

The Reactivity of Diphosphenes towards Electrophilic and Nucleophilic Reagents

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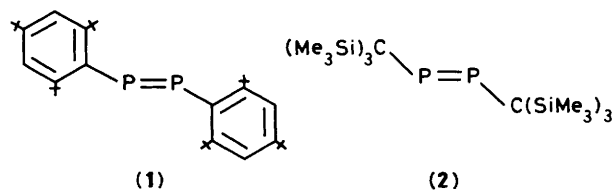
The reaction of $P_2[C(SiMe_3)_3]_2$ (**2**) with a stoichiometric quantity of HCl leads to $(Me_3Si)_3CP(H)-P(Cl)C(SiMe_3)_3$ whilst an excess of this reagent causes P=P cleavage and results in the formation of $PH(Cl)[C(SiMe_3)_3]$. The corresponding reaction with $RP=PR$ ($R = 2,4,6-Bu^tC_6H_2$), (**1**), results in $PH(Cl)R$, even when 1 equivalent of HCl is used. Protonation of compound (**2**) with $HBF_4 \cdot Et_2O$ at $-78^\circ C$ results in the phosphonium salt $[PH_3\{C(SiMe_3)_3\}][BF_4]$. Protonation of (**1**) with $HBF_4 \cdot Et_2O$ is more complex and leads ultimately to P=P bond cleavage and insertion of a cationic phosphorus centre into a C-H bond of an *ortho*- Bu^t group. The dication $[R(Ag)P=P(Ag)R]^{2+}$ and the monocation $[R(Ag)P=PR]^+$ and $[RP=P(AuPEt_3)R]^+$ are formed on treatment of (**1**) with $Ag[SO_3CF_3]$ or $[Au(PEt_3)][PF_6]$. The reaction of (**1**) with excess of sulphur in the presence of 1,5-diazabicyclo[5.4.0]undec-5-ene results in P=P bond cleavage and formation of a cyclic dithiophosphinic acid. The diphosphene, (**1**), reacts with $LiMe$ to afford the anion $[RP-P(Me)R]^-$. Quenching with MeOH affords the diphosphine $R(H)P-P(Me)R$, whilst treatment of $[RP-P(Me)R]^-$ with OH^- causes P-P bond cleavage and formation of the phosphine oxides PH_2RO and $PH(Me)RO$. Treatment of $[RP-P(Me)R]^-$ with $HBF_4 \cdot Et_2O$ produces PH_2R and the phosphonium salt $[PH_2(Me)R][BF_4]$. Treatment of (**1**) with $LiBu^t$ also results in anion formation, viz. $[RP-P(Bu^t)R]^-$, as the major product which on protonation with MeOH gives the diphosphine $R(H)P-P(Bu^t)R$. The corresponding reaction with $LiBu^n$ gives the related anion and diphosphine. The reaction of (**1**) with $K[BHBU_3]$ results only in the diphosphine $R(H)P-P(H)R$.

In recent years the syntheses of compounds featuring double bonds between the heavier Group 4¹ and 5² elements has been achieved by the use of bulky R groups. In the context of Group 4 this has led to the isolation of disilenes¹ ($R_2Si=SiR_2$), digermenes³ ($R_2Ge=GeR_2$), and a distannene⁴ ($R_2Sn=SnR_2$), whilst in Group 5 the synthesis of diphosphenes² ($RP=PR$), arsaphosphenes² ($RP=AsR$), diarsenes² ($RA=AsR$), and a stibaphosphene² ($RP=SbR$) has been accomplished. Preliminary reports of silaphosphenes⁵ ($RP=SiR_2$) and germaphosphenes⁶ ($RP=GeR_2$) have also appeared. Initial studies on these novel compounds centred around synthetic methodology, structure elucidation, and spectroscopic characterisation. More recently, however, reactivity studies have begun to emerge, particularly on disilenes⁷ and diphosphenes.⁸⁻¹¹

The reactivity patterns of diphosphenes fall into three categories, namely co-ordination chemistry, attack by electrophiles, and attack by nucleophiles. The co-ordination chemistry of diphosphenes (and heavier congeners) has been studied in considerable detail.^{2,12} Somewhat less is known, however, about the behaviour of diphosphenes towards electrophiles and nucleophiles, and it is these areas that are addressed in the present work. From a theoretical standpoint, we note that diphosphenes are anticipated to exhibit both electrophilic and nucleophilic reactivity. Thus, molecular orbital (m.o.) calculations on the model diphosphene, *trans*- P_2H_2 , indicate that the highest occupied levels are closely spaced and correspond to P=P π -bond and phosphorus lone-pair m.o.s.¹³ The lowest unoccupied molecular orbital (l.u.m.o.) possesses considerable P=P π^* character and is relatively low lying.

Results and Discussion

Reactivity towards Electrophiles.—Initial studies on the reactivity of diphosphenes towards electrophiles were concerned with the reaction of HCl with $P_2(C_6H_2Bu^t-2,4,6)_2$ (**1**) and $P_2[C(SiMe_3)_3]_2$ (**2**). Treatment of a solution of compound (**2**) in Et_2O at $-20^\circ C$ with an equimolar quantity of dry,



gaseous HCl led to a fading of the yellow-orange colour and the formation of a white solid, (**3**). A $^{31}P\{-^1H\}$ n.m.r. spectrum of this material comprised two AX spectra in approximate ratio 2:1. The corresponding proton-coupled ^{31}P spectrum indicated the presence of a single P-H group per diphosphorus unit. These data (Table), together with high-resolution mass spectral (h.r.m.s.) data (Experimental section) are consistent with the composition $(Me_3Si)_3CP_A(H)-P_B(Cl)C(SiMe_3)_3$, (**3**), which exists in two isomeric forms, (**3a**) and (**3b**).^{8a}

The production of two diastereomers of (**3**) stems from the presence of a chiral centre at each phosphorus atom. Note also that each diastereomer consists of a D,L enantiomeric pair. Model building indicates that, due to their substantial steric bulk, the $(Me_3Si)_3C$ groups will be constrained to mutually *trans* positions. The isomers (**3a**) and (**3b**) can therefore be represented by the following Newman projections. On the basis of the relative magnitudes of $^1J_{PP}$ and assuming that the sign of

