Semistable Molecules in the Laboratory and in Space
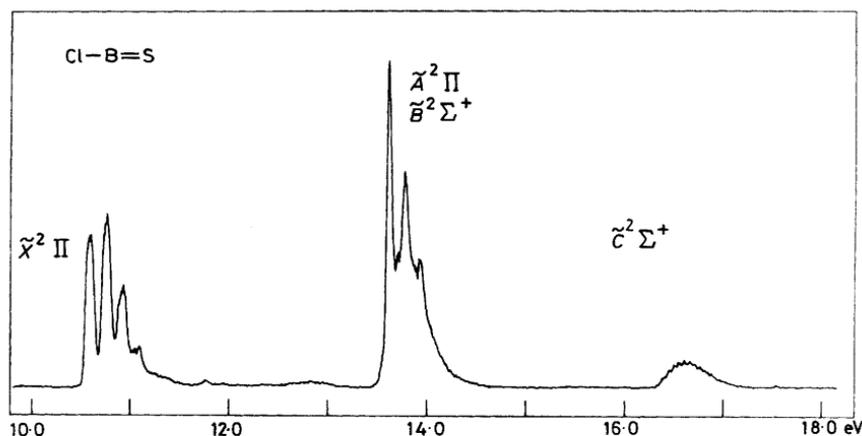

Figure 13 *The fast flow p.e. of* ClB=S.[46] *ClBS is produced by passing* Cl_2S_2 *over solid boron at 1100 °C and this spectrum indicates that the resulting vapour phase product is essentially pure ClBS. Note that the* 2nd *and* 3rd *ionization potentials coincide closely*

Table 2 *Spectroscopic data on sulphidoboron and selenidoboron species*

Species	r(X—B)/Å	r(B=S)/Å	μ/Debye	Ionization Potential/eV	Ref.
HB=S	1.169	1.599	2.098	11.1 13.55 15.84	41—44
FB=S	1.284	1.606	1.086	10.9 14.2 17.2 19.62	46, 51
ClB=S	1.681	1.606	1.45	10.57 13.55 13.63 16.36	49, 50
BrB=S	1.831	1.608	—	10.42 12.77 13.43	46
CH₃B=S	1.535	1.603	2.573	—	48
ClB=Se	1.664	1.751	—	—	52

is passed over B at 1100 °C. The spectrum is much more difficult to detect than that of ClBS. This is the first example of a selenidoboron compound and there is no obvious reason why other analogues should not be detectable.

C. Carbon–Phosphorus Multiple Bonds.—*Phospha-alkenes and Phospha-alkynes.* In 1961 Gier at Du Pont showed that phosphaethyne, HC≡P, the phosphorus analogue of HCN is produced when PH_3 is passed through a carbon arc discharge.[53] Subsequently Tyler at NRC studied the microwave spectrum[54] and the optical spectrum with Johns and Shurvell.[55] The existence of this molecule immediately suggested various possible consequences. Could analogues be made and might there be an associated chemistry parallel to that of the nitriles? The chemistry of the C≡P group might be equally, if not even more,

[53] T. E. Gier, *J. Am. Chem. Soc.*, 1961, **83**, 1769.
[54] J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.
[55] J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, *Can. J. Phys.*, 1969, **47**, 893.
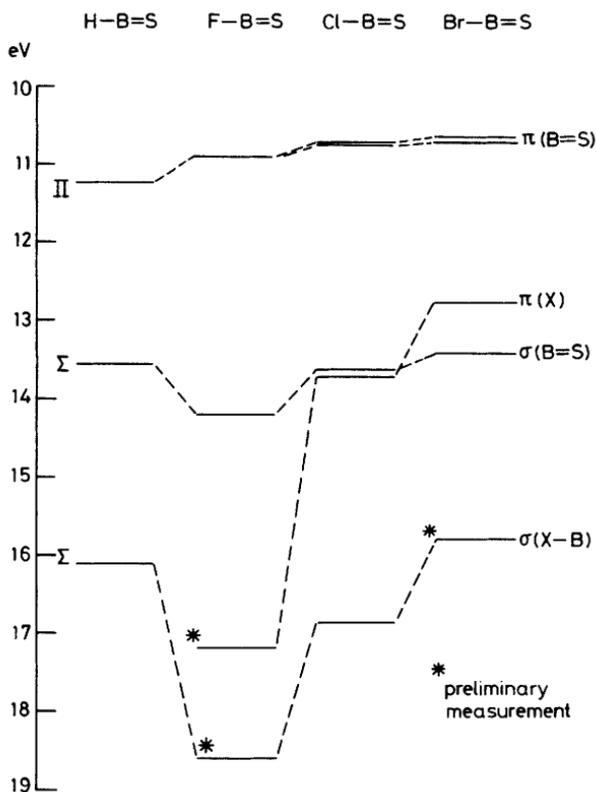
456

H. W. Kroto

Figure 14 *Correlation diagram showing the variation in observed ionization energy[46] for the various molecular orbitals of the sulphidoboron halides*

diverse and important relative to that of the nitriles. The possibilities for reactions such as condensation reactions, polymerization processes, inorganic and organometallic complex formation seemed endless. The questions were clear but the techniques for solving them much less obvious.

Although nitriles are well known stable systems the doubly bonded imino $>C=N^{\diagup}$ species are much less so, indeed it is only fairly recently that Johnson and Lovas[56] succeeded in identifying the simplest molecule $CH_2=NH$ by microwave spectroscopy in the products of pyrolysing CH_3NH_2. This experiment together with the existence of $HC\equiv P$ point to the distinct possibility that phosphaethene $CH_2=PH$ might be detectable in the pyrolysis of such species as CH_3PH_2 *etc*. Indeed some work by Haszeldine and co-workers[57,58] postulated
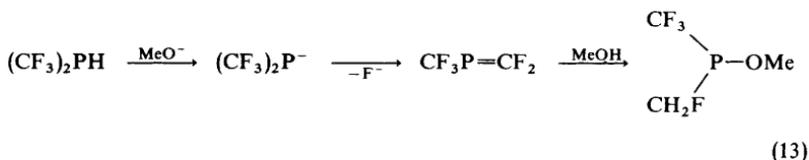
[56] D. R. Johnson and F. J. Lovas, *Chem. Phys. Lett.*, 1972, **15**, 65.

[57] H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *J. Chem. Soc.*, 1965, 6875.

