Tetrahedron Letters No. 36, pp 3179 - 3182, 1974. Pergamon Press. Printed in Great Britain.

PROBING THE ELECTRONIC STRUCTURE OF PHOSPHORINS (PHOSPHABENZENES) BY ^{13}C NMR SPECTROSCOPY

T. Bundgaard and H. J. Jakobsen
Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

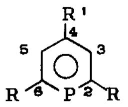
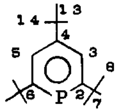
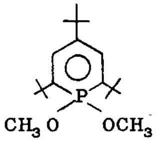
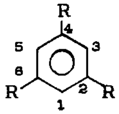
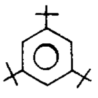
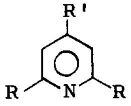
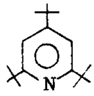
K. Dimroth and H. H. Pohl
Department of Organic Chemistry, University of Marburg/Lahn,
3350 Marburg/Lahn, Germany

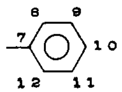
(Received in UK 17 July 1974; accepted for publication 31 July 1974)

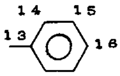
^{13}C NMR has proven an extremely useful tool in studies of organophosphorus compounds. Valuable information on their geometrical and molecular electronic structure may be obtained from three sets of parameters: (i) ^{13}C chemical shifts, (ii) ^{13}C-^{31}P nuclear spin couplings (including their signs), and (iii) ^{13}C spin-lattice relaxation times (T_1) [1,2]. In connection with our current studies on phospholes [3] we have undertaken a ^{13}C NMR investigation on some phosphorins (phosphabenzenes) with the purpose of probing their electronic structure. CNDO/2 and PE spectral approaches to this problem have recently been performed [4]. In this paper we report on the first determination of ^{13}C chemical shifts and ^{13}C-^{31}P coupling constants in λ^3- and λ^5-phosphorins [5].

^{13}C NMR parameters (Table 1) were obtained for the λ^3-phosphorins 2,4,6-tri-*t*-butylphosphorin, <u>1</u>, and 2,4,6-triphenylphosphorin, <u>2</u>, and for the λ^5-phosphorin 2,4,6-tri-*t*-butyl-1,1-dimethoxyphosphorin, <u>3</u>. The ^{13}C NMR spectra were obtained at 25.16 MHz in the FT (Fourier transform) mode on a Varian XL-100-15 spectrometer (S124-XL FT accessory, Varian 620L 16K computer) using noise and single-frequency proton decoupling. Assignments of the spectra were made on the basis of relative intensities, NOE (nuclear Overhauser enhancement) effects, and selective proton decoupling experiments. For the phenyl-substituents the known order of the ortho and meta ^{13}C chemical shifts in biphenyl [6] and a comparison of the proton decoupling frequencies with the relative order of the ortho, meta, and para ^{1}H chemical shifts observed for a series of phenyl-substituted aromatic compounds [7] were also used. Relative signs for some of the ^{13}C-^{31}P coupling constants were determined using double resonance techniques described elsewhere [8]. The results are summarized in Table 1 along with the parameters obtained for similarly trisubstituted pyridines and benzenes. These permitted an estimation of the ^{13}C chemical shifts for the unsubstituted phosphorins.

TABLE 1. ^{13}C Chemical Shifts and ^{13}C-^{31}P Coupling Constants in Some 2,4,6-Trisubstituted λ^3- and λ^5-Phosphorins (1, 2, and 3). ^{13}C Chemical Shifts in Analogously Substituted Benzenes and Pyridines (4, 5, 6, and 7).[a]

