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Synthesis and Selectivity in the Formation of Cyclophosphazene-Derived 1,3-Cyclohexadienes from Reactions of RCpCo(COD) [R = MeOC(O)] with Alkynes and Alkenes

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The first examples of mono and bisfluorophosphazene derived [η^5-cyclopentadienyl] [η^4-1,3-cyclohexadiene] cobalt complexes have been prepared along with the sandwich compound [η^5-carbomethoxycyclopentadienyl] [η^4-1,3-bis(pentafluorocyclotriphosphazenyl)-2,4-diphenylcyclobutadiene] cobalt and acetylene trimerized products from the reactions of [η^5-MeOC(O)C$_5$H$_4$]Co[COD], PhC≡CP$_3$N$_3$F$_5$ and phenylacetylene in the presence or absence of an additional cycloalkene or indene. Formation of these mono and bis fluorophosphazene derived cobalt cyclohexadiene complexes provide experimental evidence for a metallacyclopentadiene pathway for cyclohexadiene formation in CpCo catalyzed reactions. Selectivity is also observed in the formation of bisfluorophosphazene derived cyclohexadienes which stems from the fact that two P$_3$N$_3$F$_5$ units cannot be accommodated on vicinal carbon atoms of a carbacycle or metallacycle. Interestingly, reactions of (β-phenylethynyl)pentafluorobenzene with [η^5-MeOC(O)C$_5$H$_4$]Co[COD] in the presence and absence of external cycloalkene under identical reaction conditions yielded only the cis and trans isomers of the metallocene [η^5-MeOC(O)C$_5$H$_4$]Co[η^4-C$_4$Ph$_2$(C$_6$F$_5$)$_2$] along with alkyne trimerized product indicating that the selectivity in cyclohexadiene formation is governed more by steric than electronic factors. All the new compounds were characterized by ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR as well as mass spectrometry and elemental analysis. Mono and bispentafluorocyclotriphosphazene derived [η^5-cyclopentadienyl] [η^4-1,3-cyclohexadiene] cobalt complexes and [η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,3-pentafluorophenyl)-2,4-diphenylcyclobutadiene] cobalt have also been structurally characterized by single crystal X-ray analysis.

Introduction

Interest in halogenated cyclophosphazenes stems not only from a host of potential applications but also from the uniqueness of structurally diverse derivatives resulting from their reactions. While the applications include their proven use as monomers for realizing phosphazene based polymers,[1] stable cores for realizing dendrimers,[2] ionic liquids,[3] as well as multidendate[4]and multianionic[5] ligands, studies on reactivity have been mainly centered on integrating chirality[6] and exploring the versatility in the reactions of difunctional reagents with the phosphorus−halogen bonds of the heterocycle.[7] Among the reactions of difunctional reagents with cyclophosphazenes, those leading to spiro and ansa substitu-

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tion have been explored in detail.[8] However, very few attempts have been made to explore and understand the formation of bridged or multiphosphazenyl assemblies having reactive P−X bonds [6d,9] which are potential precursors for realizing phosphazene based condensation polymers, dendrimers, and multidendate ligands.

Use of organocobalt reagents in realizing multiphosphazenyl assemblies were initially reported by Allen and coworkers in a conference paper using the phosphazene derived alkyne, $PhC{\equiv}CP_3N_3F_5$ and cobalt carbonyls.[10] Reaction of fluorophosphazene derived alkynes with $Co_2(CO)_8$ and $CpCo(CO)_2$ had resulted in the formation of novel phosphazene derived cobalt carbonyls and cyclobutadiene complexes.[11] We have recently shown in a detailed study that the reactions of $PhC{\equiv}CP_3N_3F_5$ with $[\eta^5\text{-}MeOC(O)\text{-}C_5H_4]Co(PPh_3)_2$ differ considerably from its reactions with $CpCo(CO)_2$ and result in the formation of metallacycles as well.[12] In this paper, we report the first reactions of $[\eta^5\text{-}MeOC(O)C_5H_4]Co[\eta^4\text{-COD}]$ [where COD = 1,5-cyclooctadiene] with $PhC{\equiv}CP_3N_3F_5$ along with cycloalkenes or indene, which has resulted in the formation of the first examples of mono and bis fluorophosphazene derived cyclohexadiene complexes of cobalt with an interesting product selectivity. The study also addressess the mechanism of cyclohexadiene formation using CpCo based reagents and provides experimental evidence for a metallacyclopentadiene pathway for the same.

Experimental Section

General Methods. All manipulations of compounds 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 were used. (β-Phenylethynyl)pentafluorocyclotriphosphazene,[11] [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt,[13] and (β-phenylethynyl)pentafluorobenzene[14] were prepared according to literature procedures.

Instrumentation. ^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, 75.47, 121, and 282 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 electrospray ionization (ESI) mode using a JEOL SX 102/DA-6000 mass spectrometer.

X-ray Crystallography. Suitable crystals of compounds **1**, **6**, and **7** were obtained by slow evaporation of their saturated solutions in pentane, and compound **8** was recrystallized from an ethylacetate/hexane solvent mixture. X-ray diffraction studies of crystals mounted on a capillary were carried out on a BRUKER AXS SMART-APEX diffractometer equipped with a CCD area detector ($K\alpha = 0.71073$ Å; monochromator, graphite).[15a] Frames were collected at $T = 298$ K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART.[15b] The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[15b] Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.[15c] Nonhydrogen 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.[15d] For compound **6,** because of poor crystal quality, we have omitted the higher 2θ reflections.

Reaction of (β-Phenylethynyl)pentafluorocyclotriphosphazene, 1,5-Cyclooctadiene, and Phenylacetylene with [η^5-Carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] Cobalt. A solution containing 0.20 g (0.6 mmol) of [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt, 0.46 g (1.3 mmol) of (β-phenylethynyl)pentafluorocyclotriphosphazene, 0.07 g (0.6 mmol) of phenylacetylene, and 0.24 g (1.8 mmol) of 1,5-cyclooctadiene in 20 mL of xylene was refluxed for 33 h. The reaction was monitored by thin layer chromatography. After completion of the reaction, all solvents were evaporated off, and the remaining crude product was chromatographed through a silica gel column using a hexane/ethylacetate mixture as the eluent. The first fraction that came out while using pure hexane as the eluent was identified as a mixture of 1,3,5- and 1,2,4-triphenylbenzene (**3** and **4**).[16] The second fraction that came out with 2% ethylacetate/hexane mixture as a viscous liquid was identified and characterized as mono(pentafluorocyclotriphosphazenyl) triphenyl benzene (**5**). Yield: 0.08 g (44%). IR (ν, cm^{-1}): 1266 vs (P = N), 1073 w, 1020 w, 940 s, and 823 s (P−F). ^1H NMR: δ 6.89–7.94 [m, 17H, −PhH]. $^{31}P\{^1H\}$ NMR: δ 7.62 [tm, $^1J_{P-F} = 885$ Hz, $-PF_2$], 33.43 [tm, $^1J_{P-F} = 980$ Hz, −PF(C)]. $^{19}F\{^1H\}$ NMR: δ −90.62 [dm, $^1J_{P-F} = 880$ Hz, $-PF_2$], −85.58 [dm, $^1J_{P-F} = 887$ Hz, $-PF_2$], −75.34 [d, $^1J_{P-F} = 981$ Hz,

