NEW HETEROCYCLES WITH HYDROCARBON CAGE SUBSTITUENTS

STEVEN B. COPP

New Heterocycles with Hydrocarbon Cage Substituents

by

Steven B. Copp

Submitted in partial fulfilment of the requirements
for the degree of Master of Science
at
Memorial University
St. John's, Newfoundland
July, 1995

National Library of Canada
Acquisitions and Bibliographic Services Branch
395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada
Direction des acquisitions et des services bibliographiques
395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

ISBN 0-612-17582-0

Table of Contents

List of Tables

List of Figures

Abstract

The proficiency with which main group ($n \geq 3$) π systems (e.g. the nitrile sulphides ($C\equiv N^{+}\text{-}S^{-}$) and phosphaalkynes ($C\equiv P$)) imitate organic chemistry has been well documented. An investigation of the ability of main group π systems to be stabilized by *mono*- and *di*-substituted hydrocarbon cages (adamantane, bicyclo[2.2.2]octane) was undertaken. These types of compounds have not been extensively reported in the literature. Adamantyl-1,3,4-oxathiazol-2-one and *bis*-(3-Mesityl-1,2,4-oxazaphosphole)bicyclo [2.2.2]octane, have been prepared for the first time. The first X-Ray crystal structures of the oxathiazolone and oxazaphosphole heterocyclic rings will also be reported. The synthesis of precursors to these compounds will be presented along with full spectral characterisation. Attempts to generate a molecule containing two independent phosphaalkyne moieties will also be discussed.

Glossary

Adm	Adamantane
$C=P$	Phosphaalkene
$C\equiv P$	Phosphaalkyne
Et	Ethyl
HMPA	Hexamethylphosphoramide
IR	Infrared
LDA	Lithium di-isopropylamide
Me	Methyl
Mes	2,4,6-trimethylbenzene
Mes*	2,4,6-tri-*tert*-butylbenzene
Mes-CNO	Mesityl nitrile oxide
MHz	Megahertz
mp	Melting Point
MW	Molecular Weight
n/a	Not Available
n/d	Not Detected
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
ppm	Parts Per Million
P(TMS)$_3$	*Tris*-(trimethylsilyl)phosphine

TMS	Trimethylsilane
TMSCl	Chlorotrimethylsilane
TMS-O-TMS	Hexamethyldisiloxane

Throughout this thesis a systematic notation, commonly used in phosphorus chemistry, will be used to describe the phosphorus atoms discussed in various molecules. In this format, λ designates the valency or oxidation state of the phosphorus atom while σ designates the coordination of the phosphorus centre. For example,

$R\text{-}C\equiv P:$	λ = trivalent	σ = mono-coordinate	$\therefore = \lambda^3\sigma^1$
$R\text{-}C=P\text{-}R$	λ = trivalent	σ = di-coordinate	$\therefore = \lambda^3\sigma^2$
PPh_3	λ = trivalent	σ = tri-coordinate	$\therefore = \lambda^3\sigma^3$
/ $R\text{-}C\equiv P$ \	λ = pentavalent	σ = tri-coordinate	$\therefore = \lambda^5\sigma^3$
$O=PPh_3$	λ = pentavalent	σ = tetra-coordinate	$\therefore = \lambda^5\sigma^4$
PCl_5	λ = pentavalent	σ = penta-coordinate	$\therefore = \lambda^5\sigma^5$

Acknowledgements

Over the past two and a half years a number of people have contributed to successful completion of this project.

First, I would like to express my gratitude to my supervisor Dr. Mel Schriver for his patience and valuable advice throughout the course of this study. I would like to thank Dr. N Gogan and Dr. C. Loader for reviewing this manuscript. I would also like to acknowledge Dr. C. Lucas, Dr. J. Bestari, Dr. J. Clyburne, Dr. J. Burnell, Dr. G. Bodwell, Dr. A. Stein, Dr. P. Golding and Dr. L. Thompson for their time and assistance. I would also like to thank the invaluable work of Dr. Jablonski and N. Brunet for NMR, Dr. Gregory and Ms. M. Baggs for Mass Spec., and Dr. M.J. Zaworotko (SMU), Dr. J. Bridson and D. Miller for the Crystallography which made this project possible.

I would especially like to thank my friends Shugaung Zhu, Valerie Jefford (bud) and Alan Swinamer for the great times in and out of the lab. I would also like to thank Donnie Hodder (Swiler's RFC baby!), Murray Park (Crib Champs!), Yvette Favaro, Geraldine Kennedy, Brian Dwyer, Sean Quinlan, Jim Farrell, Chris Sheppard, and Neil Squires for the fun times in NF and are all people I will never forget. Special thanks to my cousin Allan Trenholm and his wife Joanne for all their help during my time in Newfoundland.

At this time I would also like to thank the secretaries of the 4th

floor (Viola, Teresa, Mary, Joan and Carolyn) and the gang in stores (Bonita, Steve, Kerry and Kevin) who have saved me more times than I would care to admit.

I appreciate the financial support and facilities provided by Memorial University of Newfoundland, NSERC and FMC.

Finally, I express my thanks to my parents and my brother Dale for their support and understanding.

Chapter 1

Preparation of Adamantyl-1,3,4-oxathiazol-2-one.

1.1 Introduction

The realization, that the heavy Main Group elements ($n > 2$), can form stable π bonds has revolutionized synthetic chemistry. Over the last 20 years, elements in the third ($n=3$) and fourth ($n=4$) rows of the periodic table have been shown to form stable π bonds such as $S{\equiv}N$[1] and $C{\equiv}P$[2] thus disproving the *double bond rule*[a]. Although these bonds are weaker than the more well known π bonds, the possibility of exploring a chemistry analogous to that of carbon now exists.

With the versatility of these new π bonds, chemists have begun to use these compounds in standard organic reactions. One class of these reactions is the 1,3-dipolar cycloaddition[3]. Like its purely organic counterparts, the 1,3-dipolar cycloaddition reaction involves the conversion of π bonds to heavier atoms to new σ bonds with the accompanying ring closure. Although examples of these new π systems are limited, a variety of new heterocycles have been characterised[4].

---

[a] In the late 1940's, the **Double Bond Rule** was developed to explain physical and theoretical observations of the periodic table as to the prominence of π bonds in elements of the second row ($n=2$) and a lack of π bonds in the heavier elements. From this rule, it was theorized that $2p\pi$-$np\pi$ ($n = 3,4,5$) would be impossible due to weak and diffuse orbital overlap[5,6].

The 1,3-dipolar cycloaddition reaction often features molecules containing the pnictogens (elements of Group 15) and chalcogens (elements of Group 16) in both the dipole, such as mesityl nitrile oxide ($C{\equiv}N\text{-}O$), and the dipolarophile, as in thiazyl chloride ($N{\equiv}S\text{-}Cl$) (See **Figure 1.1**).

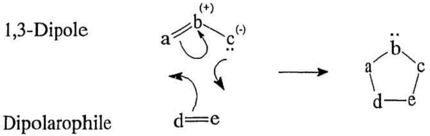


Figure 1.1 The 1,3-Dipolar Cycloaddition Reaction.

Recent research in the area of 1,3-dipolar cycloaddition reactions includes 1,3-dipoles such as the nitrile sulphides ($C{\equiv}N\text{-}S$) and dipolarophiles such as the phosphaalkynes ($\text{-}C{\equiv}P\text{:}$). The range of reactions that these compounds are capable of are indicated in **Figure 1.2**.

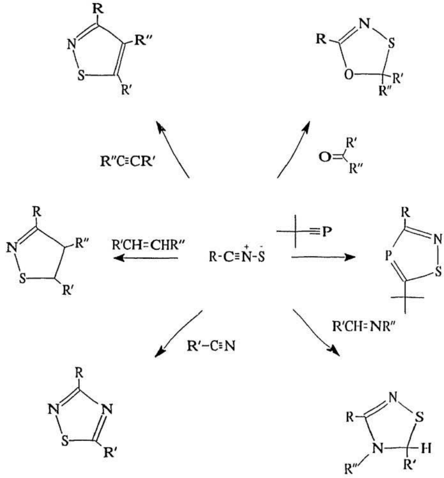


Figure 1.2 Some of the Heterocycles which can be prepared from nitrile sulphides *via* 1,3-Dipolar Cycloaddition Reaction[4].

The nitrile sulphides ($C{\equiv}N^{+}\text{-}S^{-}$) are a well known family of propargyl-allenyl type of 1,3-dipole (See **Figure 1.3**) which are very similar to the nitrile oxides ($C{\equiv}N^{+}\text{-}O^{-}$) and have been the subject of several recent review articles[22]. The nitrile oxides are much more stable than the nitrile sulphides with respect to their decomposition products ($R\text{-}C{\equiv}N$ and O_2 or S_8) and are isolable when sufficient steric protection is provided to prevent intermolecular cycloaddition reactions.

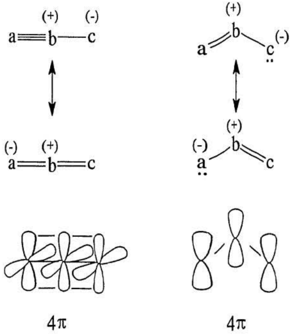


Figure 1.3 The π-Manifolds of the Propargyl-Allenyl 1,3-Dipole and the Allyl 1,3-Dipole.

Nitrile sulphides can be described as containing a formal sulphur-nitrogen π bond and have not yet been isolated. They are typically generated *in situ* from a precursor due to their high reactivity and instability. In our case, 1,3,4-oxathiazol-2-ones were used as the source of nitrile sulphides (See **Figure 1.4**). The 1,3-dipole can be generated in the presence of a suitable dipolarophile by thermal decarbonylation to give heterocyclic compounds.

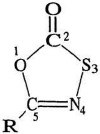


Figure 1.4. The 1,3,4-Oxathiazol-2-one Heterocycle.

First prepared by Senning[7] and Muhlbauer and Weiss[8] in the late 1960's, 1,3,4-oxathiazolones are moisture and air stable and may be stored on the bench for extended periods. The preparation of oxathiazolone derivatives from chlorocarbonyl-sulfenyl chloride and an amide is a well known reaction (See **Figure 1.5**). During the addition of ClC(O)SCl, two equivalents of hydrogen chloride gas are evolved. Early observations of the thermolysis of

1,3,4-oxathiazol-2-ones detected the presence of nitrile, CO_2 and S_8. This is common for reactions in which nitrile sulphides are generated in the absence of dipolarophiles. In the presence of a suitable dipolarophile, a [3+2] cycloaddition results in the formation a new five membered heterocycle.

To prolong the lifetime of the nitrile sulphide and therefore increase the probability of cycloaddition, the use of stabilizing large aryl and alkyl groups is very important. Generally, kinetic stabilization is brought about by bulky substituent groups and overall steric protection. However, the use of these groups compromises the reactivity of the 1,3-dipole. Yoshifugi[9] [2,4,6-tri-*t*-butylphenyl (Mes*)] and later Cowley[10] [$(TMS)_3C$] established the importance of steric shielding in the protection of Main Group π systems from self reaction or decomposition. The use of saturated cage hydrocarbons also has been effective in stabilising Main Group π systems as they provide kinetic stabilisation without excessive inhibition of reactivity. These groups have not been investigated for use in the stabilisation of nitrile sulphides.

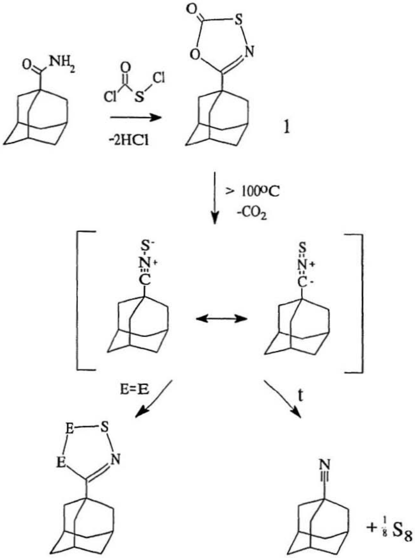


Figure 1.5. The Preparation of Adamantyl-1,3,4-oxathiazol-2-one 1 and generation of the Adamantyl Nitrile Sulphide.

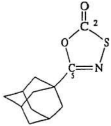
These cage hydrocarbons, including adamantane and the bicyclooctanes, contain two or more tertiary positions sometimes called bridgehead centres which can be substituted with various functional groups. Although their group electronegativities are very similar to a *t*-Butyl group[11], these cages are much more rigid and do not have as large a cone angle. The structures of cage hydrocarbons make possible multiple functionality within the same molecule without compromising protection or reactivity. In this chapter, we will investigate the use of bridgehead containing hydrocarbons in the stabilisation of nitrile sulphide 1,3-dipoles.

1.2 Experimental

1.2.1 *General Procedures*

$C_{10}H_{15}C(O)Cl$ (Aldrich) was used as received. The $C_{10}H_{15}C(O)NH_2$ was prepared following a literature procedure[12]. The solvent was dried with the appropriate drying agent [$C_6H_5CH_3$ (Na)] and distilled under nitrogen prior to use. Melting points were determined on a Mel-Temp II melting point apparatus and are uncorrected. Elemental analyses were performed by the Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. IR spectra were recorded from Nujol mulls on KBr plates using a Mattson Polaris FT-IR instrument. NMR spectra were recorded on a General Electric 300 MHz instrument [^1H, ^{13}C] or on a Bruker AMX 400 MB instrument (^{14}N) at the Atlantic Regional Magnetic Resonance Center. Chemical shifts are reported in ppm relative to internal standards (^1H, ^{13}C : TMS) or external standards (^{14}N : CH_3NO_2). EI Mass Spectra were recorded on a VG Micromass 7070 double focusing spectrophotometer. X-Ray crystallographic data were obtained by Dr. Michael Zaworotko on an Enraf-Nonious CAD-4 diffractometer.

1.2.2 *Preparation and Characterisation of Adamantyl-1,3,4-oxathiazol-2-one, 1.*



$C_{10}H_{15}$- $\overline{\text{COC(O)SN}}$, 1

Neat chlorocarbonylsulfenyl chloride, ClC(O)SCl (5.37g, 41.0 mmol) was added to a mixture of toluene (~100 mL) and adamantyl amide, $C_{10}H_{15}C(O)NH_2$ (4.92, 27.0 mmol) under nitrogen to give a clear yellow solution over a white solid. The solution was brought to reflux (at which point the solid dissolved) and maintained at 110°C for three hours. The resulting yellow-brown solution was poured into a crystallizing dish and allowed to evaporate to dryness to afford a dark brown crystalline solid which was recrystallised from hexanes to give clear, colourless plate-shaped crystals of
$C_{10}H_{15}$- $\overline{\text{COC(O)SN}}$, 1, (1.12g, 4.72 mmol, 17.5%). The solid was transferred to a sublimation apparatus and heated to 90°C [10^{-3} mmHg] for 20 hours to give clear colorless crystals which were suitable for X-Ray

crystallography. mp 79-81°C, IR (cm^{-1}): 1809 (sh), 1766 (s), 1594 (ms), 1236 (m), 1101 (w), 1072 (m), 996 (ms), 907 (ms), 570 (w). NMR ^{1}H ($CDCl_3$) δ [ppm]: 2.09, 1.96, 1.76 ^{13}C ($CDCl_3$) δ [ppm] (assignment): 174.8 (C2), 167.3 (C5), 38.9 (CH_2), 38.5 (C_{quat}), 36.1 (CH_2), 27.5 (CH) ^{14}N δ ($\Delta\nu^{1/2}$ Hz) -160 (950). Mass Spectrum [IE, 70 eV] *m/e* (%, assignment): 237 (12, $C_{10}H_{15}$-COC(O)SN), 193 (1, $C_{10}H_{15}$-CNS), 161 (12, $C_{10}H_{15}$-CN), 135 (100, $C_{10}H_{15}$), 95 (24), 79 (18), 41 (16). Anal. calcd. for $C_{12}H_{15}NO_2S$: C 60.73, H 6.37, N 5.90; found C 59.27, H 6.27, N 5.71.

1.3 Results and Discussion

1.3.1 Preparation of Adamantyl-1,3,4-oxathiazol-2-one.

The synthesis of adamantyl-1,3,4-oxathiazol-2-one, **1** from hot toluene solution produced a mixture of products with **1** being the major component. Other products identified were adamantyl nitrile and elemental sulphur which are consistent with decomposition of the 1,3-dipole. Attempts[13], such as longer reaction times and lower temperatures, to optimise the yield failed to improve the overall yield. Compound purity was improved by sublimation that removed a small amount of brown impurity and filtration on a silica gel column to remove nitrile and sulphur. Subsequent recrystallisation of the pure product gave a 17.2% yield. Fractional crystallisation produced large quantities of pure **1** but a significant amount could still be detected in the remaining crude material. Crystals of **1** were clear and colourless but upon storage would acquire a faint violet colour. This did not, however, cause any noticeable change in any of the physical or spectroscopic properties of **1**.

1.3.2 Spectroscopic Analysis of 1.

The product 1 was characterised by NMR (^{1}H, ^{13}C, ^{14}N), IR, Mass Spectroscopy and X-Ray Crystallography. The characteristic resonances in the ^{13}C NMR spectra of oxothiazolone derivatives at 174.2 ± 0.6 ppm and 162 ± 5.2 ppm are consistent with the observed peaks of 174.8 ppm (C1) and 167.3

ppm (C2) of the carbon atoms in the heterocyclic ring. The mass spectrum also confirms the structure and fragments corresponding to the loss of CO_2, S, and CN in sequence.