[58] M. Green, R. N. Haszeldine, B. R. Iles, and D. G. Rowsell, *J. Chem. Soc.*, 1965, 6879.

Semistable Molecules in the Laboratory and in Space

that species of the type $R_2C=PX$ were intermediates in the reactions of certain perfluoroalkylphosphines with bases, in for instance scheme (13).

$$(CF_3)_2PH \xrightarrow{\text{MeO}^-} (CF_3)_2P^- \xrightarrow[-F^-]{} CF_3P=CF_2 \xrightarrow{\text{MeOH,}} \begin{array}{c} CF_3 \\ \diagdown \\ P-OMe \\ \diagup \\ CH_2F \end{array}$$

$$(13)$$

The combined microwave and photoelectron technique which had already been successful in studying such species as $CH_2=S^{16}$ and $CF_2=S^{20,21}$ (isoelectronic with the feasible species $CH_2=PH$ and $CF_2=PH$ respectively) as well as CS^{13} and $HB=S^{43}$ (both isoelectronic with $HC\equiv P$) thus seemed ideally suited to the detection of the hitherto *unknown* phospha-alkenes as well as *new* phospha-alkynes related to the lone species $HC\equiv P$. Accordingly some exploratory microwave investigations were initiated at Sussex together with John Nixon. These met with immediate success in that three members of the phospha-alkene family, a new structural type, including the simplest, $CH_2=PH$, were produced and characterized.[59] In addition the first substituted phospha-alkyne, $CH_3C\equiv P$, the phosphorus analogue of acetonitrile was produced.[60] At the same time, Becker[61] observed a rearrangement in a P-silylated acyl phosphine to form $PhP=C(Bu^t)OSiMe_3$.

In the first experiment attempted, the pyrolysis of dimethyl phosphine Me_2PH, a microwave transition of the species $CH_2=PH^{59}$ was detected according to equation (14).

$$(CH_3)_2P \xrightarrow{\Delta} CH_2=PH + CH_4 \qquad (14)$$
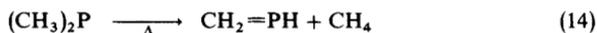
Further evidence for the assignment came with the detection of the same transition in the pyrolysis of CH_3PH_2 and subsequently, more efficiently, of $Me_3SiCH_2PH_2$.[62,63] Furthermore this detection was immediately followed[59] by the identification of $CH_2=PCl$ in the reaction (15)

$$CH_3PCl_2 \xrightarrow{\Delta} CH_2=PCl + HCl \qquad (15)$$

and the molecule $CF_2=PH^{59}$ in the reaction (16)

$$CF_3PH_2 \xrightarrow{\Delta} CF_2=PH + HF \qquad (16)$$
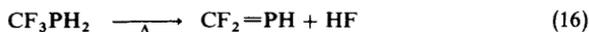
The microwave spectra for the pyrolysis of CH_3PCl_2 are shown in Figure 15. A second and very important result is also to be found in this spectrum in that at 39.952 GHz the $J = 1 \leftarrow 0$ transition of $HC\equiv P$ is readily detectable.

[59] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513.

[60] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *Chem. Phys. Lett.*, 1976, **42**, 460.

[61] G. Becker, *Z. Anorg. Allg. Chem.*, 1976, **423**, 242.

[62] H. W. Kroto, J. F. Nixon, K. Ohno, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1980, 709.

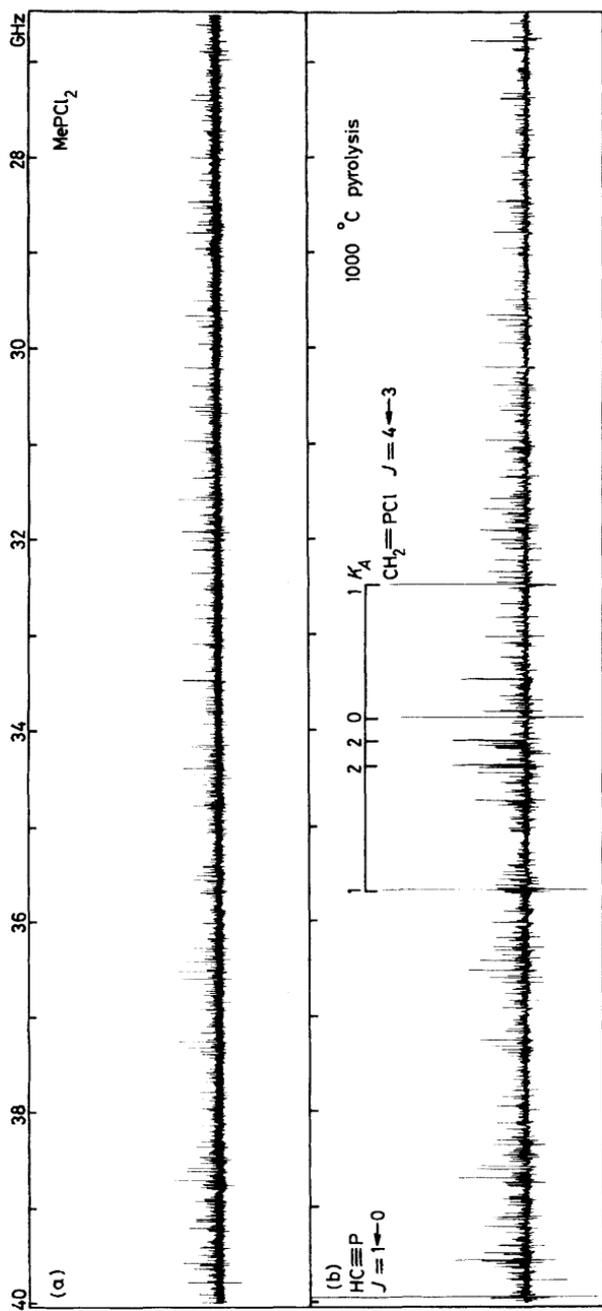[63] H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 367.