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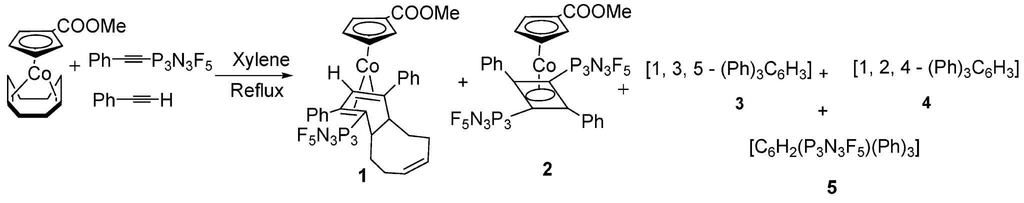
Scheme 1



−PF(C)]. MS (ESI) [*m*/*e* (species)]: 534 [M − 1]$^+$. Anal. Calcd for $C_{24}H_{17}F_5N_3P_3$: C, 53.85; H, 3.20; N, 7.85. Found: C, 53.78; H, 3.04; N, 7.46.

The red fraction that came out next using a 4% ethylacetate/hexane mixture was identified as [η^5-carbomethoxycyclopentadiene] [η^4-1-mono(pentafluorocyclotriphosphazene)-2,3-diphenyl-4a,5,6,9,10,10a-hexahydro[8]annulene] cobalt (**1**) Yield: 0.13 g (27%). Mp: 165–170 °C. IR (ν, cm^{-1}): 1713 s (C=O), 1272 vs (P=N), 1146 w, 926 s and 828 s (P−F). ^{1}H NMR: δ 0.88−1.25 [m, 3H, $-CH_2$], 1.51 [m, 4H, $-CH_2$], 2.4 [m, 4H, $-CH_2$], 3.82 [s, 3H, $-COOCH_3$], 4.28 [s, 1H, −CpH], 4.60 [s, 1H, −CpH], 4.89 [s, 1H, −CpH], 5.12 [s, 1H, −CpH], 5.56−5.74 [m, 2H, −olefinic H], 7.35−7.41 [m, 6H, −PhH), 7.62−7.84 [m, 4H, −PhH]. $^{13}C\{^1H\}$ NMR: δ 25.18, 28.63, 30.48, 30.92, 31.99, 50.26 [saturated cyclooctene C], 51.68 [$-CH_3$], 83.33, 87.29, 90.11 [C_5 ring C], 126.60, 128.33, 128.59, 128.83, 130.90, 144.12 [Ar C, olefinic C], 167.14 [−C=O]. $^{31}P\{^1H\}$ NMR: δ 7.51 [tm, $^1J_{P-F}$ = 879 Hz, $-PF_2$], 45.27 [dm, $^1J_{P-F}$ = 968 Hz, −PF(C)]. $^{19}F\{^1H\}$ NMR: δ −92.5 (dm, $^1J_{P-F}$ = 882 Hz, $-PF_2$), −87.34 (dm, $^1J_{P-F}$ = 884 Hz, $-PF_2$), −76.55 [d, $^1J_{P-F}$ = 970 Hz, −PF(C)]. MS (ESI) [*m*/*e* (species)]: 723 [M$^+$]. Anal. Calcd for $C_{31}H_{30}CoF_5N_3O_2P_3$: C, 51.47; H, 4.18; N, 5.81. Found: C, 51.21; H, 3.98; N, 5.69. The fourth red fraction that came at 6% ethylacetate/hexane mixture was identified as [η^5-carbomethoxycyclopentadienyl] [η^4-1,3-bis(pentafluorocyclotriphosphazenyl)-2,4-diphenylcyclobutadiene] cobalt (**2**) in 21% yield. The identity of **2** was confirmed by comparing its ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR and IR spectral data to reported data in the literature.[12]

Reaction of (β-Phenylethynyl)pentafluorocyclotriphosphazene and Dicyclopentadiene with [η^5-Carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] Cobalt. A solution of 0.15 g (0.5 mmol) of [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt, 0.34 g (1.0 mmol) of (β-phenylethynyl)pentafluorocyclotriphosphazene, and 0.20 g (1.5 mmol) of dicyclopentadiene in 20 mL of xylene was refluxed for 24 h. The reaction was followed up by thin layer chromatography and after completion of the reaction, all solvents were evaporated off. The remaining crude product was chromatographed through a silica gel column using hexane/ethylacetate mixture as the eluent. The cyclohexadiene complex [η^5-carbomethoxycyclopentadiene] [η^4-3,6-bis(pentafluorocyclotriphosphazene)-4,5-diphenyl-endo-tetracyclo[6.5.1.0.^{2,7}0^{9,13}] trideca-3,6,10-triene] cobalt (**6**) came out as the second fraction while using 2% ethylacetate/hexane mixture**.** Yield: 0.18 g (36%). Mp: 200–205 °C. IR (ν, cm^{-1}): 1721 s (C=O), 1265 vs (P=N), 1145 w, 938 s and 828 s (P−F). ^{1}H NMR: δ 0.85 [d, 1H], 1.09 [d, 1H], 1.34 [d, 1H], 1.47 [d, 1H], 2.26 [m, 2H], 2.28 [m, 1H], 2.33 [m, 1H], 2.40 [m, 1H], 2.98 [m, 1H], 3.89 [s, 3H], 5.46 [m, 1H], 5.61 [d, 2H], 5.82 [d, 1H], 5.90 [d, 2H], 7.18–7.57 [m, 10H]. $^{13}C\{^1H\}$ NMR: δ 26.92, 31.90, 34.44, 40.62, 41.45, 44.19, 44.94, 45.91, 52.52, 76.59 [saturated dicyclopentene C], 51.94 [$-CH_3$], 85.80, 88.42, 88.62 [$-C_5$ ring C], 127.60, 128.19, 128.27, 128.57, 129.14, 129.86, 131.29, 131.94, 132.45, 132.51, 133.01 [ArC, olefinic C], 166.23 [−C=O]. $^{31}P\{^1H\}$ NMR: δ 7.25 [tm, $^1J_{P-F}$ = 949 Hz, $-PF_2$], 44.88 [dm, $^1J_{P-F}$ = 961 Hz, −PF(C)]. $^{19}F\{^1H\}$ NMR: δ −70.45 [dm, $^1J_{P-F}$ = 941 Hz, $-PF_2$], −65.55 [dm, $^1J_{P-F}$ = 945 Hz, $-PF_2$], −64.87 [dm, $^1J_{P-F}$ = 953 Hz, $-PF_2$], −53.75 [dm, $^1J_{P-F}$ = 956 Hz, −PF(C)]. MS (ESI) [*m*/*e* (species)]: 977 [M + 1]$^+$. Anal. Calcd for $C_{33}H_{29}CoF_{10}N_6O_2P_6$: C, 40.59; H, 2.99; N, 8.61. Found: C, 40.65; H, 2.91; N, 8.54. The third red fraction that came at 6% ethylacetate/hexane mixture was identified as the sandwich compound **2** with 15% yield.

