

Azomethine Derivatives. Part 18.¹ Diphenyl-, Di-*p*-tolyl-, and Di-*t*-butyl-methyleneamino-derivatives of Phosphorus

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Reactions between methyleneaminolithium reagents $\text{Li}(\text{N}:\text{CR}_2)$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{Me-}p, \text{or Bu}^t$) and the phosphorus chlorides $\text{PCl}_3, \text{PPh}_2\text{Cl}$, or PCl_3O have been used to prepare methyleneamino-derivatives of phosphorus of the following formula types: $\text{PCl}_2(\text{N}:\text{CR}_2), \text{P}(\text{N}:\text{CR}_2)_3, \text{PPh}_2(\text{N}:\text{CR}_2), \text{P}(\text{N}:\text{CR}_2)_3\text{O}, \text{PCl}(\text{N}:\text{CR}_2)_2\text{O}$, and $\text{PCl}_2(\text{N}:\text{CR}_2)\text{O}$. Features of their i.r., ^1H and ^{31}P n.m.r., and mass spectra are reported and discussed.

In earlier parts of the present series (see, for example, ref. 1 and refs. therein) the suitability of methyleneamino-groups $\text{N}:\text{CR}_2$ as ligands for exploring aspects of metal-nitrogen or semi-metal-nitrogen multiple bonding has been discussed, and evidence for linear or near-linear $\text{C}=\text{N}=\text{M}$ units and short $\text{N}=\text{M}$ distances has been reported for systems containing co-ordinatively unsaturated main-group metals^{2,3} or semi-metals.⁴ For some systems $\text{M}(\text{N}:\text{CR}_2)\text{X}_2$ it was possible to deduce

derivatives $\text{P}(\text{N}:\text{CR}^1\text{R}^2)\text{X}^1(\text{X}^2), \text{P}(\text{N}:\text{CR}^1\text{R}^2)\text{S}(\text{X}^1)\text{X}^2$, and $[\text{PMe}(\text{N}:\text{CR}^1\text{R}^2)\text{X}^1(\text{X}^2)]\text{I}$ ($\text{X} = \text{Ph}, \text{Me}, \text{Cl}$, or OMe ; $\text{R} = \text{Ph}, \text{OMe}$, or OEt).

RESULTS AND DISCUSSION

In the present work we have prepared compounds of the following formula types: $\text{PCl}_2(\text{N}:\text{CR}_2), \text{P}(\text{N}:\text{CR}_2)_3, \text{PPh}_2(\text{N}:\text{CR}_2), \text{P}(\text{N}:\text{CR}_2)_3\text{O}, \text{PCl}(\text{N}:\text{CR}_2)_2\text{O}$, and $\text{PCl}_2(\text{N}:\text{CR}_2)\text{O}$ ($\text{R} = \text{Ph}, \text{C}_6\text{H}_4\text{Me-}p, \text{or Bu}^t$; see Tables 1