Figure 15 (a) The wide band scan of the microwave spectrum of CH_3PCl_2. This molecule is fairly asymmetric and gives rise to a very complicated multitude of weak rotational lines which fall into few, if any, recognisable patterns. (b) On pyrolysis of CH_3PCl_2 a new group of lines appears which is readily assigned to the $J = 4 \leftarrow 3$ transition of $CH_2=PCl$. In addition the strong $J = 1 \leftarrow 0$ line of $HC\equiv P$ appears at 39.952 GHz indicating that two HCl fragments have been eliminated

Semistable Molecules in the Laboratory and in Space

The second part of these initial investigations relating to the phospha-alkynes was now clear and pyrolysis of the species $EtPCl_2$ according to equation (17)

$$CH_3CH_2PCl_2 \xrightarrow{\Delta} CH_3C{\equiv}P + 2HCl \tag{17}$$

was immediately confirmed by microwave[60,64] and photoelectron[65] investigations. The microwave spectrum is shown in Figure 16.
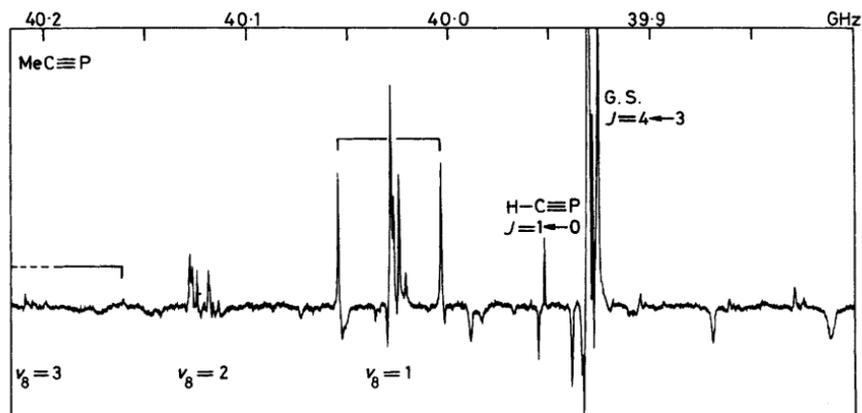

Figure 16 *The $J = 4 \leftarrow 3$ transition of $MeC{\equiv}P$ produced by pyrolysing $EtPCl_2$. The ground vibrational state lines for this symmetric top molecule with $K = 0$—3 bunch together at* ca. *39 930 MHz. When the lowest vibrational mode, the C—C—P bend, is excited the molecule changes from a symmetric to an asymmetric rotor and the $v = 1$ vibrational satellite shows a pattern which has characteristics similar to those of a slightly asymmetric rotor. The $J = 1 \leftarrow 0$ line of HCP is also in this region and it shows a nice example of a simple Stark modulated microwave line. The positive line is the zero-field frequency and the negative lobe is the frequency in the presence of the perturbing field. For the simple $J = 1 \leftarrow 0$ case one only observes a Stark shift. In general one observes splittings when higher values of J are involved (see Figure* 17)

A careful search for FCP formed by thermally eliminating two HF fragments from CF_3PH_2 continuing equation (16) was also carried out and the $J = 3 \leftarrow 2$ transition, Figure 17, was identified even though it was rather weak.[66] When this experiment was modified to prevent the possible back reaction of HF with FCP, by passing the pyrolysed products over solid KOH, it was discovered that HF could be eliminated directly by a reaction between the precursor CF_3PH_2 and KOH—no heating was necessary,[66] Figure 17. The reaction (18)

$$CF_3PH_2 \xrightarrow[KOH]{-HF} CF_2{=}PH \xrightarrow[KOH]{-HF} FC{\equiv}P \tag{18}$$
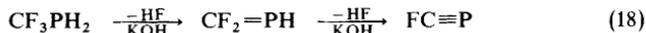
takes place at room temperature. These techniques have also confirmed the importance of phospha-alkenes as intermediates in reactions between primary

[64] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1979, **77**, 270.

[65] N. P. C. Westwood, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Dalton Trans.*, 1979, 1405.

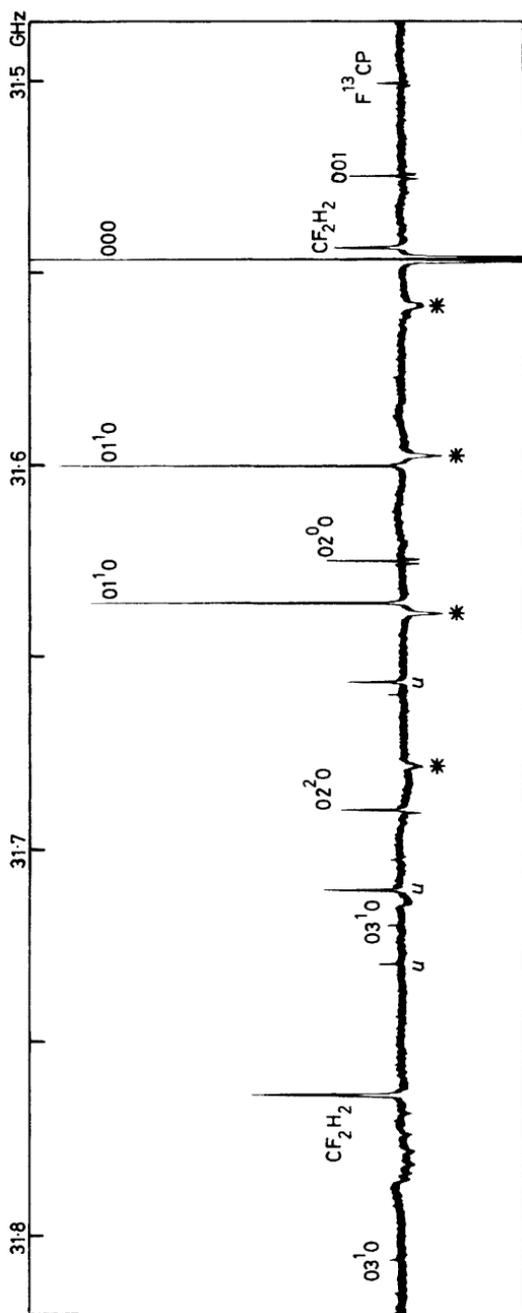[66] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1980, **82**, 185.