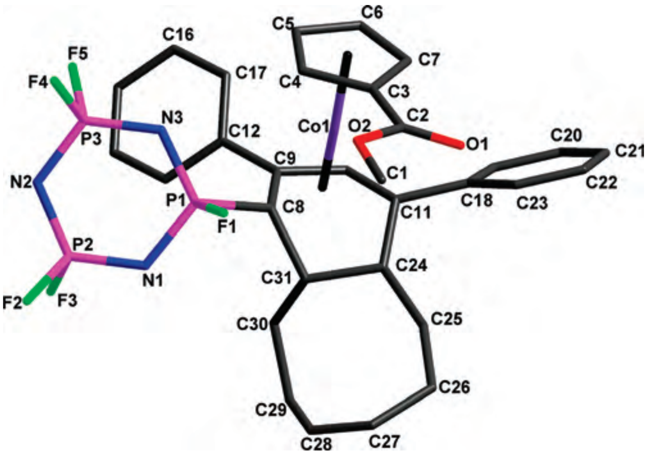
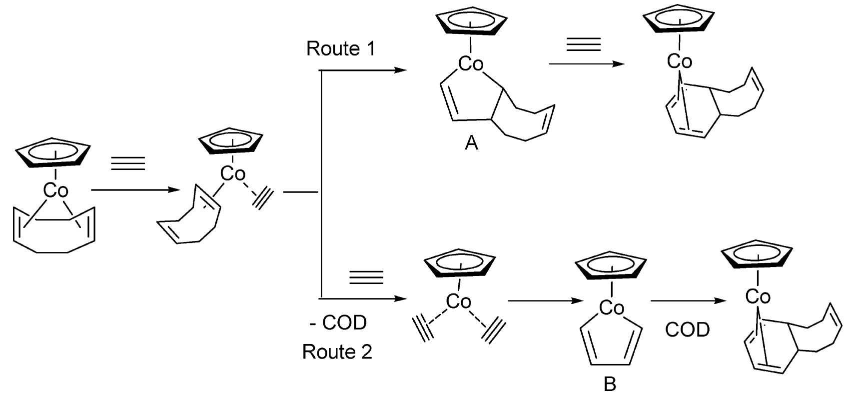


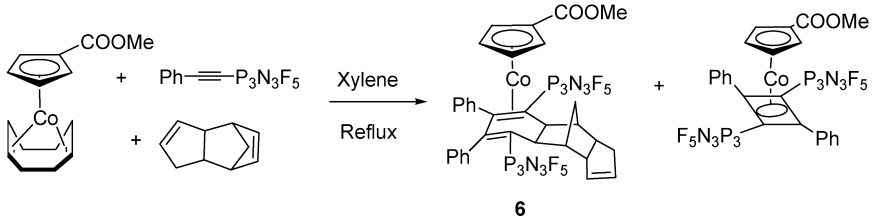
Figure 1. Molecular structure of compound **1** (H atoms are omitted for clarity).

Reaction of (β-Phenylethynyl)pentafluorocyclotriphosphazene and Indene with [η^5-Carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] Cobalt. A solution containing 0.50 g (1.7 mmol) of [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt, 1.14 g (3.4 mmol) of (β-phenylethynyl)pentafluorocyclotriphosphazene, and 0.58 g (5.1 mmol) of indene in 20 mL of xylene was refluxed for 24 h. The reaction was followed by thin layer chromatography, and after completion of the reaction, all solvents were evaporated off. The remaining crude product was chromatographed through a silica gel column using hexane/ethylacetate mixture as the eluent. Unreacted starting materials were removed by passing pure hexane through the column. The cyclohexadiene complex, [η^5-carbomethoxycyclopentadiene] [η^4-1,4-bis(pentafluorocyclotriphosphazene)-9,9a-dihydro-4aH-fluorene] (**7**) came out as the third fraction while using 2% ethylacetate/hexane mixture as the eluent. Yield: 0.64 g (40%). Mp:146–148 °C. IR (ν, cm^{-1}): 1720 s (C=O), 1621 (C=C), 1265 vs (P=N), 936 s and 831s (P−F). ^{1}H NMR: δ 3.07 [m, 1H], 3.35 [m, 1H], 3.54 [m, 1H], 3.91 [s, 3H, $-C(O)OCH_3$], 4.07 [m, 1H], 5.53 [s, 2H, CpH], 6.05 [s, 2H, CpH], 6.72, 7.08–7.24, 7.36–7.50, 7.83 [m, 14H, ArH]. ^{13}C NMR: δ 27.53, 29.71, 38.91 [aliphatic C], 52.15 [$-CH_3$], 85.82, 86.66, 89.08 [C_5 ring C], 124.32, 126.22, 126.87, 127.44, 127.57, 128.04, 128.08, 128.15, 128.59, 128.69, 129.93, 132.24, 141.44, 141.56 [Ar C, olefinic C], 166.19 [−CO]. $^{31}P\{^1H\}$ NMR: δ 6.87 [tm, $^1J_{P-F}$ = 949 Hz, $-PF_2$], 45.27 [dm, $^1J_{P-F}$ = 960 Hz, −PF(C)]. $^{19}F\{^1H\}$ NMR: δ −70.57 [dm, $^1J_{P-F}$ = 940 Hz, $-PF_2$], −65.45 [dm, $^1J_{P-F}$ = 937 Hz, $-PF_2$], −64.34 [dm, $^1J_{P-F}$ = 955 Hz, $-PF_2$], −54.32 [dm, $^1J_{P-F}$ = 950 Hz], −51.30 (dm, $^1J_{P-F}$ = 970 Hz). MS (ESI) [*m*/*e* (species)]: 961 [M + 1]$^+$. Anal. Calcd for $C_{32}H_{25}CoF_{10}N_6O_2P_6$: C, 40.02; H, 2.62; N, 8.75.