1.3.3 Structural Analysis of 1.

Although there are a wide variety of aromatic and alkyl derivatives of the 1,3,4-oxathiazol-2-one heterocycle known, we have reported[13] the characterisation of the first adamantyl derivative of this ring and the first crystal structure of any 1,3,4-oxathiazol-2-one derivative. The ORTEP[14] perspective view is presented in **Figure 1.6.** The crystal data, fractional atomic coordinates and the bond lengths and angles are also given in **Appendix 1.**

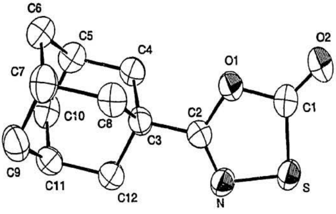
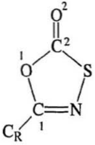


Figure 1.6. ORTEP View of Adamantyl-1,3,4-oxathiazol-2-one, **1.**

The phenyl derivative has subsequently been studied crystallographically[15] and the gas phase structures of the 1,3,4-oxathiazol-2-ones ($R=H^{16}$, Me^{17}) are also known. Comparisons of the important bond angles and distances with the 1,3,4-oxathiazol-2-ones reveal no significant difference ($\Delta \geq 3\sigma$) regardless of the substituent (**Table 1.1**). The heterocyclic ring was planar with no atom deviating more than 0.10(4) Å from the plane. The C-N bond was not significantly different from the accepted value of a carbon-nitrogen double bond (1.272(5)Å vs. 1.28Å)[18]. The S-N bond was also similar to the sulphur-nitrogen bond found in the 1,2,3,5-dithiadiazolyl family of heterocycles (1.687(3)Å vs. 1.683Å). The C-C distance between the heterocycle and substituent groups in these compounds were significantly different (See **Table 1.1**) which can be attributed to the degree of resonance between the alkyl group and the heterocycle. The adamantyl and methyl derivatives showed little or no conjugation with the 1,3,4-oxathiazol-2-one ring and the C-C bond distances were therefore longer than in the conjugated phenyl derivative (1.491(5)Å and 1.487(3)Å vs. 1.463(7)Å and 1.457(6)Å respectively). The difference in the endo-ring C-O bond distances for the phenyl derivative was attributed to increased delocalisation of the benzene ring[15]. The adamantyl group was identical to others reported in the literature for small molecules bonded at the bridgehead position[23].

Table 1.1. Comparison of Structural Data for 1,3,4-oxathiazol-2-ones.



Bond	R = Adamantyl[a]	R = Phenyl[15,a]	R = Methyl[17,b]	R = H[10,b]
C_R-C_1	1.491(5)	1.463(7) 1.457(6)	1.487(3)	n/a
C_1-N	1.272(5)	1.268(6) 1.267(6)	1.289(4)	1.286(2)
N-S	1.687(3)	1.682(4) 1.677(4)	1.685(2)	1.690(2)
S-C_2	1.750(4)	1.754(5) 1.751(5)	1.768(2)	1.767(2)
C_2-O_1	1.392(5)	1.380(6) 1.388(6)	1.391(6)	1.402(3)
O_1-C_1	1.377(5)	1.379(5) 1.380(5)	1.367(9)	1.356(3)
C_2-O_2	1.188(5)	1.187(6) 1.184(6)	1.198(2)	1.192(2)

a Data was obtained from solid state X-ray crystallographic studies.

b Data was obtained from gas phase electron diffraction studies.

A bond order analysis[19,20] (See **Figure 1.7**) also supports the localisation of π bonds within the heterocycle. This is consistent with the expected placement of π bonds in the lowest energy Lewis structure.

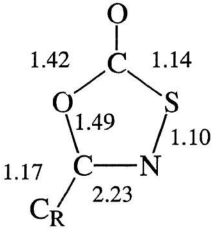


Figure 1.7 Bond Order Analysis of **1**.

1.4 Conclusion

The first adamantyl derivative of 1,3,4-oxathiazol-2-one heterocyclic family was successfully prepared by the general route to these heterocycles. Spectroscopic characterization of this compound proved to be consistent with known derivatives of this family and the first X-ray crystallographic study of the 1,3,4-oxathiazol-2-one ring was described. A bond order description using the experimental bond lengths indicated that the π bonds in the heterocycle are mostly localised between the expected atoms.

1.5 Further Work

The synthetic utility of the alkyl-based 1,3,4-oxathiazol-2-ones has been largely carried out by Shugaung Zhu[13,21]. His work with mono- and bi-functional adamantyl and polymeric phenyl derivatives has shown the generality of this route to 1,3,4-oxathiazol-2-ones and the synthetic utility of the nitrile sulphides.

Chapter 2

Preparation and Chemistry of Carbon-Phosphorus π Bonds.

2.1 Introduction

Phosphaalkynes are molecules which contain a carbon-phosphorus triple bond[24]. This moiety includes a trivalent, mono-coordinate ($\lambda^3\sigma^1$) phosphorus atom which is *sp* hybridized and bears a lone pair[a]. The π bond is a result of a 2pπ-3pπ interaction which was long thought to be an unstable bonding situation due to the predictions of the *double bond rule* (See **Section 1.1**). The carbon atom is also *sp* hybridized and, for steric and electronic reasons, the substituent bonded to this atom is the main factor in the kinetic stability of the molecule[24].

$$\mathrm{R{-}C{\equiv}P}\!:$$

Figure 2.1 The Phosphaalkyne Moiety.

The phosphaalkyne π bond is very interesting because it has been shown to have two distinct patterns of reactivity[28]. The carbon-phosphorus triple bond can react in a pattern similar to its purely organic counterpart, the alkynes (-C$\equiv$C-). On the other hand, the lone pair on the phosphorus atom can also be involved in chemistry analogous to the lone pair of a nitrile (-C$\equiv$N:) or phosphine (R_3P:).

---

[a] See **Glossary** for definition of σ and λ notation in Phosphorus chemistry.

Characterised by Gier in 1961[27], the first reported phosphaalkyne was generated from an electrical discharge between graphite electrodes in an atmosphere of phosphine (**Figure 2.2**). This highly reactive phosphorus product was a part of a mixture with by-products of acetylene and ethylene that was frozen out at -198°C. Gier observed that this compound was highly reactive and that it polymerised to a black solid upon warming to -78°C. Characterisation by IR spectroscopy determined that this product undoubtedly contained a carbon-phosphorus bond analogous to hydrogen cyanide. He called this molecule phosphaacetylene. Due to the transient nature of this molecule at room temperature and its extreme sensitivity to air and moisture, few chemical reactions with this compound have been reported.

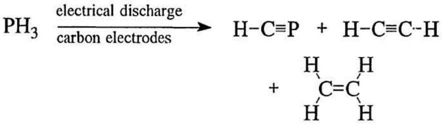
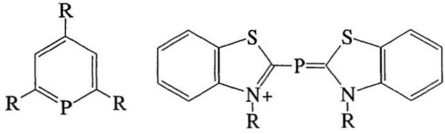


Figure 2.2 Gier's Synthesis of Phosphaacetylene.

In the next 20 years a variety of carbon-phosphorus double bonds have been generated in a number of chemical environments[26]. This continued to cast doubt on the application of the *double bond rule* to phosphorus π systems. The synthesis of phosphabenzene[28] and phosphamethine cations[29] demonstrated the ability of phosphorus to mimic the bonding environments and chemistry of carbon (**See Figure 2.3**).



R= Aryl, H

R= Me, Et

Figure 2.3 Early Examples of Carbon-Phosphorus π Bonding.

During the late 1970's, a number of new phosphaalkenes were reported such as $CF_2=PH$, $CH_2=PH$, and $CH_2=PCl$[30]. Later reports of $R\text{-}C\equiv P$ ($R = H, CH_3, CF_3, Cl$) showed that phosphaalkynes could be generated by pyrolysis of halo-phosphaalkenes at 900°C by the elimination of hydrogen halides[31]. Although these compounds were equally as sensitive to air and moisture as phosphaacetylene, the potential for the development of a family of phosphaalkynes was shown. Due to the difficulty of synthesis and their extreme sensitivity to air and moisture at room temperature, however, the chemistry of these compounds was not extensively explored.

In 1981, Gerhard Becker and his co-workers described the preparation of a phosphaalkene that contained a stable, isolated double bond and could be prepared by the addition of *tris*-trimethylsilylphosphine [$P(TMS)_3$] to common organic acid chlorides[32]. Initial addition of $P(TMS)_3$ resulted in the nucleophilic attack of the phosphine on the carbonyl and the elimination of trimethylsilyl chloride to generate an intermediate which could not be isolated. This intermediate spontaneously underwent a 1,3-trimethylsilyl shift from the phosphorus to the oxygen atom to give the isolable phosphaalkene. This reaction sequence was significant because it allowed a facile route to stable $\lambda^3\sigma^1$ phosphaalkynes by catalytic elimination of hexamethyldisiloxane from the phosphaalkene by reaction with sodium hydroxide. This discovery revolutionized phosphaalkyne chemistry because this family of compounds could now be reached synthetically on the bench at room temperature under inert atmospheres.

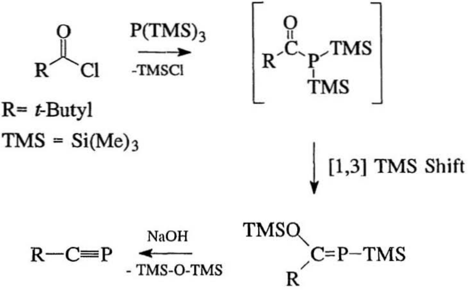


Figure 2.4 Becker's General Procedure for Phosphaalkynes.

Subsequently, Manfred Regitz and his co-workers optimized this procedure and described a number of thermally stable phosphaalkynes with substituent groups ranging from isopropyl to adamantyl[33]. Other similar methods of preparation have been in the same vein as Becker's with elimination of thermodynamically stable small molecules such as HF[34], HCl[35], and TMSCl[36] to generate phosphaalkynes. There is now an extensive review literature on the preparation and chemistry of the phosphaalkynes[24].

Descriptions of $\lambda^5\sigma^3$-phosphaalkynes have also been published. They are generated from phosphino diazo compounds by photochemical or thermal means by elimination of N_2. These compounds have recently been reviewed by Bertrand[37].

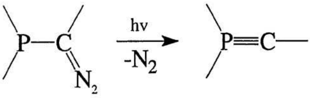


Figure 2.5 $\lambda^5\sigma^3$-Phosphaalkynes.

There are other triple bonds that contain the phosphorus atom. For example, at temperatures greater than 800°C white phosphorus (P_4) is in equilibrium with $P \equiv P$ diatomic molecules[38]. Phosphorus (III) nitrides ($P \equiv N$) can be generated thermally from P_3N_5[39]. Also, iminophosphenium cations have been described such as $Mes^{*}\text{-}^{+}N \equiv P$ which display triple bond character[40]. Other examples of $np\pi$-$np\pi$ ($n > 3$)bonding include $C=Si$, $Si=Si$, and $As=As$[41].

Phosphaalkynes are clear colourless liquids or solids depending on the substituent that stabilizes the π bond. *t*-Butyl phosphaalkyne is a thermally stable liquid that boils at 61°C whereas adamantyl phosphaalkyne is a solid (mp = 69-70°C) at room temperature. Sensitivity towards atmospheric oxygen is also decreased with the increase in steric protection provided by the R group to the point where Regitz has indicated that their air sensitivity is "overrated"[24]. In their pure form phosphaalkynes are typically short lived species and are best handled in dilute solutions to avoid decomposition[7]. Even bulky R groups only induce short half lives as demonstrated in **Table 2.1**.

Table 2.1 Relative Stabilities of Phosphaalkynes under an Inert Atmosphere[13].

R Group	Half life
R = H	only stable at -198°C
R = Ph	7 minutes at 0°C
R = TMS	50 minutes at 20°C
R = adamantane	Indefinitely Stable at 20°C

The spectroscopic data that has been reported for the C≡P triple bond is of particular interest. The chemical shifts of the ^{13}C NMR resonances vary from 150-201 ppm. The carbon atoms show coupling with the phosphorus atom ($I = 1/2$) that greatly varies with the substituent group ($^{1}J_{C,P}$ = 14-56 Hz). The chemical shifts of the ^{31}P NMR resonances have a variable chemical shift ranging from +34.4 ppm (R = Me) to -69.2 (R = adamantyl). Long range coupling due to the phosphorus atom [$^2J_{C,P}$ and $^3J_{C,P}$], is also commonly observed in the spectra of these compounds. The C≡P stretch has been reported at 1559cm^{-1}. Photoelectron spectroscopic data show that the electronic ionization energies are lower than those of C≡N indicating the phosphorus lone pair is more tightly held than the electrons in the π bond[26].

Structurally, carbon-phosphorus bonds can have bond distances[26] ranging from 1.54Å for C≡P, 1.70Å for C=P, and 1.80Å for C-P. $\lambda^3\sigma^1$ phosphaalkynes are generally linear with the R - C - P angle approaching 180°.

Phosphaalkynes are iso-electronic with alkynes but are crystallographically iso-structural with nitriles. *Ab initio* studies by Jayasuriya[42-44] have shown that the chemical behaviour of a phosphaalkyne closely resembles that of an alkyne with much of its chemistry occurring with the π bond rather than the lone pair. These studies have also revealed that a substituent effect in which electron donating groups will enhance chemical behaviour. Both experimentally and theoretically, however, the most likely site for chemical attack (electrophilic) would be at the C≡P π bond rather than the localized lone pair.

The main areas of interest in phosphaalkyne compounds include the chemistry of the π bond in cycloaddition reactions and ability of the phosphaalkyne to act as a ligand. In these cycloadditions reactions, a $\lambda^3\sigma^1$ phosphorus atom becomes a trivalent bicoordinate phosphorus atom ($\lambda^3\sigma^2$). This can be achieved in [1+2], [2+2], [3+2], and [4+2] cycloaddition reactions[2,24]. The versatility of the phosphaalkynes has been proven in a number of reactions that have produced a wide variety of phosphorus containing heterocycles.

Another area of interest includes the use of phosphaalkyne compounds in organometallic chemistry. Nixon predicted[28] that the C≡P moiety should act as a ligand in a similar fashion to an alkyne, primarily from photoelectron studies. This has been established in a number of transition metal complexes in which the C≡P coordinates in a "side on" fashion as an η^2 ligand[45]. However, Nixon has also shown[46] that a phosphaalkyne may behave like a nitrile by coordination through the lone pair on the phosphorus with the appropriate transition metal complex in which "side on" bonding is prevented by bulky ligands and "end on" ligation is favoured (See **Figure 2.6**). Cyclodimerisation of the C≡P unit in the presence of cobalt, rhodium and iridium has been described as well as a number of complexes with heterocycles formed originally from R-C≡P[47]. Other interesting complexes include a variety of "ferrocene-like" complexes and the generation of clusters of metal complexes from the utilization of the phosphorus lone pair after the initial metal complex is formed to join more than one complex together[48] (See **Figure 2.7**).

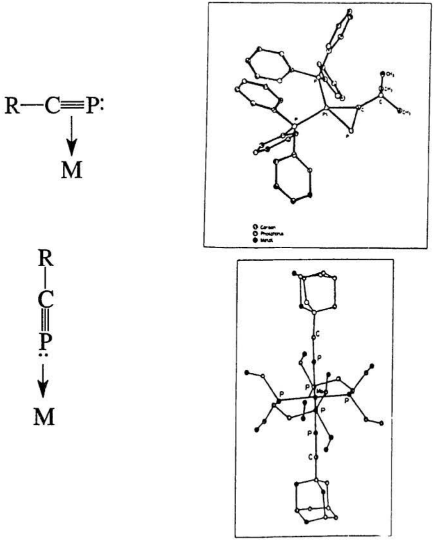


Figure 2.6 "Side on" and "End on" Coordinations of Phosphaalkynes.

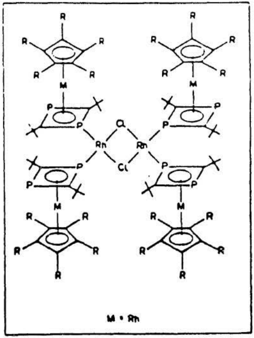


Figure 2.7 Metal Complexes and Clusters derived from Phosphaalkynes.

An area of more recent interest is the work involved with the cyclotetramer of phosphaalkynes, the phosphacubane. First described by Regitz[49], a cubane, containing only carbon and phosphorus at the corner positions, was prepared in a very low yield (< 5%) from heating neat *t*Bu-C$\equiv$P in a sealed tube at 130°C. Although little chemistry could be carried out on this molecule due to the low yield, discovery of a zirconium catalyst ([Zr(η^8-

$C_5H_5)_2(P_2C_2t\mathrm{Bu})_2])$ which greatly increased the yield to 60 - 70% has allowed some very interesting chemistry to be reported[50](See **Figure 2.8** and **2.9**). The chemistry leading to the phosphacubane has led to the discovery of other carbon-phosphorus clusters[51].

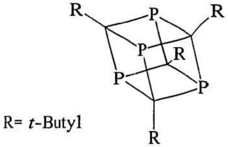


Figure 2.8 The Phosphacubane.

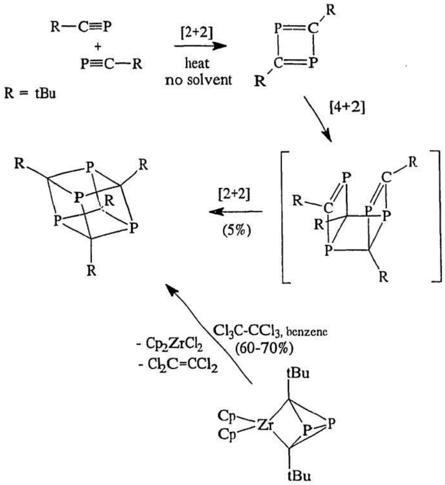


Figure 2.9 Synthesis of Phosphacubanes.

