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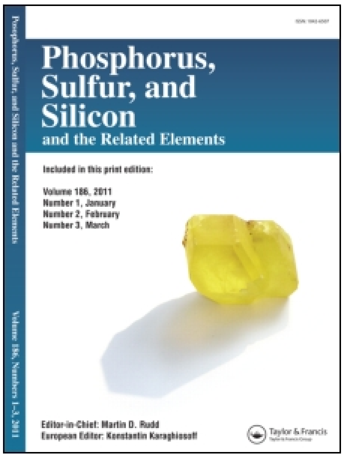

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THE REACTIONS OF ALKYNLCYCLOPHOSPHAZENES WITH METAL CARBONYLS

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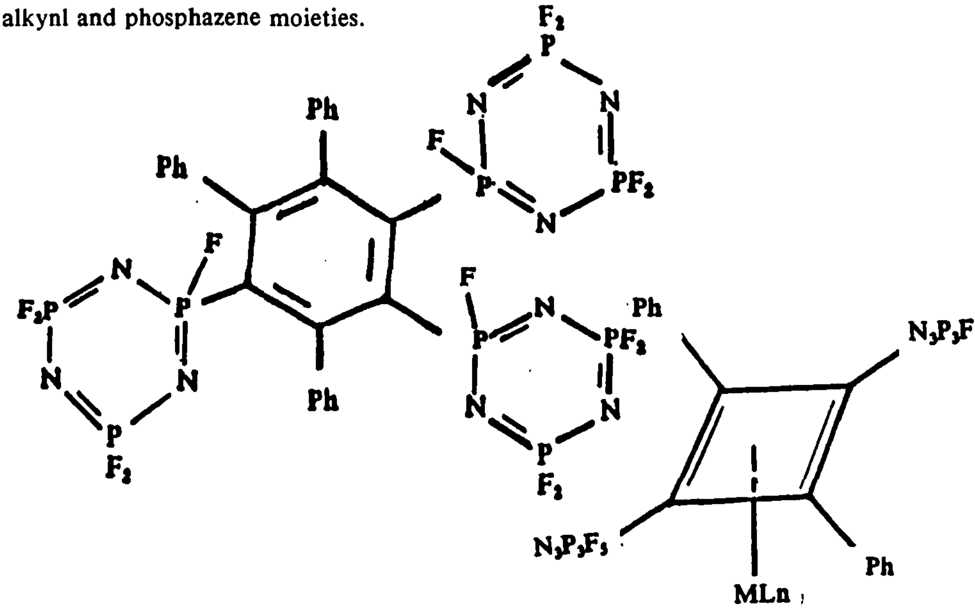
Abstract The reaction of $N_3P_3F_5C\equiv CR$ (R=Ph, Me_3Si, n-C_4H_9) with $Co_2(CO)_8$ leads to $N_3P_3F_5C\equiv CR \bullet Co_2(CO)_6$. The corresponding reaction with 2,2-$N_3P_3F_4(C\equiv CPh)_2$ produces the novel, structurally characterized, tetracobalt species 2,2-$N_3P_3F_4(C\equiv CPh \bullet Co_2(CO)_6)_2$. In the case of the previously reported $N_3P_3F_5C\equiv CPh$ complex, we now report that reaction with excess phosphazene leads to the cyclotrimerized material 1,2,4-$(N_3P_3F_5)_3Ph_3C_6$(I). Detailed dynamic ^{19}F NMR spectroscopy studies of this material shows detectable barriers to rotation about the phosphorus-carbon bond of the central arene. The reaction of a more reactive catalyst, η^5-$C_5H_5Co(CO)_2$, with $N_3P_3F_5C\equiv CPh$ gives rise to a variety of cyclooligomerized products. A cyclodimerized material, $(N_3P_3F_5)_2Ph_2C_4$(II) is isolated as the colbalt stabilized entity II•CoCp. The carbonyl insertion product of the cyclodimerized complex has been isolated as well as I and its colbalt complex I•CoCp (which is believed to contain an η^4 arene). The reaction of $Fe(CO)_5$ with $N_3P_3F_5C\equiv CPh$ gives the iron stabilized cyclodimer, II•$Fe(CO)_3$. The corresponding reaction with $Fe_2(CO)_9$ gives a plethora of products including the cyclodimerized material noted above and its carbonyl insertion product. Other characterized products include I•$Fe(CO)_3$ (also believed to be an η^4 material), an iron containing metallocycle and unique derivative in which the alkyne bridges iron and cyclopentadienone fragments.