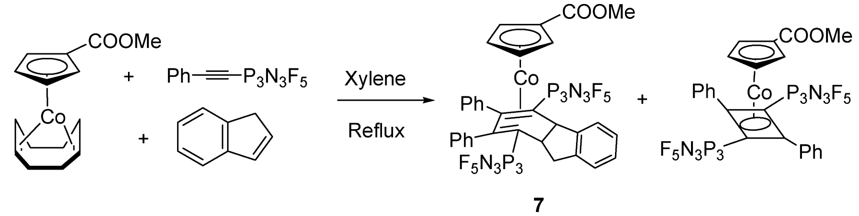
Scheme 2



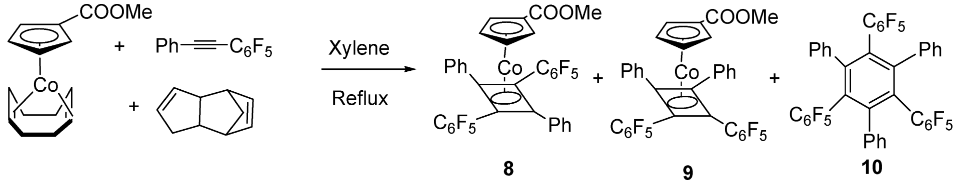
Scheme 3



Scheme 4



Scheme 5



Found: C, 39.39; H, 2.42; N, 8.62. The fourth red fraction which came at 6% ethylacetate/hexane mixture was identified as the sandwich compound **2** with 18% yield.

Reaction of (*β*-Phenylethynyl)pentafluorobenzene and Dicyclopentadiene with [η^5-Carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] Cobalt. A solution of 0.20 g (0.6 mmol) of [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt, 0.37 g (1.3 mmol) of (*β*-phenylethynyl)pentafluorobenzene and 0.23 g (1.8 mmol) of dicyclopentadiene in 20 mL of xylene was refluxed for 24 h. The reaction was followed up by thin layer chromatography, and after completion of the reaction, all solvents were evaporated off. The remaining crude product was chromatographed through a silica gel column using hexane/ethylacetate mixture as the eluent. Unreacted starting materials were removed by passing pure hexane through the column. 1,3,5-tris(pentafluorophenyl)-2,4,6-triphenylbenzene (**10**) came out as the first fraction while using pure hexane as the eluent, which was confirmed by comparing the values of ^{1}H, ^{13}C NMR and IR spectral data with the values reported in the literature.[17] The sandwich compound [η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,3-pentafluorophenyl)-2,4-diphenylcyclobutadiene] cobalt (**8**) came out as the second fraction while using 4% ethylacetate/hexane mixture as the eluent and was further purified by crystallization. Yield: 0.25 g (50%). Mp: 210–215 °C. IR (ν, cm^{-1}): 1704 vs (C=O), 1287 vs (C−F). ^{1}H NMR: δ 3.34 [s, 3H, −COOCH$_3$], 4.94 [s, 2H, −CpH], 5.48 [s, 2H, −CpH], 6.99–7.31 [m, 10H, PhH]. ^{13}C{^{1}H} NMR: δ 51.35 [−CH$_3$], 62.14, 76.43 [C$_4$ ring C], 84.89, 86.46, 88.09 [−CpC], 126.26, 127.42, 128.36, 134.70, 142.45 [PhC], 165.65 [−C=O]. ^{19}F{^{1}H} NMR: δ −161.30 (m), −153.95 (m), −130.92 (m). MS (ESI) [*m*/*e* (species)]: 718 [M$^+$]; Anal. Calcd for $C_{35}H_{17}CoF_{10}O_2$: C, 58.51; H, 2.39. Found: C, 58.34; H, 2.01.

[η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,4-pentafluorophenyl)-2,3-diphenylcyclobutadiene] cobalt (**9**) which could not be purified fully because of contamination of **8** was identified by spectral data. Yield: 11%. ^{1}H NMR: δ 3.42 [s, 3H, −COOCH$_3$], 4.96 [s, 2H, −CpH], 5.33 [s, 2H, −CpH], 6.84–7.54 [m, 10H, PhH].

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(17) Yang, J.; Verkade, J. G. *Organometallics,* **2000**, *19*, 893–900.

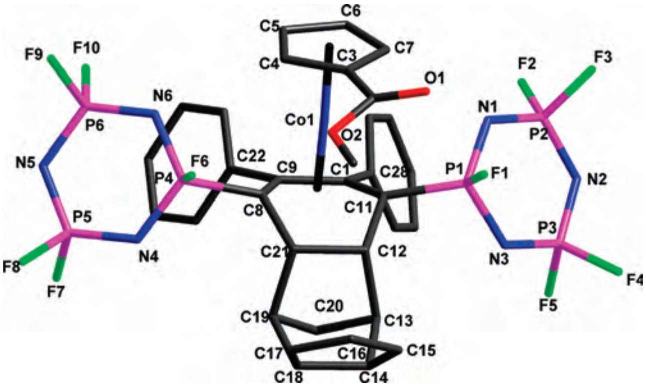

Figure 2. Molecular structure of compound **6** (H atoms are omitted for clarity).

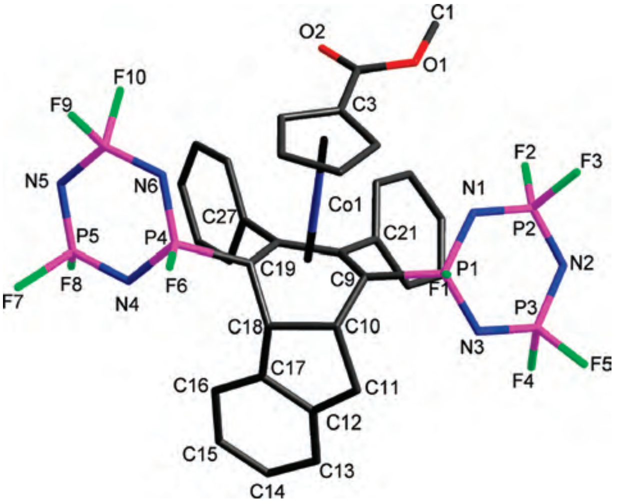

Figure 3. Molecular structure of compound **7** (H atoms are omitted for clarity).