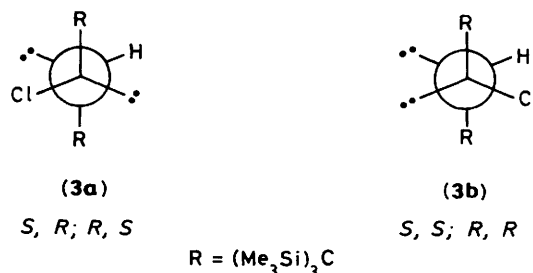


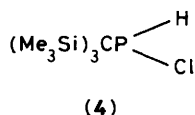
Table. ^{31}P N.m.r. data

Compound	$\delta(\text{P})/\text{p.p.m.}^{a,b}$	Coupling constant/Hz ^b
(3a)	$P_A -36.7 (-38.3), P_B 173.5 (170.0)$	$^1J(P_A P_B) = 224.7 (226.5), ^1J(P_A H) = 201.6 (203.0), ^2J(P_B H) = 26.7 (26.5)$
(3b)	$P_A -29.4 (-24.9), P_B 154.1 (148.7)$	$^1J(P_A P_B) = 380.8 (379.5), ^1J(P_A H) = 213.9 (211.8), ^2J(P_B H) = 25.3 (26.5)$
(4)	70.5 (69.5)	$^1J_{\text{PH}} = 160.6 (169)$
(5)	26.4	$^1J_{\text{PH}} = 215.0$
(6)	-56.3	$^1J_{\text{PH}} = 502.2$
(7)	$P_A -86.1, P_B 10.6$	$^1J(P_A P_B) = 290.0, ^1J(P_A H_A) = 229.0, ^2J(P_A H_B) = 6.6, ^1J(P_B H_B) = 481.0, ^2J(P_B H_A) = 9.8, ^2J(P_B H_{\text{CC}}) \text{ ca. } 5$
(8)	17.7	$^1J_{\text{PH}} = 528$
(9)	$P_A 403, P_B 358, P_X 41.5$	$^1J(P_A P_B) = 555, ^2J(P_B P_X) = -320, ^3J(P_A P_X) = 8$
(10)	$P_A 435, P_B 378$	$^1J(P_A P_B) = 549, ^1J(P_B^{109}\text{Ag}) = -751, ^1J(P_B^{107}\text{Ag}) = -750, ^2J(P_A^{109}\text{Ag}) = 12, ^2J(P_A^{107}\text{Ag}) = 11.5$
(11)	355	$^1J_{\text{PP}} = 480, ^1J_{\text{PAg}} = -760, ^2J_{\text{PAg}} = 13, ^3J_{\text{AgAg}} = -35$
(16)	75	
(18)	-77	
(20)	$P_A -94.0, P_B -43.0$	$^1J(P_A P_B) = 408$
(21)	$P_A -60.4, P_B -45.0$	$^1J(P_A P_B) = 201.0, ^1J(P_A H) = 207.0, ^3J(P_A \text{Me}) = 1.0, ^2J(P_B H) = 12.0, ^2J(P_B \text{Me}) = 5.7$
(23)	24	$^1J_{\text{PH}} = 575$
(25)	-28.5	$^1J_{\text{PH}} = 521, ^2J_{\text{PMe}} = 17$
(26)	$P_A -57.0, P_B 72.5$	$^1J(P_A P_B) = 325$
(27)	$P_A -116, P_B 7$	$^1J(P_A P_B) = 458$
(28)	$P_A -78.9, P_B 42.4$	$^1J(P_A P_B) = 325, ^1J(P_A H) = 209, ^2J(P_B H) = 2, ^3J(P_B \text{Bu}') \text{ ca. } 3$
(29)	-72.0	$^1J_{\text{PH}} = 218$
(31)	$P_A -87.2, P_B -8.2$	$^1J(P_A P_B) = 353$
(32)	$P_A -64.1, P_B -23.2$	$^1J(P_A P_B) = 224, ^1J(P_A H) = 208, ^2J(P_B H) = 10$

^a Chemical shifts relative to external 85% H_3PO_4 . Positive values to high frequency and *vice versa*. ^b Values in parentheses are those reported in ref. 11a. ^c Average $^{109}\text{Ag}/^{107}\text{Ag}$ couplings, see text.

this coupling constant is negative,¹⁶ we propose that the phosphorus lone pairs in (3a) and (3b) adopt mutually *trans* and *gauche* orientations. The reason for the production of unequal amounts of isomers (3a) and (3b) is not clear. Similar observations have been reported by Escudié *et al.*,^{11a} the only significant difference in our results being an even greater preponderance of the isomer (3a) [(3a):(3b) = 83:17]. It is therefore possible that the isomeric ratio is sensitive to small differences in reaction conditions.

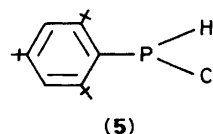
Treatment of compound (2) with an excess of HCl causes cleavage of the P=P bond and results in the formation of $\text{PH}(\text{Cl})[\text{C}(\text{SiMe}_3)_3]$ (4). This formulation is consistent with the



h.r.m.s. and with the proton-coupled ^{31}P n.m.r. spectrum (Table). Phosphines of the type $\text{PH}(\text{Cl})\text{R}$ are interesting because they are normally unstable with respect to loss of HCl and consequent oligomerisation to cyclopolyphosphines, $(\text{RP})_n$, the only previous exceptions being where $\text{R} = \text{CF}_3$ ¹⁷ or when the $\text{PH}(\text{Cl})\text{R}$ unit is co-ordinated to a transition metal.¹⁸ Compound (4) has been reported independently by Escudié *et al.*^{11a}

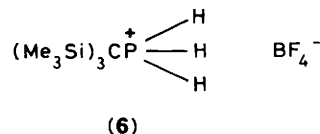
The diphosphene (1) also reacts with HCl under similar conditions; however, in this case it was not possible to isolate a HCl addition product analogous to (3).^{*} Even with a stoichiometric quantity of HCl, P=P bond cleavage occurs