INTRODUCTION

In recent years it has been shown that the range of cyclo- and polyphosphazene derivatives can be dramatically expanded by synthetic transformations of organofunctional units attached to the phosphorus atoms.[1,2] In previous, and ongoing, investigations we have explored the reactions of alkenes attached to cyclophophazenes particularly with respect to polymer synthesis.[3] A logical extension of this interest would be to investigate the reactions of alkynes attached to cyclophosphazenes. Previous work in this area is restricted to the preparation of $N_3P_3F_5C\equiv CPh \bullet Co_2(CO)_6$ by Chivers[4] and a study by Allcock et.al. of the cyclotrimerization of propargylchlorocyclotriphosphazenes and cocyclotrimerization of propynlchlorocylotriphosphazenes and acetylenes all through the alkyne bridged dicobalt hexacarbonyl derivatives.[5] Given these initial studies and the tremendous range of chemistry which has been reported from metal carbonyl mediated reactions of alkynes,[6] we have begun a systematic study of the reactions of alkynlphosphazenes with low valent transition metal complexes. The aims of these studies include construction of structurally complex phosphazene derivatives which are not available from direct synthetic routes, generation of redox active phosphazene substituents, and to examine the effect of the strongly electron withdrawing phosphazene function[7] on the products derived from these reactions.

RESULTS AND DISCUSSION

Initial studies have involved expansion of the number of known alkynlphosphazene bridging dicobalt complexes, $N_3P_3X_nY_mC{\equiv}CR{\bullet}Co_2(CO)_6$. We have prepared complexes of this type from $N_3P_3F_5C{\equiv}CR(R{=}SiMe_3$[8], $n\text{-}C_4H_9$[9]) and $N_3P_3F_3(OC_2H_5)_2C{\equiv}CH$[8]. A novel tetracobalt cluster, $2,2\text{-}N_3P_3F_4(C{\equiv}CPh.Co_2(CO)_6)_2$, has been obtained from the reaction of the alkynlphosphazene with $Co_2(CO)_8$. The crystal structures of the free alkynlphosphazene and the tetracobalt cluster have been determined and allow for the evaluation of structural perturbation of the cyclophosphazene which occur upon coordination of the dicobalt unit to the alkyne. Electrochemical reduction of both the di-and tetracolbalt species has been accomplished using cyclic voltametry. A reversible one electron reduction to a stable anion is followed by an irreversible second step. The epr spectrum of the first reduction product shows that the reduction is primarily metal based. The potentials for the first reduction are equal for the di- and tetracolbalt species indicating the absence of any significant electronic communication between the alkynl and phosphazene moieties.

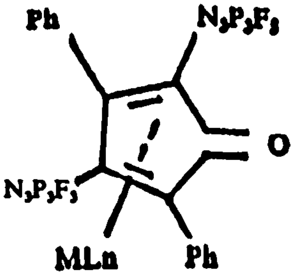


I

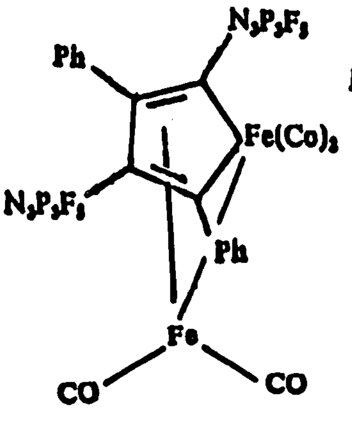
IIa $M{=}Co;L_n{=}\eta^5C_5H_5$
b $M{=}Fe;L_n{=}(CO)_3$

The reaction of the known[4] $N_3P_3F_5C{\equiv}CPh{\bullet}Co_2(CO)_6$ complex with excess $N_3P_3F_5C{\equiv}CPh$ produces a cyclotrimerized material, $(N_3P_3F_5)_3Ph_3C_6$(I). The ^{19}F NMR spectrum in the fast exchange limit shows that the major component is the 1,2,4-regio isomer about the central arene (as shown for I). A small amount of the symmetric (1,3,5) isomer was also observed. The ratio of the symmetrical to unsymmetrical regio isomers can be significantly increased if $Ni(PPh_3)_4$ is used as the cyclooligomerization catalyst. Full line shape analysis of the dynamic ^{19}F NMR spectra shows that restricted rotation occurs about the phosphorus-carbon bond in I and that all three phosphazenes rotate at different rates.

