−C(10)	133.21(36)	N(6)−P(4)−N(4)	116.28(20)
P(6)−N(5)−(P(5)	120.03(24)		

Table 4. Selected Bond Lengths and Bond Angles of Compound **4**

Bond Lengths (Å)			
P(1)−C(1)	1.810(2)	C(2)−C(3)	1.495(3)
P(1)−N(1)	1.576(2)	P(2)−F(3)	1.522(8)
P(3)−F(5)	1.517(7)	P(3)−F(4)	1.519(2)
P(2)−F(2)	1.512(7)		
P(1)−N(3)	1.581(9)		
Bond Angles (deg)			
C(1)−C(2)−C(3)	122.10(17)	C(2)−C(1)−P(1)	118.34(14)
C(1)−P(1)−F(1)	103.35(8)	N(1)−P(1)−N(3)	116.46(11)
P(2)−N(2)−P(3)	119.71(14)	P(1)−C(1)−C(2)	118.34(14)

However, no significant changes in the yields of the products were observed. The relative yields of **1**−**3** were found to vary with a change in reaction time. Reactions carried out under reflux conditions in toluene for 24 h gave yields of 11, 20, and 15%, respectively, whereas refluxing for 48 h gave 10, 15, and 10% yields of **1**−**3**, respectively. A reaction carried out for 7 h in refluxing toluene gave the same compounds **1**−**3** in lower yields (11, 6, and 4%, respectively) in addition to a red viscous liquid that was obtained at the end of the column with a polar solvent mixture as eluant. This viscous liquid was found to disappear when the reaction period was increased to 48 h. Analysis of this liquid by mass spectral and ^{31} P NMR studies suggests a possible intermediate with one or two phosphines replaced by (β-phenylethynyl)pentafluorocyclotriphosphazene. The projected overall low yields of products in these reactions are a result of the fact that the reactive reagent η^5-(MeOC(O)C$_5$H$_4$)Co(PPh$_3$)$_2$ generated in situ is formed in only around 50% yield as observed from separate studies. In addition to compounds **1**−**3**, Ph$_3$P and Ph$_3$PO were also separated from the reaction mixture. No examples of alkyne-trimerized products were isolated from these reactions.

Table 5. X-ray Crystallographic Data for Compounds **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{41}H_{32}CoF_{10}N_6O_2P_7$	$C_{41}H_{32}CoF_{10}N_6O_2P_7$	$C_{23}H_{17}CoF_{10}N_6O_2P_6$	$C_{30}H_{20}F_{10}N_6P_6$
fw	1106.45	1106.45	844.18	840.34
space group	$P1$	$P1$	$P2_1/c$	$Pbca$
a (Å)	10.563(3)	11.7729(8)	7.3106(11)	13.352(1)
b (Å)	11.418(3)	12.2864(9)	22.024(3)	13.708(1)
c (Å)	20.883(5)	16.5497(12)	19.681(3)	18.695(6)
α (deg)	82.733(5)	84.5950(10)	90	90
β (deg)	76.226(4)	85.9960(10)	94.876(3)	90
γ (deg)	72.190(5)	70.9650(10)	90	90
V (Å3)	2325.1(11)	2251.0(3)	3157.2(8)	3422.0(5)
Z	2	2	4	4
T (K)	298(2)	100(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm^3)	1.580	1.632	1.776	1.631
μ (mm^{-1})	0.694	0.717	0.943	0.403
R1[a], wR2[b] ($I > 2\sigma(I)$)	0.0848, 0.1925	0.0352, 0.0949	0.0480, 0.0985	0.0395, 0.1121

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

This reaction differs considerably when compared to the reaction of $CpCo(CO)_2$ with (β-phenylethynyl)pentafluorocyclotriphosphazene, which, although it gave (η^5-cyclopentadienyl)−[η^4-1, 3-bis(pentafluorocyclotriphosphazenyl)−2, 4-diphenylcyclobutadiene]cobalt, did not result in the formation of any cobaltametallacycle compounds.[12] Further, under similar reaction conditions, the reaction of diphenylacetylene with η^5-$(MeOC(O)C_5H_4)Co(PPh_3)_2$ gave exclusively (η^5-$(MeOC(O)C_5H_4)Co(\eta^4$-$C_4Ph_4)$).[14] The cobaltametallacycles **1** and **2** have enhanced thermal stability compared to tetrakis pentafluorophenyl and tetraphenyl analogues. Whereas compounds **1** and **2** are stable as such in refluxing toluene, the tetrakis(pentafluorophenyl) cobaltametallacycle is stable only in refluxing benzene; tetraphenyl cobaltametallacycle converts to the metallocene, [η^5-$CpCo(\eta^4$-$C_4Ph_4)$], in refluxing benzene.[13c,20]