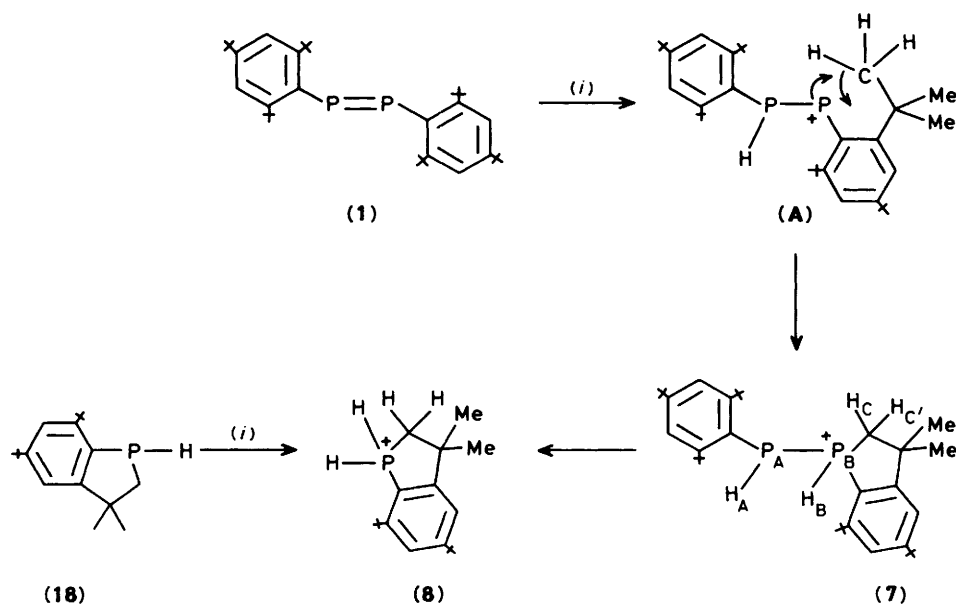
* Such a compound can, however, be produced by another synthetic route (A. M. Arif, A. H. Cowley, M. Pakulski, and G. J. Thomas, unpublished work).



resulting in (5), a chlorophosphine analogous to (4). The isolation of (4) and (5) highlights an interesting problem relating to the decomposition of phosphines of the type $\text{PH}(\text{Cl})\text{R}$. There seems to be no obvious reason why such species should not undergo unimolecular HCl elimination and formation of diphosphenes in a fashion analogous to the production of cyclopolyphosphines from chlorophosphines bearing smaller R groups. We therefore suggest that the decomposition of phosphines $\text{PH}(\text{Cl})\text{R}$ may be bimolecular and that with very bulky R groups formation of the transition state is precluded.

Protonation in the presence of a non-co-ordinating anion was examined by treatment of compounds (1) and (2) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.^{8a} The characteristic yellow-orange colour of (2) faded rapidly upon mixing with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 solution at -78°C . $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectroscopic assay of the reaction mixture revealed the presence of many products. After *ca.* 2 h, however, the spectrum simplified greatly and comprised only a singlet at -56.3 p.p.m. The corresponding proton-coupled spectrum consisted of a quartet ($^1J_{\text{PH}} = 502.2$ Hz) which is indicative of the phosphonium salt (6). The mechanism of formation of (6) remains obscure, as are the identities of the products produced in the initial stages of the reaction.



Scheme 1. (i) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$

The corresponding reaction of compound (1) with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ at -78°C takes a different course. Even in the early stages of the reaction only one product, (7), is detectable by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy. The proton-coupled ^{31}P spectrum is basically an AX system with additional couplings which are indicative of one hydrogen attached to each phosphorus atom plus additional fine structure relating to P_B . On the basis of these data we propose the structure for (7) shown in Scheme 1. Note that the additional coupling to P_B is due to the diastereotopic methylene protons in the five-membered phosphacyclic ring, H_C and $\text{H}_{\text{C}'}$. Presumably, protonation of (1) results initially in intermediate (A). The two-co-ordinate phosphonium centre thus generated then inserts into a C-H bond of an *ortho*-Bu¹ group of the aryl ring. The insertion of phosphonium centres into C-H bonds has been observed previously.¹⁹

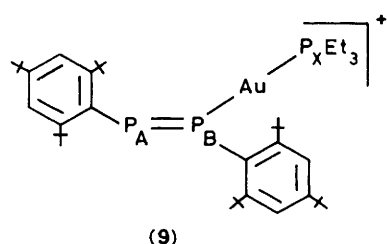
If solutions of compound (7) are allowed to warm to room temperature, P-P bond cleavage occurs resulting in (8) (Scheme 1). The proton-coupled ^{31}P n.m.r. spectrum of (8) comprises a triplet (Table) with a large $^1J_{\text{PH}}$ coupling characteristic of a secondary phosphonium cation. This structural assignment was confirmed by protonation of (18) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ which resulted in a product with an identical ^{31}P n.m.r. spectrum.

The foregoing results indicate that protonation of compounds (1) and (2) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ is not straightforward since P=P bond cleavage occurs in both cases. In an attempt to model this reaction, the reactivity of (1) towards the gold cation $[\text{Au}(\text{PEt}_3)]^+$ was investigated since it has been demonstrated that this species is isolobal with H^+ , and in many cases behaves similarly to H^+ in its reactions with transition-metal clusters.²⁰

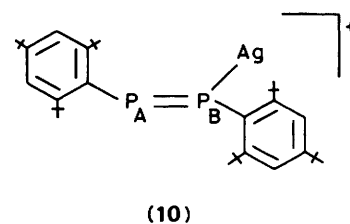
Treatment of compound (1) with $[\text{Au}(\text{PEt}_3)\text{Cl}]$ in the presence of TiPF_6 in tetrahydrofuran (thf) solution results in the

formation of (9). Whilst it was not possible to isolate (9) as a stable crystalline species, its identity and the clean nature of the reaction was demonstrated by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy which revealed an ABX spin system (Table). These data are in full accord with the above structure for (9) and preclude other possible structures in which the $\text{Au}(\text{PEt}_3)$ moiety symmetrically bridges the P=P bond or more than one such group is co-ordinated to the diphosphene.

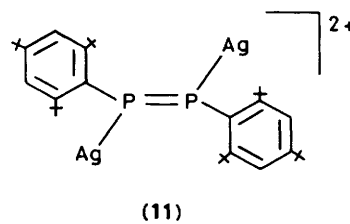
Similar reactions involving the silver cation, Ag^+ (derived from $\text{Ag}[\text{SO}_3\text{CF}_3]$), result in compounds (10) and (11) which



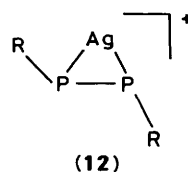
(9)



