DALTON PERSPECTIVE

Organo-P–S and P–Se heterocycles

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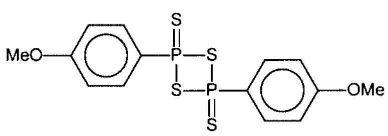
P–S heterocycles provide reagents for simple thionations as well as a range of other organic transformations. Advances in this area, as well as in P–Se chemistry, are reported.

It is widely recognised that organometallic reagents have a pivotal role in organic synthesis but the significance of main group based reagents is not always so well appreciated. Lawesson's reagent (**LR**) has widely been used in organic chem-

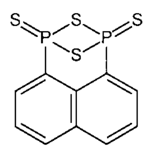


Lawessons Reagent **LR**

istry as a reagent for the conversion of ketones, amides, and esters into their thio-analogues.[1,2] This perspective is concerned with the synthesis and new organic chemistry of this and related thionation reagents and their metal complexes. We will also highlight some advances in related selenium chemistry.

Synthesis

Lawesson's reagent and many other dithiadiphosphetane disulfides are made (Table 1) by heating aromatic compounds or alkenes with P_4S_{10}.[3–8] The reaction of 1-bromonaphthalene

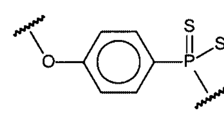


NpP_2S_4

with P_4S_{10} at temperatures above 245 °C gives 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (**NpP_2S_4**); the substituted analogue (**$MeONpP_2S_4$**) is obtained from P_4S_{10} and 1-methoxynaphthalene.[8–11] The reactions of *tert*-butyldichlorophosphine with lithium sulfide,[12] treatment of alkyldichlorophosphine sulfides with hydrogen sulfide,[13] and P_4S_{10} with thiols[14] have also been used as alternative methods of synthesis. The disproportionation reaction of 2,4,6,8-tetramesityl-1,3,5,7,2,4,6,8-tetrathiatetraphosphocine also gives a dithiadiphosphetane disulfide.[15]

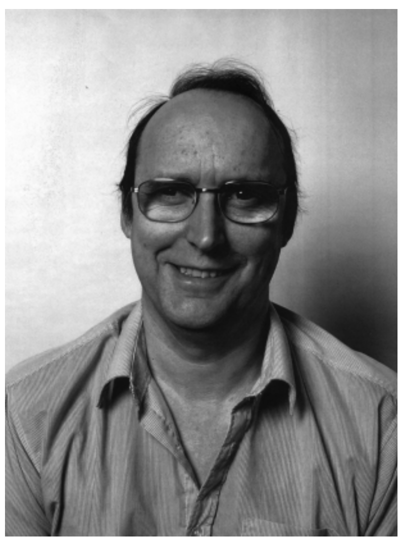
Decomposition reactions

In addition to the reaction with water, which is likely to occur for any potent thionation reagent, two thionation reagents



Mark Foreman was born in 1973 in Beckenham, Kent. After studying for his first degree at Imperial College, Mark moved to Loughborough where he obtained his PhD, working on dithiadiphosphetane disulfides. Since obtaining his PhD, Mark has worked as a research fellow at both Masaryk (Brno, Czech Republic) and Aberdeen Universities.

Mark Foreman



J. Derek Woollins

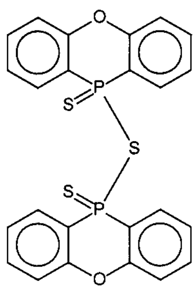
Professor J. Derek Woollins obtained his PhD at UEA in 1979 and after spells working as PDF in Vancouver, Michigan and Leeds moved to Imperial College as a lecturer where he stayed for 11 years until moving to the Chair of Inorganic Chemistry at Loughborough in 1994. Last summer he took up a new Chair in Synthetic Chemistry at St Andrews. His interests centre around the chemistry of Group 15 and 16 elements. He was awarded the RSC 1997 prize for Main Group Element Chemistry. His hobbies include weight-lifting and DIY.

Table 1 Typical syntheses of dithiadiphosphetane disulfides

Arene/Alkene	Yield (%)	Conditions	Abbreviation for product	t/h
Anisole[3]	80	Heat under reflux	**LR**	6
Phenetole (Ethoxybenzene)[3]	63	165 °C		5
Butoxyphenyl[4]	—	Heating		
Naphthalene[3]	37	170–180 °C		24
Benzene[3]	45	Autoclave at 225 °C		24
Xylene[3]	48[a]	Autoclave at 185 °C		24
2-Isopropylnaphthalene[3]	11[a]	170–175 °C		8
Cyclohexene[5]	58	Heat under reflux		108
Diphenyl ether[6]	75	Heat under reflux in *o*-$C_6H_4Cl_2$	**LR′**	0.42
Diphenyl sulfide[6]	65	Heat under reflux in *o*-$C_6H_4Cl_2$		0.42
Thiophene[7]	87	Heat under reflux		48
2-*tert*-Butylanisole[8]	47	120–140 °C	**LR***	1.5
Ferrocene[8,9]	78	Heat under reflux in xylenes	**$Fc_2P_2S_4$**	0.5

[a] Yield of the *P*-organophosphonic acid.

