Chemistry of 2,3-Dihydro-2-metallaphenalenes. Part 2.[1] Formation of $[CHMMe_2C(MMe_3)C_{10}H_6]^x$ *via* Base Decomposition of $[1,8\text{-}(Me_3MCH_2)_2C_{10}H_6]^y$ (M = Ge, $x = 2-$, $y = 0$; M = P, $x = 0$, $y = 2+$); Crystal Structures of the Novel Bis-ylide $CHPMe_2C(PMe_3)C_{10}H_6$ and of a Distorted *peri*-Ylide, $1\text{-}Me\text{-}8\text{-}(Me_3PCH)C_{10}H_6$ †

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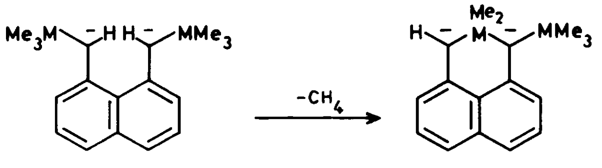
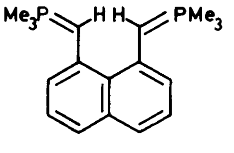
Treatment of $1,8\text{-}(Me_3GeCH_2)_2C_{10}H_6$, derived from a Grignard *in situ* trapping reaction, with $Li(Me_2NCH_2CH_2NMe_2)Bu^n$ in hexane yields the germanium heterocyclic dianion $[CHGeMe_2C(GeMe_3)C_{10}H_6]^{2-}$, characterized as its protonolysis product. Potassium hydride and $[1,8\text{-}(Me_3PCH_2)_2C_{10}H_6]Cl_2$ in tetrahydrofuran affords the novel bis-ylide $HC{=}PMe_2C({=}PMe_3)C_{10}H_6$, (**4**), and small amounts of the mono-ylide $1\text{-}Me\text{-}8\text{-}(Me_3P{=}CH)C_{10}H_6$, (**5**). The ring system in (**4**) is planar, the heteroatom excepted (0.50 Å deviation), with C_{ylide}–P to P–C_{ylide} to C_{ylide}–P distances of 1.742(4), 1.700(5), and 1.726(5) Å; *cf.* P–C_{Me} *ca.* 1.8 and P–C_{ylide} 1.69(1) Å in (**5**). The aromatic rings in (**5**) are twisted, the ylide carbon, which is almost 'co-planar' with the adjacent ring, and *peri*-methyl carbon being skewed in opposite directions.

In Part 1 [1] of the current series we reported the synthesis of the organodilithium complex $[\{Li(tmen)\}_2\{1,8\text{-}(Me_3MCH)_2C_{10}H_6\}]$ (M = Si, tmen = *NNN'N'*-tetramethylethylenediamine), the dianion of which, (**1a**), decomposes with loss of methane to a silicon heterocyclic dicarbanion $[CHSiMe_2C(SiMe_3)C_{10}H_6]^{2-}$, (**2a**), equation (1). The impetus for this process is most likely the release of steric compression within the so called 'fjord' region between the two CH^- groups of (**1a**). By inference from structural studies on dianions related to (**1a**), notably $[\{Li(tmen)\}_2\{o\text{-}(Me_3SiCH)_2C_6H_4\}]$ [2] and $[\{Li(tmen)\}_2\{(2\text{-}Me_3SiCHC_6H_4)_2\}]$,[3] the *peri*-carbon centres that bear the trimethylsilyl groups prefer to be trigonal planar. This, however, would result in unfavourable non-bonding interactions between the protons attached to the *peri*-carbons, resulting in the dianion adopting a strained structure with twisted aromatic rings. Benzo[*c*]phenanthrene can be considered as a model for such a structure. It has both trigonal planar *peri*-carbons and twisted aromatic rings.[4] Hindered substituents (*e.g.* Bu^t or $SiMe_3$) in the 1,8 positions of naphthalene result in a similar distortion of the aromatic rings.[5–7]

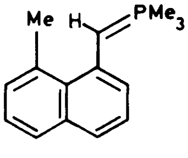


(1)

	M		M
(**1a**)	Si	(**2a**)	Si
(**1b**)	Ge	(**2b**)	Ge



(**3**)



(**5**)

Herein we report (*i*) a study of the synthesis and decomposition of $[1,8\text{-}(Me_3GeCH)_2C_{10}H_6]^{2-}$, (**1b**), to (**2b**), that is analogous to the corresponding silicon species, and (*ii*) results of the attempted synthesis of the bis-phosphonium ylide, (**3**), *via* reactions of $[1,8\text{-}(Me_3PCH_2)_2C_{10}H_6]Cl_2$ with KH in tetrahydrofuran (thf). As to the latter a compound isolated, albeit in low yield, and structurally characterized was $CHPMe_2C(PMe_3)C_{10}H_6$ (**4**) which possibly originates from elimination of CH_4 from (**3**). Attention is drawn to the isolobal relationships between (**1a**), (**1b**), and (**3**), and between (**2a**), (**2b**), and (**4**).