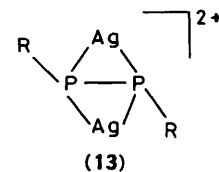
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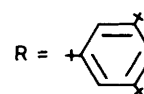
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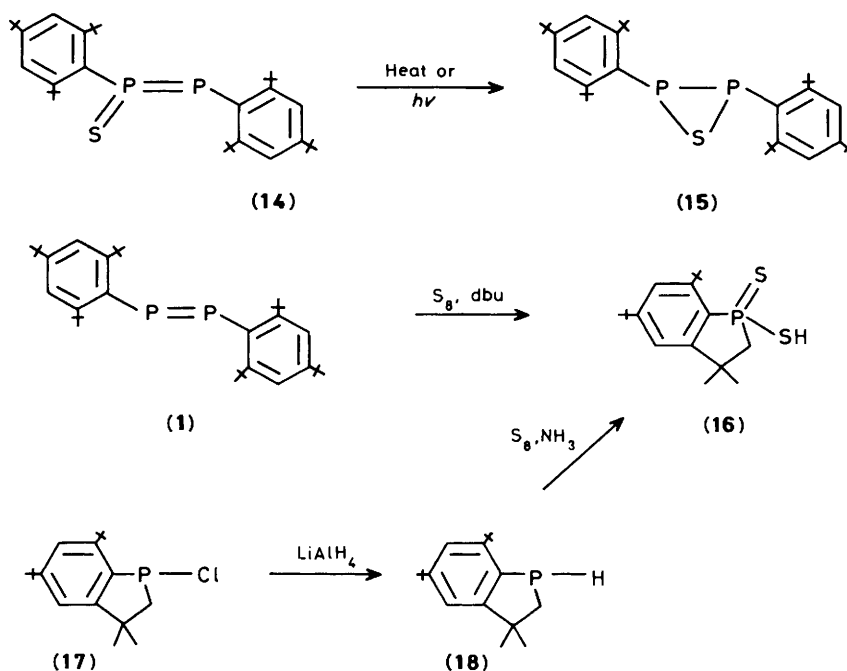


(12)



(13)

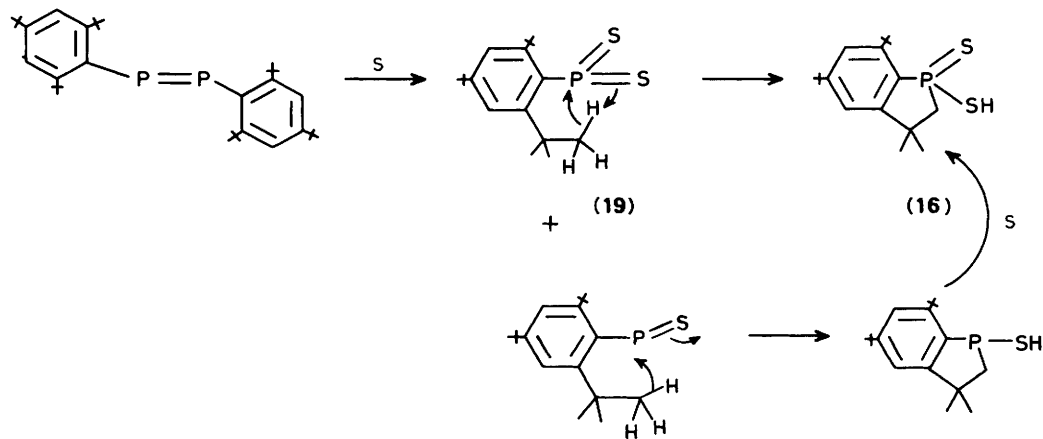




feature 1 and 2 equivalents of Ag^+ respectively. In each case it is assumed that molecules of thf are loosely co-ordinated to the silver atoms in solution. Unlike the gold compound, (9), the silver complexes, (10) and (11), are fluxional on the n.m.r. time-scale. Thus, while the low temperature ^{31}P n.m.r. spectra (-90°C) are consistent with the structures drawn, the spectra recorded at 25°C indicate equivalent phosphorus environments for (10) and show a broad singlet for (11). The original spectral patterns reappear upon cooling to -90°C . The ^{31}P n.m.r. spectrum of compound (10) is of the ABX type where X is ^{109}Ag and ^{107}Ag . The phosphorus chemical shifts do not differ noticeably depending on whether X is ^{109}Ag or ^{107}Ag and separate couplings to both isotopes were observed. The ^{31}P n.m.r. spectrum of (11) is of the AA'XX' type; however, only average $^{109}\text{Ag}/^{107}\text{Ag}$ couplings to phosphorus were observed in this case (Table). We note also that possible structures involving bridging Ag atoms, (12) and (13), can be eliminated as ground-state configurations since these would give rise to A_2X and A_2X_2 spectra respectively. Nevertheless, they are possibly involved as intermediates in the room-temperature fluxional process.

The reactivity of compound (1) towards elemental sulphur has also been examined. This reaction was first reported by Yoshifuji *et al.*^{9d,e} who isolated the monosulphide compound, (14). Upon either heating or photolysis, (14) rearranges to the episulphide, (15). If (1) is treated with elemental sulphur in the presence of catalytic quantities of dbu (1,5-diazabicyclo[5.4.0]undec-5-ene) a different reaction course is followed resulting in P=P bond cleavage and formation of the dithiophosphinic acid, (16).^{8c} Support for the indicated structure of (16) is provided by its independent synthesis from (17) and (18).^{8c,21} The mechanism by which (1) is converted into (16) is unclear. However, a possible sequence of intermediates is outlined in Scheme 2. Compound (19) has, in fact, been isolated and structurally characterised.²² However, its rearrangement to (16) under the reaction conditions employed here has yet to be demonstrated.

Reactions with Nucleophiles.—As mentioned in the Introduction, theoretical calculations on the model diphosphene, $\text{HP}=\text{PH}$, indicate a relatively low-lying l.u.m.o. of $\text{P}=\text{P}$ π^* character.¹³ In turn, this result suggested that diphosphenes

