Organophosphazenes. 25. The synthesis and electrochemistry of the dicobalt hexacarbonyl complexes of phenylethynylcyclophosphazenes¹

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Abstract: The syntheses of the dicobalt hexacarbonyl complexes, $N_3P_3F_{6-n}(C=CPhCo_2(CO)_6)_n$ (n = 1 (3), n = 2 (4)), is reported. The introduction of the organometallic fragment allows for simplification of the NMR spectra and separation of the isomers of the disubstituted (4) derivatives. Electrochemical studies show that 3 undergoes a reversible one-electron reduction. At 233 K, the geminal isomer of 4 undergoes two separate reversible one-electron reductions. The ESR spectra of the radical anions of 3 and 4 have been obtained and show the absence of delocalization of unpaired spin density from the organometallic cluster to the phosphazene.

Key words: cyclophosphazenes, cobalt-alkyne clusters, electrochemistry, ESR.

Résumé : On a réalisé la synthèse de complexes de dicobalt hexacarbonyle, $N_3P_3F_{6-n}(C\equiv CPhCo_2(CO)_6)_n$ (n = 1 (**3**), n = 2 (**4**)). L'introduction du fragment organométallique simplifie les spectres RMN et la séparation des isomères des dérivés disubstitués (**4**). Des études électrochimiques montrent que le composé **3** subit une réduction réversible à un électron. À 233 K, l'isomère géminé du composé **4** subit deux réactions séparées de réductions réversibles à un électron. Les spectres RPE des anions radicaux des composés **3** et **4** ont été mesurés et ils mettent en évidence l'absence de délocalisation de la densité de spin non pairée de l'agrégat organométallique vers le phosphazène.

Mots clés : cyclophosphazène, agrégats cobalt-alcyne, électrochimie, RPE.

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Introduction

The reactions of main group organometallic reagents with halocyclophosphazenes has lead to the formation of a broad array of organophosphazene derivatives (1, 2). Within this class of compounds, the aryl derivatives have attracted the most attention (1, 3–5). The ethenyl derivatives have been widely exploited as monomers in olefin addition polymerization reactions leading to carbon chain polymers with cyclophosphazene substituents (6–8). By way of contrast, significantly less interest has been shown in the corresponding ethynyl derivatives, in which a direct phosphorus — ethynyl carbon bond exists. The first examples of this class of compounds, N₃P₃F_{6–n} (C=CPh)_n (n = 1,2), and the dicobalt hexacarbonyl derivative of N₃P₃F₅C=CPh were reported by Chivers (9). Utilization of the reactions of lithioethynyl (10),

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This paper is dedicated to Professor Tris Chivers who has continually demonstrated the ability to produce outstanding chemistry while retaining the highest standards of collegiality and personal integrity.

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alkylethynyl (11), and mixed aryl-phenylethynyl derivatives (12). Indirect routes involve catalyzed rearrangements of propargyl derivatives (13) and byproducts in the reaction of lithiopropene with $N_3P_3F_6$ (14). The electronic structure of these materials has been probed by UV–photoelectron spectroscopy (15). In this paper, we present the results of a study of the synthesis and redox processes of the dicobalt hexa-carbonyl derivatives of phenylethynylfluorocyclotriphosphazenes. These investigations provide additional insights into the nature of the interactions between unsaturated organic substituents and the cyclophosphazene ring. A preliminary report of certain aspects of this work has appeared (16).

Experimental

Materials

Hexachlorocyclotriphosphazene $(N_3P_3Cl_6)$ was converted to $N_3P_3F_6$ (17), which in turn was converted to $N_3P_3F_5(C\equiv CPh)$ (1), $N_3P_3F_4(C\equiv CPh)_2$ (2) (9, 10), and $P_3N_3F_5C_6H_4CMe=CH_2$ (5) by previously reported procedures. Butyllithium (2.5 M in hexane) and phenylacetylene were obtained from Aldrich Co. Dicobalt octacarbonyl (Johnson Matthey) was sublimed and used immediately. All manipulations were performed under nitrogen. All solvents were distilled from the appropriate drying agents prior to use, and further purification of the solvents for electrochemical and ESR experiments was achieved by three freeze–pump–thaw cycles followed by vacuum distillation.