Although described as being model compounds for condensation polymerization reactions of cyclophosphazenes, the bridged derivatives of cyclophosphazenes are some of the most difficult to obtain.[21] Becuase of the multiplicity and reactivity of the phosphorus−halogen bonds, reactions carried out to prepare such derivatives often result in polymerized products. A few examples of alkoxy-bridged cyclophosphazenes are known in the literature and some of these have been found to undergo a bridged-to-spiro transformation in the presence of catalysts.[22] By carrying out a reaction of the cobaltametallacycle **1** with diphenylacetylene, we have been able to prepare, in reasonably good yields, aryl-bridged fluorophosphazenes with pentafluorophosphazenyl units para-substituted on the aryl ring. The 1,4-bisfluorophosphazene-substituted aryl derivative **4** is the first example of an aryl-bridged phosphazene molecule (Scheme 2). The cobaltametallacycle was found to convert to the highly stable sandwich compound [η^5-$(MeOC(O)C_5H_4]Co(\eta^4$-$C_4Ph_4)$] (**5**).[14]

A reaction similar to that of **1** with phenyl acetylene gave the 1,4-disubstituted compound **6** with one phenyl group less than in **4**. This reaction also resulted in a phenylacetylene trimerized product, which is in agreement with the observation of trimerization of 2-ethynylpyridine in its reaction with $CpCo(PPh_3)_2$.[23] The reaction indicates a wider scope is possible for such reactions in realizing a variety of novel aryl- and heteroaryl-bridged fluorophosphazenes by varying substituents on the reactants (Scheme 3).

Spectral Studies on Compounds 1−6. The ^{1}H NMR spectrum of compound **2** differs considerably from the ^{1}H NMR spectra of compounds **1** and **3**. Whereas the four protons present in the cyclopentadienyl ring gave only two different signals in the case of compounds **1** and **3**, for compound **2**, four different signals for these protons (δ, 4.65, 5.09, 5.27, and 5.52 ppm) were observed, which indicated the lesser symmetry of molecule **2**. In addition, the chemical shift values of the phenyl ring protons were shifted downfield in comparison to compounds **1** and **3**. In case of compound **2**, the two PF moieties are present in different environments and hence have different chemical shifts in their ^{31}P and ^{19}F NMR spectra. For the ^{31}P NMR spectrum of compound **2**, the signal at 19.09 ppm is due to the PF(C) group that is away from the metal center and the signal at 35.81 ppm is due to the PF(C) group that is nearer to the metal center, whereas the ^{31}P NMR spectrum of compound **1** gave only one signal at 37.33 ppm for both the PF(C) groups (Figure 1). The presence of triphenylphosphine on **1** and **2** makes the ^{13}C NMR of these compounds complex especially for the phenyl groups compared to compounds **3** and **4**. ^{19}F NMR spectra of all compounds gave two sets of doublet of multiplets at different chemical shifts for the PF_2 groups ($^1J_{P-F} \sim 900-1000$ Hz) due to the diasterotopic nature of the fluorine atoms of the $N_3P_3F_5$ units. Compound **2** gave two different signals for two −PF(C) groups, both as doublets at −53.24 and −40.67 ppm indicating its less symmetric nature compared to compound **1**. The $-PF_2$ groups of compound **2** were also observed as a complex multiplet in the range −69.25 to −65.07. However for all compounds the ^{31}P NMR spectra were much simpler and gave the expected number of signals which were assigned to the PF(C) and PF_2 groups.

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(20) (a) Gastinger, R. G.; Rausch, M. D.; Sullivan D. A.; Palenik G. J. *J. Am. Chem. Soc.* **1975**, *98*, 719−723. (b) Nakamura, A.; Hagihara, N. *Bull Chem. Soc. Jpn*. **1961**, *34*, 452−458.

(21) Chandrasekhar, V.; Muralidhara, M. G. R.; Selvaraj, I. I. *Heterocycles* **1990**, *31*, 2231−2266.

(22) Vij, A.; Geib, S. J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1996**, *35*, 2915−2929 and references therein.

(23) Wakatsuki, Y.; Yoshimura, H.; Yamazaki, H. *J. Organomet. Chem.* **1989**, *366*, 215−221.