Also from a reaction in (*ii*) small amounts of a material shown by an *X*-ray structure determination to be $1\text{-}Me\text{-}8\text{-}(Me_3PCH)C_{10}H_6$, (**5**), were isolated. This structure is of interest in relation to steric compression across the *peri* positions, discussed above. It is noteworthy that phosphonium ylides have trigonal planar ylide carbon centres that are coplanar with any adjacent aromatic ring(s)[8] so that the driving force of (**3**) ⟶ (**4**) is likely to be as for (**1**) ⟶ (**2**). Ylide carbon centres are in general coplanar with electron-withdrawing groups, including benzoyl[9] and methoxycarbonyl groups,[10] which tend to have a stabilizing influence by conjugation.

Results and Discussion

Germanium Chemistry.—A Grignard *in situ* trapping reaction involving $GeMe_3Cl$, $1,8\text{-}(ClCH_2)_2C_{10}H_6$, and magnesium powder in thf gave $1,8\text{-}(Me_3GeCH_2)_2C_{10}H_6$, (**6a**), in modest yield. Choice of organo-dichloride over dibromide and reaction conditions were as for the synthesis of the analogous silicon compound.[1] Under the conditions employed the dibromide was found to be susceptible to intramolecular

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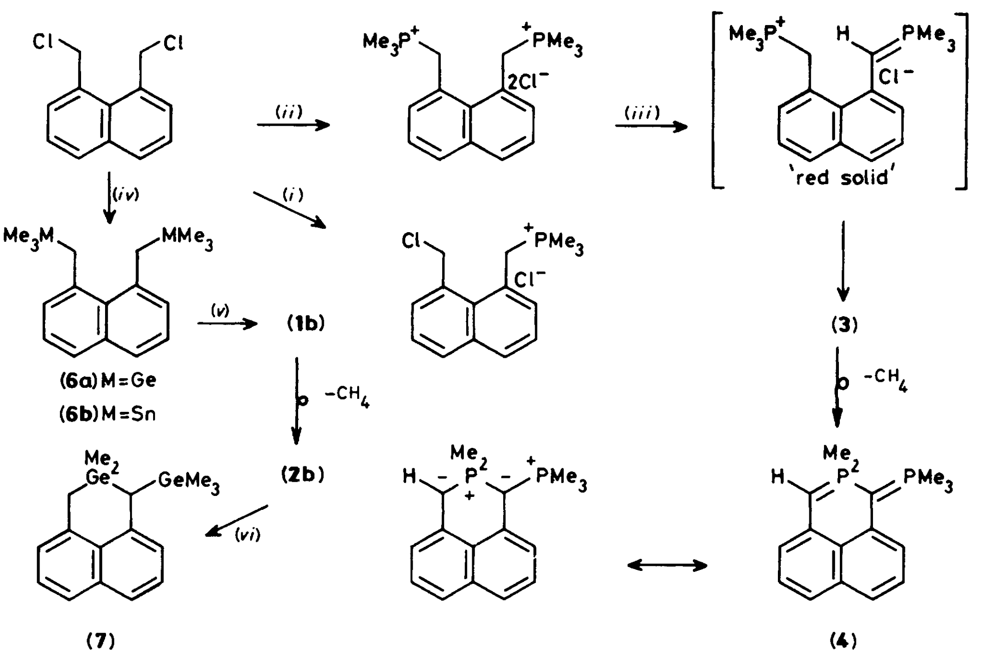
† 2,2-Dimethyl-1-trimethylphosphonio-2λ⁵-phosphaphenalen-1-ide and (8-methyl-1-naphthyl)(trimethylphosphonio)methanide respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: 1 mmHg ≈ 133 Pa.



Scheme. Summary of reactions: (*i*) PMe_3, benzene or thf, or thf–MeOH for (*ii*), *ca.* 20 °C; (*iii*) KH, thf, *ca.* 20 °C; (*iv*) Mg, thf, $GeMe_3Cl$ or $Mg(anth)(thf)_3$ then $SnMe_3Cl$, *ca.* 20 °C; (*v*) $Li(tmen)Bu^n$ in hexane *ca.* 0 °C; and (*vi*) $HCl–H_2O$, *ca.* 20 °C

cyclization, yielding acenaphthylene rather than the trapped di-Grignard reagent, and $GeMe_3Cl$ is not reduced by magnesium. The latter contrasts with rapid reduction of $SnMe_3Cl$ to $(SnMe_3)_2$, and to prepare $1,8-(Me_3SnCH_2)_2C_{10}H_6$, (**6b**), albeit in low yield (*ca.* 10%), preformed di-Grignard reagent was quenched with $SnMe_3Cl$ [^1H n.m.r. of (**6b**) purified on alumina (60 MHz, $CDCl_3$): δ −0.05 (s, 18 H, $SnMe_3$), 2.8 (s, 4 H, CH_2), and 7.25 (m, 6 H, $C_{10}H_6$)]; the di-Grignard reagent was generated by our recently established general method of forming benzylic Grignards that involves treating an organic halide, in the present case the chloride, with $Mg(anth)(thf)_3$ (anth = anthracene) (Scheme).[11] The method, however, suffers from the generation of anthracene in the reaction mixture.

Metallation of (**6a**) using $Li(tmen)Bu^n$ in hexane gave a deep red solution from which deposited a red oil after several days at room temperature. Treatment of the oil with aqueous HCl yielded the germanacycle, (7) (Scheme). The assumed formed dianion (**1b**), like the silicon[1] analogue, is thus intrinsically unstable with respect to elimination of methane and formation of a novel heterocyclic dianion.