TABLE 1
Analytical data for the methyleneaminophosphorus(III) compounds

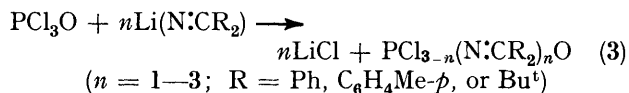
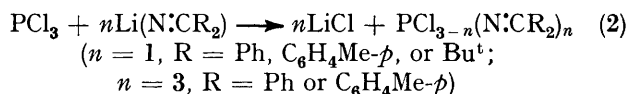
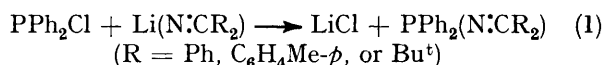
Compound	State	M.p. ($\theta_c/^\circ\text{C}$) ^a	Analysis (%) ^b					<i>M</i>
			C	H	Cl	N	P	
$\text{P}(\text{N}:\text{CPh}_2)_3$	Red crystals ^c	118—120	78.2 (82.0)	5.7 (5.3)	0 (0)	7.1 (7.4)	5.4 (5.4)	580 (571)
$\text{P}[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]_3$	Dark green solid ^c	50—52	80.5 (82.5)	6.4 (6.4)	0 (0)	6.2 (6.4)	4.8 (4.7)	680 (655)
$\text{PCl}_2(\text{N}:\text{CPh}_2)$	Yellow crystals ^d	39—40	54.1 (55.3)	3.9 (3.6)	26.3 (25.2)	5.3 (5.0)	11.4 (11.0)	250 (282)
$\text{PCl}_2[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]$	Yellow crystals ^c	43—45	56.9 (58.1)	4.4 (4.5)	24.9 (23.0)	4.2 (4.5)	9.9 (10.0)	300 (310)
$\text{PCl}_2(\text{N}:\text{CBu}^t_2)$	Yellow oil	[80 (0.5 mmHg)]	44.6 (44.6)	8.4 (7.4)	29.4 (29.3)	5.7 (5.8)	12.7 (12.8)	260 (242)
$\text{PPh}_2(\text{N}:\text{CPh}_2)$	Yellow needles ^d	105—107	83.4 (82.2)	5.4 (5.5)	0 (0)	3.8 (3.8)	8.3 (8.5)	380 (365)
$\text{PPh}_2[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]$	Yellow needles ^d	84	84.4 (82.4)	6.5 (6.1)	0 (0)	3.6 (3.6)	8.1 (7.9)	370 (393)
$\text{PPh}_2(\text{N}:\text{CBu}^t_2)$	Yellow needles ^e	41	76.6 (77.4)	8.8 (8.7)	0 (0)	4.5 (4.3)	9.3 (9.5)	340 (325)

^a Boiling points are given in square brackets. ^b Calculated values are given in parentheses. ^c From toluene-light petroleum. ^d From benzene-pentane. ^e From pentane.

whether their CNM units were linear or bent from the azomethine stretching frequencies, $\nu(\text{C}=\text{N})$, in their i.r. spectra, and from the equivalence or non-equivalence of their substituents R as revealed by their n.m.r. spectra.⁵ For other systems, such as derivatives $\text{M}(\text{NCR}_2)_x\text{X}_{4-x}$ of Group 4 elements M , the structural implications of their i.r. and n.m.r. spectra were less clear-cut, however.¹

The present study of a series of phosphorus derivatives was undertaken to see whether for these systems (which were expected to contain bent $\text{C}=\text{N}-\text{P}$ units) the spectra might be more informative. Earlier work on methyleneaminophosphorus compounds had included a brief study⁶ of the tris(methyleneamino)-derivatives $\text{P}[\text{N}:\text{C}(\text{CF}_3)_2]_3, \text{PCl}_2[\text{N}:\text{C}(\text{CF}_3)_2]_3$, and $\text{P}[\text{N}:\text{C}(\text{CF}_3)_2]_3\text{O}$, and a more extensive study⁷⁻⁹ of the mono(methyleneamino)-

and 2) using reactions (1)—(3). The reactions were carried out by mixing pentane or hexane solutions of the



reagents at low temperature ($< -78^\circ\text{C}$) and then allowing them to warm to room temperature, at which they were stirred for *ca.* 2 h for $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me-}p$; systems with $\text{R} = \text{Bu}^t$ were held at *ca.* 60°C for 1—4 d

¹ Part 17, J. Keable, D. G. Othen, and K. Wade, *J.C.S. Dalton*, 1976, 1.

² H. M. M. Shearer, R. Snaith, J. D. Sowerby, and K. Wade, *Chem. Comm.*, 1971, 1275.

³ J. B. Farmer, H. M. M. Shearer, J. D. Sowerby, and K. Wade, *J.C.S. Chem. Comm.*, 1976, 160.

⁴ G. J. Bullen, *J.C.S. Dalton*, 1973, 858.

⁵ M. R. Collier, M. F. Lappert, R. Snaith, and K. Wade, *J.C.S. Dalton*, 1972, 370.

⁶ R. F. Swindell, D. P. Dabb, T. J. Ouelette, and J. M. Shreeve, *Inorg. Chem.*, 1972, **11**, 242.