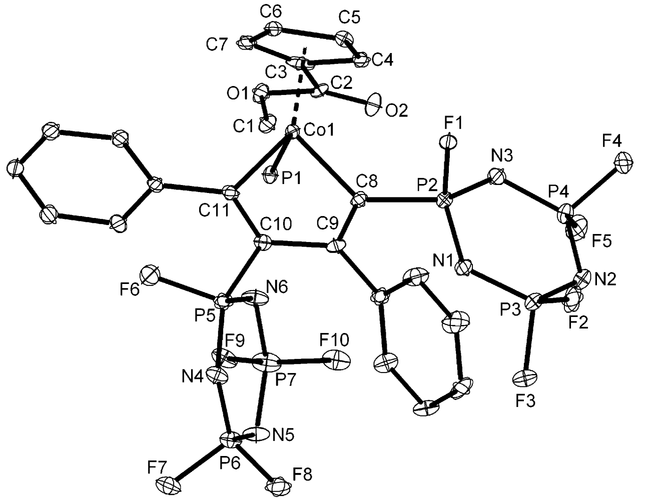

Figure 3. Thermal ellipsoid view of compound **2** with 30% probability factor (hydrogen atoms and the phenyl groups attached to the triphenylphosphine moiety have been omitted for clarity).

Compound **6** gave two different signals for two $-PF$ groups, both as doublets at -58.16 and -47.64 ppm, which was similar to the spectral pattern shown by compound **2**. Further the $-PF_2$ groups showed two signals at -73.00 and another at -67.25 ppm. The difference in the ^{19}F NMR of compounds **4** and **6** showed that the orientations of the phosphazene moieties in compound **6** are not the same as that of compound **4**, and suggests a possible conformation where the two phosphazene units are eclipsed to each other, similar to compound **2**. However, in the absence of suitable crystals for structure determination, structural features of compound **6** could not be confirmed.

X-ray crystal structures of compounds 1−4. The crystal structure of compound**1** is given in Figure 2. The cobalt triphenylphosphine bond distance [Co(1)−P(1) 2.219(4) Å, Table 1] was shorter than the values of 2.327 (4), and 2.339 (1) Å[24] found in cobaloxime complexes, and 2.234 Å in 1-(η^5-cyclopentadienyl)-1,3-bis(pentafluorophosphazenyl)-2,4-bis(phenyl)cobalt complex.[20] The two C−P distances connecting the fluorophosphazene units to the metallacycle are found to be same [1.775(8) Å]. The P−F bond distances [P(2)−F(1) 1.552(6) and P(5)−F(6) 1.548(6) Å] which are directly attached to the carbon atom of metallacycle were found to be longer than the P−F bond distances which are away from the metal center [P(3)−F(3) 1.530(6) and P(6)−F(7) 1.533(7) Å]. The two phosphazene units present in the metallacycle were oriented in the gauche form with respect to each other. Selected bond angles and bond distances for compounds **1**−**4** are given in Tables 1−4, respectively.

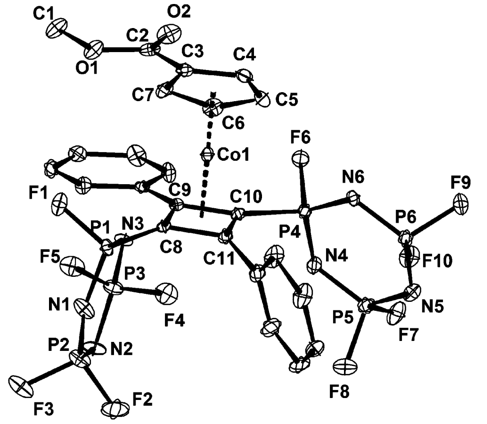

Figure 4. Thermal ellipsoid view of compound **3** with 30% probability factor (hydrogen atoms have been omitted for clarity).

Molecular structure of compound **2** differs from **1** in such a way that one of the pentafluorophosphazene units and one phenyl group exchanged their positions to make an arrangement having two phosphazene units and two phenyl rings occupying alternate positions in the metallocyclic ring (Figure 3). It is interesting to note that the distance of the P−F bond closer to the metal atom [P(5)−F(6) 1.549(2) Å] is slightly shorter than the distance of P−F bond which is away from the cobalt atom [P(2)−F(1) 1.558(2) Å], which confirms the upfield shift of the former in the ^{31}P NMR and ^{19}F NMR spectra compared to the latter. The two phosphazene units which are present in the metallacycle are eclipsed to each other, which is in contrast to the relative orientation of two phosphazene units in compound **1**. The ester group present in the cyclopentadienyl ring of compound **2** shows disorder and the atoms O1, O2, C1 and C2 were occupying two crystallographically independent positions. The site occupancy factors of these atoms were refined and these factors were fixed at 0.55.