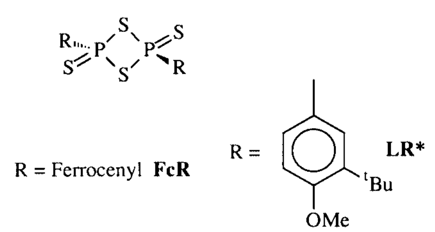
have been shown to undergo other decomposition reactions. On prolonged heating **LR** gives a polymeric compound in one decomposition route.[3] whilst 2,4-bis(4-phenoxyphenyl)-dithiadiphosphetane disulfide (**LR′**) undergoes bridge cleavage to give a compound containing a pair of PC_4O heterocycles.[16]



New organic chemistry

Thionation

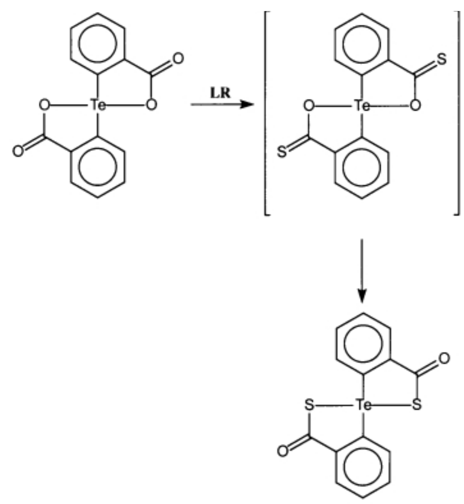
We have recently reported a comparative study of the thionation ability of **LR, LR***, **FcR** and **NpP_2S_4** towards some common organic substrates.[8] It would appear that **LR*** and **FcR**



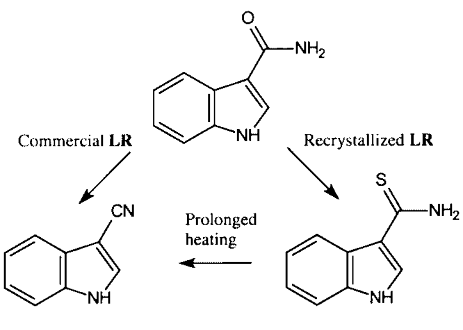
offer some improvements over **LR**. Furthermore, the traditional (often high temperature) conditions which are employed for thionation reactions may benefit from re-examination.

1,1′-Spirobi(3*H*-2,1-benzotellurole)-3,3′-dione reacts with **LR** to form (eqn. 1) 1,1′-spirobi(3*H*-2,1-benzothiatellurole)-3,3′-dione; this compound is thought to be a rearrangement of the initial product of the thionation reaction.[17]

LR may function as a dehydration agent (eqn. 2); the commercial product converts an electron rich amide into a nitrile, while after recrystallisation **LR** gives a reasonable yield of the thioamide.[18] Prolonged heating of the reaction mixture results in conversion of the thioamide into the nitrile. The rapid formation of the nitrile when using commercial **LR** is believed to be due to impurities in the **LR**.[18] The use of **$Fc_2P_2S_4$** and **$MeONpP_2S_4$** gave slightly lower yields of the thioamide, whilst far less of the nitrile was formed.[18] **LR*** gave a similar yield to **LR** with almost none of the nitrile being obtained.[18]



(1)



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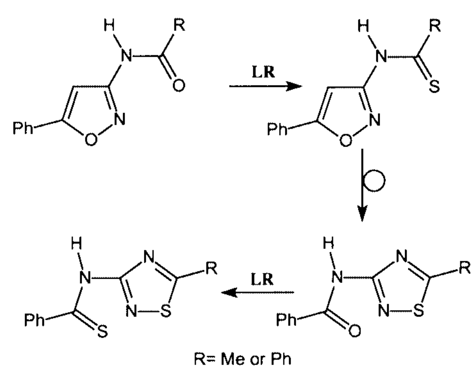
Reactions forming cyclic compounds

LR converts an 1,2-oxazole into a 1,2,4-thiadiazole. This reaction proceeds *via* a thioamide intermediate which after rearrangement is converted into a thioamide (Scheme 1).[19]

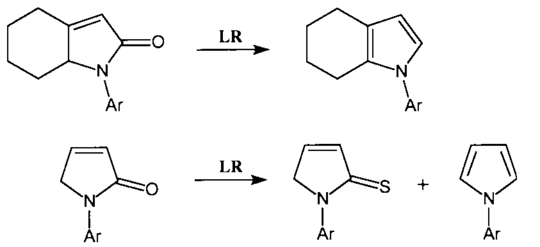


Scheme 1 Thionation followed by rearrangement.

Table 2 LR/$AgClO_4$ acting as a Lewis acid catalyst[27]

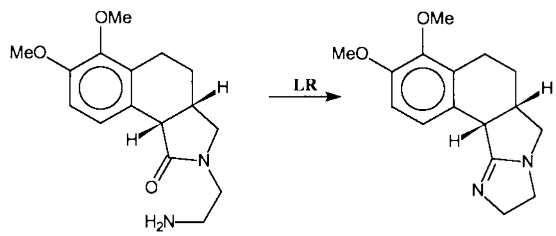
Alcohol	Yield (%)	α:β ratio
3-Phenylpropan-1-ol	97	5:95
Cyclohexanol	93	5:95
Cholesterol	90	4:96
Methyl-2,3,4-tri-*O*-benzyl-D-glycoside	79	24:76

When 1,4,5,6,7,7a-hexahydro-2*H*-indol-2-ones are treated with **LR** they do not give the expected thioamides, but instead furnish the 4,5,6,7-tetrahydroindoles.[20] However, 1,5-dihydropyrrol-2-ones give the thioamides with pyrroles as minor products (Scheme 2).[20]



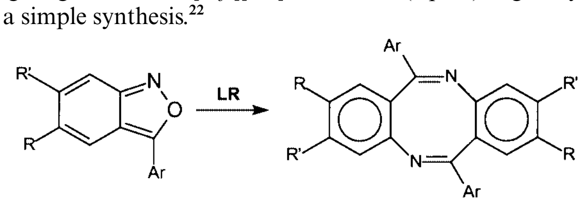
Scheme 2 Synthesis of pyrroles.