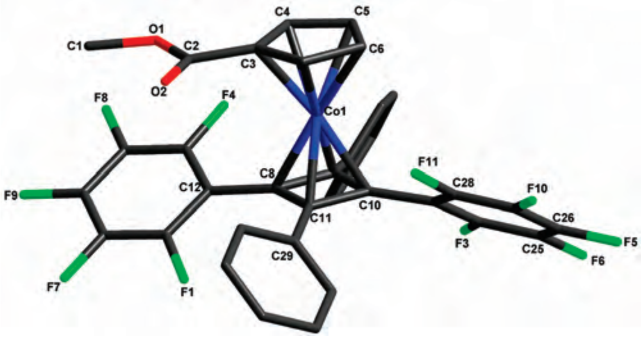

Figure 4. Molecular structure of compound **8** (H atoms are omitted for clarity).

$^{19}F\{^1H\}$ NMR: δ −161.92 (m), −154.67 (m), −131.93 (m). MS (ESI) [*m/e* (species)]: 719 $[M + 1]^+$.

Results and Discussion

While exploring the reactions of $PhC{\equiv}CP_3N_3F_5$ with RCpCo(COD), the inadvertent presence of phenylacetylene in the reaction mixture was found to give traces of a unique phosphazene derived cyclohexadiene compound. This observation initiated our study on the reactions of RCpCo(COD) with a combination of alkynes and cycloalkenes. A reaction of $PhC{\equiv}CP_3N_3F_5$ and phenylacetylene with [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt in the 2:1:1 molar ratio gave the novel cobalt cyclohexadiene complex [η^5-carbomethoxycyclopentadiene] [η^4-1-mono-(pentafluorocyclotriphosphazene)-2,3-diphenyl-4a,5,6,9,10,10a-hexahydro[8]annulene] cobalt **1** along with the sandwich compound [η^5-carbomethoxycyclopentadienyl] [η^4-1,3-bis(pentafluorocyclotriphosphazenyl)-2,4-diphenylcyclobutadiene] cobalt (**2**),[12] in addition to alkyne trimerized products, 1,3,5-$Ph_3C_6H_3$ (**3**), 1,2,4-$Ph_3C_6H_3$ (**4**), [16] and $[C_6H_2(P_3N_3F_5)(Ph)_3]$ (**5**) (Scheme 1). The nature of compound **1** indicates an unprecedented participation of the 1,5-cyclooctadiene present in CpCo(COD) in a [2 + 2 + 2] cycloaddition leading to the formation of a cyclohexadiene complex. Compound **1**, which has been structurally characterized, is also the first example of a phosphazene derived CpCo complexed cyclohexadiene (Figure 1). Such compounds are potential precursors for a host of novel phosphazene derived aryl and cyclohexadiene compounds which can be obtained by removal of the RCpCo fragment.[18]

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

	Bond Lengths (Å)		
Co1−C3	2.075(5)	Co1−C8	2.034(4)
Co1−C10	1.979(5)	Co1−C9	1.966(4)
Co1−C11	2.081(6)	C11−C24	1.532(5)
P1−C8	1.773(4)	P1−F1	1.547(3)
P3−F5	1.523(4)	P3−F4	1.524(4)
P1−N1	1.597(4)	P2−N2	1.566(5)
P3−N2	1.554(7)	P1−N3	1.592(4)
	Bond Angles (deg)		
Co1−C9−C12	128.49(17)	Co1−C11−C18	118.73(16)
Co1−C8−P1	116.14(12)	C3−Co1–11	115.30(9)
C5−Co1−C9	109.76(9)	C5−Co1–10	128.49(10)
C29−C30−C31	117.77(20)		

Table 2. Selected Bond Lengths and Bond Angles of Compound **6**

	Bond Lengths (Å)		
Co1−C3	2.064(8)	Co1−C8	2.059(8)
Co1−C10	2.024(7)	P4−C8	1.781 (7)
P4−F6	1.548(5)	P5−F7	1.524(10)
C13−C20	1.527(13)	C16−C17	1.405(19)
P1−N1	1.581(6)	P4−N4	1.586(7)
P4−N6	1.589(8)	P5−N5	1.550(9)
	Bond Angles (deg)		
Co1−C8−P4	119.57(39)	Co1−C10−C28	133.73 (52)
C18−C19–C21	109.98(63)	P4−C8−C9	118.71(53)
N1−P1−N3	114.16(34)	F2−P2−F3	97.69(32)
C11−P1−F1	101.30(3)		

Table 3. Selected Bond Lengths and Bond Angles of Compound **7**

	Bond Lengths (Å)		
Co1−C3	2.124(5)	Co1−C6	2.069(4)
C2−O2	1.185(7)	C2−O1	1.317(6)
C19−P4	1.779(4)	C9−P1	1.792(4)
P1−F1	1.547(4)	P1−N1	1.569(4)
C11−C12	1.484(9)		
	Bond Angles (deg)		
Co1−C20−C27	132.77(26)	C3−Co1−C20	125.00(15)
C9−P1−F1	99.97(19)	N1−P1−N3	114.25(20)
O2−C2−O1	125.09(47)	C9−C10−C11	115.85(33)
C17−C18−C19	116.38(31)		

The [2 + 2 + 2] cyclooligomerization of alkynes and alkenes using CpCo based catalysts has been known as an elegant method for the preparation of 1,3-cyclohexadiene derivatives, often with chemo-, regio-, and stereo-selectivity.[19] While several mechanisms have been proposed for the

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(18) Macomber, D. W.; Verma, A. G.; Rogers, R. D. *Organometallics*, **1988**, *7*, 1241–1253.