In compound **3**, the cyclobutadiene contains two pentafluorophosphazene units are trans to each other (Figure 4). Unlike compound **2**, which showed two different bond distances for the P−F bonds, compound **3** has almost equal bond distances for the P−F bonds [P(1)−F(1) 1.538 (3) Å and P(4)−F(6) 1.537(3) Å] which are closer to the metal center. Further the P−F groups of both the phosphazene moieties are involved in weak intramolecular C−H...F interaction with one of the phenyl rings (C(13)−H(13)...F(1) 2.389(5) and C(17)−H(17)...F(6) 2.369(3) Å). These distances are in good agreement with the values reported for weak C−H...F interactions.[10a] This weak interaction is probably making one of the phenyl rings to be in the plane of the cyclobutadiene ring. The other phenyl ring which does not involve in any weak interactions lies almost perpendicular to the plane of the cyclobutadiene ring. The two phosphazene units present in the cyclobutadiene ring are eclipsed to each other at a particular orientation.

The molecular structure of compound **4** is given in the Figure 5. Compound **4** is the first example of a structurally characterized aryl bridged cyclophosphazene. The four phenyl groups are oriented at an angle to the central aryl ring while the two phosphazene units are anti to each other. The mean plane containing two opposite phenyl rings makes an angle of 64.82° with the plane of the central benzene ring. Similarly the mean plane containing the other two phenyl rings makes an angle of 66.48° with the plane of the central benzene ring. The two phosphazene units are anti to each other and the closest P−F bonds to the central aryl ring makes a torsional angle of 150.92°. The fluorine atoms of

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(24) (a) Bruckner, S.; Randacclo, L. *J. Chem. Soc., Dalton Trans.* **1974**, 1017−1021. (b) Adams. W. W.; Lenhert, P. G. *Acta Crystallogr., Sect. B* **1973**, *29*, 2412−2414.

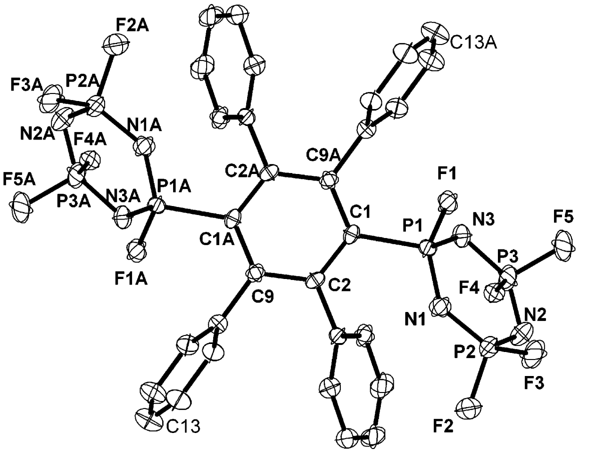

Figure 5. Thermal ellipsoid view of compound **4** with 30% probability factor (hydrogen atoms have been omitted for clarity). Atoms labeled with the suffix A were generated by the symmetry code ($1 - x$, $-y$, $1 - z$).

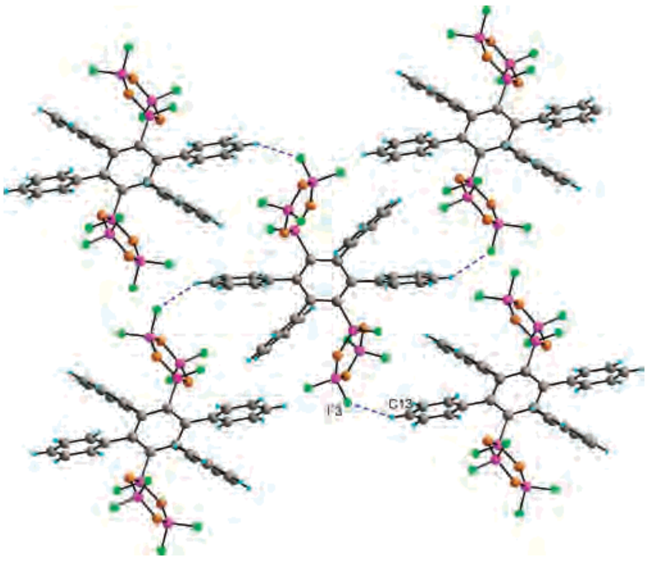

Figure 6. Molecular structure **4** showing weak intermolecular C−H···F interactions.