Lawesson's reagent converts a β-aminoamide into an imidazoline (eqn. 3) with the stereochemistry at the carbon α to the amide carbonyl carbon being unaffected.[21]



(3)

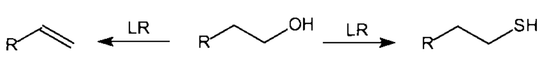
The reaction of 3-aryl-2,1-benzisoxazoles with Lawesson's reagent gives dibenzo[*b*,*f*][1,5]-diazocines (eqn. 4) in good yield in a simple synthesis.[22]



(4)

Reactions forming other organic compounds

A direct route from aliphatic alcohols to thiols using **LR** exists[23] though it unlikely that this reaction could be used for forming thiols from phenols because of competing reactions,[24] eqn. (5). As a side reaction of the above thiol synthesis, alkenes



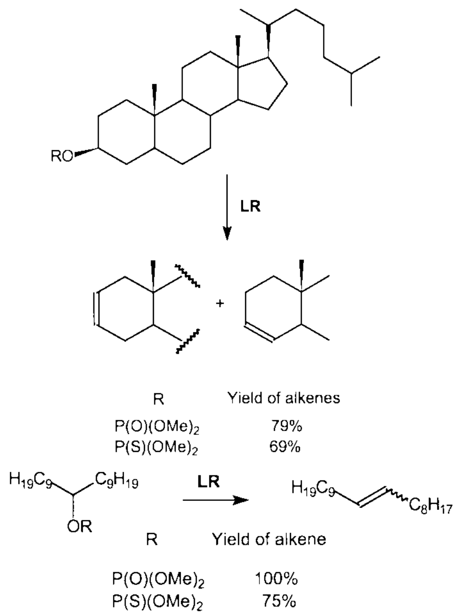
(5)

may also be formed.[23] In a related fashion, the treatment of alkyl phosphates and alkyl thiophosphates with Lawesson's reagent gives alkenes (eqn. 6) in high yield.[25]

The combination of Lawesson's reagent and silver perchlorate acts as a very effective catalytic system both for the Diels–Alder reactions of α,β-unsaturated ketones (Scheme 3),[26] as well as for the formation of β-D-ribofuranosides from D-ribofuranose and alcohols (Scheme 3 and Table 2).[27]

1,2,3-Thiadiazoles can be prepared by treating α-diazoketones with Lawesson's reagent (Scheme 4); this reaction works especially well for α-diazoketones where the ketone and the diazo group are held *cis*.[28,29] When the size of R^1 is increased the reaction forming the thiadiazole requires more forcing conditions.[29] No thiadiazole formation was observed for azobenzil, eqn. (7), which would be reasonable as the molecule is not likely to be in the *cis* arrangement.[28]

Thiophenes and furans can be formed[30–32] by treating 1,4-diketones (eqn. 8) with **LR**. The reaction gives better yields and



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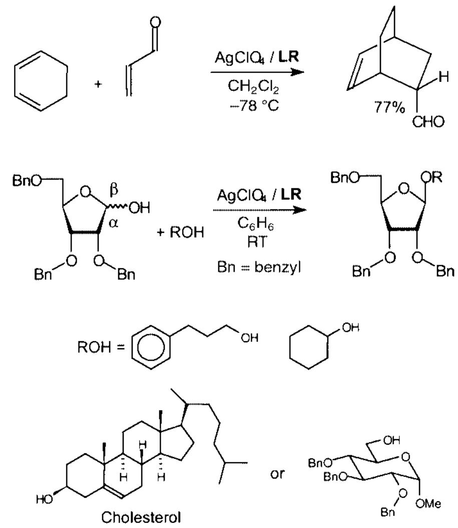
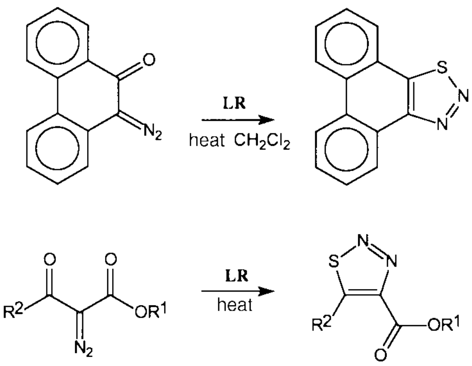
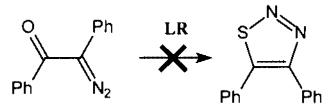


Scheme 3 LR/$AgClO_4$ acting as Lewis acid catalyst.[27]



R^1 can be allyl, Me, Bn, *tert*-butyl and $CH_2CH_2SiMe_3$
R^2 can be Me, Et, cyclopentyl and *tert*-butyl

Scheme 4 Synthesis of 1,2,3-thiadiazoles.