H. W. Kroto

Figure 17 *The $J = 3 \leftarrow 2$ microwave transition of $FC{\equiv}P$ is a beautiful example of a linear molecule rotational spectrum. The ground vibrational state line is assigned (000) i.e. $(v_1 = 0, v_2 = 0, v_3 = 0)$. The bending vibration v_2 is doubly degenerate and the satellite splits into two lines by an interaction called l-type doubling. The effect is loosely related to the asymmetry splitting of $K_A = 1$ lines in asymmetric tops due to the fact that on bending the molecule is no longer linear and $B \neq C$. These are the two lines labelled (01^10). The superscript indicates the quantum number for vibrational angular momentum, l. The $2v_2$ state gives rise to a state with $l = 2$, i.e. (02^20) and a state with $l = 0$ (02^00). The 02^00 state is shifted by a Fermi resonance with the v_3 state (001), see Figure 21. The asterisks indicate Stark lobes belonging to the two (01^10) lines. The U-lines are unidentified and belong to another species*

461

Semistable Molecules in the Laboratory and in Space

or secondary polyfluoroalkyl phosphines with nucleophiles such as alkoxides and amines. In particular the species $CF_3P{=}CF_2$, postulated as an intermediate in the methanolysis of $(CF_3)_2PH$, equation (13), has been trapped and identified by n.m.r.[67] The obvious step of treating $CF_3CF_2PH_2$ with KOH to observe $CF_3C{\equiv}P$ was not successful, though this species has been detected in the pyrolysis products of the precursor in rather low yield.[68]

Having detected the phospha-alkenes $CH_2{=}PH$, $CH_2{=}PCl$, $CF_2{=}PH$, and $CF_3P{=}CF_2$ and the phospha-alkynes $FC{\equiv}P$, $CH_3C{\equiv}P$, and $CF_3C{\equiv}P$ in these preliminary experiments, the programme was developed in wider and more general directions. Not only were new members of these two groups sought but more efficient synthetic routes and new chemical applications, for instance as ligands in transition-metal complexes, were explored. In addition, the chemistry of these species is now being studied by several other groups such as those of Becker, Appel, Bickelhaupt, and Issleib. Below, the contributions made by this research programme in collaboration with John Nixon are summarized, with contributions from other groups included where appropriate. Reviews of these systems are now beginning to appear.[69−72]
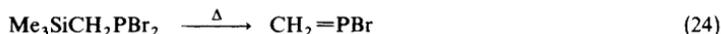
(i) *Production of Phospha-alkenes.* As indicated above, the thermal elimination route has proven very successful, especially for spectroscopic purposes. Thus, the general scheme shown in equation (19)

$$RCX_2PY_2 \xrightarrow{\Delta} RCX{=}PY + XY \quad (19)$$

has led to $CH_2{=}PH$, $CF_2{=}PH$, and $CH_2{=}PCl$[59] and Klebach *et al.*[73] have shown that a phospha-alkene is produced according to equation (20).

$$RPCl_2 \longrightarrow RPClCHPh_2 \longrightarrow RP{=}CPh_2 \text{ (R = mesityl)} \quad (20)$$

where the resulting compound is stabilized by the substituents. The elimination step can, in the case of CF_3PH_2 and $(CF_3)_2PH$, be carried out by treatment with base to form $CF_2{=}PH$ and $CF_3P{=}CF_2$ respectively (previous Section). Studies, together with David Walton, of routes involving silyl sub-stituted phosphines are in progress and have resulted in phospha-alkenes by equations (21)—(24)

$$\xrightarrow{\Delta} CH_2{=}PCl \quad (21)$$

$$Me_3SiCH_2PCl_2 \xrightarrow{SbF_3} Me_3SiCH_2PF_2 \xrightarrow{\Delta} CH_2{=}PF \quad (22)$$

$$\xrightarrow{LiAlH_4} Me_3SiCH_2PH_2 \xrightarrow{\Delta} CH_2{=}PH \quad (23)$$

$$Me_3SiCH_2PBr_2 \xrightarrow{\Delta} CH_2{=}PBr \quad (24)$$

[67] H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Organomet. Chem.*, 1979, **181**, C1.
[68] N. P. C. Simmons, H. W. Kroto, and J. F. Nixon, to be published.
[69] H. W. Kroto and J. F. Nixon in 'Phosphorus Chemistry', ed. L. D. Quin and J. Verkade, A.C.S. Symposium Series 171, American Chemical Society, 1981, p. 283.
[70] J. C. T. R. Burckett-St. Laurent, T. A. Cooper, H. W. Kroto, J. F. Nixon, O. Ohashi, and K. Ohno, *J. Mol. Struct.*, 1982, **79**, 215.
[71] R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731.
[72] H. W. Kroto and J. F. Nixon, to be published.
[73] T. C. Klebach, R. Lourens, and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886.

H. W. Kroto

The route (23) to $CH_2=PH$ is more efficient than the original one, equation (14), and has allowed an accurate structural study to be made.[63] Since this work, $CH_2=PCl$ has also been detected in the pyrolysis of CH_3OPCl_2.[74] The review by Appel *et al.*[71] contains details of other phospha-alkenes.

(ii) *Spectroscopic Data on Phospha-alkenes.* From the microwave studies accurate structures for the two phospha-alkenes $CH_2=PH$[63] and $CH_2=PCl$[74,75] have been determined (5) and (6) where the bond lengths are in Å and angles in degrees.

(5)   (6)
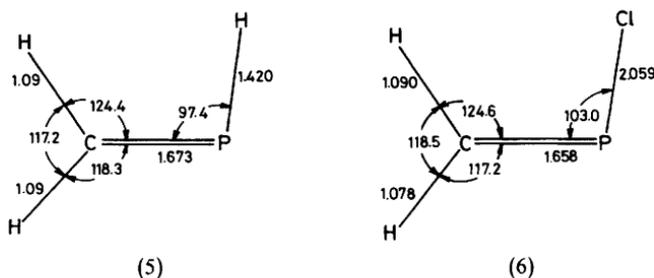
In addition to $CH_2=PH$ and $CH_2=PCl$, microwave studies have also been carried out on $CH_2=PF$,[76] $CH_2=PBr$,[77] and $CF_2=PH$.[59,78] The rotational constants of some of the species studied are given in Table 3 and some of the more

Table 3   *Rotational constants of phospha-alkenes*

Species*	A_0/MHz	B_0/MHz	C_0/MHz	Ref.
$CH_2=PH$	138 503.2	16 418.105	14 649.084	62, 63
$CH_2=PD$	93 513.75	16 098.885	13 701.898	
$CH_2=PF$	28 454.9	8890.30	6760.13	76
$CH_2=P^{35}Cl$	22 712.5	4667.318	3865.535	59, 75
$CH_2=P^{37}Cl$	22 657.0	4539.161	3735.677	
$CH_2=P^{79}Br$	21 608.48	2904.010	2586.750	77
$CH_2=P^{81}Br$	21 603.06	2879.260	2537.48	
$CF_2=PH$	11 107.108	4766.393	3330.787	59, 78
$CF_2=PD$	10 676.036	4672.806	3246.213	

* Species containing ^{12}C, ^{31}P, and ^{19}F

important structural parameters (some of which are preliminary) are collected in Table 4. Some dipole moment data are also included in this Table. Ohno *et al.*[79] have obtained vibrational frequencies from an i.r. study of $CF_2=PH$: v_1(PH stretch) = 2326.9 and v_2(C=P stretch) = 1349.5 cm^{-1} (see Section 3Cii). This system has also been studied by n.m.r. (see Section 3Cii).