Our interest in phosphaalkynes results from an observation that Regitz made about his inability to generate a *bis*-phosphaalkyne[52] (See **Figure 2.10**). The synthesis of a *bis*-phosphaalkene was successful and the product was characterised by NMR. The compound however, instead of undergoing the desired elimination of hexamethyldisiloxane, underwent a [2+2] intramolecular cycloaddition reaction to form a bicyclic compound. This thesis suggests that the proximity of the two phosphaalkyne units and the flexibility of the organic framework favours the intramolecular cycloaddition and precludes the possibility of isolated C≡P units.

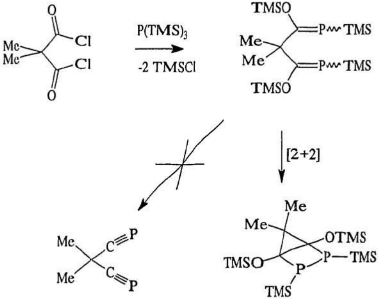


Figure 2.10 Regitz's attempt at a *bis*-phosphaalkyne.

A review of the literature reveals relatively few examples of *bis*-phosphaalkenes. Chernega et al.[53] obtained the crystal structure of a *bis*-phosphaalkene which is stabilized by extensive delocalization rather than steric protection (See **Figure 2.11**). This molecule, however, lacks the potential to form a *bis*-phosphaalkyne due to the phosphorus-phosphorus single bond. Other examples of *bis*-phosphaalkenes by Geoffrey[54], Yoshifugi[55] and Appel[56,57] (See **Figure 2.11**), are generally trapped as ligands in transition metal complexes due to the high reactivity of these species as well as being extremely sterically protected. These *bis*-phosphaalkenes, however, cannot generate a *bis*-phosphaalkyne by known methods.

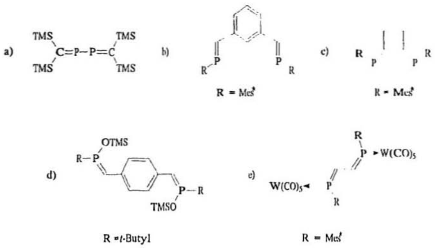


Figure 2.11 Known *bis*-Phosphaalkenes: a) Chernega, b) Geoffrey, c) Yoshifugi, d) and e) Appel.

This thesis proposes that cage hydrocarbon moieties, such as adamantane and bicyclo[2.2.2]octane, can be used as a substituent to produce an isolable *bis*-phosphaalkyne. The use of this type of substituent group should give us a number of advantages. For example, the bicyclo[2.2.2]octane group can be disubstituted at the bridgehead centres and positioning the functionalities at 180° with respect to each other should allow sufficient separation of the C≡P units to prevent intramolecular reaction. This hydrocarbon cage is also suitable for the generation of a bis-phosphaalkyne because of the observed stability of other bridgehead stabilized phosphaalkynes. Substituent groups such as triptycene (9,10-*o*-benzeno-9,10-dihydroanthracene), and adamantyl have been shown to give the most stable phosphaalkynes known because of the presence of a bridgehead carbon and they benefit from the lack of β-protons (preventing a 1,3 hydride shift). Bridgehead carbons have been shown in other Main Group systems to be useful in stabilizing reactive π systems[13].

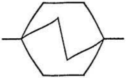


Figure 2.12 Bicyclo[2.2.2]octane.

Bridgehead carbon atoms are sp^3 hybridized carbon atoms which are not bonded to protons. They are effective in stabilizing π systems because of a) steric protection (since bridgehead carbons are usually found as part of larger hydrocarbon cages) and b) an inability to form intermediates which require the bridgehead carbon to form double bonds through resonance or planar intermediates during electrophilic or nucleophilic attack such as in the S$_N$2 reaction [Bredt's Rule].

The greater stability of the proposed *bis*-phosphaalkynes from the increased steric protection, stability from the bridgehead carbon and the prevention of intramolecular attack, should favour the generation of a *bis*-phosphaalkyne which is stable and isolable.

Bicyclo[2.2.2]octane is an eight carbon hydrocarbon cage made up of three ethylene bridges with two bridgehead carbon-substituent bonds located on a C$_3$ axis 180° apart. A number of syntheses have been reported involving Diels Alder methodology or alternative methods that typically have low yields[58-60]. A synthesis reported by Della, however, involving the alkylation of a the monoenolates of a cyclohexane diester with a 1,2-dihalo ethane followed by a base induced cycloaddition, has produced the bicyclo[2.2.2]octane in good yield[61].

The chemical advantages of a *bis*-phosphaalkyne are two fold. Initially it should allow us a facile route to *bis*-heterocycles similar to others that have been recently published[13]. Also, the tremendous ability of phosphaalkynes to cyclise should offer the possibility for preparation of polymeric species with interesting conductive and thermal properties due to alternating heterocycles and "spacer" units (See **Figure 2.13**).

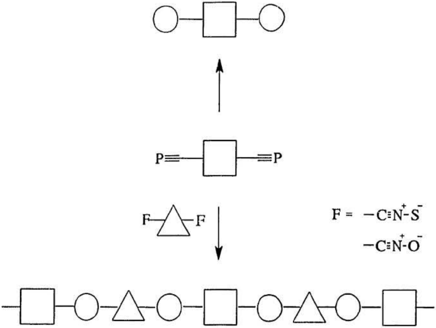


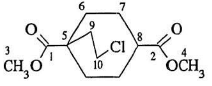
Figure 2.13 Possible Chemistry of *bis*-Phosphaalkynes.

2.2 Experimental

2.2.1 *General Procedures.*

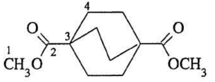
The reagents used in the synthesis (dimethyl cyclohexane-1,4-dicarboxylate, 1-bromo-2-chloroethane, 2.0M lithium diisopropylamide (LDA) in heptane/tetrahydrofuran/ethylbenzene, 1,3-adamantyl dicarboxylic acid, hexamethylphosphoramide (HMPA), thionyl chloride ($SOCl_2$)) were purchased from Aldrich and used as received. *Tris*-trimethylsilyl phosphine [$(PTMS)_3$] was prepared following a literature procedure[62] and distilled prior to use. Mesitylaldehyde (2,4,6-trimethyl benzaldehyde) was prepared from mesitylene[63] and converted to mesityl nitrile oxide[64]. Solvents were dried overnight with the appropriate drying agent [methylene chloride (P_2O_5), pentane (CaH_2), tetrahydrofuran (Na, benzophenone)] and distilled under nitrogen prior to use. The procedures used for spectroscopic and chemical analysis are given in Section **1.2**. X-ray crystallographic data were obtained, solved and refined by Dr. John Bridson and Mr. David Miller on a Rigaku AFC6S diffractometer.

2.2.2 *Preparation and Characterisation of Dimethyl 1-(2'-Chloroethyl) cyclohexane-1,4-dicarboxylate,* ***2***



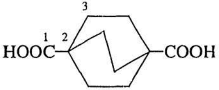
A flame dried, three neck, round bottom flask equipped with a magnetic stir bar was charged with 2.0M lithium diisopropylamide in heptane/ tetrahydrofuran/ethylbenzene (79.0 mL, 0.158 mol) under a nitrogen atmosphere. The flask was then equipped with a thermometer, a nitrogen inlet and a rubber septum. The solution was cooled in an ethanol/ice bath (approximately -30°C) and 50 mL of dry tetrahydrofuran was added carefully so that the temperature did not exceed 0°C. The resulting red solution was then cooled to -80°C using an acetone/dry ice bath. Addition of hexamethylphosphoramide (90.0 mL, 0.517mol) to the reaction mixture was followed by further cooling to -90°C using a hexanes/N_2 bath. A solution of dimethyl cyclohexane-1,4-dicarboxylate (30.0 g, 0.150 mol) in 50 mL of tetrahydrofuran was added over approximately 10 minutes. The resultant mixture was allowed to stir for 40 minutes. Neat 1-bromo-2-chloroethane (25.78g, 0.180 mol) was added dropwise over 5 minutes and was left to stir for a further 5 minutes. The bath was then removed and the solution allowed to warm to room temperature gradually over two hours. The resulting orange solution was then quenched with a saturated solution of aqueous ammonium chloride (100 mL) producing an immediate white precipitate. Workup of the solution involved concentration of the reaction mixture under reduced pressure and dilution with water (200 mL). Extraction with pentane (3 x 200 mL) afforded a pale yellow solution. The extracts were washed twice with water, dried (Na_2SO_4) and evaporated to yield a yellow oil (36.0g). The oil was then passed down a silica gel column (1:1 ether/petroleum ether 30-60), followed by fractional vacuum distillation (10^{-3} mmHg) at 90-98°C which yielded **2** as a colourless liquid (31.78g, 0.121 mol, 76.5%) ^1H ($CDCl_3$) δ [ppm] (assignment): 1.2-2.7, m, 11H (ring and CH_2-C-Cl), 3.42-3.45, 2H (CH_2Cl), 3.651, 3H (OCH_3), 3.72, 3H (OCH_3). ^{13}C ($CDCl_3$) δ [ppm] (assignment)[61]: 25.7 (C9), 39.6 (C6), 40.3 (C7), 42.9 (C10), 43.9 (C5), 45.9 (C8), 51.3 (C4), 51.7 (C3), 174.8 (C2), 175.4 (C1).

2.2.3 *Preparation and Characterisation of Dimethyl bicyclo[2.2.2] octane-1,4-dicarboxylate,* **3**



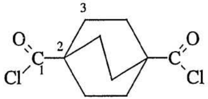
A solution of 2.0M LDA in heptane/tetrahydrofuran/ethylbenzene (31.5 mL, 0.063 mol) was cooled to -78°C. In a separate flask, a solution of **2** (16.0g, 0.061 mol) in THF (220 mL) and HMPA (45 mL, 0.259 mol) was prepared in a three necked round bottom flask equipped with a magnetic stir bar, thermometer, N_2 gas inlet and a rubber septum. The solution was then cooled to -78°C under a N_2 atmosphere. The LDA solution was then added dropwise through a transfer line over 30 minutes such that the temperature did not exceed -70°C. The yellow solution now became darker in colour and was left to stir for 30 minutes at -78°C. The solution was then allowed to warm to room temperature over 2 hours and left to stand for an additional hour. The reaction mixture was then quenched with a saturated solution of aqueous ammonium chloride (50 mL). This afforded a white precipitate and a yellow solution which was concentrated under reduced pressure and diluted with water (100 mL). Extraction with pentane (3 x 100 mL), back extraction with water (2 x 100 ml) and drying with Na_2SO_4 gave a yellow oil (12.5 g) which upon standing gave a significant mass of crystalline diester. Analysis of this oil showed the presence of the diester and an alkene impurity. The oil and solid was then passed through a silica gel column (ether/petroleum ether 30-60) impregnated with 20% silver nitrate[65] to afford a white solid, **3** (8.4g, 0.038mol, 60.5%). Mp 58-60°C IR (cm^{-1}) 1742 (s), 1248 (s), 1163 (s) ^{1}H ($CDCl_3$) δ [ppm] (assignment): 1.810, s, 12H (CH_2 ring), 3.645, s, 6H (OCH_3). ^{13}C ($CDCl_3$) δ [ppm] (assignment): 27.4 (C4), 38.3 (C3), 51.4 (C1), 177.4 (C2).

2.2.4 *Preparation and Characterisation of 1,4-Bicyclo[2.2.2]octane dicarboxylic acid*, 4



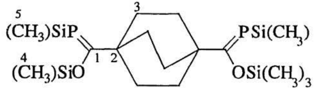
Potassium hydroxide (8.67 g, 0.155 mol) was dissolved in a 2:1 mixture of methanol and water. This clear, colourless solution was then added dropwise to the diester **3** (10.0 g, 0.0442 mol) over a period of 15 minutes and brought to reflux. After 24 hours of stirring under reflux, the pale yellow solution which resulted was made acidic (pH 1) with concentrated HCl. This afforded a white solid. This mixture was then diluted with 200mL of water and extracted with ethyl acetate (3 x 200 mL). A white solid remained in the aqueous phase. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure to afford a white solid. This was washed with water (3 x 50 mL) to give **4** (7.12 g, 0.360 mol, 81.4%). Mp >300°C IR (cm^{-1}): 3500-2650 (b), 1704 (s), 1453 (s), 1196 (b), 1040 (m), 747 (m) ^1H ($CD_3S(O)CD_3$) δ [ppm] (assignment): 1.664, s, 12H (CH_2-ring), 12.042, 2 , 2H (COOH). ^{13}C ($CD_3S(O)CD_3$) δ [ppm] (assignment): 27.5 (C3), 39.2 (C2), 178.5 (C1)

2.2.5 *Preparation and Characterisation of bis-1,4-(chlorocarbonyl) bicyclo[2.2.2]octane*, 5



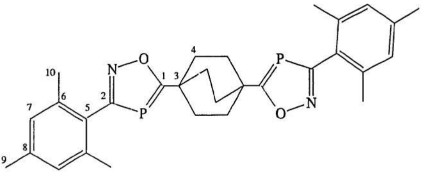
Dry diacid **4** (7.12g, 0.0360 mol) was placed in a round bottom flask with a magnetic stir bar and condenser under an argon atmosphere. Thionyl chloride (100 mL) was added to the insoluble diacid. The resulting mixture was brought to reflux and left to stir for 18 hours by which point the diacid had dissolved. The $SOCl_2$ was distilled off under vacuum (10^{-3} mmHg). The remaining solid was placed in the dry box and loaded into a sublimator. The solid sublimed at 58-62°C to yield a white crystalline solid, **5** which was stored in the dry box.(7.25g, 0.0308 mol, 85.7%). Mp 58-62°C (sub., 10^{-3} mmHg) ^1H (CD_2Cl_2) δ [ppm] (assignment): 1.91, s, 12H (CH_2-ring). ^{13}C (CD_2Cl_2) δ [ppm] (assignment): 28.2 (C3), 50.0 (C2), 179.3 (C1).

2.2.6 *Preparation and Characterisation of bis-(Trimethylsiloxy-methylidene-trimethylsilylphosphine)-1,4-bicyclo[2.2.2] octane*,**6.**



Freshly distilled *tris*-(trimethylsilyl)phosphine (4.01g, 0.016mol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of the diacid chloride **5** (1.88g, 0.0080 mol) in CH_2Cl_2 (10 mL) with stirring under a positive flow of argon. The resulting solution was pale yellow and was stirred for 7 days when the solvent was removed under vacuum and further evacuated for 60 hours with the round bottom flask immersed in a water bath at 35 ± 5°C. The recovered product was a yellow, extremely viscous oil, which was a crude mixture of **6**, TMSCl, TMS-O-TMS and other phosphorus containing impurities. (3.84 g). ^{13}C ($CDCl_3$) δ [ppm] (assignment): 1.25, 1.49 $^2J_{C,P}$ = 10 Hz (C4), 2.1 (C5), 30.5, 30.7 $^3J_{C,P}$ = 13 Hz (C3), 50.7, 51.1 $^2J_{C,P}$=28 Hz (C2), 224.1, 225.1 $^1J_{C,P}$ = 75 Hz (C1).

2.2.7 *Preparation and Characterisation of bis-(3-mesityl-1,2,4-oxazaphosphole)-1,4-bicyclo[2.2.2]octane*, **7**.



A mixture containing the bis-phosphaalkene, **6** (4.3g) generated from the procedure described previously, was dissolved in CH_2Cl_2 (75 mL) under an argon atmosphere. Dropwise addition of a solution of mesityl nitrile oxide (1.33g, 0.0165mol) in CH_2Cl_2 (25 mL) immediately changed the colour of the solution from yellow to a much darker orange. After stirring for 24 hours, the solvent was removed under vacuum (10^{-3} mmHg) to give an orange solid. Addition of pentane caused the solid to partially dissolve and left a pale yellow crystalline solid (2.4g). Extraction of the solid with benzene gave small quantities of **7** as a white crystalline solid (1.2g, 0.0024mol, 21.4% from **5**). X-ray quality crystals were obtained from slow diffusion of hexanes into a dilute solution of **7** in benzene. mp 182-4°C (decomp). ^1H (C_6D_6) δ [ppm]

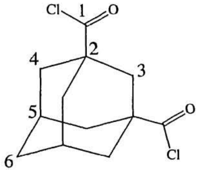
(assignment): 1.81, s, 12H ([2.2.2] ring), 2.13, s, 6H (CH_3 p-mesityl), 2.22, s, 12H (CH_3 o-mesityl) 6.78, s, 4H (CH m-mesityl). ^{13}C (C_6D_6) δ [ppm] (assignment): 21.2 (C9), 21.5 (C10), 32.2, 32.1 $^3J_{C,P}$= 7 Hz (C4), 41.0, 40.8 $^2J_{C,P}$= 12 Hz (C3), 128.5 (C8), 128.7 (C7), 136.633 (C6), 138.590 (C5), 179.436, 180.241 $^1J_{C,P}$= 61 Hz (C2), 224.4, 225.2 (C1) $^1J_{C,P}$= 64 Hz (C1). ^{31}P δ +76.6, s. M.S.(IE, 70 eV) *m/e* (assignment, % intensity): 517.96 (M^+ + 2, 3.22), 517.09 (M^+ + 1, 32.98), 516.09 (M^+, 100.00), 489.15 (1.88), 488.23 (M^+ - $C_2H_4^+$ 8.85), 371.06 (M^+ -MesC≡N, 11.26), 344.13 (6.17), 343.11 (M^+-MesC≡N,-$C_2H_4^+$, 36.46), 145.12 (Mes-C≡N, 51.47), 129.99 (85.25). Anal. calcd.: C 69.76 H 6.63 N 5.42; found: C 64.45 H 6.63 N 5.51

2.2.8 *Attempted generation of bis-(Methylidynephosphine)-1,4-bicyclo[2.2.2]octane,* 8.