Measurements

Infrared spectra were recorded on a PerkinElmer 1430 spectrophotometer. Mass spectrometry was carried out on a Finnigan 4610 spectrometer operating at 70 eV. NMR spectra were recorded on a Bruker WM250 spectrometer operating at: 250.1 MHz (¹H); 62.9 MHz (¹³C); 235.35 MHz (¹⁹F); 101.2 MHz (³¹P) and using CDCl₃ for a lock compound. Tetramethylsilane (TMS) (¹H and ¹³C) was used as an internal reference, while 85% H₃PO₄ (³¹P) and CFCl₃ (¹⁹F) were used as external references. Chemical shifts upfield from the reference are negative. Broad band ¹H decoupling was used for the ¹³C, ¹⁹F, and ³¹P spectra. ESR measurements were performed on a modified Varian E-3 spectrometer with external diphenylpicrylhydrazide (DPPH) as a standard. Elemental analyses were performed by Robertson Laboratory, Inc. Electrochemical measurements were carried out using a Princeton Applied Research Model 173 potentiostat with a Hewlett-Packard 7004B x-y recorder as described in the literature (18). Solutions for cyclic voltammetry (CV) contained 0.5 mM of the metal complex and also contained 0.1 M Bu₄NPF₆ as the supporting electrolyte in THF. Potentials are reported vs. Ag/AgCl. Low-temperature CV solutions contained 0.1 M Bu₄NCF₃SO₃ as the supporting electrolyte. Low temperature was achieved by immersing the voltammetry cell in a dry ice - acetone slush bath. For rotating platinum electrode (RPE) measurements, a Sargent synchronous rotor (1800 rpm) was employed.

Syntheses of (dicobalt hexacarbonyl phenylethynyl) pentafluorocyclotriphosphazene $(N_3P_3F_5C=CPhCo_2(CO)_6)$ (3)

This preparation is a modification of a previously reported procedure (9). (β-Phenylethynyl)pentafluorocyclotriphosphazene $(N_3P_3F_5C \equiv CPh, 1)$ (0.74 g, 2.25 mmol), and dicobalt octacarbonyl (0.78 g, 2.25 mmol), were allowed to react in hexane (40 mL) in a nitrogen filled flask connected to a gas bubbler system. The reaction mixture was stirred at room temperature. The reaction was monitored by IR spectroscopy and found to be complete within 30 min. After the solvent was removed, the material was chromatographed on silica gel with hexane and methylene chloride (90:10 v/v) as the eluent. The product eluted as a red band. The red compound was isolated and crystallized from hexane as red microcrystalline material. MW: calcd. 616; found 617 (CI-MS). ¹³C NMR δ : 99.5 ([$C \equiv CC_6H_5 \cdot Co_2(CO)_6]_2$), 136.5 $([C \equiv CC_6H_5Co_2(CO)_6]_2)$, 130.0, 129.0, 128.8, (C_6H_5) , 197.3 $(Co_2(CO)_6)$. ¹⁹F NMR δ : 57.4 (d, $J_{PF} = 974$ Hz, $\equiv PF[C \equiv CC_6H_5Co_2(CO)_6])$, 72.9 (d, $J_{PF} = 919$ Hz, $PF_2[cis])$, 72.2 (d, $J_{PF} = 946$ Hz, $\equiv PF_2[trans])$. ³¹P NMR δ : 9.4 (t, $J_{PF} = 920$ Mz δ) (c) $f_2 = 200$ (c) f929 Hz, \equiv PF₂), 38.0 (d of t, $J_{PF} = 975$ Hz, ${}^{2}J_{PP} = 68.8$ Hz, $\equiv PF[C \equiv C_6H_5Co_2(CO)_6]).$

Synthesis of bis(dicobalt hexacarbonylphenylethynyl)tetrafluorocyclotriphosphazene (2,2-