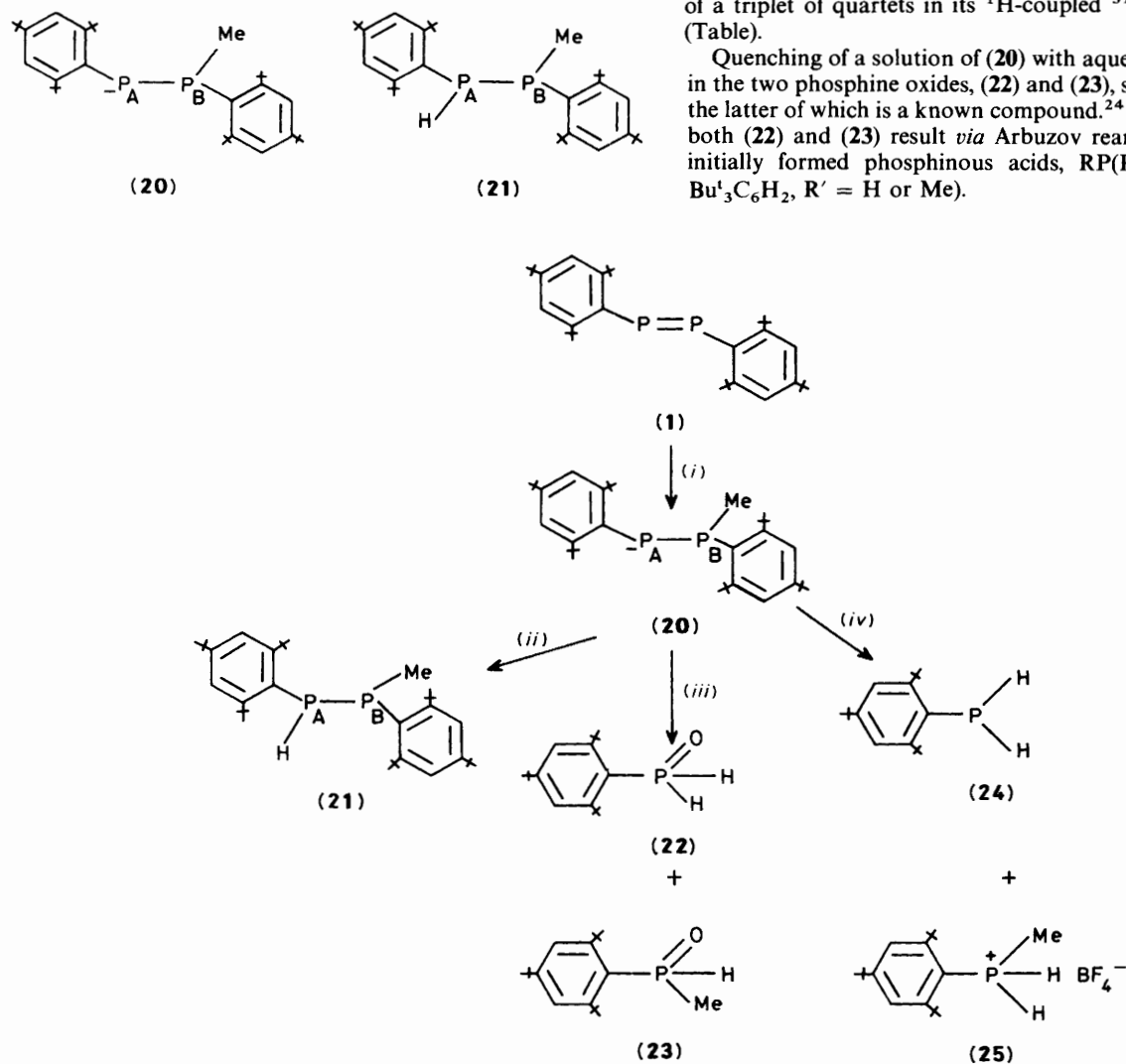


Scheme 2.

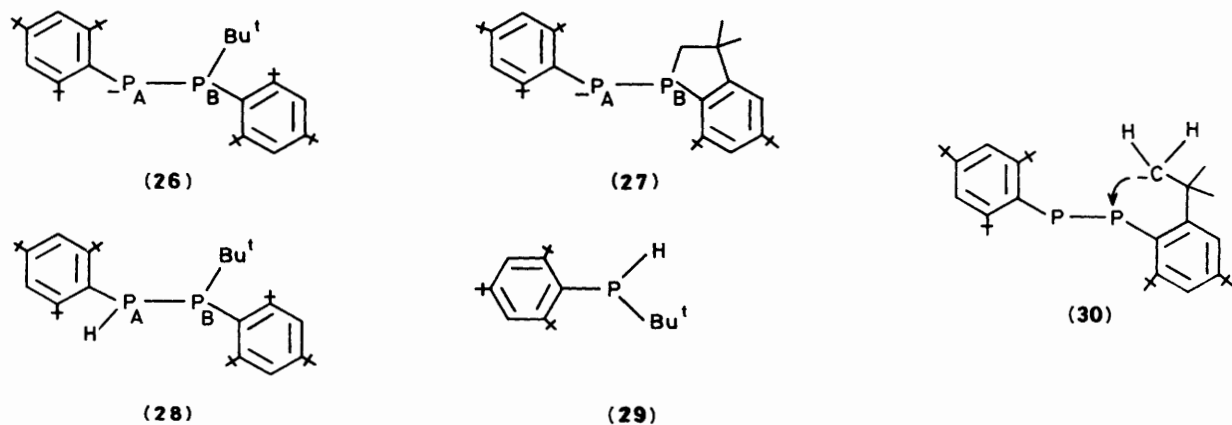
should be reactive towards nucleophiles. Accordingly, the reaction of compound (1) with LiMe was investigated.^{8b} Addition of an equimolar quantity of LiMe to a thf solution of (1) at -78°C afforded a deep red solution. The observation of an AB pattern in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum was consistent with the formation of the anion (20). This species proved too unstable to isolate and characterise more fully. However,