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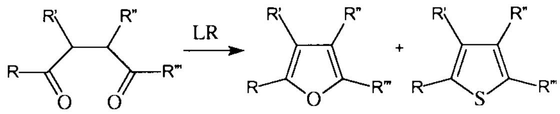
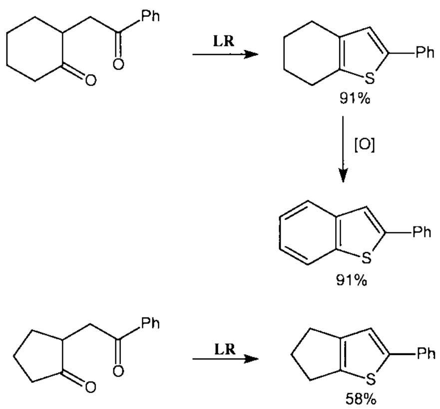


(8)

occurs under milder conditions than the synthesis using P_4S_{10}.[30] The formation of the thiophenes is thought to go *via* a 1,4-dithioketone that then undergoes the ring closing reaction,[30] eqn. (9). The reactions of more substituted diketones give

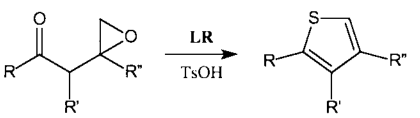


(9)

significant yields of the furans, also the presence of electron-donating groups on the aromatic groups at the 1 and 4 positions increases the yield of furans while electron withdrawing groups in these locations lowers their yield.[33] An alternative mild method for forming thiophenes from 1,4-diketones is treatment with a tin/sulfur/boron system.[31,34]

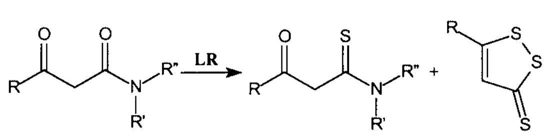
LR has been used in the attempted synthesis of [10](2,5)thiopheneophane but instead the furan was formed.[35]

A related thiophene synthesis is the reaction of epoxycarbonyls with **LR** in the presence of tosic acid,[36] eqn. (10). (Ts = toluene-*p*-sulfonyl).



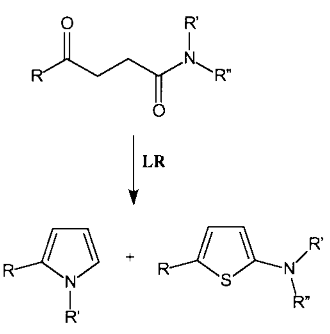
(10)

The reaction of ketoamides with **LR** makes a wide range of different products accessible.[37] For the β-ketoamides a mixture of the thioamide and a sulfur heterocycle (eqn. 11) was



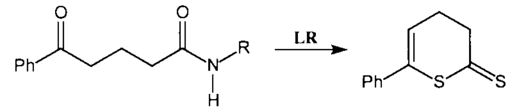
(11)

obtained.[37] However, with γ-ketoamides pyrroles and thiophenes (eqn. 12) were obtained,[37] and with the 5-ketoamides



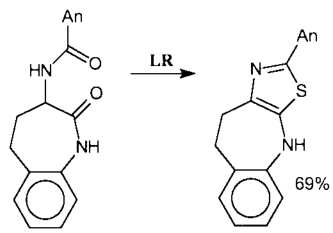
(12)

small yields of 6-phenyl-3,4-dihydro-2*H*-thiine-2-thione were obtained (eqn. 13).[37]



(13)

Ring forming chemistry has been extended to the synthesis of 5-aminothiazoles from diamides (eqn. 14).[38] (An = *p*-$MeOC_6H_4$.)



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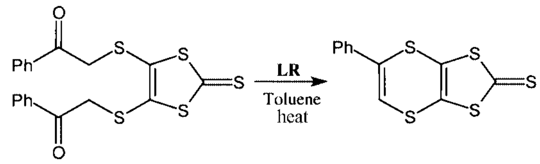
1,8-Diketones react with **LR** to form five- and six-membered sulfur heterocycles with the loss of some carbon atoms (eqns. 15–17)[39] and unsaturated diketones react with **LR** to give a



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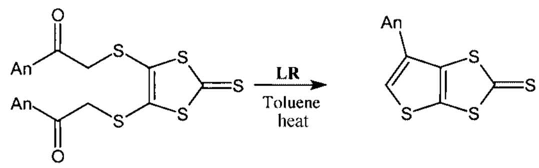

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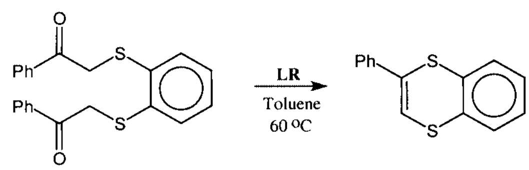
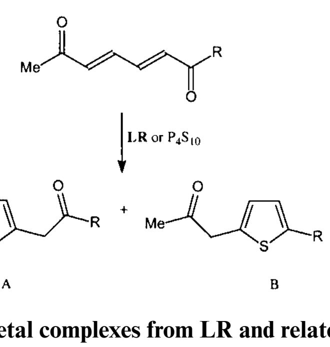


(17)

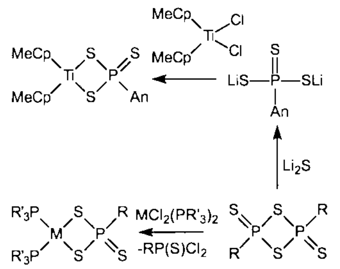
mixture of the two possible isomers (eqn. 18).[40] When the reaction is performed in the presence of boron trifluoride the product ratio changes.[40]



(18)

The formation of metal complexes from LR and related compounds

LR and $\mathbf{Fc_2P_2S_4}$ both form platinum complexes on reaction with $[PtCl_2(PR_3)_2]$.[9,41,42,] A titanium complex of similar structure can be obtained (eqn. 19) by sequential treatment of **LR** with lithium sulfide and $TiCl_2(Cp)_2$.[43] In contrast direct reaction of **LR** with titanocene dicarbonyl gives a complex containing a five-membered TiSPPS ring,[43] eqn. (20). Triiron dodecacarbonyl reacts with **LR** to form $[Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}P(S)An)]$ in low yield (eqn. 21).[44]