⁷ A. Schmidpeter and W. Zeiss, *Angew. Chem.*, 1971, **83**, 397; *Chem. Ber.*, 1971, **104**, 1199.

⁸ A. Schmidpeter, W. Zeiss, and H. Eckert, *Z. Naturforsch.*, 1972, **B27**, 769.

⁹ W. Zeiss and A. Schmidpeter, *Tetrahedron Letters*, 1972, 4229.

to ensure complete reaction. Products were separated from the by-product, LiCl, either by vacuum distillation [in the case of $\text{PCl}_2(\text{N}:\text{Bu}^t_2)$], or by extraction with the solvents indicated in the Tables (after the reaction mixtures had been evaporated to dryness).

Even using prolonged heating, we could not prepare

although several give brown solutions in benzene or toluene.

The monomeric state of association of the compounds was established by cryoscopy on benzene solutions, and supported by mass-spectroscopic studies in which no fragments of m/e greater than those values appropriate

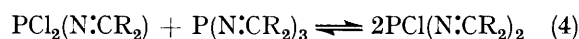
TABLE 2
Analytical data for the methyleneaminophosphorus(v) compounds

Compound	State	M.p. ($\theta_c/^\circ\text{C}$)	Analysis (%) ^a					M
			C	H	Cl	N	P	
$\text{P}(\text{N}:\text{CPh}_2)_3\text{O}$	Yellow solid ^b	46—48	79.9 (79.7)	5.4 (5.1)	0 (0)	7.1 (7.2)	5.5 (5.3)	620 (587)
$\text{P}[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]_3\text{O}$	Green-blue solid ^c	72—73	77.8 (80.5)	5.9 (6.3)	0 (0)	6.1 (6.3)	4.6 (4.6)	690 (671)
$\text{P}(\text{N}:\text{CBu}^t_2)_3\text{O}$	Yellow crystals ^d	60—61	67.4 (69.4)	11.7 (11.6)	0 (0)	8.7 (9.0)	6.9 (6.7)	480 (467)
$\text{PCl}_2(\text{N}:\text{CPh}_2)_2\text{O}$	Colourless crystals ^e	50	69.3 (70.5)	4.7 (4.5)	8.2 (8.0)	6.1 (6.3)	7.3 (7.0)	420 (442)
$\text{PCl}_2[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]_2\text{O}$	Brown solid ^e	65	70.9 (72.2)	5.8 (5.6)	6.9 (7.1)	5.5 (5.6)	6.3 (6.2)	520 (498)
$\text{PCl}_2(\text{N}:\text{CBu}^t_2)_2\text{O}$	White powder ^f	49—51	58.3 (59.6)	9.7 (9.9)	10.0 (9.8)	7.6 (7.7)	8.8 (8.6)	390 (362)
$\text{PCl}_2(\text{N}:\text{CPh}_2)\text{O}$	Cream crystals ^e	47—49	51.4 (52.3)	3.4 (3.4)	24.2 (23.8)	4.8 (4.7)	10.2 (10.4)	310 (298)
$\text{PCl}_2[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]\text{O}$	Yellow-orange solid ^g	75—76	53.9 (55.2)	4.3 (4.3)	22.3 (21.8)	4.1 (4.3)	9.8 (9.5)	340 (326)
$\text{PCl}_2(\text{N}:\text{CBu}^t_2)\text{O}$	Colourless crystals ^h	53—54	43.2 (41.9)	6.7 (7.0)	27.7 (27.5)	5.4 (5.4)	11.9 (12.0)	270 (258)

^a Calculated values are given in parentheses. ^b From toluene-light petroleum. ^c From benzene-light petroleum. ^d From benzene-hexane. ^e From benzene. ^f From hexane. ^g From toluene. ^h From hexane-light petroleum.