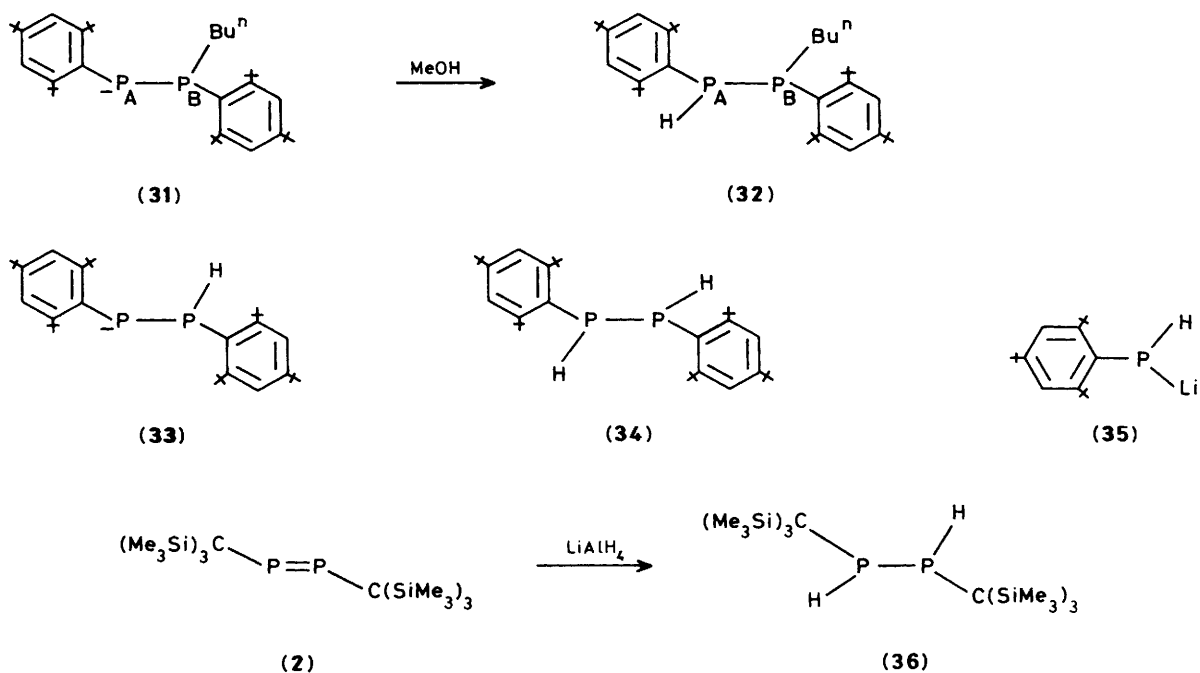
protonation of (20) with methanol produced the diphosphine (21). The latter was characterised unambiguously on the basis of the ^1H -coupled ^{31}P n.m.r. spectrum which consisted of an ABM_3X spin system (Table). Attempted protonation of (20) with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ failed to produce the diphosphine (21) but gave instead the known phosphine (24)²³ and the phosphonium salt (25) (Scheme 3) which was characterised by the appearance of a triplet of quartets in its ^1H -coupled ^{31}P n.m.r. spectrum (Table).

Quenching of a solution of (20) with aqueous LiOH resulted in the two phosphine oxides, (22) and (23), shown in Scheme 3, the latter of which is a known compound.²⁴ It is suggested that both (22) and (23) result *via* Arbuzov rearrangements of the initially formed phosphinous acids, $\text{RP}(\text{R}')\text{OH}$ ($\text{R} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$, $\text{R}' = \text{H}$ or Me).



Scheme 3. (i) LiMe; (ii) MeOH; (iii) LiOH (aq); (iv) $\text{HBF}_4\cdot\text{Et}_2\text{O}$





The reaction of compound (1) with LiBu^t in thf solution proved to be more complex than the corresponding reaction with LiMe as evidenced by ^{31}P n.m.r. spectroscopy. After 12 h at 25°C , an initially complex spectral pattern simplified into that anticipated for the anion (26) and signals due to a minor product which is assigned structure (27). Treatment of a solution of these anions with MeOH resulted in protonation of (26) to form the anticipated diphosphine, (28), together with some P–P cleavage resulting in a small amount of the phosphine (29).^{15c} We suggest that in the reaction of (1) with LiBu^t a competition exists between nucleophilic attack at phosphorus and deprotonation of an *ortho*- Bu^t group. The former process gives rise to (26) directly whilst the latter may be considered to give rise to an intermediate such as (30) from which (27) is formed *via* intramolecular nucleophilic attack.

The reaction of compound (1) with LiBu^n proceeded in a similar fashion to that with LiMe . Thus, initial treatment of (1) with LiBu^n at -78°C resulted in the anion (31) from which the diphosphine (32) was formed by quenching with methanol. ^{31}P N.m.r. spectroscopic data for (31) and (32) are presented in the Table.

In view of the facile reactivity of (1) towards the anions Me^- , Bu^t^- , and Bu^n^- , it was anticipated that this compound would react with a source of hydride such as $\text{K}[\text{BHBU}_3]$. Unexpectedly, however, ^{31}P n.m.r. spectroscopic investigation

of mixtures of (1) and $\text{K}[\text{BHBU}_3]$ in thf solution revealed no evidence for the presence of anion (33). There was, however, evidence for the slow production of diphosphine (34) over 4 d. An attempted preparation of (33) *via* deprotonation of (34) with LiBu^n afforded only the known monophosphide (35).^{14b}

The formation of (34) as the only observable product from the reaction of (1) with $\text{K}[\text{BHBU}_3]$ is similar to the reaction reported by Escudié *et al.*^{11a} between (2) and LiAlH_4 , giving the diphosphine (36). There is, however, an interesting difference between these two reactions. In both (34) and (36) the phosphorus centres are chiral giving rise to the possibility of diastereomers. As is the case with the isomers of (3), it is assumed that because of the large steric bulk of the R groups these must adopt mutually *trans* positions, giving rise to the isomers shown. In the case of compound (36) these are formed in the ratio 3:2 whilst in the case of (34) one isomer predominates. The cause of this stereoselectivity is at present unclear.

Experimental

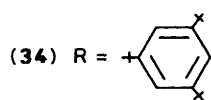
General Considerations.—All experiments were performed under an atmosphere of dry dinitrogen with the use of standard Schlenk techniques. All solvents were distilled over CaH_2 or sodium or potassium diphenylketyl immediately prior to use.

Spectroscopic Measurements.—Proton n.m.r. spectra were recorded on Varian EM390 and Nicolet NT200 instruments operating at 90.0 and 200.0 MHz respectively, ^{31}P n.m.r. spectra on Varian FT80A and Nicolet NT200 instruments operating at 32.384 and 81.03 MHz. The ^1H spectra were referenced to SiMe_4 (0.0 p.p.m.) whilst ^{31}P spectra were referenced to 85% H_3PO_4 , positive values to high frequency in both cases. All ^{31}P n.m.r. data are summarized in the Table. N.m.r. data were collected in CH_2Cl_2 or CD_2Cl_2 solution unless stated otherwise.

Medium- and high-resolution mass spectra (h.r.m.s.) were measured on Du Pont-Consolidated model 21-491 and 21-100 spectrometers respectively. Perfluorokerosene was used as the calibrant.



S,R,R,S



(36) $R = (\text{Me}_3\text{Si})_3\text{C}$

$S,S;R,R$

Starting Materials.—The diphosphenes (1)^{14a} and (2)^{14b,15} were prepared according to the literature methods. The compounds HCl(g), HBF₄·Et₂O, LiMe, LiBu^t, LiBuⁿ, Ag[SO₃CF₃], [Au(PEt₃)Cl], and S₈ were obtained commercially and used without further purification.