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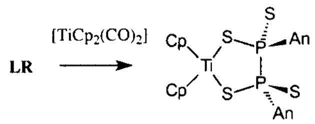

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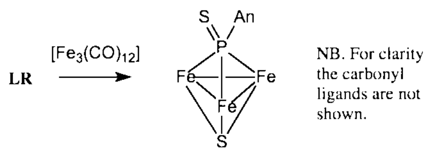

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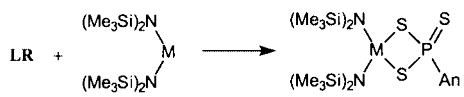
In closely analogous reactions to those above bis[bis-(trimethylsilyl)amino]-germanium(II) and -tin(II) both asymmetrically cleave the P_2S_2 ring in **LR,** forming MSPS rings in 10 and 90% yields (eqn. 22).[45] Other similar germanium com-



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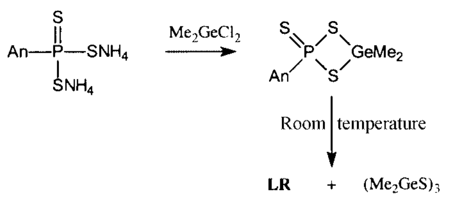
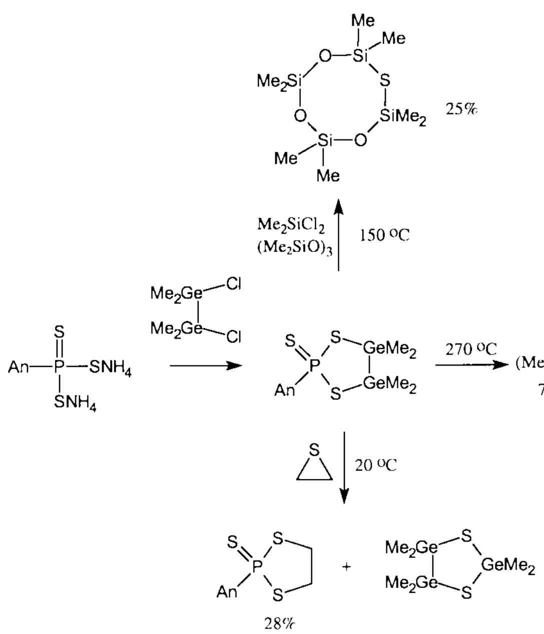
pounds have been reported (eqn. 23) though some of these are



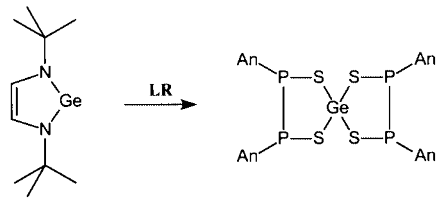
(23)

unstable.[46] The five-membered Ge_2S_2P heterocycle is more stable and has been used as a starting material for further chemistry (Scheme 5).[46]



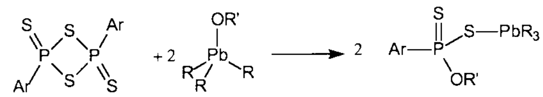
Scheme 5 Reactions of $AnPS_3(GeMe_2)_2$.

In contrast to eqn. (22), 1,3-di-*tert*-butyl-1,3,2-diazagermol-2-ylidene reacts with **LR** to give a spirocyclic compound (eqn. 24) in 20% yield.[45] The phosphorus has been reduced to the III oxidation state.



(24)

Treatment of dithiadiphosphetane disulfides with triethyl- and triphenyl-(alkoxy)plumbanes in benzene results in symmetric ring cleavage to form triethyl- and triphenyl-lead(IV) *S*-(*O*-alkyl 4-alkoxyphenyldithiophosphonates),[47] eqn. (25). In a



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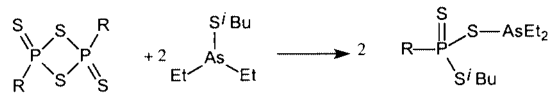
Ar	R	R′	Yield (%)
p-$MeOC_6H_4$	Et	Bu^i	65
p-$EtOC_6H_4$	Et	Bu^i	63
p-$MeOC_6H_4$	Ph	Me	61
p-$EtOC_6H_4$	Ph	Me	98

similar way treatment with a *S*-alkyl organoarsenic compound results in symmetric cleavage of the dithiadiphosphetane ring (eqn. 26).[48]



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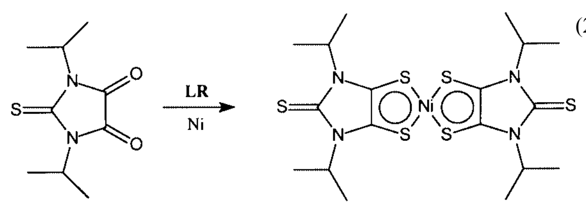
R	Yield (%)
EtS	83
p-$MeOC_6H_4$	76

Thionation chemistry used in metal co-ordination chemistry

The reaction of 1,3-diisopropyl-4,5-dioxoimidazolidine-2-thione with **LR** and nickel powder gives a nickel complex (eqn. 27).[49] Attempts to isolate the trithione intermediate failed.[49]



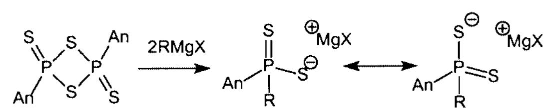
(27)