Table 4. Selected Bond Lengths and Bond Angles of Compound **8**

Bond Lengths (Å)			
Co1−C3	2.038(3)	Co1−C8	1.983(3)
C2−O2	1.186(5)	C2−O1	1.337(5)
C10−C23	1.466(4)	C9−C18	1.475(5)
C24−F3	1.336(4)	C17−F4	1.332(4)
Bond Angles (deg)			
Co1−C10−C23	127.68(20)	Co1−C9−C18	130.82(23)
C3−Co1−C11	123.78(12)	Co1−C11−C29	131.76(22)

formation of CpCo complexed 1,3-cyclohexadienes, all of them begin with a sequential displacement of the ligands bound to the $CpCoL_2$ complex by alkyne or alkene units.[20] For successive steps, theoretical studies reported on the reactions provide two possible pathways involving metallacycles, one involving a metallacyclopentene and the other a metallacyclopentadiene. The former is expected to form by the sequential complexation of one alkyne and one alkene unit displacing the ligands already present in the cobalt complex followed by an oxidative coupling. The latter is envisaged in a similar way but by the oxidative coupling of two alkyne units coordinated to the cobalt center.[21]

The possibility of formation of both these intermediates is supported by structurally characterized examples in the literature for iridium[22] and cobalt[23] based metallacyclopentenes and metallacyclopentadienes. Wakatsuki, Yamazaki, and co-workers using carefully planned reactions have also shown that triphenylphosphine ligated cobaltacyclopentadienes and cobaltacyclopentenes on reaction with alkenes or alkynes, respectively, can lead to the formation of CpCo(η^4-cyclohexadiene) complexes.[23] However, recent theoretical studies by Gandon et al. has shown that out of the two pathways, the formation of a metallacyclopentadiene intermediate is energetically more favored (about 10 kcal/mol) than the metallacyclopentene intermediate.[21] In this context, we were interested to see the type of mechanism involved in the reaction of $PhC{\equiv}CP_3N_3F_5$ with RCpCo(COD) and an alkene.

The formation of **1** can be explained by two possible mechanisms. The first, a shorter route, involves association of one mole of alkyne to the cobalt center by changing the coordination of the complexed cyclooctadiene from an η^4 to η^2 mode followed by an oxidative coupling of the η^2 bound COD and the alkyne leading to a metallacyclopentene intermediate A (Scheme 2; route 1). The presence of η^2 bound 1,5-COD transition metal complexes is well documented in the literature.[24] The second involves a mechanism in which the COD falls off completely from the complex and is replaced by two molecules of alkyne which undergo oxidative coupling to form a cobaltacyclopentadiene intermediate B (Scheme 2; route 2). Complexation of another molecule of the alkyne on the cobalt center of A or complexation of COD on B in η^2 mode followed by insertion and reductive elimination can result in the CpCo(η^4-cyclohexadiene) compound **1**.

To identify between these two possible mechanisms, we have carried out the same reaction under identical reaction conditions; however, after adding an additional amount (1 mole) of 1,5-cyclooctadiene. Interestingly, the reaction resulted in the formation of same set of products but with different yields, and the yield of RCpCo(η^4-cyclohexadiene) compound **1** increased from 8 to 18%. Further, an increase in yield of compound **1** (up to 27%) was observed by increasing the amount of 1,5-cyclooctadiene added to 3 moles. This indicates that the COD which took part in the reaction need not be the one complexed to the metal, and for a purely intramolecular pathway involving a metallacyclopentene intermediate, the yield of compound **1** should not have increased.

Further to confirm the evidence of the metallacyclopentadiene pathway for the formation of 1,3-cyclohexadiene complexes, two reactions of $PhC{\equiv}CP_3N_3F_5$ with [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt were carried out with additional alkenes; one by adding 3 moles of dicyclopentadiene and other by adding 3 moles of indene instead of 1,5-cyclooctadiene (Schemes 3 and 4). Interestingly, both the reactions resulted in the formation of RCpCo-complexed cyclohexadienes **6** and **7** having two phosphazenyl units adjacent to the added cycloalkene units. Both reactions also yielded compound **2**, the cyclobutadiene sandwich compound having the phosphazene units trans to each other. A reaction of $PhC{\equiv}CP_3N_3F_5$ and phenylacetylene with $MeOC(O)C_5H_4Co(COD)$ in the presence of 3 moles of dicyclopentadiene also gave compounds **2** and **6** in addition to the alkyne trimerized products, and formation of **1** was not observed in the same. The absence of compound **1** and the incorporation of dicyclopentadiene or indene in the cyclohexadiene unit in these reactions clearly indicates an intermolecular cobaltacyclopentadiene pathway for the formation of cyclohexadiene complexes (Scheme 2; route 2).

To determine if there is any specific role of pentafluorophosphazenyl ($N_3P_3F_5$) units in forming the RCpCo stabilized cyclohexadiene complex, we have carried out reactions of $PhC{\equiv}CC_6F_5$ with the [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt complex in the absence of external alkene as well as in the presence of dicyclopentadiene. These reactions were undertaken as C_6F_5 is closest to $N_3P_3F_5$ when

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Table 5. X-ray Crystallographic Data for Compounds **1**, **6**, **7**, and **8**

	1	**6**	**7**	**8**
empirical formula	$C_{31}H_{30}CoF_5N_3O_2P_3$	$C_{33}H_{29}CoF_{10}N_6O_2P_6O_2$	$C_{32}H_{25}CoF_{10}N_6O_2P_6$	$C_{35}H_{17}CoF_{10}O_2$
fw	723.42	976.37	960.33	718.43
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$Pbca$
a (Å)	10.830(3)	17.9726(19)	9.2110(14)	20.620(4)
b (Å)	11.497(3)	11.8081(12)	12.6795(19)	10.9120(18)
c (Å)	12.943(3)	19.162(2)	17.506(3)	25.222(4)
α (deg)	88.369(4)	101.704(2)	78.019(2)	90
β (deg)	88.369(4)	101.704(2)	78.019(2)	90
γ (deg)	89.931(4)	90	74.057(2)	90
V (Å3)	1540.2(7)	3982.1(7)	1885.1(5)	5675.1(16)
Z	2	4	2	8
T (K)	298(2)	298(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm^3)	1.560	1.629	1.692	1.682
μ (mm^{-1})	0.779	0.760	0.801	0.705
θ range	1.65−25.50	1.42−21.00	1.21−25.17	1.61−25.50
R1^a, wR2^b ($I > 2\sigma(I)$)	0.0399, 0.1116	0.0783, 0.1701	0.0587, 0.1507	0.0533, 0.1263

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

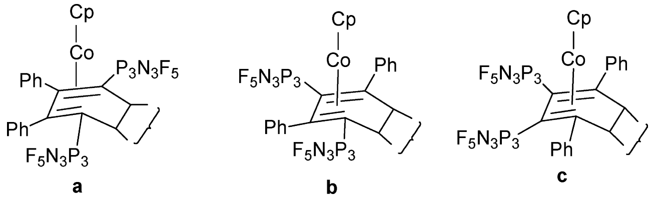


Figure 5. Three possible isomers of bisfluorophosphazene derived cyclohexadiene complexes.