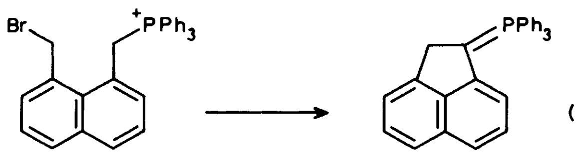
Crystalline complexes of (**1b**) and/or (**2b**) were inaccessible which is surprising given that the silicon system gave red needles of $[\{Li(tmen)\}_2\{1,8-(Me_3SiCH)_2C_{10}H_6\}]$, and two polymorphs of $[\{Li(tmen)\}_2\{CHSiMe_2C(SiMe_3)C_{10}H_6\}]$ (both structurally authenticated).[1] The former has been used to good effect in the synthesis of metallacycles *via* halogen/alkyl exchange reactions, *viz.* *meso*-$SiMe_2L$[1] and *meso*-$[M(\eta-C_5H_5)_2L]$ $\{M = Zr$ or Hf, $L = [1,8-(Me_3SiCH)_2C_{10}H_6]^{2-}\}$.[12]

Metallation of (**6b**) was not attempted because of isolation problems, and the well known nucleophilic attack at metal centres in $SnR_3(CH_2R^1)$ (R^1 = aryl) type species, yielding $Li(CH_2R^1)$, instead of α-proton abstraction.[13]

Phosphorus Ylide Chemistry.—The bis-quaternary phosphonium salt (Scheme) was obtained analytically pure in high yield by treating $1,8-(ClCH_2)_2C_{10}H_6$ with two equivalents of PMe_3 in MeOH–thf. Using thf (or benzene) as the solvent a white precipitate of the mono-quaternary phosphonium salt contaminated with a few percent of the bis-quaternary salt (*ca.* 7%, ^{31}P n.m.r.) was obtained, even for one equivalent of PMe_3.

Treatment of the bis-quaternary salt with potassium hydride in thf gave initially a yellow solution and rapid formation of a red precipitate, most likely of the ylide-quaternary salt (Scheme), that disappeared after *ca.* 15 min at which stage the reaction mixture was rapidly filtered. On cooling to −30 °C overnight yellow prisms of the novel bis-ylide (**4**) were obtained which presumably arise from decomposition of (**3**). This is in accord with the instability of (**1a**)[1] and (**1b**) which are isolobal with (**3**), and yield species isolobal with (**4**).

Work-up of the mother-liquor obtained on isolation of (**4**) yielded a small quantity of a material shown by an *X*-ray structure determination to be (**5**) (see structural commentary). Nucleophilic displacement of PMe_3 by H^- for the mono-ylide depicted in the Scheme, or reduction/ylide formation of traces of $[1-(ClCH_2)-8-(Me_3\overset{+}{P}CH_2)C_{10}H_6]$ arising from incomplete quaternization, are possible routes to (**5**). The latter, however, is unlikely since we were unable to isolate (**5**) on treating this mono-quaternary phosphonium salt with KH in thf, and that the related salt in equation (2), and other non-congested systems, gives a cyclization product.[14,15]



(2)

In assuming compound (**4**) originates from decomposition of (**3**) it is interesting to note that the bis-ylide with phenyl groups in place of methyls in (**3**) is thermally stable, which is typical of bis-ylides[14,16] {exception: that derived from $[C_6H_4(PPh_2Me)_2$-*o*$]^{2+}$ which rearranges to $MePh_2P=C=CPPh_3$[17]}.

To our knowledge $HC=PPh_2CH_2C_{10}H_6$, reported by Schmidbaur and Mörtl,[18] and (**4**) are the only examples of 2-

Table 1. Non-hydrogen atom co-ordinates for (**4**)

Atom	*x*	*y*	*z*
C(1)	0.060 6(4)	0.096 6(4)	0.377 9(3)
C(2)	−0.096 2(4)	0.122 8(4)	0.327 1(3)
C(3)	−0.169 8(5)	0.063 5(4)	0.239 6(3)
C(4)	−0.321 3(5)	0.073 8(5)	0.193 0(4)
C(5)	−0.397 7(5)	0.145 1(5)	0.231 4(4)
C(6)	−0.328 8(5)	0.212 8(4)	0.313 3(3)
C(7)	−0.408 5(5)	0.290 4(5)	0.345 9(4)
C(8)	−0.341 1(6)	0.364 2(5)	0.424 7(4)
C(9)	−0.189 5(5)	0.360 7(4)	0.473 3(3)
C(10)	−0.103 9(5)	0.283 8(4)	0.441 8(3)
C(101)	0.047 7(5)	0.292 2(4)	0.489 2(3)
C(11)	−0.175 0(4)	0.206 0(4)	0.362 2(3)
P(1)	0.138 2(1)	−0.020 1(1)	0.338 00(9)
C(12)	0.166 5(6)	0.013 8(5)	0.231 2(4)
C(13)	0.315 2(5)	−0.064 3(5)	0.419 1(4)
C(14)	0.041 9(6)	−0.164 0(4)	0.320 2(4)
P(2)	0.163 4(1)	0.191 2(1)	0.471 06(8)
C(21)	0.264 7(5)	0.112 1(5)	0.579 0(3)
C(22)	0.307 1(5)	0.272 9(4)	0.450 9(3)

Table 2. Non-hydrogen atom co-ordinates for (**5**)