LR has been treated with a polyanion $[PW_{11}NbO_{40}]^{4-}$ replacing one oxygen atom by sulfur (eqn. 28).[50] Grignard

$$[Bu_4N]^+{}_4\,[PW_{11}NbO_{40}]^{4-} \xrightarrow[\text{MeCN/AcOH}]{\textbf{LR}} [Bu_4N]^+{}_4\,[PW_{11}NbO_{39}S]^{4-} \quad (28)$$

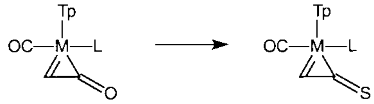
60%

reagents react with **LR** forming carbon–phosphorus bonds in $[R(An)PS_2]^-$ anions (eqn. 29) which have (as expected) a signifi-



(29)

cant co-ordination chemistry.[51–53] Metal ketenyl complexes of molybdenum and tungsten react with **LR** to form thioketenyl complexes in high yields (eqn. 30).[54]

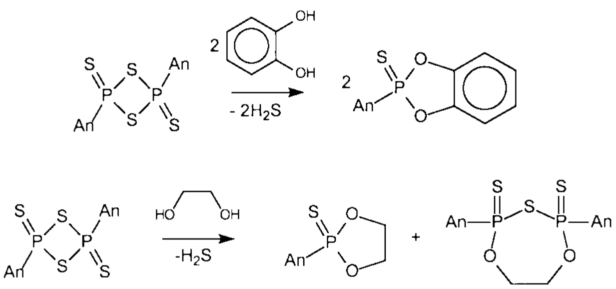


(30)

M	L
W	PPh_3
Mo	PPh_3
W	PMe_2Ph
Mo	$P(OMe)_3$

Reactions forming oxygen heterocycles

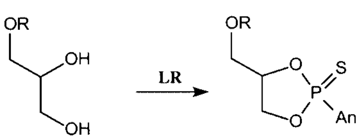
The reactions of simple oxygen nucleophiles are mentioned in an existing review so they will not be considered in depth here. Oxygen nucleophiles containing two sites for reaction such as ethylene glycol can react with a dithiadiphosphetane disulfide using one or two sites. The reactions of 1,2-diols[55] and catechols[56] with **LR** have recently been investigated. While the reactions of catechols only give five-membered rings,[56] those of 1,2-diols gave a mixture of similar five-membered heterocycles and seven-membered rings.[55] Mechanistically these reactions can be rationalised as being due to an SH group acting as a leaving group (Scheme 6); hydrogen sulfide gas will be formed.



Scheme 6 Reactions of catechol and ethylene glycol with **LR**.

The product of treating $\mathbf{Fc_2P_2S_4}$ with catechol has been subject to crystallographic investigation.[9]

Recently some dioxaphospholane phospholipid analogues have been reported to exhibit selective herbicidal activity against rape (eqn. 31).[57]

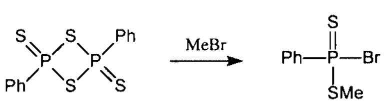


(31)

R= $C_{14}H_{29}$, $C_{16}H_{33}$ or $C_{18}H_{37}$

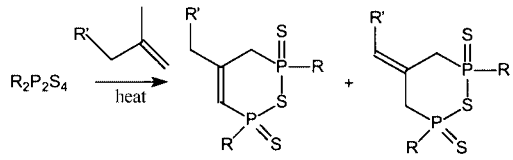
Synthesis of organo sulfur phosphorus compounds

The reaction of an excess of methyl bromide with diphenyldithiadiphosphetane disulfide in a sealed tube gives (in almost quantitative yield) methyl phenylphosphonobromidodithioate (eqn. 32).[58]



(32)

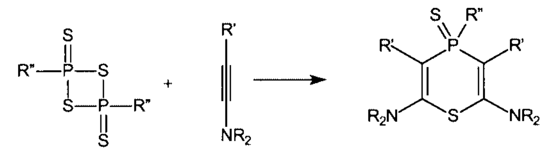
The reaction of dithiadiphosphetane disulfides with alkenes has been used in the synthesis of antisludge additives for engine oils[59] (eqn. 33); R′ may be a variety of alkyl and aryl groups including phenyl, *tert*-butyl, and straight chain alkyl groups, R can be Me, An, and 3,5-di-*t*-butyl-4-hydroxyphenyl.[59] The



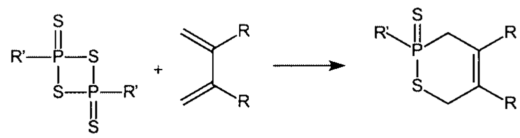
(33)

154 **155**

reactions of electron rich alkynes are known to give thiaphosphorines (eqn. 34)[60,61] and 1,3-dienes react with dithiadiphosphetane disulfides in Diels–Alder reactions (eqn. 35).[62–66]

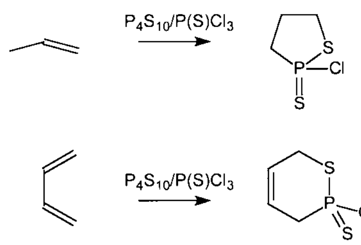


(34)



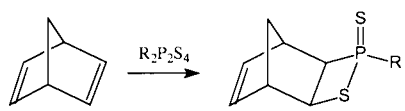
(35)

It is noteworthy that a mixture of P_4S_{10} and $P(S)Cl_3$ will react with alkenes and dienes as a synthon for $ClPS_2$, in the formation of cyclic compounds (Scheme 7).[67]



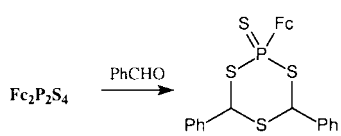
Scheme 7 The reactions of propene and butadiene with $P_4S_{10}/P(S)Cl_3$.