							
	1	2	3[b]	4	5	6	7
δ_{C2}	172.93	182.94	97.73	143.26	150.34	151.14	167.69
δ_{C3}	132.42	127.14	136.61	125.61	119.72	117.53	112.82
δ_{C4}	145.23	152.30	119.78	143.26	150.34	147.00	160.41
δ_{C7}	144.15	39.35	35.64	141.84	35.30	140.39	38.12
δ_{C8}	128.50	33.31	33.00	128.14	31.84	127.91	30.59
δ_{C9}	129.87			129.76		129.47	
δ_{C10}	128.95			128.45		129.89	
δ_{C13}	142.75	36.68	34.64	141.84	35.30	139.56	35.38
δ_{C14}	128.68	31.69	32.59	128.14	31.84	128.15	31.01
δ_{C15}	129.95			129.76		129.94	
δ_{C16}	128.97			128.45		129.91	
$^{1}J_{C2-P}$	51.72	56.63	134.22				
$^{2}J_{C3-P}$	12.17	12.44	10.26				
$^{3}J_{C4-P}$	13.84	14.29	17.37				
$^{2}J_{C7-P}$	24.28	21.87	5.64				
$^{3}J_{C8-P}$	12.88	12.61	4.49				
$^{4}J_{C9-P}$	~0						
$^{5}J_{C10-P}$	2.01						
$^{4}J_{C13-P}$	3.32	2.00	1.69				
$^{5}J_{C14-P}$	1.80	1.54	0.98				
$^{6}J_{C15-P}$	0.60						
$^{7}J_{C16-P}$	0.97						

R = 

R' = 

[a] Chemical shifts and coupling constants were measured from expanded spectra obtained using 256 Hz spectral width and 8K data points. Chemical shifts are in ppm downfield from internal TMS ($\nu_{TMS-^{13}C}$ = 25.1605 MHz; internal lock: ^{2}H, $(CD_3)_2CO$) with errors less than ±0.01 ppm. Coupling constants are in Hz with errors ±0.03 Hz. All solutions are in $(CD_3)_2CO$ containing ca. 3% v/v TMS: 1 0.09 m, 2 1.13 m, 3 0.50 m, 4 0.11 m, 5 1.10 m, 6 0.14 m, and 7 0.90 m.

[b] δ_C (OCH_3) = 51.70 ppm; $^{3}J_{\underline{P}-O-\underline{C}}$ = −1.74 Hz (sign opposite to that of $^{3}J_{\underline{P}-O-C-\underline{H}}$).

λ^3-Phosphorins. It is seen (Table 1) that the relative order of the ^{13}C chemical shifts for the λ^3-phosphorins, 1 and 2, is similar to that obtained for the benzene and pyridine derivatives. However, a pronounced downfield shift is observed for the C2 carbons of 1 and 2 (relative to the benzene and pyridine series); this effect is similar to the extreme downfield H2 proton chemical shift reported for unsubstituted λ^3-phosphorin [9]. Table 2 shows that the differences in substituent effects on the ^{13}C chemical shifts for 1 and 2 exhibit the same trends as for the analogous benzene and pyridine compounds, the magnitudes being nearly the same as for the benzene series. Thus, using the observed substituent effects for 4 and 5, we have estimated (Table 3) the ^{13}C chemical shifts for the unsubstituted λ^3-phosphorin. This shows that the relative order of the C3 and C4 chemical shifts in λ^3-phosphorin apparently is reversed as compared to that in pyridine.

TABLE 2. Differences in Substituent Effects on the Ring-^{13}C Chemical Shifts in Triphenyl- and Tri-*t*-butyl- λ^3-Phosphorins (1 and 2), Benzenes (4 and 5), and Pyridines (6 and 7): $\Delta\delta_C = \delta_C^{\text{phenyl}} - \delta_C^{t\text{-butyl}}$ (ppm).

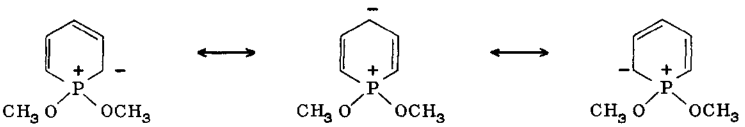
	λ^3-Phosphorins 1 and 2	Benzenes 4 and 5	Pyridines 6 and 7
$\Delta\delta_{C2}$	-10.01	-7.08	-16.55
$\Delta\delta_{C3}$	+5.28	+5.89	+4.71
$\Delta\delta_{C4}$	-7.07	-7.08	-13.41

TABLE 3. Estimated ^{13}C Chemical Shifts (δ_C, ppm) in λ^3-Phosphorin (Phosphabenzene) and 1,1-Dimethoxy-λ^5-phosphorin from Observed Values in 1, 2, and 3 (Table 1) and from Substituent Effects in 4 and 5. Observed ^{13}C Chemical Shifts in Benzene and Pyridine (Solvent: Acetone-d_6).