A mixture containing **6** (3.84 g) was dissolved in anhydrous ethylene glycol dimethyl ether (50 mL) in a two necked round bottomed flask under argon. The yellow viscous oil dissolved immediately to a clear yellow solution. Two NaOH pellets (≈0.2 g) were then retrieved from the dry box in a Schlenk tube and crushed under argon and transferred to a two necked round bottomed flask under argon. Using a filter stick, the solution containing **6** was added to the solid NaOH. The NaOH was not soluble and the suspension was stirred for 4 days. After 4 days, the solvent was removed under vacuum to afford a yellow solid (1.48 g). This solid was insoluble in a variety of organic solvents ranging from pentane to DMSO. The ^{31}P NMR showed that no soluble phosphorus containing products were in solution.

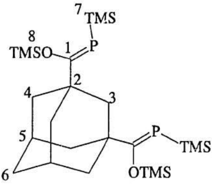
Other attempts to prepare the desired compound by varying the solvent (pentane, chloroform, methylene chloride, toluene) or amount of NaOH (5 mg to 0.5 g) failed to improve results and all observations were consistent with those described above.

2.2.9 *Preparation and Characterisation of bis-1,3-(chlorocarbonyl) adamantane*, **9**.



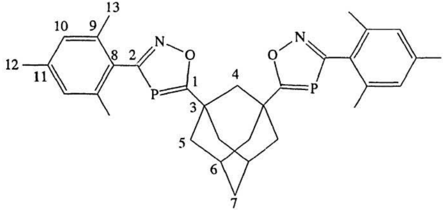
Dry diacid (6.00g 0.0267 mol) was placed in a round bottom flask with a magnetic stir bar and condenser under an argon atmosphere. Thionyl chloride (100 mL) was added to the insoluble acid. The resulting mixture was brought to reflux and left to stir for 18 hours at which point the diacid dissolved. The $SOCl_2$ was distilled off under vacuum (10^{-3} mmHg). The remaining solid was placed in the dry box and loaded into a sublimator. The solid sublimed at 65-68°C to yield a white crystalline solid, **9**, which was stored in the dry box.(6.46 g, 0.0246 mol, 92.56%). mp 65-68°C (sub., 10^{-3} mmHg) ^{1}H (CD_2Cl_2) δ [ppm] (assignment): 1.70-2.35, m, 12H (CH_2-ring). ^{13}C (CD_2Cl_2) δ [ppm] (assignment): 27.7 (C6), 34.6 (C5), 37.8 (C4), 39.8 (C3), 51.2 (C2), 178.6 (C1).

2.2.10 *Preparation and Characterisation of bis-(Trimethylsiloxymethylidene-trimethylsilylphosphine)-1,3-adamantane,* **10.**



Freshly distilled *tris*-(trimethylsilyl)phosphine (4.80 g, 0.0192 mol) in CH_2Cl_2 (25 mL) was slowly added dropwise (one drop every 12 seconds) to a solution of the diacid chloride, **5**, (1.80g, 0.00687 mol) in CH_2Cl_2 (25 mL) with stirring under a positive flow of argon. The resulting solution was pale yellow and was stirred for 7 days at which point the solvent was removed under vacuum. The resultant product was a yellow, extremely viscous oil, which was a crude mixture of **10**, TMSCl, TMS-O-TMS and other phosphorus containing impurities. (4.12 g). ^{13}C ($CDCl_3$) δ [ppm] (assignment): 1.3, 1.6 $^2J_{C,P}$ = 19 Hz (C7), 2.2 (C8), 28.9 (C6), 35.1 (C5), 40.4, 40.5 $^3J_{C,P}$ = 8 Hz (C4), 40.7, 40.8 $^3J_{C,P}$ = 8 Hz (C3), 47.8, 48.1 $^2J_{C,P}$ = 20 Hz (C2), 225.8, 226.9 $^1J_{C,P}$ = 79 Hz (C1).

2.2.11 *Preparation and Characterisation of bis-(3-mesityl-1,2,4-oxazaphosphole)-1,3-adamantane*, 11

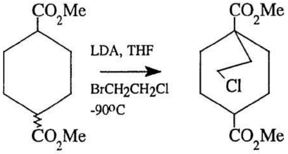


A mixture containing bis-phosphaalkene, **10**, (4.12g) generated from the procedure described previously, was dissolved in pentane (100 mL) under an argon atmosphere. Dropwise addition of a solution of mesityl nitrile oxide (2.898 g, 0.0165mol) in pentane (50 mL) immediately generated a yellow precipitate. After stirring for 24 hours, the solvent was removed under vacuum (10^{-3} mmHg) to afford a yellow-white solid, **11**, (0.75 g). Characterisation of the solid revealed a mixture of bifunctional and mono-functional heterocycles as well as other alkyl impurities. Further optimisation of this procedure was carried out on the bicyclo[2.2.2]octane derivative. ^{13}C ($CDCl_3$) δ [ppm] (assignment): 0-175, m (See **Appendix 3**) 178.9, 179.7 ${}^{1}J_{C,P}$= 61 Hz (C2), 223.5, 224.4 (C1) ${}^{1}J_{C,P}$= 68 Hz (C1).

2.3 Results and Discussion

2.3.1 Generation of the Hydrocarbon Cage Substrate.

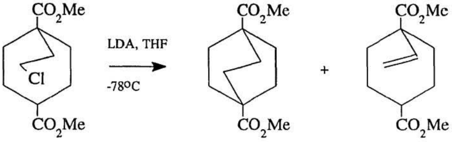
The general synthesis reported by Della et al.[61] was utilized in the preparation of the disubstituted bicyclo[2.2.2]octane moiety. This procedure required a dimethyl-1,4-cyclohexane dicarboxylate as starting material (See **Figure 2.14**).



2

Figure 2.14. Alkylation of Dimethyl 1,4-Cyclohexane Dicarboxylate.

Using dimethyl cyclohexane-1,4-dicarboxylate the mono-enolate was prepared under low temperature (kinetic) conditions from the reaction of lithium disopropylamide (LDA), HMPA and THF. This enolate was then alkylated with 1,2-chlorobromoethane to form **2**. The dimethyl 1-(2'-chloroethyl)cyclohexane-1,4-dicarboxylate, **2**, was fractionally distilled before base induced cyclization with LDA. (See **Figure 2.15**).



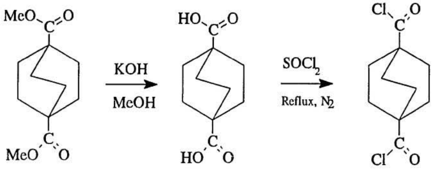
2

3

Figure 2.15 Preparation of 1,4-Bicyclo[2.2.2]octane Diester, 3, with the Alkene Impurity.

The initial reaction generated a mixture of 3 and an alkene impurity. Elution of the mixture down a 20% silver nitrate impregnated silica gel column(15) with ether/petroleum ether (50/50) and subsequent oxidation with $KMnO_4$ did indeed remove the alkene. The best results and higher overall yield were however obtained by fractional crystallization of the diester from the oil.

The diester, 3, was converted to the diacid, 4, and subsequently to the *bis*-acid chloride, 5, using standard procedures (See **Figure 2.16**). The *bis*-acid chloride, 5, was sublimed to ensure high purity and was stored under nitrogen prior to use. At each step in the procedure, the product was fully characterised by NMR, IR and melting point and was found to be consistent with the literature and structures presented.



3 4 5

Figure 2.16 Functional Group Conversion of Bicyclo[2.2.2]octane *bis*-Ester, **3** to the *bis*-Acid Chloride, **5**.

2.3.2 Generation of *bis*-(Methylidenephosphine)-1,4-bicyclo[2.2.2]octane, 6.

The procedure reported by Regitz[33] in preparation of adamantyl phosphaalkyne using *tris*-trimethylsilylphosphine was used to generate the *bis*-phosphaalkene, due to the similar properties of our substrate ie. cage hydrocarbon and bridgehead centres. Reaction of $P(TMS)_3$ with the *bis*-acid chloride, **5**, did indeed generate the *bis*-(trimethylsiloxymethylidene-trimethylsilylphosphine)-1,4-bicyclo[2.2.2]octane, **6**, which was identified by its NMR spectrum (See **Figure 2.17**). This *bis*-phosphaalkene, **6**, was present in a yellow viscous oil as a part of a mixture containing excess $P(TMS)_3$, TMSCl, and TMS-O-TMS identified by NMR (See **Figure 2.18**). The reaction was monitored by ^{13}C NMR spectroscopy which did not indicate the presence of the *bis*-acid chloride, **5**, starting material (^{13}C = 178.5 ppm) or unexpected impurities. The literature procedure for purification of adamantyl phosphaalkyne, involved fractional distillation to resolve the mixture. This was unsuccessful in our reaction due to the high temperatures required to distill the high molecular weight phosphaalkene, **6**, (MW > 500). The higher temperatures may initiate polymerisation (ie. similar to early cubane syntheses) or the temperature required to distil these compounds is too high for the compound itself to survive without decomposing. Under these conditions the reaction mixture generated an insoluble yellow solid prior to any observable distillation. Other attempts at purifying **6** such as fractional crystallization or long periods of evacuation failed to completely remove the $P(TMS)_3$.

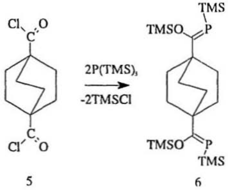


Figure 2.17 Preparation of *bis*-(Trimethylsiloxymethylidene-trimethylsilylphosphine)-1,4-bicyclo[2.2.2]octane, **6**.

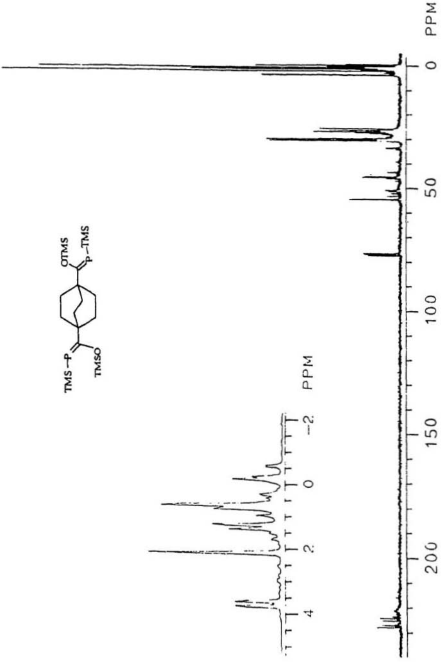


Figure 2.18 Typical ^{13}C NMR Spectra of the Mixture containing 6.

Although **6** was only observed as part of a mixture, spectroscopically it was very similar to the variety of known *mono*-phosphaalkenes. ^{13}C NMR spectroscopy was used for identification of **6** in the presence of the other constituents of the mixture ($P(TMS)_3$, TMS-O-TMS and TMSCl) and showed characteristic doublets at 224.1 ppm [with $^1J_{C,P}$ of 75 Hz for the C = P] and 1.4 ppm [$^2J_{C,P}$ = 10 Hz] corresponding to the silyl group on the phosphorus atom (**CH_3**-Si-P = C) and a singlet at 2.1 ppm resulting from the siloxy group on the carbon atom of the phosphaalkene (**CH_3**-Si-O-C = P). (See **Table 2.2**)

Table 2.2 Comparison of ^{13}C NMR Spectra (ppm) of **6** with other known phosphaalkenes.

R Group	**C** = P ($^1J_{C,P}$ Hz)	**CH_3**-Si-P = C ($^2J_{C,P}$ Hz)	**CH_3**-Si-O-C = P
R = bicyclo[2.2.2] octane	224.1 (75)	1.4 (10)	2.1
R = adamantane[33]	226.8 (78.6)	1.4 (9.4)	2.6
R = *t*-Butyl[32]	227.0 (80.5)	2.0 (10)	3.0

2.3.3 Preparation and Characterisation of *bis*-(Methylidynephosphine)-1,4-bicyclo[2.2.2]octane, 8.

Attempts to generate the phosphaalkyne from this mixture by reaction of the *bis*-phosphaalkene, **6** in solution with solid NaOH were not successful (See **Figure 2.19**). Although the *bis*-phosphaalkene, **6** mixture was stable and could be dissolved repeatedly, addition of NaOH and removal of solvent yielded an yellow solid which would not redissolve. This result was unlikely to be due to atmospheric hydrolysis or oxidation because vacuum line procedures were strictly followed. The generation of this compound was consistently observed despite changing a number of reaction conditions (absence of light, solvent, temperature and stoichiometry). The exact cause of this reaction and the identity of the yellow precipitate are not known. Contributors to this problem could be the presence of $P(TMS)_3$ in the mixture, poor quality NaOH (containing oxides or impurities) or catalytic intermolecular oligimerisation. Characterisation of this yellow solid was very difficult due to its insolubility and the chemical composition of this compound or mixture (mp > 300"C) could not be accurately determined spectroscopically.

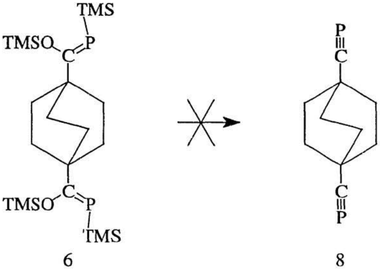


Figure 2.19 Attempted Generation of *bis*-(Methylidynephosphine)-1,4-bicyclo[2.2.2]octane, **8**.

2.3.4 1,3-Dipolar Cycloaddition Reactions of *bis*-(Methylidenephosphine)-1,4-bicyclo[2.2.2]octane, 6.

Since the *bis*-phosphaalkyne, 8,could not be generated or isolated, a "trapping reaction", to show the unequivocal presence of a *bis*-phosphaalkene, 6, as well as the potential of this route to *bis*-phosphaalkynes was proposed.

Early literature reports[66] of the *synthetic equivalency*[b] of the phosphaalkene to the phosphaalkyne, in the reaction with the well known 1,3-dipole Mes-C≡N-O[64] to generate an heterocycle called a 1,2,4-oxazaphosphole, presented the possibility of "trapping" the phosphaalkene while showing the generation of a synthetically equivalent *bis*-phosphaalkyne is possible (See **Figure 2.20**).

---

[b] Compounds are **synthetically equivalent** when their reactions produce the same product even though they feature different compositions and structure.

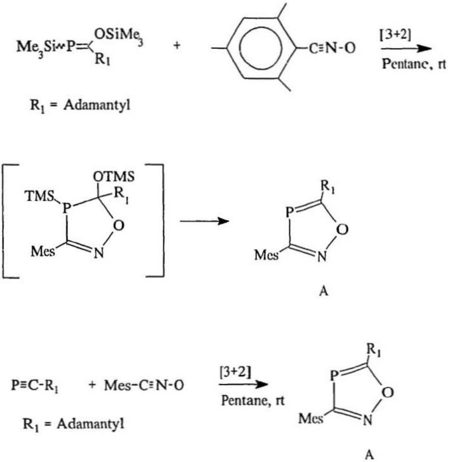


Figure 2.20 The Reaction of Mesityl Nitrile Oxide with Phosphaalkenes and Phosphaalkynes to generate 1,2,4-Oxazaphosphole Rings via the 1,3-Dipolar Cycloaddition Reaction.

This procedure is useful due to the high yield and selectivity afforded from the 1,3-dipolar cycloaddition reaction. The cycloaddition reaction generates a five membered ring termed a 1,2,4-oxazaphosphole[67]. The reaction is very sensitive to steric influences and a large substituent on the 1,3-dipole generally will control selectivity. The ring system in **B** contains two π bonds (C=N and C=P). Reported reactions indicate that the heterocycle with the P-O bond, **C** would not be favoured. This observed reaction[68] (See **Figure 2.21**) is expected because of the steric influences of the bicyclo[2.2.2]octane will dominate the dipole-dipolarophile interaction despite the oxygen atom's high affinity for phosphorus. The carbon-phosphorus π bond within the heterocycle has been shown to possess the potential for further chemistry by forming a second ring in a second 1,3-dipolar cycloaddition[68].

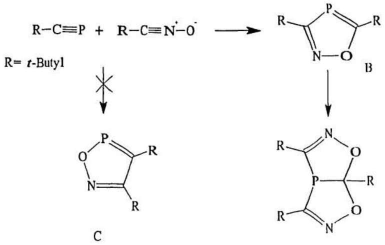


Figure 2.21 Regiochemistry of the 1,3-Dipolar Cycloaddition with Mes-CNO.

The 1,3-dipole, Mes-CNO, is a reactive but isolable species and is conveniently prepared from mesitylene in a multi-step procedure[63,64] (**See Figure 2.22**).

The reaction of the *bis*-phosphaalkene, 6 with Mes-CNO initially was unsuccessful due to a side reaction with unreacted $P(TMS)_3$ present in the reaction mixture (See **Figure 2.23**). The abstraction of the oxygen atom by the phosphine has been previously been reported[64] [Mes-CNO and PR_3 R = alkyl]. These phosphines readily adopt an equilibrium called the Arbuzov-Michaelis rearrangement[67] ($(RO)_3P \leftrightarrow (RO)_2P(O)R$). This side reaction was not immediately identified.