[74] B. Bak, N. A. Kristiansen, and H. Svanholt, *Acta Chem. Scand., Ser A*, 1982, **36**, 1.

[75] H. W. Kroto, J. F. Nixon, O. Ohashi, K. Ohno, and N. P. C. Simmons, to be published.

[76] H. W. Kroto, J. F. Nixon, K. Ohno, and D. R. M. Walton, to be published.

[77] H. W. Kroto, J. F. Nixon, and K. Ohno, to be published.

[78] H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, to be published.

[79] K. Ohno, H. Matsuura, H. W. Kroto, and H. Murata, *Chem. Letts.*, 1982, 981.

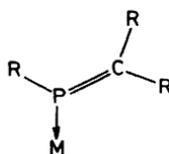*Semistable Molecules in the Laboratory and in Space*

Table 4   *Structural and dipole moment data for phospha-alkenes*

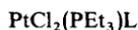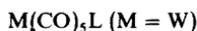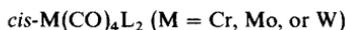|	$r(CP)/Å$	$r(PX)/Å$	$\angle(CPX)/°$	μ_A	$\mu_B/Debye$	μ	*Ref.*
$CH_2=PH$	1.673	1.420	97.4	0.731	0.470	0.869	63
$CH_2=PF$	1.67^a	1.58^a	104.0	—	—	—	76
$CH_2=PCl$	1.658	2.059	103.0	—	—	—	75
$CH_2=PBr$	1.65^a	2.22^a	104	—	—	—	77
$CF_2=PH$	1.67^a	1.42^a	(100)	0.705	0.533	0.884	78

(*a*) preliminary data

(iii) *Phospha-alkene Complexes.* On production of the first phospha-alkenes the possibility of their use as ligands with transition metals was investigated. This has resulted in the synthesis of several organometallic complexes of the form (7).


(7)

The complexes which have been made[80] are $(L = MesP=CPh_2)$:

cis-$M(CO)_4L_2$ (M = Cr, Mo, or W)

$M(CO)_5L$ (M = W)

$RhCl(PPh_3)L$, $RhCl(CO)L_2$, $Rh(C_9H_7)L_2$, PtX_2L_2 (X = Cl, I, or Me)

$PtCl_2(PEt_3)L$

The last compound has been the subject of an X-ray structure analysis,[81] from which the main structural parameters are: $r(C=P) = 1.668\,Å$, $\angle(C=P—C) = 112°$, $r(Pt—P) = 2.193\,Å$, $\angle(C=P—Pt) = 120.2°$.

(iv) *Production of Phospha-alkynes.* The original Gier method[53] required a rather complicated cooled carbon arc device to be made and the reaction between graphite and PH_3 produced a mixture of *ca.* 4:1 C_2H_2:HCP. It appears to be almost impossible to separate these two as their physical properties are very similar.

The method of production that has been most fruitful has been the thermal elimination route (25)

$$RCX_2PY_2 \xrightarrow[\Delta]{-2XY} RC\equiv P \ (XY = HCl \ or \ FH) \qquad (25)$$
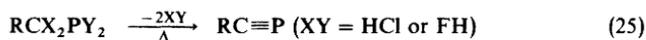
Using this straightforward method at temperatures of *ca.* 1000 °C or so, the

[80] H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.,* 1981, 199.

[81] H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew, and K. W. Muir, *Polyhedron,* 1982, 1, 89.

464

molecules $HC\equiv P$,[59] $FC\equiv P$,[66] $CH_3C\equiv P$,[60,64,65] $CF_3C\equiv P$,[68] and $CH_2=$ $CHC\equiv P$[82] have all been detected by microwave spectroscopy. Photoelectron studies indicate that the yield is good in the case of HCP,[83] fair for CH_3CP,[65] and poor for the rest. Pure HCP can now be produced from CH_3PCl_2 by titrating off the HCl with NH_3.[83] FCP can be produced in good yield by treating CF_3PH_2 with KOH (see Section 3Cv).

During experiments aimed at detecting $HC\equiv C-C\equiv P$ which involved an attempted synthesis of $HC\equiv CCH_2PCl_2$, the sought species was detected.[84] To produce the precursor, the Grignard of $HC\equiv CCH_2Cl$ was treated with PCl_3 and the resulting products flow pyrolysed, which gave rise to a weak but readily identifiable spectrum of HC_3P. The precursor was not, however, $HC\equiv CCH_2PCl_2$, which did not appear to be formed, but the original starting materials $HC\equiv CCH_2Cl$ and PCl_3. In fact the strongest spectrum was observed using a 10:1 PCl_3:$HC\equiv CCH_2Cl$ mixture. This result suggested that HC_3P might be formed in reaction (26),

$$HC\equiv C-CH_3 + Cl_3P \xrightarrow{\Delta} HC\equiv C-C\equiv P + 3HCl \qquad (26)$$

which indeed turned out to be the case. In fact the reaction, equation (1), has now been generalized with $R = HC\equiv C$, $N\equiv C$, and Ph to produce not only $HC\equiv C-C\equiv P$ but also $N\equiv C-C\equiv P$, and $PhC\equiv P$. Most recently the molecule NC_5P has been detected by equation (27) the first new species to be detected by this route.[85]
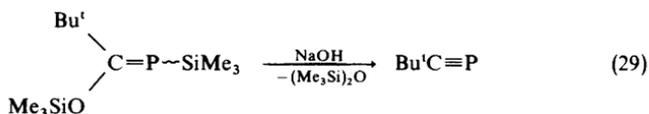
$$N\equiv C-C\equiv C-CH_3 + Cl_3P \xrightarrow{\Delta} N\equiv C-C\equiv C-C\equiv P + 3HCl \qquad (27)$$
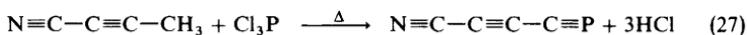
$N\equiv C-C\equiv P$ had originally been detected by co-pyrolysing HCP with NCN_3,[86] equation (28).

$$N\equiv CN_3 + HC\equiv P \xrightarrow{\Delta} N\equiv C-C\equiv P + \cdots \qquad (28)$$

The PCl_3/CH_3CN route is at least as good for spectroscopic purposes.