$\text{P}(\text{N}:\text{CBu}^t_2)_3$ from PCl_3 and $3\text{Li}(\text{N}:\text{CBu}^t_2)$. Studies on boron,^{5,10} silicon,¹¹ and germanium¹ systems have shown that it is generally more difficult to attach two or more di-*t*-butylmethyleneamino-groups, $\text{N}:\text{CBu}^t_2$, than a similar number of diphenylmethyleneamino-groups, $\text{N}:\text{CPh}_2$, to these elements, a difference attributed to steric hindrance, although our successful preparation of both $\text{PCl}_2(\text{N}:\text{CBu}^t_2)_2\text{O}$ and $\text{P}(\text{N}:\text{CBu}^t_2)_3\text{O}$ in the present work shows that this is not the only factor involved.

We also failed to prepare bis(methyleneamino)-phosphorus(III) chlorides, $\text{PCl}(\text{N}:\text{CR}_2)_2$, from PCl_3 and $2\text{Li}(\text{N}:\text{CR}_2)$, or from $\text{PCl}_2(\text{N}:\text{CR}_2)$ and $\text{P}(\text{N}:\text{CR}_2)_3$, attributed to the reversibility of reaction (4). This



conclusion is supported by ³¹P n.m.r. studies on $\text{PCl}_2(\text{N}:\text{CR}_2)\text{-P}(\text{N}:\text{CR}_2)_3$ systems (see below). Elsewhere, methyleneamino(chloro)-derivatives of boron,^{5,10} aluminium,¹⁰ silicon,^{1,11,12} and germanium¹ have been found to be unstable with respect to similar disproportionation reactions.

With the exception of $\text{PCl}_2(\text{N}:\text{CBu}^t_2)$, all the new methyleneaminophosphorus compounds we have prepared are solids, although generally low-melting (see Tables 1 and 2). The tris(methyleneamino)-compounds $\text{P}(\text{N}:\text{CR}_2)_3$ and $\text{P}(\text{N}:\text{CR}_2)_3\text{O}$ decompose slowly in moist air, typically turning colourless during *ca.* 48 h and deliquescing. The methyleneaminophosphorus chlorides, like other phosphorus chlorides, are more sensitive to moisture, decomposing rapidly in moist air. The intense colours of the compounds $\text{P}(\text{N}:\text{CPh}_2)_3$, $\text{P}[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]_3$, and $\text{P}[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}p)_2]_3\text{O}$ contrast with the relatively pale colours (yellow, off-white, or brown) of the other derivatives (see Tables 1 and 2),

¹⁰ J. B. Farmer, E. A. Petch, R. Snaith, and K. Wade, unpublished work.

¹¹ J. B. Farmer, R. Snaith, and K. Wade, *J.C.S. Dalton*, 1972, 1501.

for monomers were observed. Fragmentation in the mass spectrometer typically involved cleavage of P-N, P-Cl, and C-R links, and migration of groups R from the azomethine carbon to the phosphorus atom. For example, the main peaks in the mass spectrum of $\text{PCl}_2(\text{N}:\text{CBu}^t_2)$ were at m/e 241 (parent ion), 206 $[\text{PCl}(\text{N}:\text{CBu}^t_2)]^+$, 184 $[\text{PCl}_2(\text{N}:\text{CBu}^t_2)]^+$, 171 $[\text{P}(\text{N}:\text{CBu}^t_2)]^+$, 140 $[\text{N}:\text{CBu}^t_2]^+$, 114 $[\text{P}(\text{N}:\text{CBu}^t_2)]^+$, 101 $[\text{PCl}_2]^+$, 83 $[\text{N}:\text{CBu}^t_2]^+$, and 66 $[\text{PCl}]^+$, while the main peaks in the spectrum of $\text{P}(\text{N}:\text{CPh}_2)_3\text{O}$ were at m/e 407 $[\text{P}(\text{N}:\text{CPh}_2)_3\text{O}]^+$, 227 $[\text{P}(\text{N}:\text{CPh}_2)_3\text{O}]^+$, 180 $[\text{N}:\text{CPh}_2]^+$, 103 $[\text{N}:\text{CPh}]^+$, 77 $[\text{Ph}]^+$, 57 $[\text{PNC}]^+$, and 47 $[\text{PO}]^+$. In the spectrum of $\text{PPh}_2(\text{N}:\text{CPh}_2)$, apart from the parent ion at m/e 365, the most intense peaks were at m/e 262 $[\text{PPh}_3]^+$, 185 $[\text{PPh}_2]^+$, and 180 $[\text{N}:\text{CPh}_2]^+$.