 $N_{3}P_{3}F_{4}(C \equiv CPhCo_{2}(CO)_{6})_{2})$ (4)

Bis(phenylethynyl)tetrafluorocyclotriphosphazene $(N_3P_3F_4[C \equiv CPh]_2)$ (0.7 g, 2.25 mmol), and dicobalt octacarbonyl (1.55 g, 4.5 mmol), were allowed to react in hexane (60 mL) in a nitrogen filled flask connected to a gas bubbler system. The reaction mixture was stirred at room temperature for 30 min and monitored by IR. After the solvent was removed,

the material was chromatographed on silica gel with hexane and methylene chloride (90:10) as the eluent. Two red fractions were isolated, which were shown to be the geminal isomer and the cis–trans non-geminal mixture. The pure geminal isomer was obtained as dark red crystals from hexane solution at -20° C (0.89 g, 40% yield). The melting point of the geminal isomer was found to be greater than 225°C. Attempts to crystallize or sublime either of the non-geminal isomers were unsuccessful, nor could the isomers be separated. A yield of 0.14 g (15%) was obtained. Anal. calcd. for $C_{28}H_{10}F_4N_3P_3O_{12}Co_2$: C 34.12, H 1.01, MW 985; found: (geminal) C 34.21, H 0.92. Molecular ion M⁺ was not observed in either EI- or CI-MS.

Geminal

IR (KBr pellet) (cm⁻¹): 2098, 2077, 2067, 2044, 2031, 2026, 2008 ($v_{terminal CO}$), 1562 ($v_{c=c}$), 1476, 1439, 1242 ($v_{as PNP}$), 1184, 926, 915 (sh) ($v_{as PF}$), 811 (($v_{sym PF}$); hexane solution), 2018, 2032 (sh), 2040, 2071, 2097 ($v_{terminal CO}$). ¹³C NMR δ : 99.5 (=P[*C*=C C₆H₅Co₂(CO)₆]₂), 136.5 (=P[*C* = *C*-6H₅Co₂(CO)₆]₂), 130.0, 129.0, 128.8 (C₆H₅), 197.3 (Co₂(CO)₆). ¹⁹F NMR δ : 72.9 (d, J_{FP} = 889 Hz, =PF₂). ³¹P NMR δ : 8.2 (t, J_{PF} = 892 Hz, =PF₂), 32.5 (t, ² J_{PP} = 50.1 Hz, =P[*C*=CC₆H₅Co₂(CO)₆]₂). MS (molecular ion ([M⁺]) not observed), *m/e* (%): 901 ([M – 3CO]⁺, 10), 845 ([M – 5CO]⁺, 1.7), 817 ([M – 6CO]⁺, 6.6), 789 ([M – 7CO]⁺, 20.8), 761 ([M – 8CO]⁺, 26), 733 ([M – 9CO]⁺, 6), 705 ([M – 10CO]⁺, 15), 677 ([M – 11CO]⁺, 8), 649 ([M – 12CO]⁺, 100).

Cis non-geminal

¹⁹F NMR δ: 68.4 (d, $J_{FP} = 912$ Hz, $\equiv PF_2[trans]$), 73.2 (d, $J_{FP} = 912$ Hz, $\equiv PF_2[cis]$), 46.5 (d, $J_{FP} = 962$ Hz, $\equiv PF(C \equiv CC_6H_5Co_2(CO)_6]$). ³¹P NMR δ: 6.2 (t of t, $J_{PF} = 997$ Hz, $^2J_{PP} = 78$ Hz, $\equiv PF_2$), 36.1 (d of d, $J_{PF} = 979$ Hz, $^2J_{PP} = 70$ Hz, $\equiv PF[C \equiv CC_6H_5Co_2(CO)_6]$). MS, cis-trans mixture (molecular ion ([M⁺]) not observed), *m/e* (%): 901 ([M – 3CO]⁺, 10), 845 ([M – 5CO]⁺, 1.7), 817 ([M – 6CO]⁺, 6.6), 789 ([M – 7CO]⁺, 20.8), 761 ([M – 8CO]⁺, 26), 733 ([M – 9CO]⁺, 6), 705 ([M – 10CO]⁺, 15), 677 ([M – 11CO]⁺, 8), 649 ([M – 12CO]⁺, 100).