The molecules $SiMe_3C\equiv P$ and $PhC\equiv P$ have been produced by pyrolysis of $ClP=C(SiMe_3)_2$ and $ClP=C(SiMe_3)Ph$ respectively by Appel and Westerhaus,[87,88] Becker *et al.*[89] have shown that the *stable* molecule $Bu^tC\equiv P$ can be produced by equation (29)

$$\begin{array}{c} Bu^t \\ \diagdown \\ \diagup C=P\sim SiMe_3 \xrightarrow[-(Me_3Si)_2O]{NaOH} Bu^tC\equiv P \\ Me_3SiO \end{array} \qquad (29)$$

[82] K. Ohno, H. W. Kroto, and J. F. Nixon, *J. Mol. Spectrosc.*, 1981, **90**, 507.
[83] M. A. King, H. W. Kroto, and J. F. Nixon, unpublished.
[84] H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512.
[85] M. Durrant, H. W. Kroto, D. McNaughton, and J. F. Nixon, to be published.
[86] T. A. Cooper, H. W. Kroto, J. F. Nixon, and O. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1980, 333.
[87] R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, 2159.
[88] R. Appel and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 197.
[89] G. Becker, G. Gresser, and W. Uhl, *Z. Naturforsch, Teil B*, 1981, **36**, 16.

Semistable Molecules in the Laboratory and in Space

(v) *Spectroscopic Data on Phospha-alkynes.* Using Gier's original method of producing HC≡P numerous spectroscopic investigations were made. The microwave spectrum was studied by Tyler,[54] the electronic spectrum by Johns *et al.*,[55] the n.m.r. spectrum by Anderson *et al.*,[90] the i.r. by Garneau and Cabana,[91] and the p.e. spectrum by Frost *et al.*[92] In some cases, particularly the last two, the acetylene contaminant obscured regions of the spectrum. This problem is obviated by producing HCP from CH_3PCl_2, allowing a p.e. spectrum of pure HCP to be observed.[83] It has also enabled the electronic fluorescence spectrum of the HCP$^+$ ion, excited by slow electron bombardment, to be observed, Figure 18.[93]
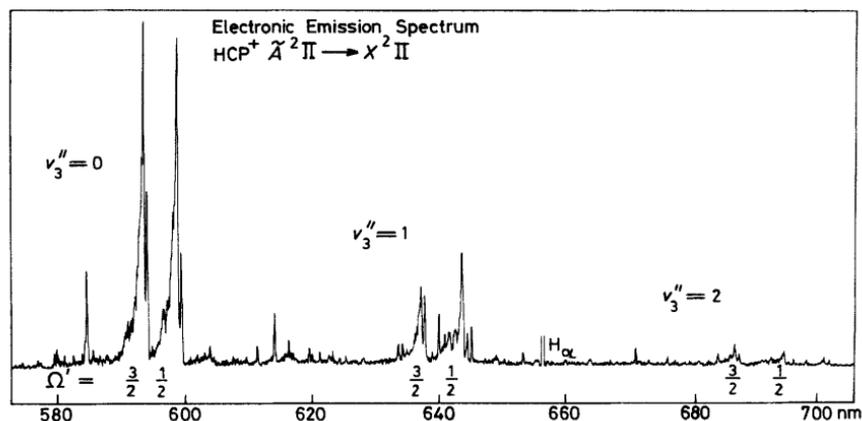

Figure 18 *The electronic emission spectrum of* HCP$^+$ *excited by slow electron bombardment of* HCP[93]

So far, CH_3CP,[60,64] FCP,[65] CF_3CP,[68] $NCCP$,[86,85] $HC≡CCP$,[84,85] $NCC≡CCP$,[85] $CH_2=CHCP$,[82] and PhCP[85,94] have all been studied by microwave spectroscopy. Indeed, all but the last compound were first identified by this technique. The more important data are collected in Table 5.

The discovery of reaction (18) enabled a thorough analysis of the microwave spectrum of FCP shown in Figure 17 to be carried out.[66] It also enabled the

[90] S. P. Anderson, H. Goldwhite, D. Ko, A. Letson, and E. Esparza, *J. Chem. Soc., Chem. Commun.*, 1975, 744.

[91] J. M. Garneau and A. Cabana, *J. Mol. Spectrosc.*, 1980, **79**, 502.

[92] D. C. Frost, T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472.

[93] M. A. King, H. W. Kroto, J. F. Nixon, D. Klapstein, J. D. Maier, and O. Marthaler, *Chem. Phys. Lett.*, 1981, **82**, 543.

[94] J. C. T. R. Burckett-St. Laurent, H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1982, **92**, 158.

Table 5 *Spectroscopic data on phospha-alkynes*

	B_0/MHz	μ/ Debye	$r(X{-}C)$/ Å	$r(C{\equiv}P)$/ Å	Ionization Potentials/ eV	Ref.
HC≡P	19 973.67	0.39	1.0667	1.5421	10.79 12.86	54, 92
HC≡P$^+$			1.11	1.596		93
CH$_3$C≡P	4991.339	1.499	1.465	1.544	9.89 12.19	64, 65
FC≡P	5257.80	0.279	1.285	1.541	10.57 13.55	66, 96
CF$_3$C≡P	1668.5644	—	1.460	1.542		68
N≡C—C≡P	2704.4803	3.44	1.382	1.547		86
H—C≡C—C≡P	2656.3944	0.754	1.382	(1.544)		84
N≡C—C≡C—C≡P	873.4803	—	1.382	(1.544)		85
CH$_2$=CHC≡P	2726.773	1.183	1.432	(1.544)		82
PhC≡P	867.6925	—	1.467	(1.544)	8.68 9.60 9.87 10.79	97
t-BuC≡P	—	—	—	—	9.61 11.44	97

p.e. spectrum shown in Figure 19 and the n.m.r. data in Figure 20 to be obtained.[95] The i.r. data of Ohno *et al.*[79] in Figure 21 give a particularly useful insight into the overall efficiency of this reaction.