Atom	*x*	*y*	*z*
C(1)	0.505(1)	0.410(1)	0.359(1)
C(2)	0.428(1)	0.381(1)	0.476(1)
C(3)	0.325(1)	0.426(1)	0.473(2)
C(4)	0.248(1)	0.380(2)	0.567(2)
C(5)	0.262(1)	0.290(1)	0.664(2)
C(6)	0.365(1)	0.256(1)	0.683(1)
C(7)	0.378(1)	0.175(2)	0.788(2)
C(8)	0.476(2)	0.135(1)	0.819(2)
C(9)	0.564(1)	0.198(1)	0.756(2)
C(10)	0.549(1)	0.270(1)	0.656(2)
C(101)	0.648(1)	0.325(1)	0.619(2)
C(11)	0.451(1)	0.301(1)	0.608(1)
P(1)	0.479 6(—)*	0.476 3(2)	0.185 6(4)
C(12)	0.601(1)	0.480(1)	0.068(2)
C(13)	0.379(2)	0.434(1)	0.056(2)
C(14)	0.448(1)	0.609(1)	0.205(2)

* Defines origin.

Table. 3. Non-hydrogen interatomic distances (Å)

	(**4**)*	(**5**)
P(1)–C(1)	1.726(5)	1.69(1)
P(1)–C(12)	1.808(6)	1.84(2)
P(1)–C(13)	1.794(5)	1.77(2)
P(1)–C(14)	1.809(5)	1.74(2)
C(1)–C(2)	1.488(5)	1.43(2)
C(2)–C(3)	1.415(6)	1.44(2)
C(2)–C(11)	1.439(7)	1.52(2)
C(3)–C(4)	1.410(6)	1.39(2)
C(4)–C(5)	1.377(8)	1.40(2)
C(5)–C(6)	1.390(7)	1.40(2)
C(6)–C(11)	1.432(6)	1.39(2)
C(6)–C(7)	1.385(8)	1.35(2)
C(7)–C(8)	1.392(7)	1.38(3)
C(8)–C(9)	1.411(7)	1.48(3)
C(9)–C(10)	1.413(8)	1.25(2)
C(10)–C(11)	1.432(6)	1.38(2)
C(10)–C(101)	1.411(6)	1.49(2)

* (**4**) only: P(2)–C(1,101,21,22), 1.742(4) 1.700(5), 1.795(4), and 1.820(6) Å.

Table 4. Non-hydrogen interatomic angles (°)

	(**4**)*	(**5**)
C(1)–P(1)–C(12)	115.0(2)	107.2(7)
C(1)–P(1)–C(13)	114.4(2)	120.3(7)
C(1)–P(1)–C(14)	114.1(3)	116.5(6)
C(12)–P(1)–C(13)	102.9(3)	108.1(8)
C(12)–P(1)–C(14)	107.7(3)	102.8(7)
C(13)–P(1)–C(14)	101.4(2)	100.4(8)
P(1)–C(1)–C(2)	119.1(3)	125(1)
C(1)–C(2)–C(3)	117.8(4)	121(1)
C(1)–C(2)–C(11)	123.1(3)	121(1)
C(3)–C(2)–C(11)	119.0(4)	117(1)
C(2)–C(3)–C(4)	120.6(5)	119(1)
C(3)–C(4)–C(5)	119.7(4)	125(2)
C(4)–C(5)–C(6)	121.7(4)	116(1)
C(5)–C(6)–C(7)	119.9(4)	115(1)
C(5)–C(6)–C(11)	120.2(5)	125(1)
C(7)–C(6)–C(11)	119.8(4)	120(1)
C(6)–C(7)–C(8)	121.0(4)	121(1)
C(7)–C(8)–C(9)	120.3(5)	116(1)
C(8)–C(9)–C(10)	120.5(4)	121(2)
C(9)–C(10)–C(11)	118.6(4)	123(1)
C(9)–C(10)–C(101)	117.4(4)	110(1)
C(11)–C(10)–C(101)	124.0(5)	126(1)
C(2)–C(11)–C(6)	118.2(4)	116(1)
C(2)–C(11)–C(10)	122.1(4)	125(1)
C(6)–C(11)–C(10)	119.7(4)	119(1)

* (**4**) only: C(10)–C(101)–P(2), 122.7(3); P(1), C(2)–C(1)–P(2), 121.7(2), 119.1(3); C(1)–P(2)–C(101, 21, 22), 107.2(2), 114.6(2), 114.0(2); C(101)–P(2)–C(21, 22), 109.8(2), 110.2(2); and C(21)–P(2)–C(22), 101.1(2)°.

phosphaphenalenes. Other 2-metallaphenalenes are 2,3-dihydro systems based on Si,[1,19] Ge (above), P,[18] the main Group 6 elements,[20] and Zr and Hf.[11]

Structural Commentary.—Results of the *X*-ray structure determinations of (**4**) and (**5**) are given in Tables 1—5, and Figures 1—4 which define the numbering schemes used; the asymmetric unit in each case is a discrete molecule. Of particular interest are (*i*) the P–C_{ylide} and C_{ylide}–C distances; and (*ii*) the disposition of the aromatic rings relative to each other and the planes of the sp^2 hybridized C_{ylide} atoms. A noteworthy feature of the structures is they are the first of trialkylphosphorus ylides; previous structural studies on phosphorus ylides have centred in triaryl systems.