TABLE 3

Azomethine stretching bands (cm^{-1}) for the methyleneaminophosphorus compounds recorded as KBr discs. $\Delta\nu = \nu(\text{C}=\text{N})(\text{phosphorus compound}) - \nu(\text{C}=\text{N})(\text{HN}:\text{CR}_2)$

Compound	R = Ph		R = $\text{C}_6\text{H}_4\text{Me-}p$		R = Bu ^t	
	$\nu(\text{C}=\text{N})$	$\Delta\nu$	$\nu(\text{C}=\text{N})$	$\Delta\nu$	$\nu(\text{C}=\text{N})$	$\Delta\nu$
$\text{P}(\text{N}:\text{CR}_2)_3$	1 607	4	1 612	2		
$\text{PCl}_2(\text{N}:\text{CR}_2)$	1 620	17	1 630	20	1 678	68
$\text{PPh}_2(\text{N}:\text{CR}_2)$	1 608	5	1 612	2	1 647 ^a	37
$\text{P}(\text{N}:\text{CR}_2)_3\text{O}$	1 619 ^b	16	1 620	10	1 670 ^c	60
$\text{PCl}(\text{N}:\text{CR}_2)_2\text{O}$	1 620	17	1 618 ^a	8	1 667 ^a	57
$\text{PCl}_2(\text{N}:\text{CR}_2)\text{O}$	1 610 ^a	7	1 607 ^d	-3	1 655	45
$\text{HN}:\text{CR}_2$	1 603 ^d		1 610 ^a		1 610 ^d	

^a Nujol mull. ^b Benzene solution. ^c Hexane solution. ^d Liquid film.

The i.r. spectra of the methyleneaminophosphorus compounds contain strong, in some cases broad, absorptions in the 1 605—1 680 cm^{-1} region attributable to the azomethine stretching vibration, $\nu(\text{C}=\text{N})$. Their frequencies are listed in Table 3, together with values

¹² L.-H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

for the parent methyleneamines $\text{HN}:\text{CR}_2$, and also values of $\Delta\nu$, the frequency difference between the methyleneaminophosphorus compound and the parent methyleneamine. The *diaryl* methyleneamino-derivatives absorb at frequencies similar to, but generally slightly higher than, that of the parent methyleneamine. The compound $\text{PCl}_2[\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2]\text{O}$ is an exception, absorbing at lower frequency than $\text{HN}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2$. The *di-t-butyl* methyleneamino-derivatives, however, have generally higher values of $\nu(\text{C}=\text{N})$ and $\Delta\nu$. This difference between the diaryl and di-*t*-butyl compounds probably arises because conjugation in the former between the aryl groups and the azomethine group reduces the sensitivity of $\nu(\text{C}=\text{N})$ to changes of the substituent at nitrogen, and is in line with observations on related methyleneamino-beryllium,¹⁰ -boron,^{5,10} -aluminium,¹⁰ -silicon,¹¹ and -germanium¹ systems, although the possibility that it reflects structural differences between the two series of phosphorus compounds cannot be excluded. [The bulk of the *t*-butyl groups might enforce a linear $\text{C}=\text{N}-\text{P}$ skeletal geometry where a bent $\text{C}=\text{N}-\text{P}$ skeleton is otherwise preferred, as in the case of the present phosphorus compounds, all of which are expected to contain bent $\text{C}=\text{N}-\text{P}$ units, established by *X*-ray crystallography for $\text{P}(\text{N}:\text{CPh}_2)_3$ ¹³ as indicated below.]