Recently we have shown that strained bicyclic alkenes react with $\mathbf{Fc_2P_2S_4}$ and other dithiadiphosphetanes to form thiaphosphetane rings (eqn. 36).[65,66]



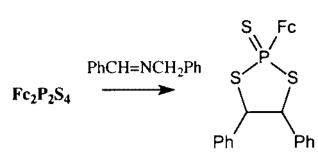
(36)

While many unhindered thioaldehydes and thioketones are unavailable due to extreme instability, they may be generated *in situ* by the action of a thionation agent on the carbonyl compound. The reaction of simple unhindered ketones and aldehydes with $\mathbf{Fc_2P_2S_4}$ forms six-membered rings (eqn. 37),[2,66,68,69]



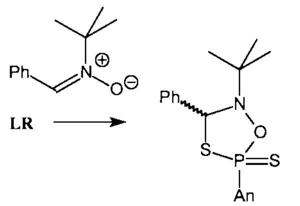
(37)

and the reaction of $\mathbf{Fc_2P_2S_4}$ with an imine gives (in low yield) a five-membered ring (eqn. 38).[66] It is thought that the imine reacts slowly forming thiobenzaldehyde at a lower concentration than that obtained by treating benzaldehyde with $\mathbf{Fc_2P_2S_4}$.[66]

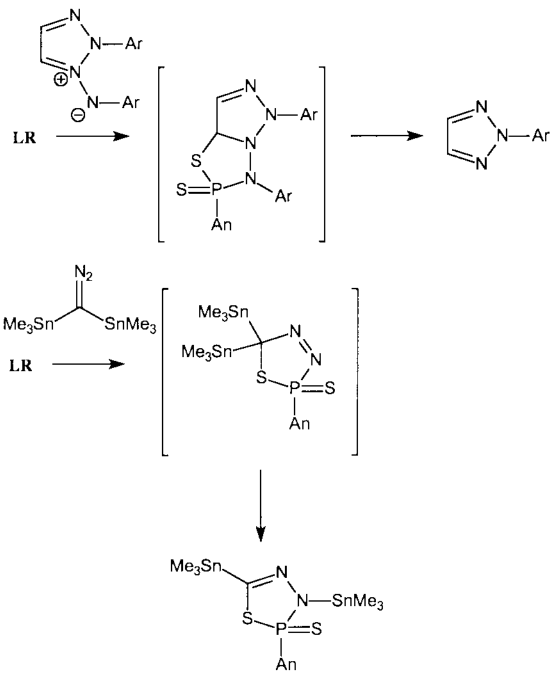


(38)

The reaction of **LR** with 1,3-dipoles also yields five-membered rings,[70–72] including some 'true' heterocycles (eqn. 39).[70] although in some cases the initial product is unstable and rearranges or decomposes (eqn. 40).[70,72]

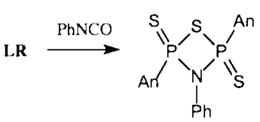


(39)



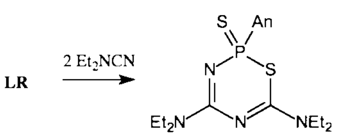
(40)

The reactions of trimethylsilyl azide,[73] heptamethyldisilazane,[74] isocyanates,[58] isothiocyanates,[58] ureas,[75] hindered amines,[76] imines,[77] and dicyclohexylcarbodiimide[77] with dithiadiphosphetane disulfides give thiazadiphosphetanes (eqn. 41).



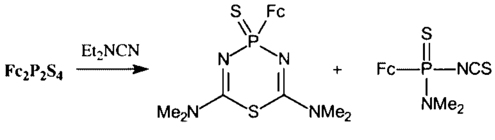
(41)

Treatment of dithiadiphosphetane disulfides with dialkyl cyanamides, was reported to give 1,3,5,2-thiadiazaphosphorines (eqn. 42) which are of possible use as plant protection



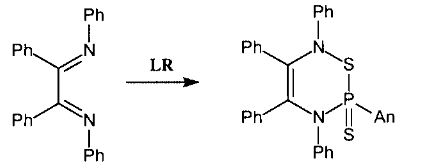
(42)

agents.[78,79] We found that treatment of **LR** and **$Fc_2P_2S_4$** with dimethyl cyanamide gives mixtures of 1,3,5,4-thiadiazaphosphorines and *P*-isothiocyanates (eqn. 43).[76,77]

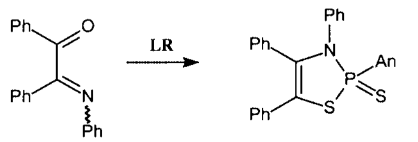


(43)

Benzil dianils[80] and anils[81] react with **LR** to form heterocycles (eqns. 44, 45); these are further examples of **LR** undergoing a symmetric cleavage reaction.