Trans non-geminal

¹⁹F NMR δ: 72.3 (complex d, $J_{FP} = 888$ Hz, $\equiv PF_2$), 52.8 (complex d, $J_{FP} = 937$ Hz, $\equiv PF[C \equiv CC_6H_5Co_2(CO)_6]$). ³¹P NMR δ: 6.2 (t, $J_{PF} = 997$ Hz, $\equiv PF_2$), 34.8 (d of d, $J_{PF} = 944$ Hz, ² $J_{PP} = 70$ Hz, $\equiv PF[C \equiv CC_6H_5Co_2(CO)_6]$).

Attempted reaction of the lithium salt of hexacarbonyl(phenylethyne)dicobalt

The reaction of LiC=CPhCo₂(CO)₆, generated from lithium diisopropylamide and HC=CPhCo₂(CO)₆, with an equimolar quantity of N₃P₃F₅C₆H₄CMe=CH₂ in hexane, resulted in a dark green solution, from which a green solid was isolated. The absence of detectable ³¹P NMR resonances indicated that the phosphazene derivative was not formed.

Chemical reduction of 3 and 4

The reduction was carried out on a vacuum line with 0.75 mmol of **3**, or the geminal isomer of **4**, and 0.18 mg (0.75 mmol) of cobaltocene, in an ESR tube. The ESR tube

was connected to the vacuum line and evacuated. Approximately 0.5 mL of 2:1 tetrahydrofuran–dichloromethane (v/v) was introduced by vacuum transfer, and subsequently the ESR tube was sealed off. After thawing the sample, the reaction was carried out at -65° C (in a dry ice – acetone slush bath) for less than 5 min, and then the sample was frozen in liquid nitrogen. The ESR spectra were then immediately recorded at liquid nitrogen temperature.

Results and discussion

The reaction of dicobalt octacarbonyl with 1 (9) and 2 lead cleanly to the respective dicobalt hexacarbonyl – alkyne cluster derivatives.

[1]
$$N_3P_3F_5C \equiv CPh + Co_2(CO)_8$$
 (1)
 $\rightarrow N_3P_3F_5(C \equiv CPhCo_2(CO)_6)$ (3)

$$[2] \qquad N_3 P_3 F_4 (C \equiv CPh)_2 + Co_2(CO)_8 (2) \rightarrow N_3 P_3 F_4 (C \equiv CPhCo_2(CO)_6)_2 (4)$$

An alternative route to the synthesis of dicobalt hexacarbonyl – alkyne complexes, via the reactions of $\text{LiC}=\text{CPhCo}_2(\text{CO})_6$ (19), was also attempted. All attempts to isolate cyclophosphazene derivatives failed. The major product was a green solid, which is believed to be an alkyne coupling product. A similar product was observed in the reactions of $\text{LiC}=\text{CSiMe}_3\text{Co}_2(\text{CO})_6$ with electrophiles, and was shown to be a dimer, $\text{Co}_2(\text{CO})_6\text{Me}_3\text{SiC}=\text{C}-\text{C}=\text{CSiMe}_3\text{Co}_2(\text{CO})_6$ (19).



Previous NMR studies have shown that **2** consists of a mixture of inseparable isomers, with the geminal (2,2-) species being in large excess over the non-geminal (2,4-) components (10). The addition of the dicobalt hexacarbonyl fragment allowed for the chromatographic separation of the geminal (**4g**) and non-geminal isomers (**4ng**). The cis and trans isomers of 2,4-[(α -methylethenyl)phenylethynyl]tetra-fluorocyclotriphosphazene have also been separated as their dicobalt hexacarbonyl complexes (12). These studies show the applicability of metal complex formation to the often intractable problem of separation of cyclophosphazene regio-and stereoisomers. The addition of the dicobalt hexacarbonyl fragment to the alkyne also had a significant effect on the ³¹P NMR spectra. A comparison of the NMR spectra of **1**