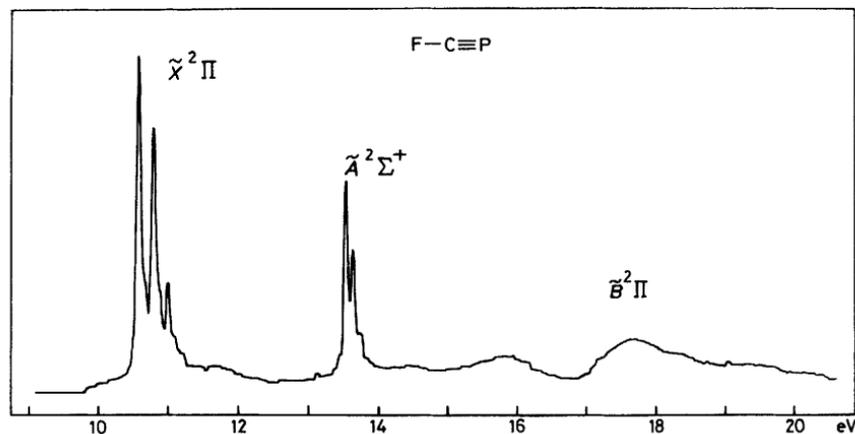As well as the earlier p.e. work on HCP,[92] CH$_3$CP,[65] and FCP,[96] more

Figure 19 *The p.e. spectrum of* FC≡P *produced by flowing gaseous* CF$_3$PH$_2$ *over solid* KOH. *The first and second bands correspond to ionizations from the* π(C≡P) *and* n(P) *orbitals respectively*[96]

[95] H. E. Hosseini, J. F. Nixon, H. W. Kroto, S. Browstein, J. R. Morton, and K. F. Preston, *J. Chem. Soc., Chem. Commun.*, 1979, 653.

[96] H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 446.
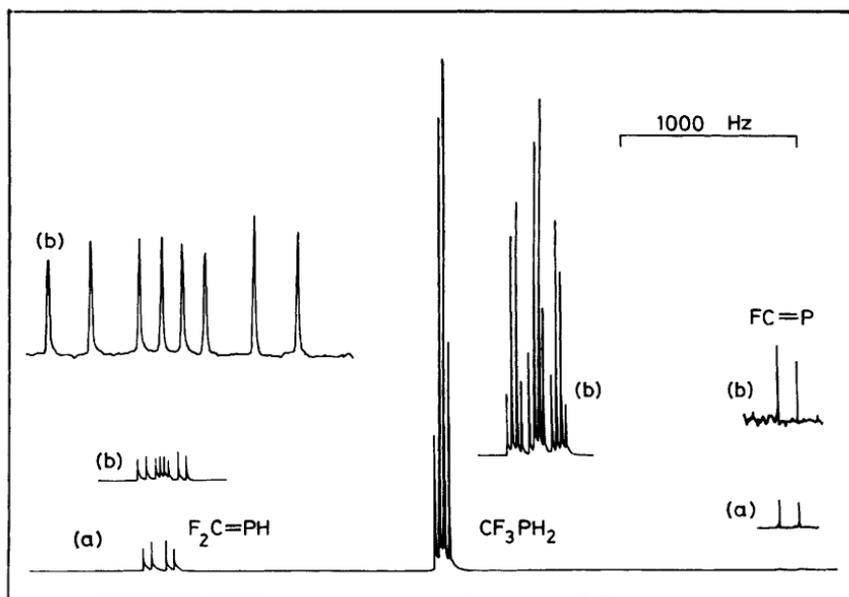
467

Figure 20 ^{31}P (ca. $-80\,°C$) *n.m.r. spectra of the products of the reaction of* CF_3PH_2 *with* KOH *at room temperature.*[95] *(a)* ^{1}H *decoupled, (b)* ^{1}H *undecoupled*

recently PhCP and t-BuCP[97] have been studied, yielding useful information on the electronic behaviour of the C≡P group. In particular, it is worth noting that the *n* and π ionization energies for HCN are almost identical, whereas for HCP the $\pi(C≡P)$ is the first at 10.79 eV and the P lone pair is the second at 12.86 eV.[92] Some ionization potential data are also collected in Table 5.

(vi) *Phospha-alkyne Complexes.* One of the more exciting prospects with phospha-alkynes is the possibility of making transition-metal complexes. A Pt complex of Bu^{t}C≡P has been made and its structure, as determined by X-ray analysis, is shown in Figure 22.[98] It is noteworthy that the angle ∠CCP has bent from 180° → 132° and the C≡P bond length has increased from *ca.* 1.544 Å (as in CH$_3$C≡P) in the free molecule to 1.672 Å in the complex reflecting the effects of back-bonding from the zero-valent platinum. The n.m.r. spectrum has also been measured.[98] Seyferth and Henderson have observed dechlorination of RCCl$_2$PCl$_2$ by Co$_2$(CO)$_8$ to form a phospha-alkyne complex.[99] A similar complex can be formed from Co$_2$(CO)$_8$ and free t-BuCP.[98]

[97] J. C. T. R. Burckett-St. Laurent, M. A. King, H. W. Kroto, J. F. Nixon, and R. J. Suffolk, to be published.

[98] J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.