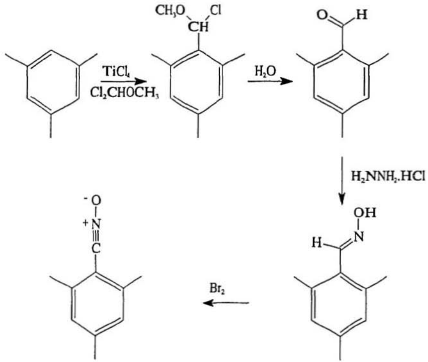


Figure 2.22 Preparation of Mes-CNO.

Confirmation of this reaction with Mes-CNO was carried out with PPh_3. The reaction quantitatively produced Mes-CN and $O=PPh_3$ and was monitored by ^{31}P NMR spectroscopy[69].

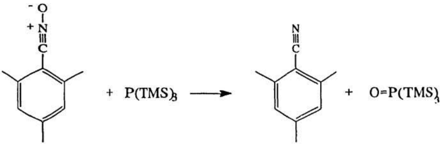


Figure 2.23 Reaction of $P(TMS)_3$ with Mes-CNO.

Synthesis of *bis*-(3-Mesityl-1,2,4-oxazaphosphole)-1,4-bicyclo[2.2.2]octane, **7** (See **Figure 2.24**) was accomplished by careful removal of the volatile contaminants in **6** by gentle heating (35 ± 5°C) and subsequent reaction with Mes-CNO in methylene chloride. In previous reports, the reaction is generally carried out in pentane because the cycloadduct is insoluble and precipitates after the cycloaddition while the starting material and reaction by-products remain in solution allowing facile separation[68]. In our case, the reaction was carried out in CH_2Cl_2 to ensure that both cyclization reactions had taken place in solution. The reaction time was also increased from 1 hour to 24 hours. The resultant mixture was then washed with pentane to separate the product from starting materials. Crystals suitable for x-ray crystallography were obtained from the mixture consisting largely of 7.

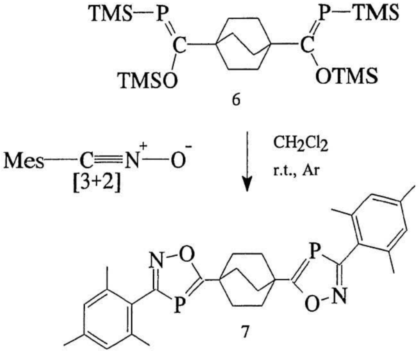


Figure 2.24 Synthesis of *bis*-(3-Mesityl-1,2,4-oxazaphosphole)-1,4-bicyclo[2.2.2]octane, **7** .

This is the first reported *bis*-1,2,4-oxazaphosphole with two independent ring systems within the same molecule. The 1,2,4-oxazaphosphole derivatives are generally colourless or pale yellow, air-stable oils or solids[87]. Such was the case with the *bis*-oxazaphosphole, **7**, melting at 182-4°C. The only described route to these molecules has been the [3 + 2] dipolar cycloaddition reaction between nitrile oxides and C = P or C ≡ P[87].

2.3.5 Spectroscopic Characterisation of *bis*-(3-Mesityl-1,2,4-oxazaphosphole)-1,4-bicyclo[2.2.2]octane, 7.

^{1}H NMR spectroscopy showed an equivalence of the mesityl ring aromatic protons as well as the *ortho*- and *para*-substituted methyl groups in solution. The completion of the reaction was demonstrated by an absence of peaks assignable to the starting materials in the ^{13}H NMR spectra (See **Figure 2.25**). The integration of the ^{1}H NMR spectrum precludes the possibility that the isolated product is the mono-derivative. ^{13}C NMR spectroscopy showed equivalence of the two mesityl and heterocyclic rings as well as the previously observed C_3 symmetry within the bicyclo[2.2.2] octane moiety (See **Figure 2.26**). The ^{13}C NMR spectrum of the heterocyclic ring showed doublets at 224 ppm and 180 ppm with $^{1}J_{C,P}$ couplings of 64 and 61 Hz respectively. Phosphorus coupling was also observed at the bridgehead carbon atom ($^{2}J_{C,P}$ = 12 Hz) and in the methylene carbon atoms in the bicyclo[2.2.2]octane ($^{3}J_{C,P}$ = 7 Hz). Phosphorus coupling ($^{3}J_{C,P}$) was not observed in the spectrum of the atoms of the aromatic substituent. These chemical shifts and couplings are consistent with other similar *mono*-oxazaphospholes (See **Table 2.3**). The ^{31}P NMR spectrum of **7** showed a singlet resonance at + 76.6 ppm which is consistent with the chemical shift reported for the adamantyl derivative at + 74.4 ppm[32,33].

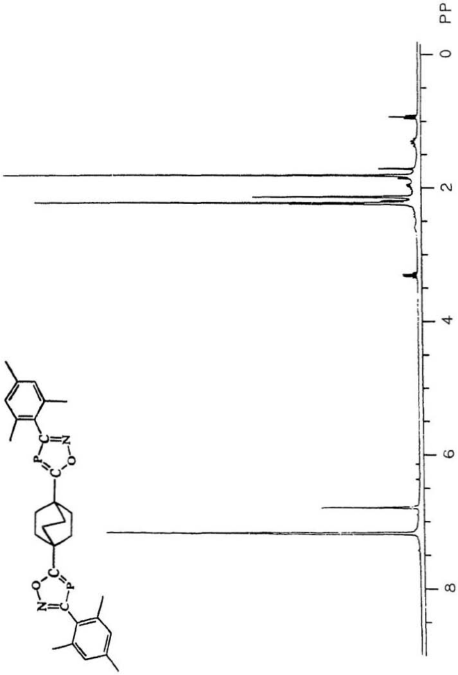


Figure 2.25 Typical ^{1}H NMR Spectrum of **7**.

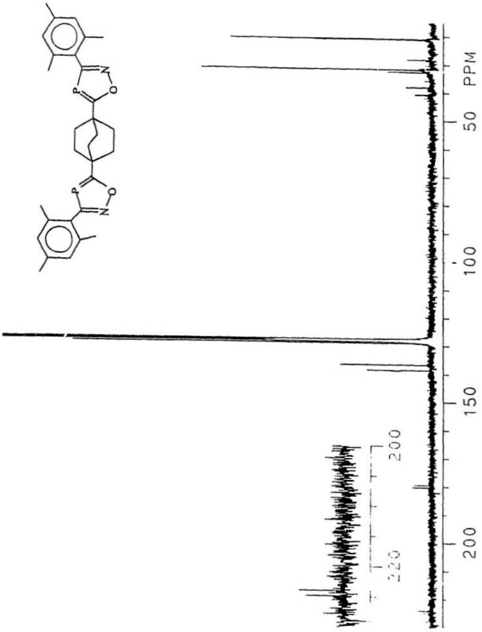


Figure 2.26 Typical ^{13}C NMR Spectrum of **7**.

Table 2.3 Characteristic ^{13}C and ^{31}P NMR spectra of 3-Mesityl-1,2,4-oxazaphospholes.

	^{13}C-NMR, δ(J, Hz)		^{31}P-NMR
	$\delta_{C\text{-}3}$ ($^1J_{C,P}$)	$\delta_{C\text{-}5}$ ($^1J_{C,P}$)	
R = [2.2.2]octane	179.4 (61.0	224.4 (64.0)	76.6
R = *t*-Butyl[32]	179.9 (61.4)	226.5 (67.1)	77.1
R = Adamantyl[33]	181.0 (61.0)	228.0 (65.0)	74.4

The mass spectrum of a sample of **7** contained the peaks assigned to the molecular ion (M^+ = 516.09) as well as significant peaks at 488 (M^+-$C_2H_4{}^+$), 371.06 (M^+-Mes-CN), 145 (Mes-C≡N) and 130. It was possible to correlate the natural isotopic abundances, using ISOMABS[70], with the observed molecular ion peaks which can be attributed to **7** (See **Table 2.4 and Figure 2.27**).

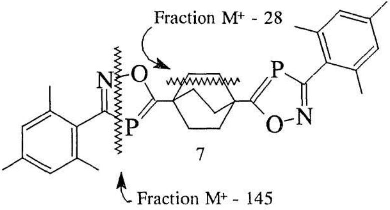


Figure 2.27 Fragmentation diagram of **7**.

Table 2.4 ISOMABS[70] analysis of atomic abundances for observed molecular ion peaks in the mass spectrum.

	Actual intensity	Calculated
516 (M)	100.00	100.00
517 (M+1)	36.46	34.681
518 (M+2)	3.22	6.232
519 (M+3)	n/d	0.700
520 (M+4)	n/d	0.064

Crystals suitable for X-ray crystallography were obtained by slow diffusion of hexanes into a dilute solution of **7** dissolved in benzene. Subsequent examination by X-ray diffraction methods identified the product unequivocally as **7** (See **Figure 2.28**). The structure obtained was the first X-ray crystal structure of a compound that contained the 1,2,4-oxazaphosphole heterocyclic ring.

A listing of crystallographic data, fractional atomic coordinates, and important bond distances and angles are given in **Appendix 2.**

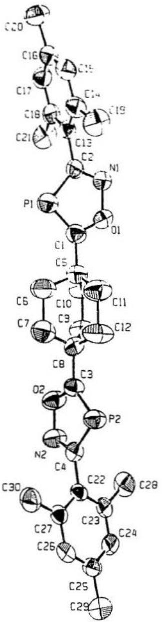
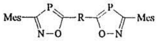
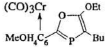
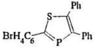
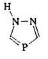


Figure 2.28 ORTEP[14] Perspective of 7.

The spectroscopic equivalence of the heterocyclic rings which was observed in solution was not observed in the solid state by crystallography, but the rings were not significantly different. The difference in bond lengths in the heterocycles reveal that the carbon-phosphorus single bonds and double bonds were clearly localized (See **Table 2.5**). A number of phosphorus containing heterocycles related to **7** are known and a comparison of the bond distances and angles around the phosphorus atom within the 1,2,4-oxazaphosphole ring is given in **Table 2.5**. We can conclude therefore, that the bonding in the heterocycle is consistent with other similar ring systems.

Table 2.5 Structural comparison of 7 with related phosphorus heterocycles.

	d C=P	d C—P	∠ C—P—C
	1.671(6) 1.675(5)	1.778(5) 1.782(5)	86.8(3) 86.8(2)
	1.705	1.772	89.5
	1.691	1.719	96.3
	1.734	n/a	87.5

The relatively small angle at the phosphorus atom [observed 86.8°, VSEPR for a sp^2 hybridized atom requires 120° ideally] was also consistent with heterocycles containing the C = P-C unit (See **Table 2.5**). This is a consequence of *orbital non-hybridization*[67,72] commonly observed in heterocycles containing phosphorus. Orbital non-hybridization is a tendency of the heavier elements **not** to hybridize in the same manner as carbon or nitrogen in chemically similar environments. Non-hybridization in effect increases the s-character of their lone pairs. Intuitively, one would expect that because the promotion energies from the s and p orbitals actually decrease[73] going from N to P that hybridization would become easier but this is not the case. This has been confirmed by *ab initio* calculations, the results of which are shown in **Figure 2.29**[73]. The small angle at the phosphorus atom is a result of this accumulation of s-character in the phosphorus non-bonding lone pairs. Therefore, the increased s-character causes the angle at phosphorus to significantly decrease from the expected 120° or because of the increasing p content of the bonding orbitals.

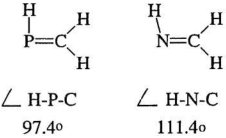


Figure 2.29 Geometrical Parameters of Mixed π-Bonded Systems.

Mes-CNO has been examined crystallographically but is disordered[74]. Similar nitrile oxides have been reported[74] with different aryl groups. In these derivatives, the bond lengths and angles in the nitrile moiety remain relatively unchanged. The expected changes from the reactant nitrile oxide to the heterocycle in **7** were observed (See **Table 2.6**) such as the lengthening of the C-N ($C{\equiv}N \rightarrow C{=}N$) and C-O bonds ($C{=}O \rightarrow C\text{-}O\text{-}C$).

Table 2.6 Comparison of **7** with known Nitrile Oxides.

Bond Length(Å) /Angle(°)	R= OMe[a]	R= Br[b]	R = bicyclo[2.2.2] octane
C-N	1.148	1.146	1.291(7) 1.272(6)
N-O	1.249	1.237	1.422(6) 1.470(6)
C_{aryl}-C	1.435	1.437	1.504(7) 1.498(8)
∠C-N-O	178.3	179.3	108.8(4) 109.4(4)
∠C-C-N	173.8	171.7	119.8(4) 119.4(4)

[a] R= **4-methoxy**-2,6-dimethylbenzonitrile oxide
[b] R= **4-bromo**-2,6-dimethylbenzonitrile oxide

The C-C distance from the benzene ring to the heterocycle lengthened with respect to the related bond in the nitrile oxide presumably due to the decrease in conjugation with the heterocycle than with the nitrile oxide. The structural features of the mesityl ring were consistent with other reported

The solid state structure of 7 also shows some unexpected conformational features. The phosphole and mesityl rings are planar as expected and have an inter-ring torsion angle that approaches 90° (P(1)-C(2)-C(13)-C(14) = 95.9(5)° and N(1)-C(2)-C(13)-C(14) = 85.0(6)°, P(2)-C(4)-C(22)-C(27) = 95.1(5)° and N(2)-C(4)-C(22)-C(27) = 83.8(6)) (See **Figure 2.30**). This conformation has been observed in other heterocycles substituted with mesityl rings[80].

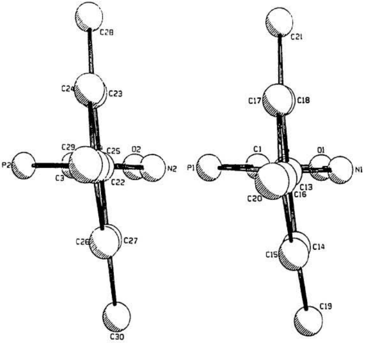


Figure 2.30 PLUTO[71] Representation of the Torsion Angle between the Phosphole and Mesityl Ring which approaches 90°.

The phosphole ring in **7** is also aligned such that the phosphorus atom is eclipsed with an C_2H_4 bridge of the bicyclo[2.2.2]octane and the oxygen and nitrogen atoms are completely staggered (See **Figure 2.31**). Each phosphole ring is aligned with a different ethylene bridge. Presumably, this conformation is a result of the small differences in distance between the oxygen and phosphorus atom from the bicyclo[2.2.2] octane cage. The smaller distance from the bridge methylene groups to the oxygen atom results in an energetic minimum favouring the observed structure.

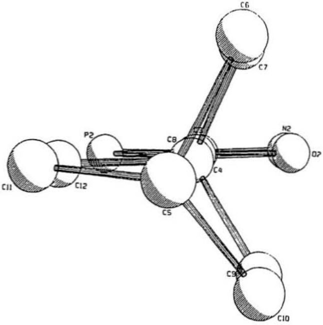


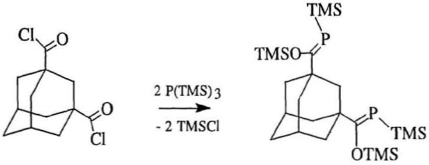
Figure 2.31 PLUTO[71] representation of the eclipsed nature of the phosphole rings with individual branches of the bicyclo[2.2.2]octane cage.

The bicyclo[2.2.2]octane cage in **7** is noticeably different from the related cage reported in the crystal structure of the 1,4-bicyclo [2.2.2]octane dicarboxylic acid derivative[75]. These differences are attributed to thermal motion and some minor disorder within the bicyclo [2.2.2]octane cage. Thermal motion within the cage is higher than the bridgehead carbons indicating some minor rotational disorder as well as higher thermal motion observed in the ethylene bridges. Also, the ethylene bridges which are eclipsed with the phosphole have greater thermal motion than the bridge which is not eclipsed which may be the cause of the observed variations (See **Appendix 2**).

2.3.6 The Attempted Generation of the Adamantyl Derivatives of 6 and 7.

The generality of the reaction described above was also explored using disubstituted 1,3-adamantyl derivatives. The commercially available 1,3-adamantyl-*bis*-carboxylic acid was easily converted to the *bis*-acid chloride, **9** from the standard procedure described for **4** → **5** (See Experimental **Section 2.2**). The *bis*-1,3-(chlorocarbonyl)adamantane, **9** was sublimed, to remove residual HCl and to ensure high purity, and stored under nitrogen prior to use.

The procedure for preparation of the *bis*-(trimethylsiloxy-methylidene-trimethylsilylphosphine)-1,3-adamantane, **10**, was identical to that described by Regitz for the adamantyl *mono*-phosphaalkene[33] and **6** (See **Figure 2.32**). As before, **10** was identified by ^{13}C NMR spectroscopy as part of a complex mixture with some other phosphorus containing compounds, $P(TMS)_3$, TMS-O-TMS, and TMSCl. Resolution of this mixture was unsuccessful due to an inability to fractionally distill the high molecular weight phosphaalkene which was consistent with initial work carried out with the 1,4-bicyclo[2.2.2]octane derivative.



9

10

Figure 2.32 Generation of the *bis*-Phosphaalkene, **10**.