In (**5**) the P–C_{ylide} distance, 1.69(1) Å, is shorter than the P–C_{methyl} distances both in (**5**) and (**4**), *ca.* 1.80 Å, and is therefore indicative of some double bond character. It is, however, significantly longer than the corresponding distance in Ph_3PCH_2, 1.661(5) Å.[21] This is consistent with the stabilizing influence in (**5**) by the classical mesomeric resonance of the naphthyl ring system which is reflected in the C_{ylide}–C_{aryl} distance of 1.43(2) Å, well below a typical C_{aryl}–C distance of 1.49 Å, *e.g.* C–C_{Me} distance in (**5**). Regrettably the imprecision of the determination precludes the identification of specific resonance contributions within the rings.

Resonance stabilization would be favoured when the plane defined by C_{ylide} and adjacent atoms is coplanar with the aromatic ring. The tendency for this in (**5**) is a consequence of the twisting of the two aromatic rings to avoid otherwise unfavourable non-bonding interactions between the ylide hydrogen and hydrogens of the methyl groups (Figures 3 and 4). The phosphorus atom is −1.15 Å out of the 'plane' defined by the aromatic carbon atoms (Table 5); the methyl carbon is skewed 0.45 Å in the opposite direction. Such twisting is prevalent amongst 1,8-substituted naphthalenes, particularly with hindered substituents.[5–7]

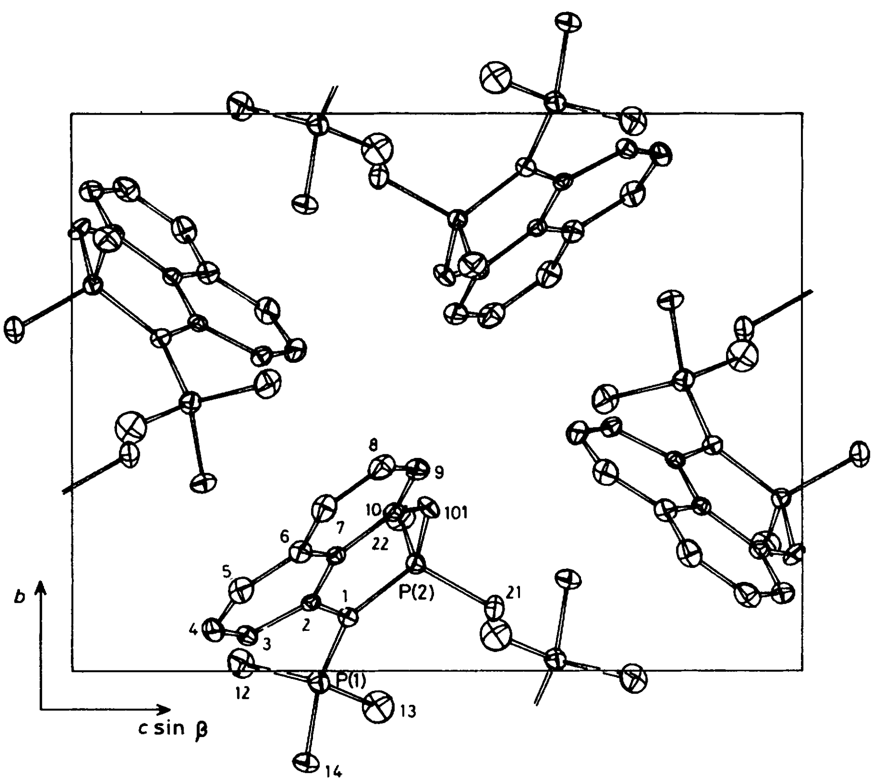


Figure 1. Unit-cell contents of (4) projected down *a*

Table 5. Least-squares planes. Least-squares planes defined by the C(2—11) skeleton are given in the form $pX + qY + rZ = s$, where the right-hand orthogonal Å frame (X, Y, Z) has X parallel to a, Z in the ac plane. Atom deviations are in Å

	(4)	(5)
10^4p	−3 604	854
10^4q	−7 452	6 597
10^4r	6 569	7 467
s	2.572	6.796
χ^2	782	482
δC(1)	0.24	−0.61
δC(2)	0.08	−0.21
δC(3)	−0.06	0.03
δC(4)	−0.06	0.15
δC(5)	0.02	0.01
δC(6)	0.05	−0.04
δC(7)	0.03	−0.06
δC(8)	−0.02	−0.09
δC(9)	−0.05	0.14
δC(10)	−0.05	0.11
δC(101)	−0.19	0.45
δC(11)	0.04	−0.04
δP(1)	0.50	−1.15
δC(12)	−0.95	−1.72
δC(13)	1.04	−2.42
δC(14)	1.85	0.04
δP(2)	0.03	
δC(21)	1.40	
δC(22)	−1.35	

Compound (4) can be formally considered as possessing two ylide centres having contributions from two classical resonance forms, namely that with a $P(d)$–$C_{ylide}(p)$ π bond and a carbanion attached to a phosphorus centre carrying a high