	λ^3-Phosphorin (Calc.)			1,1-Dimethoxy-λ^5-phosphorin (Calc.)	Benzene (Observed)	Pyridine (Observed)
From	4	5	Mean	5		
δ_{C2}	158.3	161.3	159.8	76.1	128.66	150.10
δ_{C3}	135.5	136.1	135.8	145.6	128.66	123.91
δ_{C4}	130.6	130.6	130.6	98.1	128.66	135.85

The magnitudes of the one-bond ^{13}C-^{31}P coupling constants in 1 and 2 (51.72 and 56.63 Hz, respectively, sign not obtained so far) are larger than $^1J_{C-P}$ in phosphines (P^{III}) which are usually small in magnitude and negative (e.g. in triphenylphosphine $^1J_{C-P} = -12.51$ Hz [10]). The larger magnitude of $^3J_{C4-P}$ relative to $^2J_{C3-P}$ in 1 and 2 (also observed for 3) is comparable to the trend observed for ${}^3J_{C4-N}$ and ${}^2J_{C3-N}$ in ^{15}N-pyridine and the ^{15}N-pyridinium ion [11]. Furthermore, ${}^2J_{C3-P}$ and ${}^3J_{H3-P}$ in 1 and 2, like ${}^2J_{C3-N}$ and ${}^3J_{H3-N}$ in ^{15}N-pyridine [7], have opposite signs. The absolute signs are unknown, however, ${}^2J_{C3-P}$ is probably negative due to the phosphorus lone pair effect on ${}^2J_{C-P}$ [1]. Finally, the large magnitude observed for ${}^2J_{C7-P}$ probably results from the geometrical dependence of ${}^2J_{C-P}$ on the orientation of the lone pair electrons on phosphorus [1].

λ^5-Phosphorins. The ring-^{13}C NMR parameters for the λ^5-phosphorin, 3, differ widely from those obtained for 1 and 2. The extreme upfield chemical shifts for the C2 and C4 carbons and the larger magnitude of ${}^1J_{C2-P}$ (= 134.22 Hz; sign not obtained, probably positive) relative to the values for the λ^3-phosphorins show the same features as recently observed in phosphorus ylides [2,12]. However, the chemical shifts estimated for the C2 and C4 carbons in 1,1-dimethoxyphosphorin (Table 3) are more downfield than in ordinary ylides [2]. This may be attributed to delocalization in the 6π-electron system as visualized in the resonance structures



Further studies, especially directed towards the determination of the ^{13}C-^{1}H (one-bond and long-range) couplings and of the signs of the ^{13}C-^{31}P and ^{1}H-^{31}P coupling constants in phosphorins, are presently being undertaken.

REFERENCES

1. S.Sørensen, R.S.Hansen, and H.J.Jakobsen, J.Amer.Chem.Soc. **94**, 5900 (1972).
2. G.A.Gray, J.Amer.Chem.Soc. **95**, 7736 (1973) and references therein.
3. T.Bundgaard and H.J.Jakobsen, Tetrahedron Letters 3353 (1972).
4. H.Oehling and A.Schweig, Tetrahedron Letters 4941 (1970). C.Batich, E.Heilbronner, V.Hornung, A.J.Ashe,III, D.T.Clark, U.T.Cobley, D.Kilcast, and I.Scanlan, J.Amer.Chem.Soc. **95**, 928 (1973).
5. K.Dimroth, "Phosphorus-Carbon Double Bonds" in "Topics in Current Chemistry 38", Springer-Verlag, Berlin, 1973.
6. T.D.Alger, D.M.Grant, and E.G.Paul, J.Amer.Chem.Soc. **88**, 5397 (1966).
7. T.Bundgaard and H.J.Jakobsen, unpublished results.
8. H.J.Jakobsen, T.Bundgaard, and R.S.Hansen, Mol.Phys. **23**, 197 (1972). S.Sørensen, R.S.Hansen, and H.J.Jakobsen, J.Amer.Chem.Soc. **95**, 5080 (1973).
9. A.J.Ashe,III, J.Amer.Chem.Soc. **93**, 3293, 6690 (1971).
10. T.Bundgaard and H.J.Jakobsen, Acta Chem.Scand. **26**, 2548 (1972).
11. R.L.Lichter and J.D.Roberts, J.Amer.Chem.Soc. **93**, 5218 (1971).
12. H.Schmidbaur, W.Buchner, and D.Scheutzow, Chem.Ber. **106**, 1251 (1973).