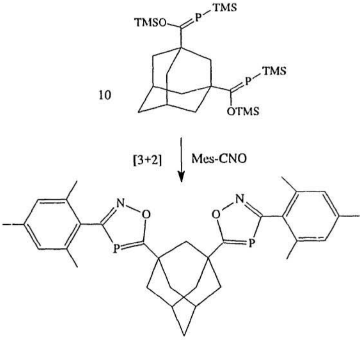
^{13}C NMR spectroscopy was used for identification of **10** and, despite the presence of a mixture, resonances were observed that were very similar to those observed for **7** and to known *mono*-phosphaalkenes (See **Table 2.7**). Characteristic doublets at 226.9 ppm [with $^1J_{C,P}$ of 79 Hz for the C=P] and 1.3 ppm [$^2J_{C,P}$ = 19 Hz] and a singlet at 2.2 ppm corresponding to the siloxy group resulting from the siloxy group on the carbon atom of the phosphaalkene (**CH_3**-Si-O-C=P).

Table 2.7 Comparison of ^{13}C NMR Spectra (ppm) of **10** with other known Phosphaalkenes.

R Group	C=P ($^1J_{C,P}$ Hz)	CH_3-Si-P=C ($^2J_{C,P}$ Hz)	CH_3-Si-O-C=P
R= 1,3-adamantane	226.9 (79)	1.3 (19)	2.2
R= bicyclo[2.2.2] octane	224.1 (75)	1.4 (10)	2.1
R= adamantane[33]	226.8 (78.6)	1.4 (9.4)	2.6
R= *t*-Butyl[32]	227.0 (80.5)	2.0 (10)	3.0

Attempts to isolate the *bis*-phosphaalkyne, **10** or the *bis*-phosphaalkyne by reaction with NaOH were not successful. As described above, a similar yellow insoluble solid was the only observed product and could not be identified (See **Section 2.3.3**).

The "trapping" of the phosphaalkene, **10**,*via* a [3 + 2] cycloaddition reaction with Mes-CNO was attempted and was successful in preparing a second *bis*-oxazaphosphole (See **Figure 2.33** and **Table 2.8**). Due to the presence of $P(TMS)_3$, however, the yield was quite low and identification was only made by ^{13}C NMR. Crystals suitable for X-ray crystallography were not obtained.



10

11

Figure 2.33 Preparation of *bis*-(3-Mesityl-1,2,4-oxazaphosphole)-1,3-adamantane, **11**.

Table 2.8 Characteristic ^{13}C and ^{31}P NMR Spectra of 3-Mesityl-1,2,4-oxazaphospholes.

	^{13}C-NMR, δ(J, Hz) $\delta_{C\text{-}3}$ ($^1J_{C,P}$)	 $\delta_{C\text{-}5}$ ($^1J_{C,P}$)	^{31}P-NMR
R= 1,3-adamantane[a]	179.7 (61.0)	224.4 (62.0)	n/a
R= bicyclo[2.2.2] octane	179.4 (61.0)	224.4 (64.0)	76.6
R= *t*-butyl[32]	179.9 (61.4)	226.5 (67.1)	77.1
R= adamantane[33]	181.0 (61.0)	228.0 (65.0)	74.4

a The peaks assigned to the 1,3-adamantyl derivative were selected from a spectrum which had other unassigned peaks present.

2.4 Conclusions

Although the generation of a *bis*-phosphaalkyne was not accomplished, this study has shown that it is indeed attainable. The synthesis as proposed was successful in generating an isolable *bis*-phosphaalkene, **6** . This phosphaalkene was indefinitely stable at room temperature with little steric protection as shown by the relative ease of cycloaddition. Characterization of this species has shown chemical similarities between the **bis-** and **mono-**substituted phosphaalkenes, suggesting the true independence of each C=P unit afforded by the bridgehead stabilization and separation.

The high molecular weight, however, of the disubstituted phosphaalkene prevented isolation and purification. It has been determined that highly pure *bis*-phosphaalkene is required to make *bis*-phosphaalkynes by traditional methods and because of this we were unsuccessful in generating a *bis*-phosphaalkyne.

The reaction mixture containing **6** was shown to have synthetic use when it was used in a 1,3-dipolar cycloaddition reaction to generate the first 1,2,4-oxazaphosphole containing two independent heterocycles within the same molecule. Along with a complete spectroscopic analysis, this molecule was also studied by X-ray crystallography revealing the first structural characterization of a 1,2,4-oxazaphosphole ring which was compared to other known phosphorus heterocycles.

Similar results were obtained by following the same reaction pathway with 1,3-disubstituted adamantane derivatives indicating that these reactions have some synthetic generality.

Since the phosphaalkene has been shown to be *synthetically equivalent* to the phosphaalkyne in the 1,3-dipolar cycloaddition reaction with Mes-CNO, our generation of **7** proves that a *bis*-phosphaalkyne may not have to be synthesized to explore the desired chemistry. We have shown that generation of two independent carbon phosphorus π systems within one molecule is possible. The chemistry of the π systems is directly analogous to that of the *mono*-phosphaalkenes but the traditional route to phosphaalkynes does not appear to work for compounds which bear two carbon phosphorus units.

2.5 Future Work

The generation of *bis*-phosphaalkyne derivatives would allow access to a variety of interesting areas which have yet to be explored. Before this chemistry can be attempted the precursor must be generated and isolated.

The primary problem with the traditional synthesis was the base catalysed elimination of TMS-O-TMS with NaOH. The reaction for *mono*-phosphaalkynes, which at best is not trivial, requires highly pure phosphaalkenes to generate the phosphaalkyne in isolable yields. This, however, is not possible for our substrates due our inability to resolve the mixture through fractional distillation. More careful examination of the yellow insoluble solids (1,4-bicyclo[2.2.2]octane, 1,3-adamantane) **(Section 2.3.3)** may be necessary to determine its origin whether through intermolecular polymerisation, caused by heat or impurity catalysis, or side reaction not yet identified.

An avenue left for this procedure would be to synthesize the *bis*-phosphaalkyne under high dilution conditions. The reactions reported in this thesis were conducted in approximately 10^{-1}M solution. More dilute solutions [$< 10^{-3}$M] may effectively minimize intermolecular interactions.

Other possible answers to the problem of generating a *bis*-phosphaalkyne, may be the elimination of a different thermodynamically stable small molecule. Elimination of a molecule of TMSCl or perhaps LiOTMS (See **Figure 2.34**) may allow a more facile separation. This procedure seems to be very appealing due to its mild conditions and spontaneous eliminations.

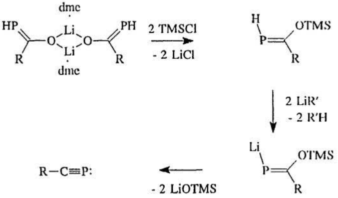


Figure 2.34 Elimination of Lithium Trimethylsilanolate to generate R-C≡P.

A more advantageous answer may be found in a comment by Regitz[2] "It has been found advantageous not to perform the reaction 12→3 [C=P → C≡P] in solution, as originally reported, but rather to work at temperatures of 120-200°C in the absence of solvent."[3] This preferred procedure is not properly described in the literature. The low yields obtained from the literature preparations of Adm-C≡P and *t*-butyl by various workers in our lab may be explained by the known difficulties of the literature procedure.

Another avenue to *bis*-phosphaalkynes that may be useful would be a three step process involving: i) 1,2-phosphonium addition to the *bis*-phosphaalkene ii) TMS-O-TMS elimination followed by iii) base induced elimination of hydrogen. Using a new reaction recently discovered in our laboratory(69), a *bis*-phosphaalkyne may be isolated from our existing mixtures. Dr. Jason Clyburne has shown, using the phosphonium cation ($H\text{-}{}^{+}PPh_3$), that this cation will add across R-C≡P quantitatively to generate $R\text{-}CH=P^{+}\text{-}PPh_3$ (See **Figure 2.35**).

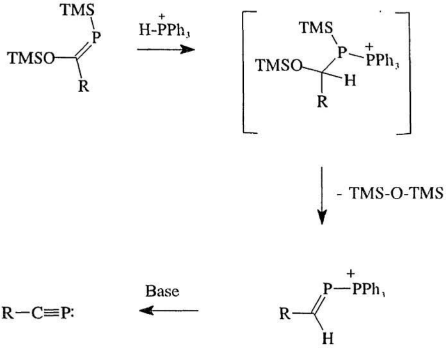


Figure 2.35 Use of a Phosphonium cation to generate Phosphaalkynes.

The generation of a member of this family of compounds has been reported[76] via a different route but it does provide an interesting potential route to phosphaalkynes. Addition of the phosphonium salt to our mixture will immediately generate a cationic species by addition across the C=P bond. Following the spontaneous elimination of TMS-O-TMS, the C=P is reformed and results in the generation of a stable cation. In spite of the $P(TMS)_3$

impurity, extraction or evacuation of the phosphine from the ionic species will allow purification of the cation. Addition of a strong base, such as BuLi, should allow elimination of the PPh_3 and facile separation of the phosphaalkyne, presumably by sublimation.

A number of chemical avenues become available following the generation of the *bis*-phosphaalkyne. Obvious chemical reactions to pursue include the generation of more heterocycles via 1,3-dipolar cycloaddition reactions and the organometallic chemistry available with a bidentate ligand (See **Section 2.1**). Also, of interest would be the possible polymerisation products which could come about using a disubstituted 1,3-dipole or generation of covalently bonded diamondoid networks while synthesizing the phosphacubane.

References

1. D.K. Padma and R. Mews. *Z. Naturforsch. B: Chem. Sci.* **42**, 699 (**1987**). W. Bludssus and R. Mews. *J. Chem. Soc. Chem. Commun.* 35 (**1979**).
2. M. Regitz. *Chem. Rev.* **90**, 191 (**1990**).
3. A. Padwa (Editor) *1,3-Dipolar Cycloaddition Chemistry.* John Wiley and Sons, New York (**1984**).
4. S. Parsons, J. Passmore, M.J. Schriver, and X. Sun. *Inorg. Chem.* **30**, 3342 (**1991**).
5. K.S.Pitzer. *J. Am. Chem. Soc.* **70**, 2140, (**1948**).
6. R.S. Mulliken. *ibid.* **72**, 4493 (**1950**).
7. A. Senning and P. Kelly. *Acta. Chem. Scand.* **21**, 1871 (**1967**).
8. E. Muhlbauer and W. Weiss Brit. 1,079,348, Aug. 16 1967; Ger. Appl. May 8, 1965; **Chem Abstr. 68**, 69000 (**1968**).
9. M. Yoshifugi, I. Shima, and N. Inamoto. *J. Am. Chem. Soc.* **103**, 4587 (**1981**).
10. A.H. Cowley, J.E. Kilduff, T.H. Newman, and M.J.Pakulski. *J. Am. Chem. Soc.* **104**, 5280 (**1982**).
11. R.J. Boyd and S.L. Boyd. *J. Am. Chem. Soc.* **114**, 1652 (**1992**).
12. B.S. Furniss, A.J. Hannaford, P.W.G. and Smith, A.R. Tactchell. *Vogel's Textbook of Practical Organic Chemistry* 5th Ed. John Wiley and Sons, New York (**1989**).
13. J.N. Bridson, S.B. Copp, M.J. Schriver, and S. Zhu. *Can. J. Chem.* **72**, 1143 (**1994**).
14. C.K. Johnson. *ORTEPII. Report ORNL-5138* Oak Ridge National Laboratory, Oak Ridge, Tennessee (**1976**).

15. M.J. Schriver and M.J. Zaworotko. *J. Chem. Cryst.* **25**, 25 (**1995**).

16. B. Bak, O. Neilson, H. Svanholt, A. Almennigen, O Bastiansen, G. Braathen, L. Fernholt, G. Gunderson, C.J. Neilsen, B.N. Cyvin and S. Cyvin. *Acta Chem. Scand.* **36A**, 283 (**1982**).

17. B. Bak, O. Neilsen, H. Svanholt, A. Almennigen, O. Bastiansen, L. Fernholt, G. Gunderson, C.J. Neilsen, B.N. Cyvin and S. Cyvin. *Acta Chem. Scand.* **32A**, 1005 (**1978**).

18. R.C. Weast. (Editor) *CRC Handbook of Chemistry and Physics* CRC Press, Florida (**1978**).

19. L. Pauling. *The Nature of the Chemical Bond* 3rd ed. Cornell University Press, Ithaca (**1960**).

20. S.C. Nyburg. *J. Cryst. Mol. Struct.* **3**, 331 (**1973**).

21. J. Bridson, M. Schriver and S. Zhu, in press / unpublished results.

22. M. Paton. *Chem. Soc. Rev.* **18**, 33 (**1989**). S. Patai and Z. Rappaport. (Editors) *The Chemistry of Functional Groups, Supplement C* John Wiley and Sons, New York (**1983**).

23. Valerie Jefford, Honours Thesis, Memorial University of Newfoundland (**1995**).

24. M. Regitz. *J. Heterocyclic Chem.* **34**, 663 (**1994**). M. Regitz and P. Binger. *Angew. Chem. Int. Ed. Engl.* **27**, 1484 (**1988**). R. Streubel *Angew. Chem. Int. Ed. Engl.* **34**, 436 (**1995**).

25. M. Regitz. *Heteroatom Chemistry* VCH Publishers, New York (**1990**).

26. J.F. Nixon. *Endeavour* **15**, 49 (**1991**). J.F. Nixon. *Chemistry and Industry* 7 June **1993** pg. 404.

27. T.E. Gier. *J. Am. Chem. Soc.* **83**, 1769 (**1961**).

28. G. Markl. *Angew. Chem. Int. Ed. Engl.* **5**, 846 (**1966**).

29. K. Dimroth and P. Hoffman. *Angew. Chem. Int. Ed. Engl.* **3**, 384 (**1964**).

30. M.J. Hopkinson, H.W. Kroto, J.F. Nixon and N.P.C. Simmons. *Chem. Commun.* 513 (**1976**).

31. H.W. Kroto, J.F. Nixon, N.P.C. Simmons and N.P.C. Westwood. *J. Am. Chem. Soc.* **100**, 446 (**1978**).

32. G. Becker, G. Gresser, and W. Uhl. *Z. Naturforsch. B.* **36**, 16 (**1981**).

33. T. Allspach, M. Regitz, G. Becker, and W. Becker. *Synthesis* 31 (**1986**).

34. E.P.O. Fuchs, M. Hermesdorf, W. Schnurr, W. Rosch, H. Heydt, and M. Regitz. *J. Organomet. Chem.* **338**, 329 (**1987**).

35. K. Ohno, H.W. Kroto, and J.F. Nixon *J. Mol. Spectrosc.* **90** 507 (**1981**). N.P.C Westwood, H.W. Kroto, N.P.C. Simmons and J.F. Nixon. *J. Chem. Soc. Dalton Trans.* 1405 (**1979**). J.C.T.R. Burckett-St. Laurent, T.A. Cooper, K. Ohno, H.W. Kroto, J.F. Nixon and O. Ohashi. *J. Mol. Struct.* **79** 215 (**1982**).

36. M. Regitz and M. Hermesdorf. unpublished results (**1989**).

37. G. Bertrand and R. Reed. *Coor. Chem. Rev.* **137**, 323 (**1994**).

38. D.E.C. Corbridge. *The Structural Chemistry of Phosphorus* Elsevier, New York (**1990**).

39. H. Bock and H. Muller. *Inorg. Chem.* **23** 4365 (**1984**).

40. E. Neicke, M. Nieger, and F. Reichert. *Angew. Chem. Int. Ed. Engl.* **27**, 1715 (**1988**).

41. A.J. Ashe. *Topics Current Chem.* **105**, 125 (**1982**).

42. K. Jayasuriya. *J. Mol. Struct.* **256**, 17 (**1992**).

43. K. Jayasuriya. *J. Mol. Struct.* **257**, 405 (**1992**).

44. K. Jayasuriya. *Int. J. of Quan. Chem.* **44**, 327 (**1992**).

45. J.C.T.R. Burckett-St. Laurent, P.B. Hitchcock, H.W. Kroto, J.F. Nixon. *Chem. Commun.* 1141 **(1981)**.

46. P.B. Hitchcock, M.J. Maah, J.F. Nixon, J.A. Zora, G.J. Leigh, and M.A. Bakar. *Angew. Chem. Int. Ed. Engl.* **26**, 474 **(1987)**.

47. R. Bartsch, P.B. Hitchcock and J.F. Nixon. *Chem. Commun.* 1146 **(1987)**.

48. P.B. Hitchcock, M.J. Maah and J.F. Nixon. *Chem. Commun.* 737 **(1986)**.

49. T. Wettling, J. Schneider, O. Wagner, C.G. Kreiter and M. Regitz. *Angew. Chem. Int. Ed. Engl.* **28**, 1013 **(1989)**.

50. P. Binger, B. Biedenbach, C. Kruger and M. Regitz. *Angew. Chem. Int. Ed. Engl.* **26**, 764 **(1987)**.

51. R. Streubel. *Angew. Chem. Int. Ed. Engl.* **4**, 34 **(1995)**.

52. M. Regitz and T. Allspach. *Chem. Ber.* **120**, 1269 **(1987)**.

53. A. Jouaiti, M. Geoffrey, and G. Bernardinelli. *J. Chem. Soc. Dalton Trans.* 1685 **(1985)**.

54. K. Toyota, K. Masaki, T. Abe and M. Yoshifugi. *Chem. Lett.* 221 **(1995)**. K. Toyota, K. Tashiro, T. Abe and M. Yoshfugi. *Heteroatom Chem.* **5**, 549 **(1994)**.