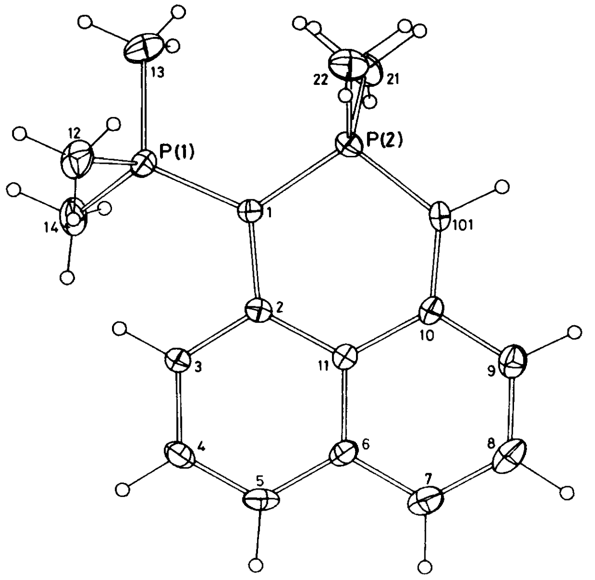


Figure 2. Single molecule of (4) showing 20% thermal ellipsoids for the non-hydrogen atoms and labelling; hydrogen atoms have an arbitrary radius of 0.1 Å

degree of negative charge (Scheme). The P–C_{ylide} distances, however, indicate that the two ylide centres cannot be considered in isolation and there is at least a contribution from $C(10)\overset{-}{C}(101)H\text{–}P(2)Me_2{=}C(1)\overset{+}{P}(1)Me_3C(2)$ (*cf.* highest occupied molecular orbital of butadiene which has a double bond between the two central carbons); P(1)–C(1) 1.726(5), P(2)–C(1)

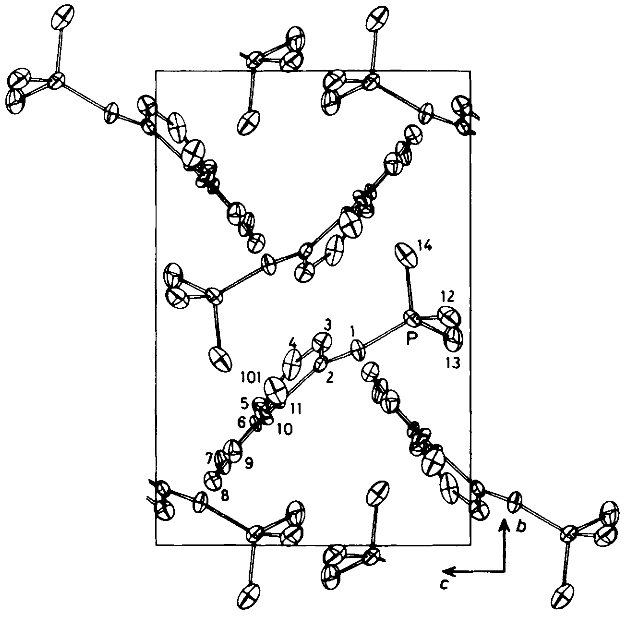


Figure 3. Unit-cell contents of (5) projected down *a*

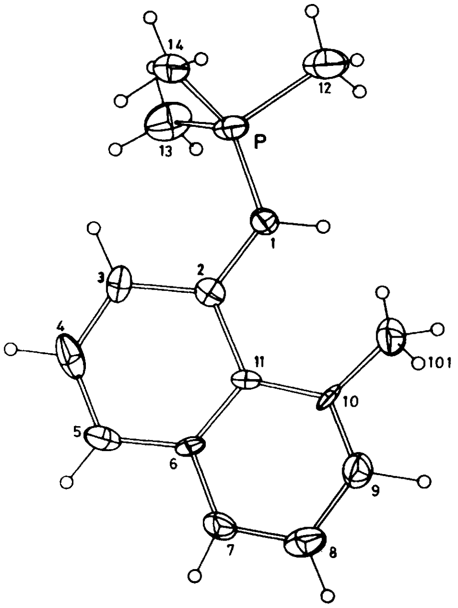
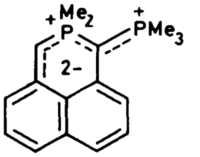


Figure 4. Single molecule of (5) as for (4) (Figure 2)

1.742(4), and P(2)–C(101) 1.700(5) Å all lie between the extremes discussed above, *viz.* 1.661(5) Å in Ph_3PCH_2,[21] and *ca.* 1.8 Å for P–C single bonds. Each ylide carbon centre has a potentially resonance stabilizing aryl ring attached. However, resonance is evident only for the ylide carbon C(101). The C(101)–C_{aryl} distance is 1.411(6) Å which is unexceptional for C_{ylide}–C_{aryl} distances[8] and compares with 1.43(2) in (5). The other C_{ylide}–C_{aryl} distance in (4) is 1.488(5) Å, typical of an 'sp^3' carbon attached to an aromatic ring and it therefore appears that this ylide carbon is resonance stabilized by the second phosphorus, demonstrated by the associated P–C distance [1.700(5) Å], rather than by the adjacent aromatic ring. The resonance representation that is most consistent with the data is shown below.



Unlike (5) the naphthalene ring system, together with the two ylide carbon atoms, defines a tolerably planar fragment (Table 5), from which the heterocyclic phosphorus atom deviates by 0.50 Å and the exocyclic phosphorus by 0.03 Å. Thus, although sp^2 C(1) and C(101) ylide carbons would tend to dictate a planar heterocycle the phosphorus within the ring resides out of the plane. This presumably is a consequence of the geometrical requirement of incorporating a rather large hetero atom in a six-membered ring. Support for this is the opening of the angles at C(2) and C(10) subtended by C(1) and C(11) [123.1(3)°], and C(11) and C(101) [124.0(5)°], respectively, being greater than 120°. The structure of the fused three ring system is similar to that of $1,8\text{-}S(CH_2)C_{10}H_6CH_2$[22] and the dianion (**2a**), which is isoelectronic with (**4**), in one of the polymorphs of $[\{Li(tmen)\}_2\{CHSiMe_2C(SiMe_3)C_{10}H_6\}]$.[1] Here the ring silicon is 0.54 Å out of the plane, the second silicon being at −0.24 Å. In the other polymorph the naphthalene rings and adjacent carbons no longer define a reasonable plane, possibly due to a strong influence of the interaction of the lithium centres with the dianion.