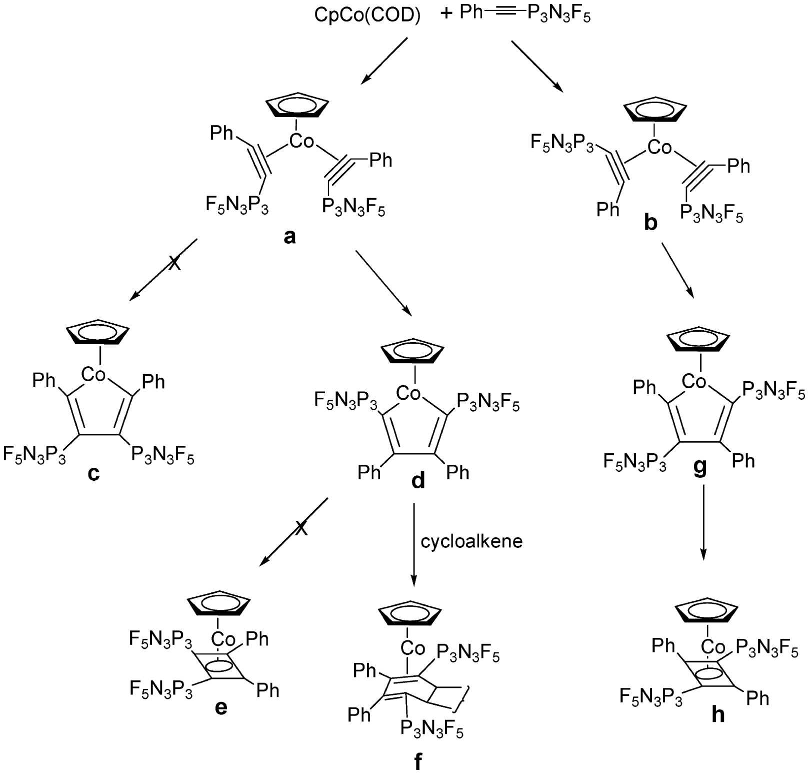
electronic factors are considered. Interestingly, the reactions resulted in the formation the cis and trans C_6F_5 substituted cyclobutadiene RCpCo complexes, [η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,3-pentafluorophenyl)-2,4-diphenylcyclobutadiene] cobalt (**8**) [η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,2-pentafluorophenyl)-3,4-diphenylcyclobutadiene] cobalt (**9**) along with a trimerized product (Scheme 5).

The above reaction did not yield any pentafluorophenyl substituted cyclohexadiene complexes analogous to compounds **1**, **6**, and **7**, and unlike the reactions involving $PhC{\equiv}CP_3N_3F_5$, it resulted also in the formation of sandwich compound **9** in which the two pentaflurophenyl moieties are present in the vicinal carbon atoms of the cyclobutadiene moiety. This difference in the nature of product formation between the alkynes $PhC{\equiv}CC_6F_5$ and $PhC{\equiv}CP_3N_3F_5$ suggests that, more than electronic factors, steric factors are involved in the formation of cyclohexadiene complexes.

X-ray Crystal Structures of Compounds 1, 6, 7, and 8. The X-ray crystal structures of compounds **1**, **6**, **7**, and **8** are given in Figures 1−4, respectively (Tables 1−5). In compounds **1**, **6**, and **7**, the cyclopentadiene ligand is coordinated in an η^5 mode, and the cyclohexadiene ring coordinated in an η^4 mode with the cobalt atom. In compounds **1**, **6**, and **7**, the cobalt atom is at a distance in the range of 1.695(2) to 1.708(1) Å with the centroids of the cyclopentadienyl rings, whereas the distance between the cobalt atom and the centroids of the four atoms of the cyclohexadiene ring which form the η^4-coordination are in the range of 1.592(2) to 1.600(l) Å. Unlike compounds **1**, **6**, and **7**, where there are differences in distances of Co- η^5-Cp centroids and Co- η^4-C centroids, in compound **8** the cobalt atom makes comparable distances of 1.680(9) and 1.688(9) Å with the centroids of the cyclopentadienyl and the cyclobutadiene rings, respectively, which are similar to that of other CpCo stabilized cyclobutadiene complexes.[12] In compound **1**, the phosphazene ring is present on the adjacent carbon atom of the added cycloalkene moiety, and the mean plane containing the phosphazene ring makes an angle of 66.52(57)° with the mean plane containing the atoms C7, C8, C9, and C10 of the cyclohexadiene unit. In compounds **6** and **7**, the two phosphazene rings are present on the carbon atoms adjacent to the alkene moieties. While in compound **6** the two phosphazene rings make angles of 71.16(92) and 68.64(43)°, respectively, with the mean plane containing the four carbon atoms C8, C9, C10, and C11 of the cyclohexadiene ring, in compound **7** the two phosphazene units are oriented at angles of 67.14(21) and 85.79(61)° with respect to the mean plane containing the atoms C8, C9, C19, and C20 of the cyclohexadiene ring. In compound **6**, the two phosphazene rings are eclipsed with respect to each other while in compound **7** the phosphazene rings are present in a skew conformation. The CpCo fragment of compound **6** is oriented on the opposite side of the bridging methano moiety of the dicyclopentene group. The six membered ring which contains the atoms C8, C9, C10, C11, C12, and C21 and the five membered ring containing the atoms C14, C15, C16, C17, and C18 are cis fused with the dicyclopentene system in compound **6**. The cis fused orientation of the five and six membered rings is similar to the orientation observed in the analogous tetraphenyl CpCo (η^4-1,3-cyclohexadiene) complex.[18] In compound **8**, the two phenyl rings are oriented at angles of 59.42(61) and 43.07(21)° with respect to the plane containing the cyclobutadiene ring, and the two pentafluorophenyl rings are oriented at angles of 30.01(91) and 35.52(21)° with respect to the plane containing the cyclobutadiene ring.