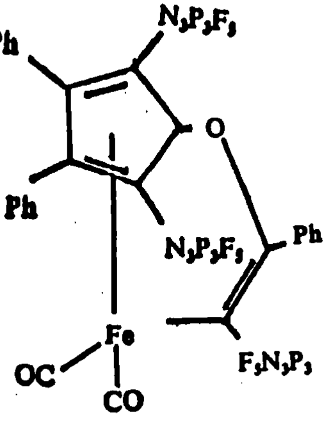
In order to expand the range of cobalt mediated chemistry, the reactions of a more active catalyst, $CpCo(CO)_2$, with $N_3P_3F_5C{\equiv}CPh$ were explored under a wide variety of conditions. The major products derived from these reactions include the cobalt stabilized cyclodimerized material IIa, for which a crystal structure has been determined, its carbonyl insertion product, IIIa, the cyclotrimer (I) and its cobalt complex I•CoCp. Both electron counting considerations and electrochemical evidence suggest that the central arene to colbalt coordination in I•CoCp is of the η^4 type. In contrast to the reactions of $Co_2(CO)_8$, $CpCo(CO)_2$ induces cyclooligomerization for other alkynlphosphosphazenes, e.g. $N_3P_3F_5C{\equiv}C\text{-}n\text{-}C_4H_9$, in addition to $N_3P_3F_5C{\equiv}CPh$.



IIIa M=Co; $L_n=\eta^5C_5H_5$
b M=Fe;$L_n=(CO)_3$



IV



V

The chemistry of iron carbonyl-alkynlphosphazene interactions is even more complex than that observed for colbalt mediated reactions. The reaction of the coordinately saturated $Fe(CO)_5$ with $N_3P_3F_5C{\equiv}CPh$ is sluggish but does yield the iron stabilized cyclodimer IIb. The crystal structure of IIb has been determined. The corresponding reactions with $Fe_2(CO)_9$ give a plethora of products including the stabilized cyclodimer, IIb, and its carbonyl insertion product IIIb. A iron complex of I, I•$Fe(CO)_3$, which is also believed to exhibit η^4 iron-central arene coordination, has been isolated. In addition to these materials and numerous trace level products, the iron metallocycle IV and a high relative yield of the unique species V have been isolated. The structure of V has been determined by x-ray crystallography and may be considered to arise from an unusual reaction of a coordinated cyclobutadienone with an alkyne. It is of interest to note that the proposed cyclobutadiene •$Fe(CO)_3$ precursor to V results from a head to head addition of alkynes as opposed to the head to tail addition which produces IIb.

In conclusion, it is clear that a wide range of new exocyclic groups can be constructed on cyclophosphazenes using transition metal-alkylphosphazene reactions and that in certain cases novel reactions or products are observed.

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REFERENCES

1. C.W. Allen in *The Chemistry of Inorganic Rings*, Eds.I Haiduc and D.B. Sowerby, Vol.2, (Academic Press, London, U.K., 1987), p.501-516
2. H.R. Allcock, *ACS Symp. Ser.*, *360*, 250 (1988).
3. C.W. Allen, *ACS Symp. Ser.*, *360*, 290 (1988).
4. T. Chivers, *Inorg. Nucl. Chem. Lett.*, *7*, 827 (1981).
5. H.R. Allcock, R.H. Nissan, P.J. Harris and R.R. Whittle, *Organometallics*, *3*, 432 (1984).
6. C. Hoogzand and W. Hubel in *Organic Synthesis via Metal Carbonyls* Eds. I. Wendu and P.Pino, Vol.I, (Wiley Interscience, N.Y. 1988), p.343-369.
7. C.W. Allen and J.C. Green, *Inorg. Chem.*, *19*, 1791 (1980).
8. C.W. Allen, J.L. Desorcie and K. Ramachandran, *J. Chem. Soc., Dalton Trans*, 1653 (1984).
9. C.W. Allen and K. Hill, unpublished observations.