Experimental

General Procedures.—All manipulations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from $LiAlH_4$ (thf), Na (benzene), $CaCl_2$ (MeOH), or CaH_2 (hexane). 1,8-Bis(chloromethyl)naphthalene was prepared according to the method outlined in ref. 1. $GeMe_3Cl$ and PMe_3 were purchased from Strem Chemicals. ^1H N.m.r., and ^{13}C and ^{31}P n.m.r., spectra were recorded on Hitachi-Perkin-Elmer R-24B and Bruker WP-80 spectrometers, respectively.

Synthesis of 1,8-*Bis*(*trimethylgermylmethyl*)*naphthalene* (**6a**).—To a suspension of magnesium powder (0.65 g, 27 mmol) in tetrahydrofuran (10 cm^3) was added 1,2-dibromoethane (0.2 cm^3). After evolution of ethylene was evident the mixture was stirred for 5 min, whereupon the thf was replaced by fresh thf (10 cm^3) and $GeMe_3Cl$ added (3.3 cm^3, 28 mmol) followed by the slow addition of 1,8-bis(chloromethyl)naphthalene (2 g, 8.9 mmol) in thf (40 cm^3) at such a rate as to maintain the temperature of the mixture close to 40 °C. After addition was complete, stirring was continued overnight at room temperature. The solvent was then removed *in vacuo* and the residue extracted with hexane (100 cm^3). The filtrate was washed with dilute hydrochloric acid (20 cm^3), dried (Na_2CO_3), and concentrated. Distillation afforded a colourless liquid (2.4 g, 71%), b.p. 114 °C (10^{-2} mmHg) (Found: C, 55.5; H, 7.2. Calc. for $C_{18}H_{28}Ge_2$: C, 55.7; H, 7.3%); ^1H n.m.r. (60 MHz, $CDCl_3$), δ −0.1 (s, 18 H, $GeMe_3$), 2.85 (s, 4 H, CH_2), and 7.25 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (20.1 MHz, ^1H decoupled, $CDCl_3$), δ −2.2 (s, $GeMe_3$), 29.6 (CH_2), 124.8, 126.6, 127.4 (CH, $C_{10}H_6$), 132.1, 136.3, 138.9 (C, $C_{10}H_6$); *m/e* 389 $(P)^+$, 182 $(P - GeMe_3)^+$ and 64 $(P - 2\ GeMe_3)^+$.

Synthesis of 2,2-*Dimethyl*-1-*trimethylgermyl*-2,3-*dihydro*-2-*germaphenalene* (**7**).—To a cooled solution of $LiBu^n$ (1.7 cm^3, 2.7 mmol of a 1.7 mol dm^{-3} solution in hexane) was slowly added tmen (0.4 cm^3, 2.6 mmol) with stirring, followed by 1,8-$(Me_3GeCH_2)_2C_{10}H_6$ (0.5 g, 1.2 mmol) yielding a red solution. During 6 d at room temperature a red oil formed. A solution of aqueous HCl (1 mol dm^{-3}, 10 cm^3) was then slowly added. After stirring for 5 min at room temperature the organic phase was separated, dried (Na_2CO_3), and the solvent removed *in vacuo* to afford a colourless liquid (0.34 g, 76%), b.p. 142 °C (0.5 mmHg); ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ −0.10 (s, 9 H, $GeMe_3$), −0.05 (s, 3 H, $GeMe_2$), 0.4 (s, 3 H, $GeMe_2$), 2.2 (J_{AX} *ca.* 0, J_{AX} 2.5, X part of ABX, CH), 2.4 (J_{AB} 17.0, J_{AX} *ca.*0 Hz, AB part of ABX, CH_2), and 7.3 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (20.1 MHz, ^{1}H decoupled, $CDCl_3$), δ −3.1 ($GeMe_2$), −2.2 ($GeMe_2$), −0.7 ($GeMe_3$), 21.0 (CH_2), 25.6 (CH), 124.8, 125.6, 127.0, 128.2, 128.9 (CH, $C_{10}H_6$), 135.7, 135.8, 140.3 (C, $C_{10}H_6$).

Synthesis of 1-*Chloromethyl*-8-(*trimethylphosphoniomethyl*)-*naphthalene Chloride*.—1,8-Bis(chloromethyl)naphthalene (0.5 g, 2.2 mmol) was dissolved in benzene (10 cm^3) or thf (10—20 cm^3). On addition of trimethylphosphine (0.68 cm^3, 6.7 mmol) a fine white precipitate of the *title compound* formed. This was filtered off, washed with thf (2 × 2 cm^3), and dried *in vacuo* (0.86 g, 85%); ^{1}H n.m.r. (60 Mz, CD_3OD), δ 1.30 (d, 9 H, J_{P-H} 14, PMe_3), 4.06 (d, 2 H, J_{P-H} 16 Hz, PCH_2), 4.78 (s, 2 H, $ClCH_2$), and 7.0—7.7 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. (20.1 MHz, ^{1}H decoupled, CD_3OD), δ 7.9 (d, J_{P-C} 56, PMe_3), 30.7 (d, J_{P-C} 50 Hz, CH_2), 50.0 (s, $ClCH_2$), and 136—124 ($C_{10}H_6$, not assigned); ^{31}P n.m.r. (32.4 MHz, ^{1}H decoupled, CD_3OD), δ 29.1.