Although, for the compounds containing more than one methyleneamino-group attached to the same phosphorus atom, more than one azomethine stretching vibration is expected to be i.r. active, we found no clear link between the number of methyleneamino-groups in a compound and the number of peaks in the 1 550—1 660 cm^{-1} region, where a characteristic ring mode at

structures could be discerned. For example, the phosphorus(v) compounds absorbed strongly in the 1 160—1 300 cm^{-1} region [$\nu(\text{P}=\text{O})$], and the hydrolysis of samples could be followed by the development of new absorptions in the N-H and C=N stretching regions (*ca.* 3 300 and 1 650 cm^{-1} respectively).

The ¹H n.m.r. spectra of the methyleneaminophosphorus compounds were recorded, using perdeuterio-benzene or -toluene solutions. The compounds having aryl substituents exhibited broad complex absorptions in the τ 2.5—3.5 region. The chemical shifts of the methyl absorptions of the *p*-tolyl and *t*-butyl compounds are listed in Table 4. These absorptions were all sharp singlets, even when solutions were cooled to -60°C .

TABLE 4

Hydrogen-1 n.m.r. chemical shifts (τ values) for the methyl resonances of the $\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2$ and $\text{N}:\text{CBu}^t_2$ derivatives in benzene

	PX_3	PCl_2X	PPh_2X
$\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2$	7.84	7.83	7.82
$\text{N}:\text{CBu}^t_2$		8.66 *	8.68 *
	PX_3O	PClX_2O	PCl_2XO
$\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2$	7.87	7.83	7.89
$\text{N}:\text{CBu}^t_2$	8.59	8.67	8.67

* In toluene.

The ³¹P n.m.r. spectra were recorded using benzene solutions. Chemical shifts are in Table 5, together with values taken from the literature for related isocyanato-,¹⁵ isothiocyanato-,¹⁵ and dimethylamino-compounds.¹⁶⁻¹⁹ The chemical shifts of the compounds $\text{PCl}_n(\text{N}:\text{CR}_2)_{3-n}$ show a close correspondence with those of related isothiocyanates $\text{PCl}_n(\text{NCS})_{3-n}$. The data given in Table 5 for $\text{PCl}(\text{N}:\text{CR}_2)_2$ were obtained using mixtures of

TABLE 5

Phosphorus-31 n.m.r. chemical shifts^a for the methyleneaminophosphorus compounds and related substances

Compound	X					
	$\text{N}:\text{CPh}_2$	$\text{N}:\text{C}(\text{C}_6\text{H}_4\text{Me-}i>p)_2$	$\text{N}:\text{CBu}^t_2$	NCO^b	NCS^b	NMe_2
PX_3	-85.5	-86.3		-97.0	-85.6	-123.0 ^c
PClX_2	-115.2	-117.3		-128.0	-114.0	-158.7 ^d
PCl_2X	-157.2	-159.0		-165.7	-155.3	-166.0 ^d
PCl_3	-220.0	-220.0	-220.0	-220.0	-220.0	-220.0 ^b
PPh_2X	-36.5	-37.3	-29.1			
PX_3O	2.3	1.5	17.7	40.9	61.0	-23.4 ^e
PClX_2O	-7.8 ^f	-7.8 ^f	4.1 ^f	26.6	41.5	-30.3 ^e
PCl_2XO	-7.9 ^f	-7.9 ^f	2.7 ^f	9.2	21.0	-18.1 ^e
PCl_3O	-2.2	-2.2	-2.2	-2.2	-2.2	-2.2 ^e

^a Measured for benzene solutions, relative to P_4O_6 as external reference, but expressed in p.p.m. relative to 85% aqueous H_3PO_4 (resonances to low field of H_3PO_4 are negative). ^b From ref. 15. ^c From ref. 16. ^d From refs. 17 and 18. ^e From ref. 19. ^f See text.

ca. 1 590 cm^{-1} was the only other absorption in the spectra of the compounds having aryl substituents. Elsewhere, the complexity of the spectra in the regions where P-O, P-N, P-C, or P-Cl vibrations are expected¹⁴ prevented unambiguous assignment of other skeletal vibrations, although features supporting the proposed

$\text{P}(\text{N}:\text{CR}_2)_3$ and $\text{PCl}_2(\text{N}:\text{CR}_2)$, which in addition to giving peaks assignable to each reagent, also absorbed at the intermediate frequencies shown. No satisfactory spectrum was obtained for $\text{PCl}_2(\text{N}:\text{CBu}^t_2)$.