(10) to **3** showed that the alkynylphosphorus center 31 P resonance undergoes a 32 ppm downfield shift while the $\equiv PF_2$ centers only change by about 2 ppm. This leads to a considerable simplification in the spectrum in 3, since in 1 the two phosphorus shifts are only separated by 2 ppm. The intraring phosphorus–phosphorus coupling constant $(^{2}J_{PP})$ decreased by 32 Hz. Similar changes were observed in a comparison of the geminal isomer of 2 to 4g, wherein the corresponding bis(alkynyl)phosphorus resonance underwent a 66 ppm downfield shift and ${}^{2}J_{PP}$ decreased by 41 ppm. The NMR spectra of the 4ng isomers were also sufficiently simplified so that the principle parameters could be measured and reported. The factors controlling the chemical shifts in cyclophosphazenes are complex and not well understood (20). In the present case, a change of the exocyclic bond angle at the phosphorus center or an introduction of a significant paramagnetic term to the shift tensor from the transition metal component are both viable proposals. The ${}^{2}J_{PP}$ values cyclophosphazenes are controlled by in the electronegativities of the phosphorus substituents (20). The carbon atoms of the phosphazene substituent change, from approximate sp hydridization in 1 and 2, to a lower s character in the organometallic derivatives, and hence the orbital electronegativity decreases, leading to the observed decrease in ${}^{2}J_{\rm PP}$.

The IR spectra for complexes 3 (9) and 4g showed five CO bands between 2000 and 2110 cm⁻¹. The IR spectrum for 3 (9) showed a PN stretching band at 1269 cm^{-1} , while the PN stretching band for 4g appeared at 1242 cm⁻¹. The PN stretching frequency showed a steady decrease in going from $P_3N_3F_6$, to 3, to 4g, which reflects an increased electron donation to the phosphazene ring by the [C=C- $C_6H_5Co_2(CO)_6$] substituent, in comparison to the fluorine atom (21). The change in the $v_{C=C}$ absorbance from 2 (2139 cm^{-1}) to 4 (1562 cm^{-1}) indicates a significant reduction in bond order, and hence in orbital electronegativity. The mass spectrum of 3 showed the parent ion and the peaks associated with the sequential loss of the six carbonyl groups. By way of contrast, in both 4g and 4ng, the $[M - 3CO]^+$ fragment is the highest mass peak, followed by the [M -5CO⁺ ion. The base peak was the [M – 12CO]⁺ ion.

The electrochemistry of alkyne – dicobalt hexacarbonyl clusters $(Co_2(CO)_6(\mu-RC_2R) (R = CF_3, Bu, Ph))$ has been examined in some detail (22-24). This background provides a frame of reference for understanding the electrochemical behavior of 3 and 4. The cyclic voltammogram (CV) of 3 showed a reversible reduction at $E^{\circ} = -0.64$ V (298 K). The anodic to cathodic (i_a/i_c) current ratios were unity over a scan rate range of 40–400 mV s⁻¹. Comparison of CV peak separations (ΔE_p), and $i_p/v^{1/2}$ with those of ferrocene, under the same experimental conditions,³ established the process as diffusion-controlled, leading to the formation of 3⁻. A second irreversible reduction was observed at -1.67 V. If one scans beyond the second reduction, the reverse scan reveals an anodic peak at -0.98 V, presumably due to a decomposition product of 3^{2-} . Low temperature CV studies did not show any change in the behavior of 3, except for shifts in the E° values (E° (**3**) = -0.55 V at 233 K) and smaller diffusion

³The variable scan rate data for **3** and **4**, Tables D1 and D2, can be found in the supplementary material. Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).