55. A.N. Chernega, V.V. Penkorskii and V.D. Romanenko. *J. Chem. USSR Eng.* **63**, 60 **(1993)**.

56. M. Neiger, N. Siabalis and R. Appel. *Z. Krystallographie* **206**, 295 **(1993)**.

57. F. Knoch, R. Appel and H. Wenzel. *Z. Krystallographie* **210**, 224 **(1995)**.

58. P.C. Guha. *Ber. Dtsch. Chem. Ges.* **46**, 4795 **(1981)**.

59. J.C. Kauer, R.E. Benson, and S.W. Parshall. *J. Org. Chem.* **30**, 1431 (**1965**).

60. J.C. Kauer. *Chem. Abstr.* **65**, 14529e (**1965**).

61. E.W. Della and J. Tsanaktsidis. *Aust. J. Chem.* **38**, 1705 (**1985**).

62. G. Becker, H. Schmidt, G. Uhl and W. Uhl. *Inorg. Syn.* **27**, 243 (**1990**).

63. A. Reiche, H. Gross, and E. Hoft. *Org. Syn.* **V** 49.

64. C. Grundmann and J.M. Dean. *J. Org. Chem.* **30**, 2805 (**1965**).

65. P.Y. Liu. *Ph.D. Thesis* Memorial University of Newfoundland (**1992**).

66. W. Rosch, U. Vogelbacher, T. Allspach and M. Regitz. *J. Organomet. Chem.* **306**, 39 (**1986**).

67. M. Regitz and O.J. Scherer (editors). *Multiple Bonds and Low Coordination in Phosphorus Chemistry* Theime Medical Publishers, Inc. New York (**1990**).

68. W. Rosch and M. Regitz. *Synthesis* 689 (**1987**).

69. J.A.C. Clyburne. personal communication (**1995**).

70. **ISOMABS** - a computor program developed by S.J. Grossert available as SHAREWARE. Dalhousie University, Halifax, NS.

71. S. Motherwell and W. Clegg. *PLUTO. A Program for Plotting Molecular and Crystal Structures.* University of Cambridge, England (**1978**).

72. P.J. Bruna, V. Krumbach, and S.D. Peyerimhoff. *Can. J. Chem.* **63**, 1594 (**1985**).

73. C.E. Moore. *Atomic Energy Levels* National Bureau of Standards, Washington, D.C. **1949**.

74. M. Shiro, M. Tamakawa, and T. Kubota. *Acta Cryst.* **B35**, 712 (**1979**).

75. O. Ermer and J.D. Dunitz. *Chem. Commun.* 567 (**1968**).

76. G. David, E. Niecke, M. Nieger, and J. Radsack. *J. Am. Chem. Soc.* 116, 2191 (1994).

Appendix
Table of Contents

---

[a] Numbers correspond to those used in Chapter 2.

Appendix 1 X-Ray Crystal Structure of 1.

Table A1.1 Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 1.

Compound	$C_{12}H_{15}NO_2S$
Color	clear
Formula Wt.	237.31
Crystal System	monoclinic
Space Group	$P2_1/c$
Temp, °C	17
Cell constants[a]	
a, Å	11.334(2)
b, Å	7.344(1)
c, Å	14.373(2)
β, °	107.740(10)
Cell Volume, $Å^3$	1139.5(3)
F(000)	504
Z	4
D_{calc}, g cm^{-3}	1.383
μ_{calc}, cm^{-1}	0.026
Scan Type	$\omega/2\theta$
Radiation	MoK_α
Max. Xtal Dimensions, mm	.40 x .33 x .15
Scan Width	$.80 + .35\tan\theta$
Transmission Range	.818, .989
Decay of Standards	±2%
Reflections Measured	1571
2θ range, °	2-45
Unique Reflections	1485
Reflections Observed[b]	1085
Computer Programs[c]	NRCVAX[d]
Structure Solution	Direct
Number Parameters	145
Weight modifier, k	.00002
G.O.F.	3.14
R	0.039
R_w	0.042
Final Diff. Map (e/$Å^3$)	0.19

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections $\theta > 14°$

[b] $I > 2.5\sigma(I)$. Corrections: Lorentz-polarization and absorption (empirical psi scan)

[c] Neutral scattering factors and anomalous dispersion corrections from reference 13;

[d] an Interactive Program System for Structure Analysis, E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, J. Appl. Cryst. **22**, 384, 1989.

Table A1.2 Final Atomic Parameters x,y,z and B_{iso} for $C_{12}H_{15}NO_2S$, 1.

	x	y	z	B_{iso}
S	.47194(10)	.40129(15)	.22348(8)	3.92 (5)
O1	.26283(23)	.3929 (4)	.09445(17)	3.76(13)
O2	.2901 (3)	.1538 (4)	.19784(22)	5.38(17)
N	.4359 (3)	.5699 (4)	.13879(21)	3.54(16)
C1	.3300 (4)	.2900 (6)	.1744 (3)	3.71(21)
C2	.3277 (4)	.5435 (5)	.0804 (3)	3.01(19)
C3	.2606 (3)	.6617 (5)	-.0033 (25)	3.03(18)
C4	.1379 (3)	.7305 (5)	.0121 (3)	3.32(19)
C5	.0677 (3)	.8500 (5)	-.0749 (3)	3.52(19)
C6	.0374 (4)	.7377 (6)	-.1691 (3)	3.69(19)
C7	.1577 (4)	.6717 (6)	-.1855 (3)	3.72(21)
C8	.2291 (3)	.5504 (5)	-.0990 (3)	3.45(19)
C9	.2372 (4)	.8350 (6)	-.1929 (3)	4.18(21)
C10	.1474 (4)	1.0129(6)	-.0816 (3)	4.14(23)
C11	.2681 (4)	.9460 (6)	-.0981 (3)	4.02(20)
C12	.3409 (4)	.8266 (6)	-.0114 (3)	3.86(20)

B_{iso} is the Mean of the Principal Axes of the Thermal Ellipsoid

Table A1.3 Selected bond lengths (Å) and angles (°) in $C_{10}H_{15}$-COC(O)SN, 1.

Bond Lengths		Bonds Angles	
S-N	1.687(3)	N-S-C(1)	93.5(2)
S-C(1)	1.750(4)	S-N-C(2)	109.6(3)
O(1)-C(1)	1.392(5)	C(1)-O(1)-C(2)	112.0(3)
O(1)-C(2)	1.377(5)	S-C(1)-O(1)	106.5(3)
O(2)-C(1)	1.188(5)	S-C(1)-O(2)	131.4(3)
N-C(2)	1.272(5)	O(1)-C(1)-O(2)	122.1(4)
C(2)-C(3)	1.491(5)	O(1)-C(2)-N	118.4(3)
C(3)-C(4)	1.557(5)	O(1)-C(2)-C(3)	115.0(3)
C(3)-C(8)	1.545(5)	N-C(2)-C(3)	126.6(3)
C(3)-C(12)	1.541(5)	C(2)-C(3)-C(4)	109.4(3)
C(4)-C(5)	1.536(5)	C(2)-C(3)-C(8)	109.4(3)
C(5)-C(6)	1.532(5)	C(2)-C(3)-C(12)	110.5(3)
C(5)-C(10)	1.519(6)	C(4)-C(3)-C(8)	108.9(3)
C(6)-C(7)	1.531(6)	C(4)-C(3)-C(12)	109.2(3)
C(7)-C(8)	1.543(5)	C(8)-C(3)-C(12)	109.3(3)
C(7)-C(9)	1.524(6)		
C(9)-C(11)	1.534(6)		
C(10)-C(11)	1.539(6)		
C(11)-C(12)	1.542(6)		

Table A1.4 Distances(Å) to the least-squares planes.

Plane no. 1

Equation of the plane :- $6.794(12)X + 3.941(11)Y + 10.755(13)Z = .778(8)$

Distances(Å) to the plane from the atoms in the plane.

S	.0002(16)	O1	.000(4)
N	-.002(4)	C1	-.002(5)
C2	.002(5)		

Chi squared for this plane .445

Distances(Å) to the plane from the atoms out of the plane.

O2	-.016(5)	C3	.023(6)

Plane no. 2

Equation of the plane :- $6.819(9)X + 3.916(7)Y + 10.776(11)Z = .761(5)$

Distances(Å) to the plane from the atoms in the plane.

S	.0006(16)	O1	.003(3)
O2	-.005(4)	N	-.006(4)
C1	.004(5)	C2	.000(5)

Chi squared for this plane 6.111

Plane no. 3

Equation of the plane :- $6.814(8)X + 3.904(6)Y + 10.800(8)Z = .763(5)$

Distances(Å) to the plane from the atoms in the plane.

S	.0011(16)	O1	.000(3)
O2	-.003(4)	N	-.010(4)
C1	.004(5)	C2	-.006(4)
C3	.009(5)		

Chi squared for this plane 14.942

Appendix 2 X-Ray Crystal Structure of 7.

Table A2.1 Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 7.

Compound	$C_{30}H_{34}O_2P_2N_2$
Color	Colorless
Formula Weight	516.56
Crystal System	monoclinic
Space Group	$P2_1/c$ (#14)
Temp, °C	26
Cell constants[a]	
a,Å	8.807(7)
b,Å	13.576(8)
c,Å	23.741(6)
b,°	97.78(4)
Cell Volume, Å^3	2813
F(000)	1096
D_{calc}, g/cm^3	1.220
μ_{calc}, cm^{-1}	1.78
Scan type	ω-2θ
Radiation	MoK_α
Max. Xtal Dimensions, mm	0.40 x 0.25 x 0.42
Scan Width	1.57 + tanθ
Reflections Measured[b]	5584
2θ range	50.2
Unique Reflections	5224
Computer Program[c]	NRCVAX[d]
Structure Solution	Direct
G.O.F.	2.64
R	0.065
R_w	0.048
Final Diff. Map(e$^-$/Å^3)	0.37

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections $\theta > 14°$

[b] $I > 2.5\sigma(I)$. Corrections: Lorentz-polarization and absorption (empirical psi scan)

[c] Neutral scattering factors and anomalous dispersion corrections from reference 13;

[d] an Interactive Program System for Structure Analysis, E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, J. Appl. Cryst. 22, 384, 1989.

Table A2.2 Final Atomic Coorinates x,y,z and B_{iso} for **7**.

Atom	x	y	z	B_{iso}
P(1)	1.0564(2)	0.5800(1)	0.07362(8)	7.3(1)
P(2)	0.2681(2)	0.3107(1)	0.12911(7)	6.37(8)
O(1)	0.8626(4)	0.6941(3)	0.1101(2)	6.6(2)
O(2)	0.5010(4)	0.2650(3)	0.1995(2)	7.0(2)
N(1)	0.9786(5)	0.7597(3)	0.0969(2)	6.7(3)
N(2)	0.3858(5)	0.1995(3)	0.2131(2)	6.8(3)
C(1)	0.8915(6)	0.5991(4)	0.0995(2)	5.1(3)
C(2)	1.0838(6)	0.7097(4)	0.0778(2)	4.3(3)
C(3)	0.4520(5)	0.3261(4)	0.1565(2)	4.7(3)
C(4)	0.2611(5)	0.2160(3)	0.1807(2)	4.2(2)
C(5)	0.7706(6)	0.5303(4)	0.1150(2)	5.3(3)
C(6)	0.8239(7)	0.4207(5)	0.1053(3)	9.2(4)
C(7)	0.6994(7)	0.3466(5)	0.1210(3)	8.8(4)
C(8)	0.5712(5)	0.3978(4)	0.1423(2)	4.7(3)
C(9)	0.6329(6)	0.4618(4)	0.1929(2)	6.6(3)
C(10)	0.7544(6)	0.5342(4)	0.1765(2)	6.6(3)
C(11)	0.6265(7)	0.5373(5)	0.0760(3)	8.1(4)
C(12)	0.5036(6)	0.4650(5)	0.0932(3)	9.2(4)
C(13)	1.2205(5)	0.7609(3)	0.0612(2)	4.1(3)
C(14)	1.2155(6)	0.8011(4)	0.0072(2)	5.2(3)
C(15)	1.3479(7)	0.8414(4)	-0.0095(2)	5.7(3)
C(16)	1.4848(7)	0.8409(4)	0.0268(3)	5.9(3)
C(17)	1.4864(6)	0.8053(4)	0.0806(3)	5.6(3)
C(18)	1.3561(6)	0.7650(4)	0.0986(2)	4.8(3)
C(19)	1.0673(6)	0.8039(5)	-0.0336(2)	8.4(4)
C(20)	1.6336(7)	0.8804(5)	0.0079(3)	9.4(4)
C(21)	1.3626(6)	0.7292(4)	0.1595(2)	7.3(3)
C(22)	0.1229(5)	0.1559(3)	0.1871(2)	3.7(2)
C(23)	0.0122(6)	0.1951(4)	0.2176(2)	4.4(3)
C(24)	-0.1215(6)	0.1429(4)	0.2199(2)	5.2(3)
C(25)	-0.1488(6)	0.0538(4)	0.1926(2)	5.3(3)
C(26)	-0.0372(6)	0.0155(4)	0.1644(2)	5.1(3)
C(27)	0.0996(6)	0.0646(4)	0.1613(2)	4.3(3)
C(28)	0.0386(6)	0.2921(4)	0.2491(2)	6.4(3)
C(29)	-0.3011(6)	0.0007(5)	0.1942(3)	8.9(4)
C(30)	0.2170(6)	0.0187(4)	0.1285(2)	7.0(3)

Table A2.3 Selected bond lengths (Å) in **7**.

Bonds	Lengths	Bonds	Lengths
P(1)-C(1)	1.671(6)	C(9)-C(10)	1.542(8)
P(1)-C(2)	1.778(5)	C(11)-C(12)	1.557(9)
P(2)-C(3)	1.675(5)	C(13)-C(14)	1.388(8)
P(2)-C(4)	1.782(5)	C(13)-C(18)	1.391(7)
O(1)-N(1)	1.422(6)	C(14)-C(15)	1.394(8)
O(1)-C(1)	1.345(7)	C(14)-C(19)	1.517(7)
O(2)-N(2)	1.420(6)	C(15)-C(16)	1.384(8)
O(2)-C(3)	1.341(6)	C(16)-C(17)	1.365(9)
N(1)-C(2)	1.281(7)	C(16)-C(20)	1.538(9)
N(2)-C(4)	1.272(6)	C(17)-C(18)	1.390(8)
C(1)-C(5)	1.498(8)	C(18)-C(21)	1.517(8)
C(2)-C(13)	1.489(7)	C(22)-C(23)	1.397(7)
C(3)-C(8)	1.504(7)	C(22)-C(27)	1.385(7)
C(4)-C(22)	1.490(7)	C(23)-C(24)	1.382(7)
C(5)-C(6)	1.586(9)	C(23)-C(28)	1.516(7)
C(5)-C(10)	1.487(8)	C(24)-C(25)	1.378(8)
C(5)-C(11)	1.469(8)	C(25)-C(26)	1.366(8)
C(6)-C(7)	1.570(9)	C(25)-C(29)	1.527(8)
C(7)-C(8)	1.473(9)	C(26)-C(27)	1.388(8)
C(8)-C(9)	1.522(7)	C(27)-C(30)	1.511(8)
C(8)-C(12)	1.534(8)		

Table A2.4 Selected Bond Angles (°) in **7**.

Bonds	Angle	Bonds	Angle
C(1)-P(1)-C(2)	86.8(3)	C(3)-C(8)-C(7)	111.2(5)
C(3)-P(2)-C(4)	86.8(2)	C(3)-C(8)-C(9)	112.1(4)
N(1)-O(1)-C(1)	113.5(4)	C(3)-C(8)-C(12)	110.1(4)
N(2)-O(2)-C(3)	113.2(3)	C(7)-C(8)-C(9)	109.4(4)
O(1)-N(1)-C(2)	108.8(4)	C(7)-C(8)-C(12)	104.9(5)
O(2)-N(2)-C(4)	109.7(4)	C(9)-C(8)-C(12)	108.7(5)
P(1)-C(1)-O(1)	114.4(4)	C(8)-C(9)-C(10)	110.4(5)
P(1)-C(1)-C(5)	132.4(4)	C(5)-C(10)-C(9)	112.8(4)
O(1)-C(1)-C(5)	113.1(4)	C(5)-C(11)-C(12)	111.5(5)
P(1)-C(2)-N(1)	116.4(4)	C(8)-C(12)-C(11)	111.2(4)
P(1)-C(2)-C(13)	123.9(4)	C(2)-C(13)-C(14)	120.2(4)
N(1)-C(2)-C(13)	119.8(4)	C(2)-C(13)-C(18)	120.3(5)
P(2)-C(3)-O(2)	114.4(4)	C(14)-C(13)-C(18)	119.5(5)
P(2)-C(3)-C(8)	131.4(4)	C(13)-C(14)-C(15)	119.6(5)
O(2)-C(3)-C(8)	114.2(4)	C(13)-C(14)-C(19)	121.1(5)
P(2)-C(4)-N(2)	115.8(4)	C(15)-C(14)-C(19)	119.3(5)
P(2)-C(4)-C(22)	124.7(3)	C(14)-C(15)-C(16)	120.9(5)
N(2)-C(4)-C(22)	119.4(4)	C(15)-C(16)-C(17)	118.9(6)
C(1)-C(5)-C(6)	108.4(5)	C(15)-C(16)-C(20)	121.5(6)
C(1)-C(5)-C(10)	112.6(4)	C(17)-C(16)-C(20)	119.7(5)
C(1)-C(5)-C(11)	112.8(5)	C(16)-C(17)-C(18)	121.6(5)
C(6)-C(5)-C(10)	104.2(5)	C(13)-C(18)-C(17)	119.5(5)
C(6)-C(5)-C(11)	102.5(5)	C(13)-C(18)-C(21)	121.0(5)
C(10)-C(5)-C(11)	115.3(5)	C(17)-C(18)-C(21)	119.5(5)
C(5)-C(6)-C(7)	109.7(5)	C(4)-C(22)-C(23)	118.8(4)
C(6)-C(7)-C(8)	111.7(5)	C(4)-C(22)-C(27)	121.3(4)
C(23)-C(22)-C(27)	119.9(4)	C(22)-C(23)-C(24)	118.9(5)
C(22)-C(23)-C(28)	121.1(4)	C(24)-C(23)-C(28)	120.1(5)
C(23)-C(24)-C(25)	121.9(5)	C(24)-C(25)-C(26)	118.3(5)
C(24)-C(25)-C(29)	120.1(5)	C(26)-C(25)-C(29)	121.7(5)
C(25)-C(26)-C(27)	122.0(5)	C(22)-C(27)-C(26)	119.0(5)
C(22)-C(27)-C(30)	121.8(4)	C(26)-C(27)-C(30)	119.2(5)

Table A2.5 Table of Least-Squares Planes for 7.