Preparation of (Me₃Si)₃CP(H)–P(Cl)C(SiMe₃)₃, (3).—A stoichiometric quantity of dry gaseous HCl (4.6 cm³) was added *via* a gas-tight syringe to a solution of compound (2) (0.1 g, 0.2 mmol) in Et₂O (10 cm³) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 24 h, during which time the characteristic orange colour of (2) disappeared and a small amount of a grey-white precipitate was formed. Filtration of the crude reaction mixture through Celite followed by removal of the solvent gave (3) as a white solid. H.r.m.s.: found 560.2095; calc. for C₂₀H₅₅ClP₂Si₆ 560.2081.

The preparation of PH(Cl)[C(SiMe₃)₃] (4) was performed in an identical manner to that described for (3) except that an excess (20 cm³) of gaseous HCl was employed. H.r.m.s.: found 298.0933; calc. for C₁₀H₂₈ClP₂Si₃ 298.0924.

Preparation of PH(Cl)(C₆H₂Bu^t₃-2,4,6), (5).—Gaseous HCl (0.036 g, 1.0 mmol) was condensed into a solution of compound (1) (0.55 g, 1.0 mmol) in CH₂Cl₂ (10 cm³) at –90 °C. The mixture was allowed to warm to room temperature and the progress of the reaction was monitored by ³¹P n.m.r. spectroscopy which revealed resonances due to (1) (+494 p.p.m.) and (5). Addition of a second equivalent of HCl at –78 °C resulted in the disappearance of the signal due to (1) leaving (5) as the sole product. H.r.m.s.: found 311.1691; calc. for C₁₈H₂₉ClP (M – 1) 311.1695.

Preparation of [PH₃{C(SiMe₃)₃}] [BF₄], (6).—Two equivalents of HBF₄·Et₂O (1.42 mmol) were added dropwise to a solution of compound (2) (0.37 g, 0.71 mmol) in Et₂O (10 cm³) at 0 °C. The stirred solution was allowed to warm to room temperature. Initial ³¹P n.m.r. monitoring of the reaction mixture revealed a large number of signals. However, after 2 h the spectrum simplified to a single resonance assigned to (6). Attempted isolation of (6) gave only decomposition products.

Reaction of Compound (1) with HBF₄·Et₂O.—Diphosphene (1) (0.11 g, 0.2 mmol) was dissolved in CH₂Cl₂ (2 cm³) and the solution placed in an 8-mm n.m.r. tube and cooled to –78 °C. To this cooled solution, was added HBF₄·Et₂O and the temperature allowed to rise to –20 °C. A colour change from orange to yellow was noted. The n.m.r. tube was then re-cooled to –90 °C and placed in the probe of the spectrometer maintained at this temperature. The ³¹P n.m.r. spectrum indicated the presence of a single compound, (7). After recording the spectrum of (7) the probe temperature was allowed to rise to 0 °C and the spectrum was remeasured. This revealed a different set of signals which are assigned to (8). By means of ³¹P n.m.r. spectroscopy, it was established that protonation of compound (18) with HBF₄·Et₂O resulted in (8), thus confirming the proposed structural assignment.

Preparation of [(2,4,6-Bu^t₃C₆H₂)P=P(AuPEt₃)(C₆H₂Bu^t₃-2,4,6)] [PF₆], (9).—Diphosphene (1) (0.11 g, 0.2 mmol) and [Au(PEt₃)Cl] (0.18 g, 0.5 mmol) were dissolved in CH₂Cl₂ (5 cm³) and the solution cooled to –78 °C. Thallium(i) hexafluorophosphate (0.175 g, 0.5 mmol) in thf (2 cm³) was added dropwise. The progress of the reaction was monitored by ³¹P n.m.r. spectroscopy which revealed a single ABX spin system (see Results and Discussion section) together with a signal due to PF₆[–] (–145 p.p.m.). Attempted isolation of (9) was precluded by its sensitivity to heat and light.

Reaction of Compound (1) with Ag[SO₃CF₃]; Preparation of (10) and (11).—Diphosphene (1) (0.11 g, 0.2 mmol) was dissolved in CH₂Cl₂ (2 cm³) and the solution placed in an 8-mm n.m.r. tube and cooled to –78 °C. A solution of Ag[SO₃CF₃] (0.05 g, 0.2 mmol) in thf (1 cm³) was added dropwise. The ³¹P n.m.r. spectrum of the reaction mixture was recorded at various temperatures as described in the text and indicated the presence of 1 equivalent of Ag⁺ per diphosphene unit, *i.e.* structure (10). Compound (11) with two silver ions per diphosphene was prepared in an analogous manner but using 2 equivalents of Ag[SO₃CF₃] (0.1 g, 0.4 mmol). As in the case of (9), the isolation of both (10) and (11) was precluded by their sensitivity to light.

Preparation of Compound (16).—Diphosphene (1) (0.55 g, 1 mmol) was dissolved in toluene (60 cm³) followed by sulphur (0.16 g, 5 mmol) and dbu (0.6 g, 4 mmol). The resulting mixture was heated to 80 °C for 3 h during which time the orange colour of (1) gradually disappeared. The reaction mixture was then treated with HCl(aq) and the toluene removed *in vacuo*. The resulting residue was redissolved in hexane and filtered through Celite. The resulting colourless filtrate was shaken with NH₃(aq) and dried with MgSO₄. Crystallisation from hexane gave (16) (0.3 g, 42%) as the ammonium salt (Found: C, 60.3; H, 9.1. C₁₈H₃₂NPS₂ requires C, 60.45; H, 9.0%).

Preparation of [(2,4,6-Bu^t₃C₆H₂)P–P(Me)(C₆H₂Bu^t₃-2,4,6)][–], (20), and (2,4,6-Bu^t₃C₆H₂)P(H)–P(Me)(C₆H₂Bu^t₃-2,4,6), (21).—Diphosphene (1) (0.11 g, 0.2 mmol) was dissolved in thf (1 cm³) and placed in an 8-mm n.m.r. tube. After cooling the reaction mixture to –78 °C, 1 equivalent of LiMe in diethyl ether was added, whereupon the colour changed from orange to deep red. The red anion, (20), was not isolated; however, quenching of the reaction mixture with excess of methanol resulted in the diphosphine (21) which was characterised by ³¹P n.m.r. (Table) and h.r.m.s. (found 568.9316; calc. for C₃₇H₆₂P₂ 568.9326).