currents.³ The room temperature CV for 4g showed two closely spaced reduction waves in the potential range where only one was observed for **3**. The first process ($E^{\circ} = -0.69 \text{ V}$) is reversible whereas the second (E = -1.08 V) is irreversible. The second process gives a follow-up product with an irreversible oxidation peak at 0.20 V, which was assigned to $Co(CO)_4^{-/0}$ (25). Other features in the potential range of 1.0 to -2.0 V are equivalent to those observed for 3. There are, however, differences in the stabilities and formal potentials for formation of **3**⁻ and **4g**⁻. For **4g**, the i_a/i_c ratio increased from 0.66 at 40 mV s⁻¹ to 0.96 at 400 mV s⁻¹. This indicates that the $4g^{0/1-}$ redox process is only chemically reversible at the higher scan rates. Assuming that the decomposition of 4g⁻ is a first-order process, a half-life of approximately 6 s can be calculated. The dianion, $4g^{2-}$, has an even smaller half-life. The decomposition step of $4g^{2-}$ can be avoided by a reduction in temperature. At 233 K, the CV of 4g showed two reversible reduction steps, at -0.61 V and -0.94 V, for the $4g^{0/-}$ and $4g^{-/2-}$ steps, respectively (Fig. 1). Scans of the waves with a rotating platinum electrode established that they are both one-electron processes. Traditional diagnostic criteria (26) were used to demonstrate diffusion control through CV scans (Supplementary material, Tables D.1, D.2).³ Within the limits of experimental error, the $i_{\rm p}/\upsilon^{1/2}$ ratios for 3 or 4g are the same (0.65 vs. 0.61) over the scan rate of 0.1 to 0.4 V s⁻¹. Thus, the following reactions (eq. [3]) govern the reductive behavior of the species under investigation. Previous investigations (22-24) have established that the lifetime of the radical anion derived from

[3] 3 + e⁻
$$\rightleftharpoons$$
 3⁻; E[°] = -0.55 V
4g + e⁻ \rightleftharpoons 4g⁻; E[°] = -0.61 V
4g⁻ + e⁻ \rightleftharpoons 4g²⁻; E[°] = -0.94 V

dicobalt hexacarbonyl – alkyne clusters decreases as the electronegativity of the alkyne substituents decrease. For example, the room temperature lifetime of $[(CF_3)_2C_2Co_2(CO)_6]^-$ is greater than 1 h, whereas that of $[Ph_2C_2Co(CO)_6]^-$ is 17 ms (27). In **3** and **4g**, the effect of the strongly electron-withdrawing phosphazene (15) and the electron-donating





Magnetic Field (Gauss)

phenyl group are counterbalanced to produce radicals of intermediate stability. The first reduction of 4g takes place at a more negative potential compared with 3, and the radical anion 3⁻ is more stable than $4g^-$. Both of these observations are a reflection of the decrease in the group electronegativity of the phosphazene substituent as a result of the replacement of a fluorine atom with the more electron donating alkyne – cobalt carbonyl cluster on going from 3 to 4g.

The moderate stability of the radical anions allows for their characterization by ESR spectroscopy in frozen solutions. Chemical reduction was accomplished using cobaltocene (Cp_2Co) as the reductant. The ESR spectra of both 3⁻ and $4g^{-}$ showed 15 lines from hyperfine coupling to the two equivalent cobalt (I = 7/2) nuclei (Fig. 2). Hyperfine coupling to phosphorus was not observed. A first-order analysis yielded values of $\mathbf{g}_1 = 2.04$ and $\mathbf{a}_1 = 67.8$ G. These values are higher than those obtained from similar complexes that were interpreted in terms of anisotropic g and cobalt hyperfine tensors (27). The absence of phosphorus hyperfine coupling indicates that the unpaired electron is localized on the organometallic fragment and not delocalized to the phosphazene. The ultraviolet photoelectron spectra of alkynyl phosphazenes have also been interpreted as showing absence of π donation of the alkyne to the phosphazene (15). Thus, alkynylphosphazenes and their organometallic complexes are similar to alkenyl (15, 28) and arylphosphosphazenes (5, 28, 29) in that the carbon–carbon π electron density is localized on the organic exocyclic substituent.

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