------------- Plane number 1 --------------

Atoms Defining Plane	Distance	esd
C(13)	0.0183	0.0048
C(14)	-0.0096	0.0054
C(15)	-0.0134	0.0054
C(16)	0.0254	0.0057
C(17)	-0.0099	0.0057
C(18)	-0.0124	0.0050

Mean deviation from plane is 0.0148 angstroms
Chi-squared: 52.7

-------------- Plane number 2 ---------------

Atoms Defining Plane	Distance	esd
P(1)	0.0005	0.0018
C(1)	-0.0043	0.0049
O(1)	0.0013	0.0035
N(1)	0.0011	0.0046
C(2)	-0.0029	0.0045

Mean deviation from plane is 0.0020 angstroms
Chi-squared: 1.4

Dihedral angles between least-squares planes

plane	plane	angle
2	1	96.95

-------------- Plane number 3 ---------------

Atoms Defining Plane	Distance	esd
P(2)	0.0007	0.0016
C(3)	-0.0049	0.0051
O(2)	0.0000	0.0039
N(2)	0.0059	0.0046
C(4)	-0.0078	0.0047

Mean deviation from plane is 0.0039 angstroms
Chi-squared: 5.5

```
      Table of Least-Squares Planes (continued)
      -----------------------------

-------------- Plane number  4 ---------------

Atoms Defining Plane      Distance      esd
     C(22)              -0.0144     0.0045
     C(23)               0.0062     0.0047
     C(24)               0.0088     0.0051
     C(25)              -0.0161     0.0055
     C(26)               0.0024     0.0050
     C(27)               0.0119     0.0047

Mean deviation from plane is 0.0100  angstroms
Chi-squared:        30.4

Dihedral angles between least-squares planes
        plane  plane   angle
          4      1     77.05
          4      2     21.79
          4      3     96.94
```

Appendix 3 Selected Spectra

Figure A3.1 ^{13}C NMR Spectrum of 2.

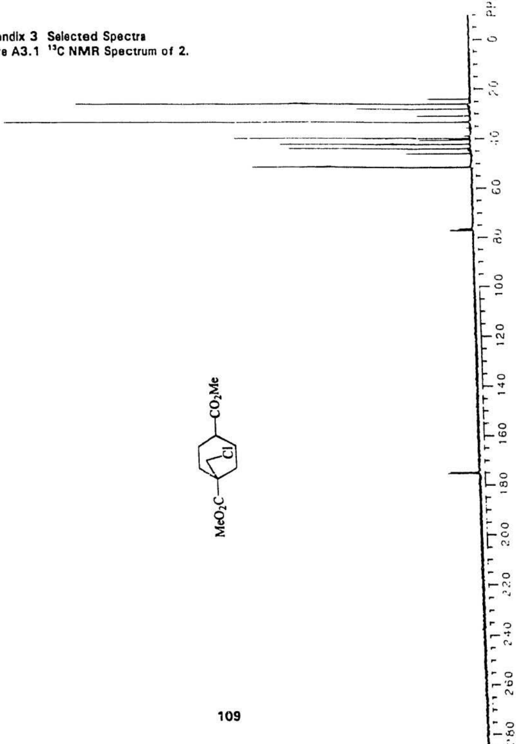


Figure A3.2 ^{13}C NMR Spectrum of 3.

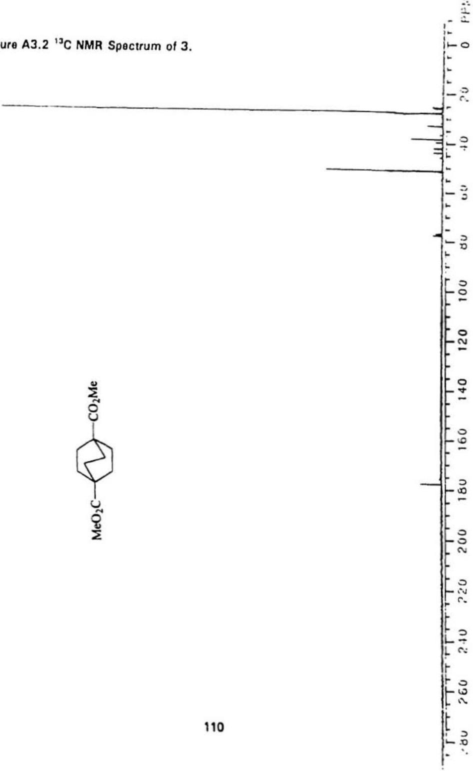


Figure A3.3 ¹H NMR of 4.

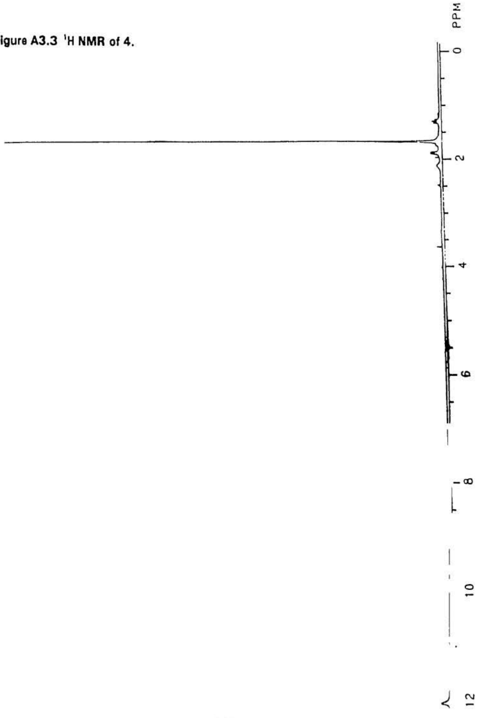


Figure A3.4 Infrared Spectrum of 4.

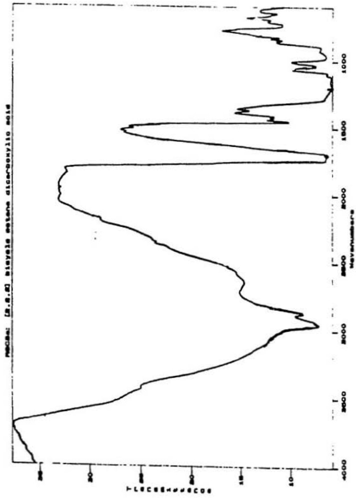


Figure A3.5 ^1H NMR Spectrum of 5.

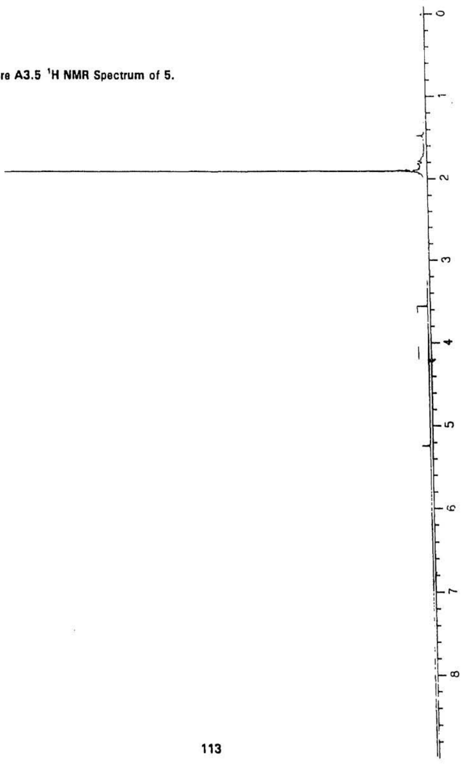


Figure A3.6 ^{13}C NMR Spectrum of 5.

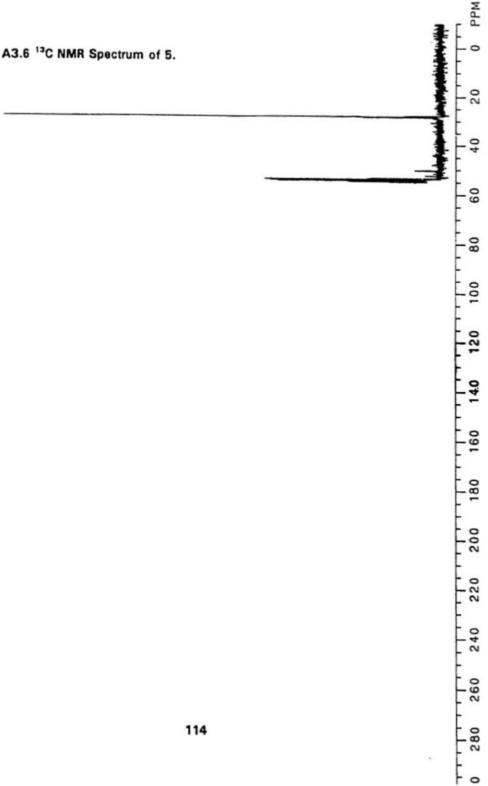


Figure A3.7 ^{13}C NMR Spectrum of 6.

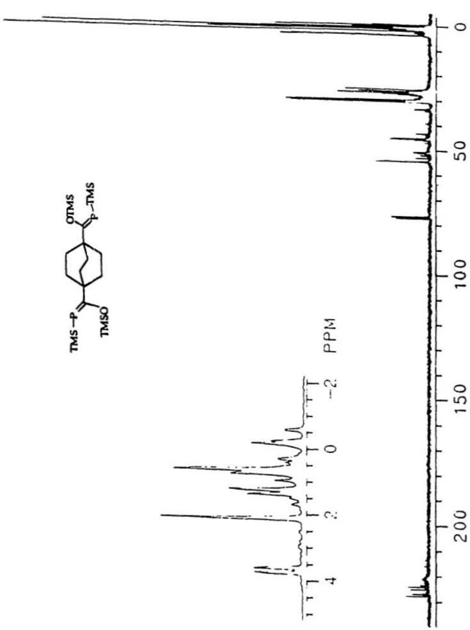


Figure A3.8 ^{1}H NMR Spectrum of 7.

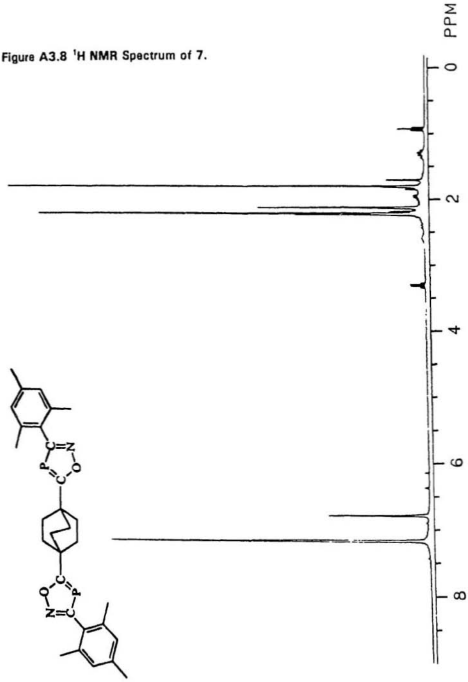


Figure A3.9 ^{13}C NMR Spectrum of 7.

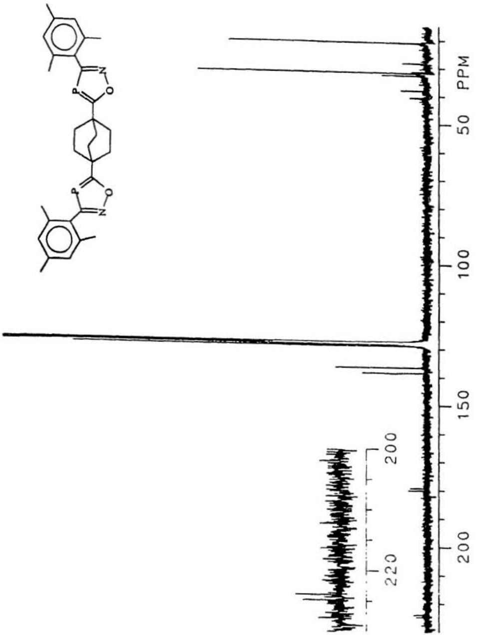


Figure A3.10 ^{31}P NMR Spectrum of **7**.

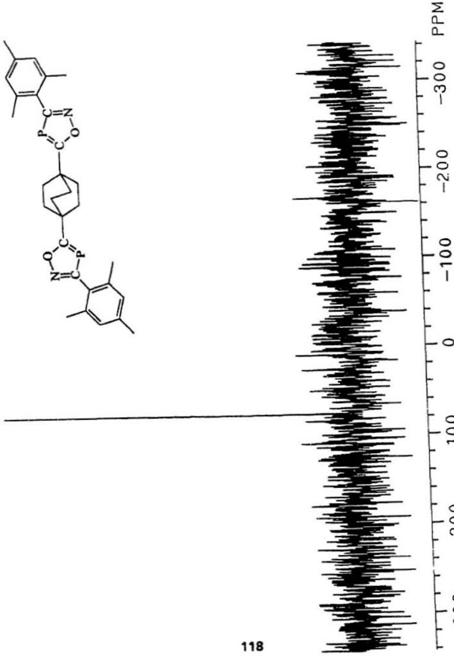


Figure A3.11 Mass Spectrum of 7.

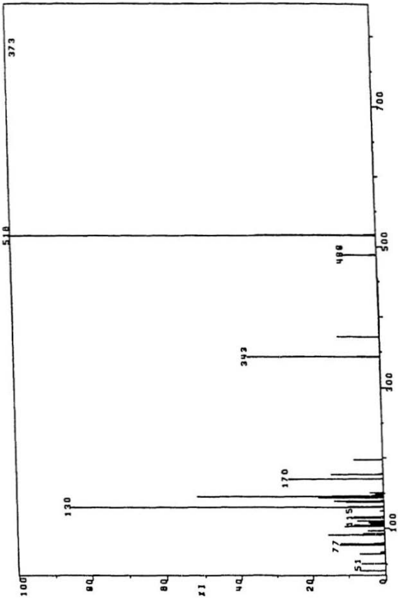


Figure A3.12 Infrared Spectrum of 7.

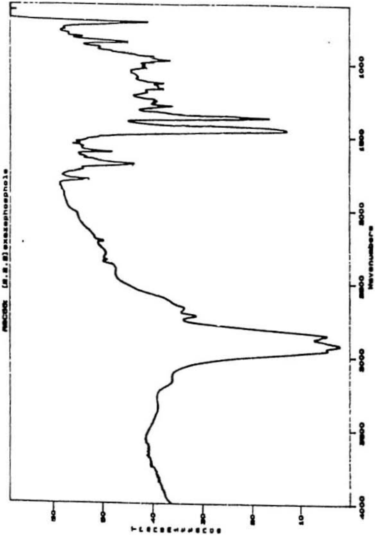


Figure A3.13 ^{13}C NMR Spectrum of 9.

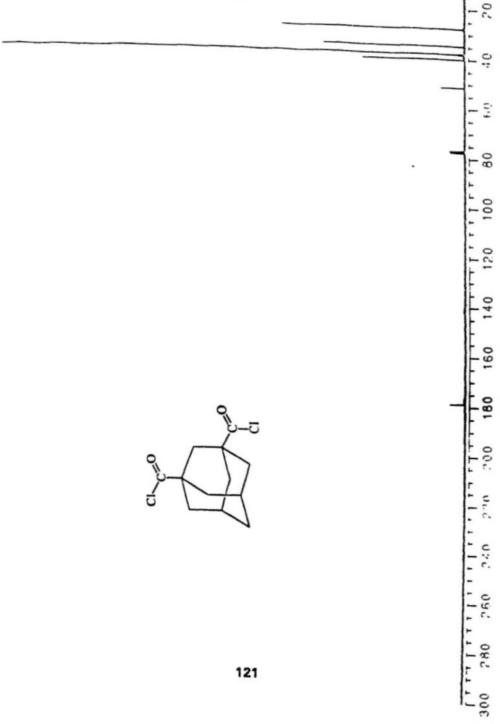


Figure A3.14 ^{13}C NMR Spectrum of 10.

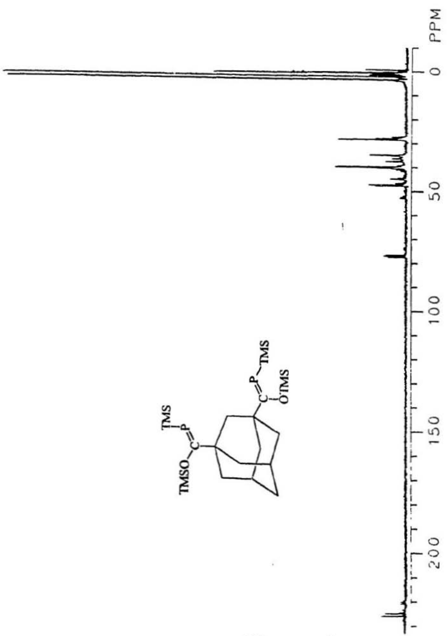


Figure A3.15 ^{13}C NMR Spectrum of 11.