The values obtained for the phosphorus(v) compounds are all in the range appropriate for four-co-ordinate

¹⁷ J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, 1964, **86**, 811.

¹⁸ K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307.

¹⁹ M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1968, **5**, 1.

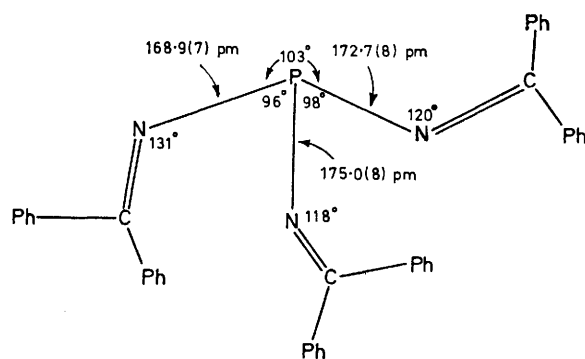
¹³ H. M. M. Shearer, personal communication.

¹⁴ D. E. C. Corbridge, *Topics Phosphorus Chem.*, 1969, **6**, 235.

¹⁵ E. Fluck, *Z. Naturforsch.*, 1964, **B19**, 869.

¹⁶ J. R. Van Wazer, C. F. Callis, J. N. Shooley, and R. C. Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715.

phosphorus compounds. The values listed for the methyleneaminophosphorus chloride oxides $\text{PCl}_n(\text{N}:\text{CR}_2)_{3-n}\text{O}$ ($n = 1$ or 2) may actually relate to rapidly equilibrating mixtures of these two species, since the



Molecular structure ¹³ of $\text{P}(\text{N}:\text{CPh}_2)_3$

spectra recorded also contained peaks attributable to the other disproportionation products $\text{P}(\text{N}:\text{CR}_2)_3\text{O}$ and PCl_3O . Detailed discussion of these values is therefore not justified.

The compound $\text{P}(\text{N}:\text{CPh}_2)_3$ has been the subject of an X-ray crystallographic study ¹³ which has established that the $\text{C}:\text{N}:\text{P}$ units are indeed bent (the average of the

²⁰ N. W. Alcock and M. Pierce-Butler, *J.C.S. Dalton*, 1975, 2469.

three CNP angles is 123°) and the co-ordination at phosphorus is pyramidal (the average of the three NPN angles is 99°). Interestingly, one of the CNP angles [$130.8(6)^\circ$] is significantly larger than the other two [$118.1(7)$ and $120.1(7)^\circ$], and the ligand involved is attached by a slightly shorter $\text{N}-\text{P}$ bond to phosphorus (see Figure), a structural feature reminiscent of the slightly differing modes of attachment to the Group 4 element of the ligands in $\text{Si}(\text{N}:\text{CPh}_2)_4$ and $\text{Ge}(\text{N}:\text{CPh}_2)_4$.²⁰ Again, the shortest and presumably strongest bond attaches the ligand with the largest CNP angle. In $\text{P}(\text{N}:\text{CPh}_2)_3$ the $\text{C}=\text{N}$ lengths are normal (128 pm).

From the spectroscopic data already discussed, we infer that similarly bent CNP units occur in the remaining diarylmethyleneaminophosphorus compounds studied, although the corresponding angles in the di-*t*-butylmethyleneamino-analogues may well be greater.

EXPERIMENTAL

The techniques and instruments used in the present work were as described in earlier parts of this series.

We thank the S.R.C. for the award of grants (to J. K. and R. S.), and Dr. H. M. M. Shearer for the crystallographic data. This paper was written whilst K.W. was a visiting professor at the Free University, Amsterdam, whose hospitality is gratefully acknowledged.

[7/1862 Received, 24th October, 1977]