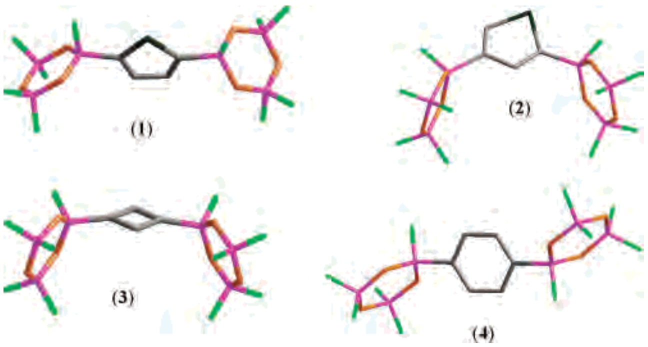

Figure 7. Molecular structures of compounds **1**−**4** showing orientations of the phosphazene moieties with respect to the central ring (other parts of the molecules have been omitted for clarity).

the phosphazene units are involved in weak intermolecular C−H...F interaction with the phenyl rings of the neighboring molecules [C(13)−H(13)...F(3) 2.652(2) Å] resulting in a two-dimensional layer type supramolecular assembly (Figure 6).

A comparison of the orientations of the two phosphazene moieties in compounds **1**−**4** shows interesting features (Figure 7). None of the compounds isolated and characterized in this study has two fluorophosphazene units present on vicinal carbon atoms of four, five and six-membered carbo or metallacyclic rings. The phosphazene units present in compounds **2** and **3** are eclipsing with each other. In the case of compounds **1**, the phosphazene units are gauche to each other, and in compound **4** the orientations of the phosphazene units are anti to each other. In the case of compounds **2** and **3**, the mean planes containing the two phosphazene units intersect each other at an angle of 52.28° and 63.66° respectively. For compound **1** the angle between the two planes is 80.99°. The number and chemical shifts of signals obtained in the ^{31}P and ^{19}F NMR spectra of compounds **1**−**4** reflects these differences in the orientations of phosphazene groups and indicates further the stability of the structure in solution phase as well.

Conclusions

In conclusion, we report the synthesis and characterization of two novel fluorophosphazene derived cobaltocyclopentadienylmetallacycles, and also provide a hitherto unknown synthetic route for making aryl bridged fluorinated cyclophosphazenes by the reaction of the metallacycles with substituted acetylenes. The PPh_3 stabilized metallacycles are prepared by the reaction of (β-phenylethynyl) pentafluorocyclotriphosphazene, $F_5P_3N_3C{\equiv}CPh$ with in situ generated η^5- $(MeOC(O)C_5H_4)Co(PPh_3)_2$. This reaction also gives a cyclobutadienyl cobaltametallocene having two fluorophosphazenyl groups trans to each other on the cyclobutadiene ring. Quite interestingly, structural studies indicate that compounds having two fluorophosphazene moieties on vicinal carbon atoms of four, five and six membered carbocyclic rings have not been formed in these reactions thus indicating selectivity in product formation. This may possibly be due the steric bulkiness of the phosphazene molecules. The metallocyclic compounds, metallocenyl compound and the aryl bridged fluorophosphazene compounds considerably differ in their spectral and structural properties and these have been compared. The method described for making bridged phosphazenes shows potential for making a host of aryl and heteroaryl fluorophosphazene derivatives, which can themselves, be precursors for a host of new molecules.

Acknowledgment. The authors thank the Department of Science and Technology (DST) of India and the Council of Scientific and Industrial Research (CSIR) of India for financial assistance in the form of research grants to A.J.E. and IIT Delhi for an equipment grant. We thank DST-FIST and IITD for funding of the single crystal X-ray diffraction facility at IIT Delhi. The authors thank Dr. N. Kurur and Prof. A. Ramanan, Department of Chemistry, IIT Delhi, for their help in recording multinuclear NMR and analyzing X-ray crystallographic data. We thank SAIF, CDRI, Lucknow, for providing mass spectral and analytical data.

Supporting Information Available: Crystallographic information files (CIF) for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0609204