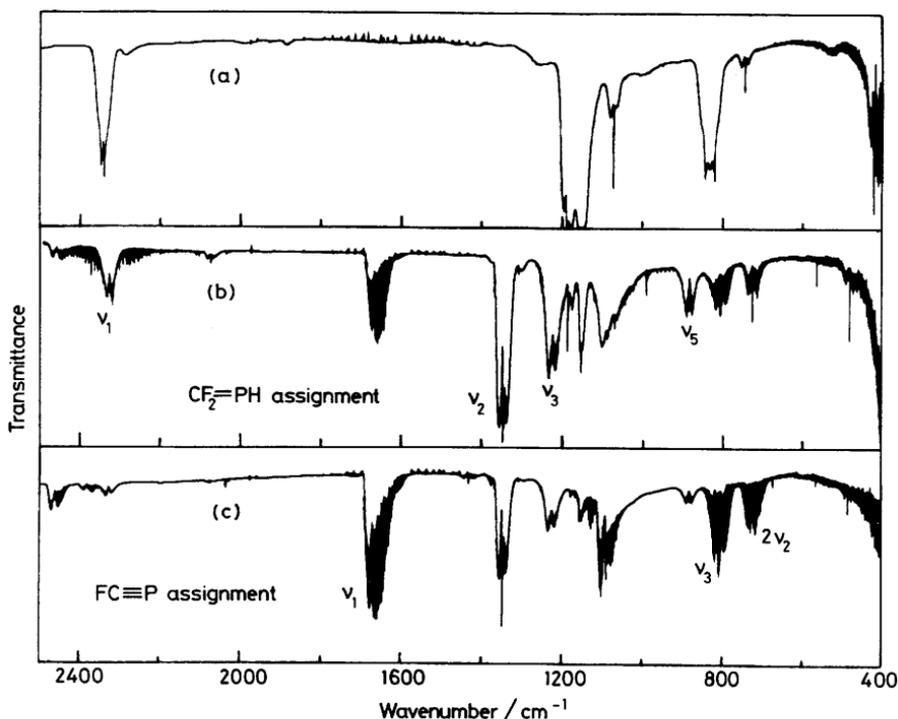[99] D. Seyferth and R. S. Henderson, *J. Organomet. Chem.*, 1978, **162**, C35.

H. W. Kroto

Figure 21 *The i.r. spectra obtained (a) for* CF_3PH_2, *(b) by passing* CF_3PH_2 *through a tube packed with* KOH, *(c) by double passage over* KOH.[79] *The strong band at ca. 1170 in (a) is the* C—P *stretch of* CF_3PH_2. *In (b) both* CF_2=PH *and FCP appear and in (c) FCP is more intense relative to* CF_2=PH, *and* CF_3PH_2 *has been almost completely eliminated. In (b) the stronger* CF_2=PH *features are* v_1(PHstr), v_2(C=Pstr), v_3(CF_2asym str) *and* v_5(CF_2sym str). *In (c) the FCP features* v_1, $2v_2$, *and* v_3 *are identified:* v_1 *appears to be an antisymmetric stretching frequency and* v_3 *a symmetric stretching frequency. Fermi resonance with* v_3 *enhances* $2v_2$. *Note the correlation with the microwave spectrum in Figure 17*

4 Poly-ynes

A. Introduction.—Linear molecules present some most interesting problems in molecular dynamics. If they are very long they flex like a cane and one can visualize rotational energy transfer *or* vibrational energy transfer depending on whether a collision is near an end or near the chain centre respectively. In general they possess the most simple spectra and the longer they are, the higher is the number of bending vibrations excited at room temperature. These types of intrinsically interesting physical ideas initiated a programme with David Walton aimed at spectroscopic study of poly-ynes. This involved the preparation of a range of simple poly-ynes, some of which are rather unstable, by a combination of traditional synthesis and novel reactions.
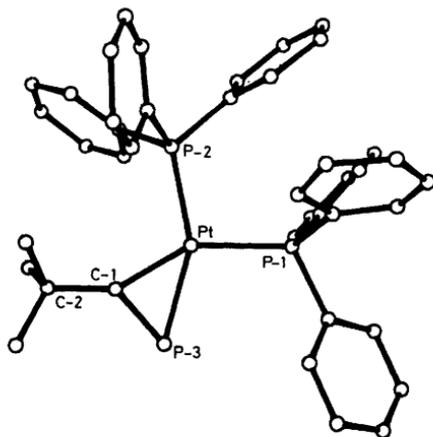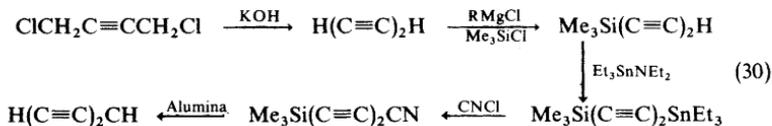
469

Semistable Molecules in the Laboratory and in Space

Figure 22 *The results of an X-ray analysis of the* t-BuC≡PPt[P(Ph)$_3$]$_2$ *π complex.*[98] ∠CCP *has changed from* 180° *in the free* t-BuCP *molecule to* 132° *in the complex*

A number of alkynes and polyalkynes were produced and their microwave spectra, and in some cases also their photoelectron, n.m.r., and i.r. spectra, were measured.[100] The length of these molecules gives rise to extended vibrational satellite structure in their microwave spectra enabling detailed rotation-vibration studies to be made.

The study of these species, in particular HC≡C—C≡C—C≡N, coincided with the exciting breakthrough in detection of interstellar molecules by radio-astronomy[101 – 103] and the microwave measurements initiated a search for interstellar poly-ynes which has led to exciting and perplexing discoveries whose implications have still to be explained.

B. Microwave Spectra of Polyacetylenes.—In a typical synthesis, HC$_5$N[104] was made as shown in equation (30)

$$ClCH_2C≡CCH_2Cl \xrightarrow{KOH} H(C≡C)_2H \xrightarrow[Me_3SiCl]{RMgCl} Me_3Si(C≡C)_2H$$

$$\Big\downarrow Et_3SnNEt_2 \quad (30)$$

$$H(C≡C)_2CH \xleftarrow{Alumina} Me_3Si(C≡C)_2CN \xleftarrow{CNCl} Me_3Si(C≡C)_2SnEt_3$$

The triethyl tin group is preferentially replaced in step 4 resulting in Me$_3$Si(C≡C)$_2$CN. This molecule is a symmetric rotor and its microwave spectrum is shown in Figure 23.[105] In this case there are so many lines, due to not

[100] A. J. Alexander, 'Spectroscopic Studies', B.Sc. Thesis, University of Sussex, 1975.
[101] G. Winnewisser, E. Churchwell, and C. M. Walmsely in 'Modern Aspects of Microwave Spectroscopy', ed. G. Chantry, Academic Press, London, 1979, p. 313.
[102] H. W. Kroto, 'Chemistry between the Stars', *New Scientist*, 1978, **79**, 400.
[103] H. W. Kroto, 'The Spectra of Interstellar Molecules', *Int. Rev. Phys. Chem.*, 1981, **1**, 309.
[104] A. J. Alexander, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1976, **62**, 175.
[105] A. J. Alexander, H. W. Kroto, and D. R. M. Walton, to be published.