Synthesis of 1,8-*Bis*(*trimethylphosphoniomethyl*)*naphthalene Dichloride*.—1,8-Bis(chloromethyl)naphthalene (0.5 g, 2.2 mmol) was dissolved in thf (10 cm^3). After addition of trimethylphosphine (0.68 cm^3, 6.7 mmol) sufficient anhydrous methanol (*ca.* 4 cm^3) was added to dissolve a white precipitate of the above chloride. The solution was then stirred at room temperature for 12 h during which a white solid of the *title compound* formed. This was filtered off, washed with thf (2 × 2 cm^3), and then dried *in vacuo* (0.76 g, 92%) (Found: C, 57.6; H, 7.25; Cl, 18.4. Calc. for $C_{18}H_{28}Cl_2P_2$: C, 57.3; H, 7.50; Cl, 18.8%); ^{1}H n.m.r. [60 MHz, $(CD_3)_2SO$], δ 1.70 (d, 18 H, J_{P-H} 13 Hz, PMe_3), 4.70 (d, 4 H, J_{P-H} 20 Hz, PCH_2), and 7.3—8.0 (m, 6 H, $C_{10}H_6$); ^{13}C n.m.r. [20.1 MHz, ^{1}H decoupled, $(CD_3)_2SO$], δ 8.0 (d, J_{P-C} 54, PMe_3), 13.7 (d, J_{P-C} 50 Hz, P–CH_2), and 136.8—124.6 ($C_{10}H_6$, not assigned); ^{31}P n.m.r. [32.4 MHz, ^{1}H decoupled, $(CD_3)_2SO$], δ 30.6.

Reaction of the above Diphosphonium Salt with Potassium Hydride.—KH (0.24 g, 6.1 mmol) in thf (20 cm^3) was added to the diphosphonium salt (2.3 g, 6.1 mmol) in thf (20 cm^3). Immediately the solution became yellow and after 4 min a red-orange precipitate formed. After 15 min most of this precipitate had reacted yielding a yellow solution and at this stage the mixture was rapidly filtered. The resulting clear solution was then reduced to half the original volume and cooled to −30 °C overnight whereupon yellow prisms of (**4**) deposited. These were collected, washed with cold thf (−30 °C), and then dried *in vacuo* (0.4 g, 22%), m.p. 158—164 °C; ^{1}H n.m.r. (80 MHz, [$^2H_8$]-thf), δ 1.61, (d, 6 H, J_{P-H} 12.5, PMe_2), 1.67 (d, 9 H, J_{P-H} 12.5 Hz, PMe_3), and 7.1 (m, 6 H, $C_{10}H_6$); ^{31}P n.m.r. (32.4 MHz, ^{1}H decoupled, [$^2H_8$]thf), δ −11.96 and −15.24. The mother-liquor was concentrated to *ca.* 5 cm^3 and warm hexane added (20 cm^3). Slow cooling to −30 °C yielded yellow prisms that were shown by *X*-ray diffraction studies to be (**5**), and colourless needles of trimethylphosphine oxide (Found: C, 39.5; H, 9.8. Calc. for C_3H_9OP: C, 39.1; H, 9.85%).

Crystallography.—Unique data sets were measured at 295 K to the specified $2\theta_{max.}$ limits using a Syntex $P2_1$ four-circle diffractometer fitted with an Mo-K_α radiation source (λ = 0.710 69 Å) and operating in conventional 2θ/θ scan mode. *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement with statistical weights and without absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included at estimated values. Residuals at convergence *R*, *R′* on |*F*| are quoted. Neutral complex scattering factors were used;[23] computation used the XTAL 83 program system[24] implemented on a Perkin-Elmer 3240 computer.

Crystal data for (**4**). $C_{17}H_{22}P_2$, M = 288.3, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 10.025(4), b = 10.924(4), c = 15.362(6) Å, β = 112.80(3)°, U = 1 551(1) Å^3, D_c (Z = 4) = 1.23 g cm^{-3}, $F(000)$ = 616, μ_{Mo} = 2.7 cm^{-1}. Specimen: 0.24 × 0.24 × 0.5 mm (capillary). $2\theta_{max.}$ = 60°. N = 3 745, N_o = 2 340; R, R' = 0.061, 0.028.

Crystal data for (**5**). $C_{15}H_{19}P$, M = 230.3, orthorhombic, space group $P2_1na$ (variant of C_{2v}^9, no. 33), a = 12.896(6), b = 12.635(13), c = 8.267(4) Å, U = 1 347(1) Å^3, D_c (Z = 4) = 1.14 g cm^{-3}, $F(000)$ = 496, μ_{Mo} = 1.8 cm^{-1}. Specimen: spheroid, 0.15 mm diameter (capillary). $2\theta_{max.}$ = 50°. N = 1 253, N_o = 866; R, R' = 0.073, 0.089 (both chiralities).

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