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References

- R. West, *Pure Appl. Chem.*, 1984, **56**, 163; 'Organosilicon and Bioorganosilicon Chemistry,' ch. 1, ed. H. Sakurai, Ellis Horwood Publishers, Chichester, 1985.
- A. H. Cowley, *Polyhedron*, 1984, **3**, 389; *Acc. Chem. Res.*, 1984, **17**, 386; A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.*, in the press.
- P. J. Davidson, D. H. Harris, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268; D. E. Goldberg, D. H. Harris, M. F. Lappert, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1976, 261; S. Masamune, Y. Hanzawa, and D. J. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 6136; J. T. Snow, S. Murakami, S. Masamune, and D. J. Williams, *Tetrahedron Lett.*, 1984, **25**, 4191.
- B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 691; B. Cetinkaya, M. F. Lappert, J. G. Stamper, and R. J. Suffolk, *J. Electron Spectrosc. Relat. Phenom.*, 1983, **32**, 133.
- C. N. Smit, F. M. Lock, and F. Bickelhaupt, *Tetrahedron Lett.*, 1984, **25**, 3011.
- J. Escudie, C. Couret, J. Satgé, M. Adrianarison, and J-D. Andriamizaka, *J. Am. Chem. Soc.*, 1985, **107**, 3378.
- M. J. Fink, D. J. DeYoung, R. West, and J. Michl, *J. Am. Chem. Soc.*, 1983, **105**, 1070; S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, *ibid.*, 1982, **104**, 1150; S. Masamune, S. Murakami, H. Tobita, and D. J. Williams, *ibid.*, 1983, **105**, 7776; M. J. Fink, K. J. Haller, R. West, and J. Michl, *ibid.*, 1984, **106**, 822; M. J. Fink, J. Michalczyk, K. J. Haller, R. West, and J. Michl, *Organometallics*, 1984, **3**, 793.

- 8 (a) A. H. Cowley, J. E. Kilduff, N. C. Norman, M. Pakulski, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, 1983, **105**, 4845; (b) A. H. Cowley and M. Pakulski, *ibid.*, 1984, **106**, 1491; (c) A. H. Cowley and M. Pakulski, *Tetrahedron Lett.*, 1984, **25**, 2125.
- 9 (a) M. Yoshifuji, I. Shima, K. Shibayama, and N. Inamoto, *Tetrahedron Lett.*, 1984, **25**, 411; (b) M. Yoshifuji, K. Ando, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, *Angew. Chem.*, 1983, **95**, 416; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 418; (c) M. Yoshifuji, K. Ando, K. Toyota, I. Shima, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1983, 419; (d) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, *ibid.*, p. 862; (e) M. Yoshifuji, K. Shibayama, and N. Inamoto, *Heterocycles*, 1984, **22**, 681.
- 10 E. Niecke and R. Rüger, *Angew. Chem.*, 1983, **95**, 154; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 155; E. Niecke, R. Rüger, M. Lysek, S. Pohl, and W. Schoeller, *Angew. Chem.*, 1983, **95**, 495; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 486.
- 11 (a) J. Escudié, C. Couret, H. Ranaivonjatovo, J. Satgé, and J. Jaud, *Phosphorus Sulphur*, 1983, **17**, 221; (b) J. Escudié, C. Couret, H. Ranaivonjatovo, and J-G. Wolf, *Tetrahedron Lett.*, 1983, **24**, 3625; (c) J. Escudié, C. Couret, J. D. Andriamizaka, and J. Satgé, *J. Organomet. Chem.*, 1982, **228**, C76.
- 12 A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, and T. C. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 7751; A. H. Cowley, J. G. Lasch, N. C. Norman, and M. Pakulski, *Angew. Chem.*, 1983, **95**, 1019; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 978; A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, and T. C. Wright, *Organometallics*, 1984, **3**, 1044.
- 13 J-G. Lee, A. H. Cowley, and J. E. Boggs, *Inorg. Chim. Acta*, 1983, **77**, L61; M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, *J. Am. Chem. Soc.*, 1983, **105**, 2495; V. Galasso, *Chem. Phys.*, 1984, **83**, 407; T-K. Ha, M. T. Nguyen, and P. Ruelle, *ibid.*, **87**, 23.
- 14 (a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587; (b) A. H. Cowley, J. E. Kilduff, T. H. Newman, and M. Pakulski, *ibid.*, 1982, **104**, 5820.
- 15 (a) C. Couret, J. Escudié, and J. Satgé, *Tetrahedron Lett.*, 1982, **23**, 4941; (b) C. N. Smit, Th. A. van der Knaap, and F. Bickelhaupt, *ibid.*, 1983, **24**, 2031; (c) A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, B. R. Whittlesey, J. L. Atwood, and W. E. Hunter, *Inorg. Chem.*, 1984, **23**, 2582.
- 16 A. H. Cowley, W. D. White, and M. C. Damasco, *J. Am. Chem. Soc.*, 1969, **91**, 1922; J. Albrand, H. Faucher, D. Gagnaire, and J. B. Robert, *Chem. Phys. Lett.*, 1976, **38**, 521; A. A. M. Ali, Ph.D. Thesis, University of East Anglia, 1979; A. A. M. Ali and R. K. Harris, *J. Chem. Soc., Dalton Trans.*, 1983, 538.
- 17 R. D. Dobbie, P. D. Goshij, and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1975, 2368.
- 18 A. Marinetti and F. Mathey, *Organometallics*, 1982, **1**, 1488.
- 19 A. H. Cowley, R. A. Kemp, and C. A. Stewart, *J. Am. Chem. Soc.*, 1982, **104**, 3239; A. H. Cowley and S. K. Mehrotra, *ibid.*, 1983, **105**, 2074.
- 20 F. G. A. Stone, *Angew. Chem.*, 1984, **96**, 85; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89 and refs. therein.
- 21 M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 933.
- 22 R. Appel, F. Knoch, and H. Kunze, *Angew. Chem.*, 1983, **95**, 1008; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 1004; J. Navech, J-P. Majoral, and R. Kraemer, *Tetrahedron Lett.*, 1983, **24**, 5885; M. Yoshifuji, K. Toyota, K. Ando, and N. Inamoto, *Chem. Lett.*, 1984, 317.
- 23 A. H. Cowley, J. E. Kilduff, M. Pakulski, and C. A. Stewart, *J. Am. Chem. Soc.*, 1982, **104**, 5820.
- 24 M. Yoshifuji, K. Shibayama, K. Toyota, and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 4227.

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