Spectral Studies on Compounds 1 and 3. All the new compounds prepared are stable to air and moisture and were analyzed by IR, multinuclear (^{1}H, ^{13}C, ^{31}P and ^{19}F) NMR, and mass spectra. The ^{31}P NMR of compound **1** gave a signal at 7.51 ppm which corresponds to the $-PF_2$ groups, and the signal at 45.27 ppm is due to the $-PF$ group. The ^{19}F NMR spectra of compound **1** gave two different signals for the $-PF_2$ fluorines (−92.5 and −87.34 ppm) because of the

Scheme 6



diastereotopic nature of the fluorine atoms attached to the same phosphorus atom. Similarly, the ^{31}P NMR of compounds **6** and **7** gave two signals in the expected multiplicity for the $-PF_2$ and the $-PF$ groups. Compared to **1**, the ^{19}F NMR spectra of both compounds **6** and **7** were complex in nature, but they showed similarity to reported examples of bis(pentafluorocyclotriphosphazene) derived cobaltametallacycles.[12] Both compounds gave three different signals for the $-PF_2$ groups which can be attributed to the diastereotopic nature of fluorines, an observation common in many bis(pentafluorocyclotriphosphazene) derived cobalt complexes.[12] While compound **6** gave only one doublet at -53.75 ppm for the $-PF$ groups, compound **7** gave two different doublets at -54.32 and at -51.30 ppm for the $-PF$ groups indicating that the orientations of the pentafluorocyclotriphosphazene moieties in compounds **6** and **7** are different. This observation can be related to the fact that from their crystal structures it is observed that in compound **6** the two phosphazene units are eclipsed while in compound **7** they are present in a skew conformation with respect to each other.

Selectivity and Mechanistic Considerations. The formation of bis pentafluorocyclotriphosphazene derived cyclohexadiene complexes **6** and **7** shows an interesting selectivity. As shown in Figure 5, there exists a possibility of forming three isomers **a**, **b**, and **c** for compounds **6** and **7**. Out of these three possible isomers, only isomer **a** is found to form; in this isomer the two fluorophosphazene units are present on the carbon atoms which are adjacent to the added dicyclopentadiene or indene moiety.

This selectivity of product formation can be explained using the following reaction mechanism (Scheme 6). In the first step, 2 moles of $PhC{\equiv}CP_3N_3F_5$ displace the cyclooctadiene present in [η^5-carbomethoxycyclopentadienyl] [η^4-cyclooctadiene] cobalt complex, and the two alkynes can coordinate with the cobalt center in two different orientations (**a** and **b**). These can undergo oxidative coupling leading to the metallacycle intermediates **c**, **d**, and **g**. The intermediate **a**, in principle, can form two different metallacyclopentadiene complexes (**c** and **d**) but the possibility of formation of the intermediate **c** is restricted as it would result in two pentafluorophosphazenyl moieties present on vicinal carbon atoms of the metallacycle. The intermediate **d**, in the presence of an external cycloalkene undergoes a [4 + 2] cycloaddition leading to the formation of the hexadiene complex (**f**). The possibility of formation of the cyclobutadiene complex (**e**) from (**d**) is not favored, as it would force two fluorophosphazene units to be present on vicinal carbon atoms of the cyclobutadiene unit, which is contrary to the experimental results obtained from all the above reactions. Further, the intermediate **b** can undergo oxidative coupling to form the metallacyclopentadiene intermediate (**g**), which in turn can readily convert to the more stable trans fluorophosphazene substituted cyclobutadiene complex (**h**) which obeys the 18 electron rule as well. In a previous work, the metallacyles **d** and **g** in their PPh_3 stabilized form have been isolated and structurally characterized, which further supports the proposed mechanism.[12] It is also of interest to note that the same reaction did not yield the PPh_3 stabilized metallacycle **c**, supporting our contention that two fluorophosphazenyl units are not accommodated on vicinal carbon atoms of a carbacycle or metallacycle.

The fact that the reactions of $PhC{\equiv}CC_6F_5$ with RCpCo(COD) did not give any cyclohexadiene complexes and also resulted in cis and trans C_6F_5 substituted cyclobutadiene RCpCo complexes indicates that the metallacycle analogues of **c** and **d** having C_6F_5 units are able to convert readily to the cis substituted cyclobutadiene complex similar to **e**. This indicates that unlike $N_3P_3F_5$, there is no difficulty for two C_6F_5 units to be present on vicinal carbon atoms of a carbacycle or metallacycle, and although electronically similar, the steric features of $N_3P_3F_5$ and C_6F_5 are significantly different. This is further confirmed by reported examples of multi pentafluorophenyl substituted aryl and cycloalkyl compounds having two pentafluorophenyl groups on adjacent carbon atoms.[25]

Conclusions

In conclusion, we report the first examples of mono and bis pentafluorocyclotriphosphazene derived [η^5-carbomethoxycyclopentadienyl] [η^4-1,3-cyclohexadiene] cobalt complexes from the reactions of MeOC(O)CpCo(COD), $PhC\equiv CP_3N_3F_5$ along with other alkynes or cyclic alkenes. These cobalt based cyclohexadiene complexes can be used as precursors for a host of aryl and cyclohexadiene derived cyclophosphazenes. Although structural isomers are possible, the reactions are found to be selective in nature, resulting in only one isomer of the cyclohexadiene complex having fluorophosphazene moieties attached to the carbon atoms adjacent to the added alkene or indene unit. The reactions also yielded only the trans [η^5-carbomethoxycyclopentadienyl] [η^4-bis(1,3-pentafluorocyclotriphosphazenyl)-2,4-diphenylcyclobutadiene] cobalt metallocene **2.** The comparison of the above reactions with the (β-phenylethynyl)pentafluorobenzene indicates that the selectivity observed in the formation of the cyclohexadiene complexes is due to steric factors more than electronic factors, and unlike pentafluorophenyl units, there is difficulty in accommodating two $N_3P_3F_5$ units on vicinal carbon atoms of a carbacycle or metallacycle.

The reactions have also contributed to the understanding of the mechanism of cobalt based [2 + 2 + 2] cycloaddition reactions of two alkynes and one alkene. Although two pathways are possible for the formation of cyclohexadiene complexes, namely, through a metallacyclopentene or a metallacyclopentadiene, calculations based on recent theoretical studies have predicted the metallacyclopentadiene pathway as energetically more feasible. While previous experimental studies have shown that both cobaltacyclopentene and cobaltacyclopentadiene can be precursors for CpCo complexed cyclohexadienes, formation of phosphazene based cyclohexadienes in this study support a cobaltacyclopentadiene intermediate, which is in agreement with the energy calculations. The bispentafluorocyclotriphosphazene based compounds synthesized in this study can also be precursors for novel cyclohexadiene and aryl bridged fluorophosphazene compounds.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **1**, **6**, **7**, and **8** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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