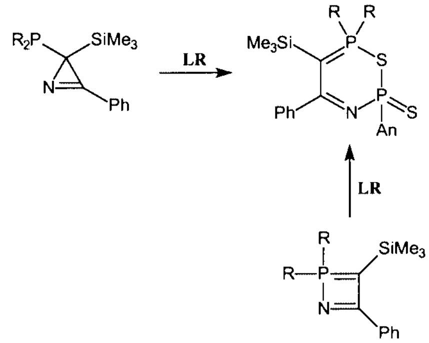


(44)



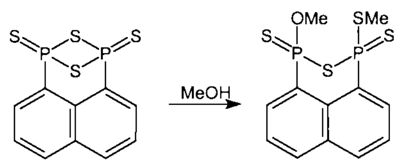
(45)

LR reacts with a phosphino-2*H*-azirine or an azaphosphete to form a heterocyclic product (eqn. 46, R = dicyclohexylamino).[82]



(46)

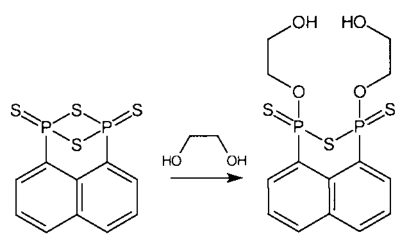
The reactions of **NpP_2S_4** with oxygen nucleophiles have been investigated. Methanol gave **1** {δ_P 79.8 (d) and 66.4 [d, $^2J(^{31}P–^{31}P) = 15$ Hz]} which cannot be explained by the simple action of methanol as a nucleophile, as one methyl group is transferred from an oxygen to a sulfur atom (eqn. 47).[83] The



NpP_2S_4 **1**

(47)

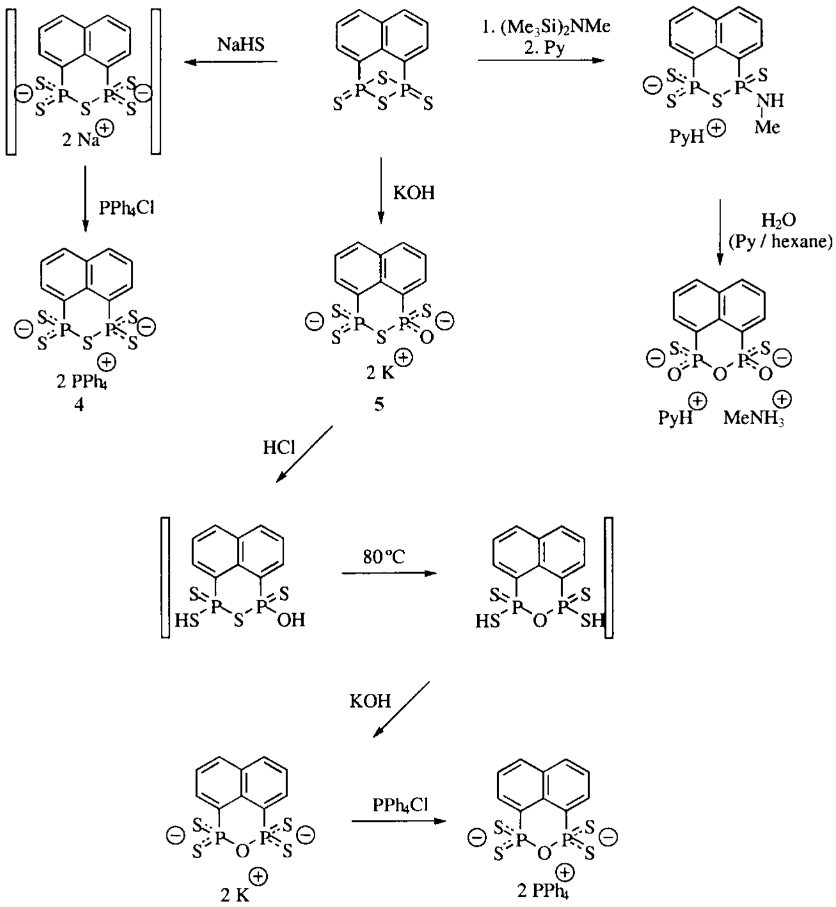
reaction of ethylene glycol with **NpP_2S_4** to give **2** (δ_P 78.6) can be explained by the nucleophilic attack of two molecules of the diol on the phosphorus centres, followed by elimination of hydrogen sulfide (eqn. 48).[84] The fact both the hydroxyl groups



2

(48)

of one molecule of the diol do not react to give a $C_2O_2P_2S$ ring is difficult to explain.[84] Further treatment of **2** with ethylene glycol at 140 °C gives **3** (δ_P 6.6), which would be the logical hydrolysis product (eqn. 49).[84] Surprisingly, attempts to form **3** by the action of water on **2** have failed.[84]

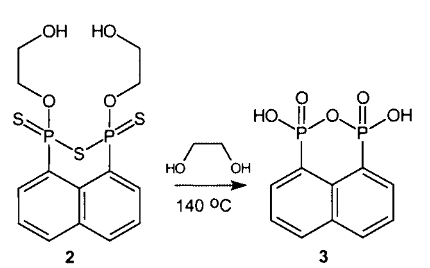


Scheme 8

In contrast to the above, the reaction of 3,5-di-*tert*-butylcatechol with $\mathbf{NpP_2S_4}$ in hot toluene gives (eqn. 50) a seven-membered ring, unlike the five-membered rings obtained by the reaction of catechols with **LR**.[11,85]

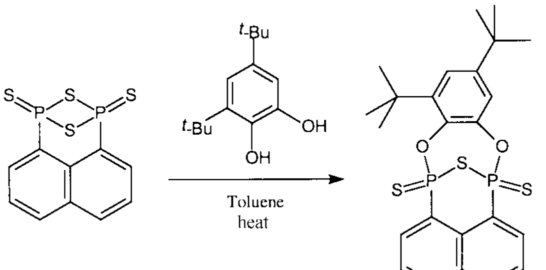
New salts of thionated (naphthalene-1,8-diyl)bis(phosphonic) acid monoanhydrides $[PPh_4^+]_2[C_{10}H_6PS_2(\mu\text{-}S)PS_2^{2-}]$ **4**

(49)



2 **3**

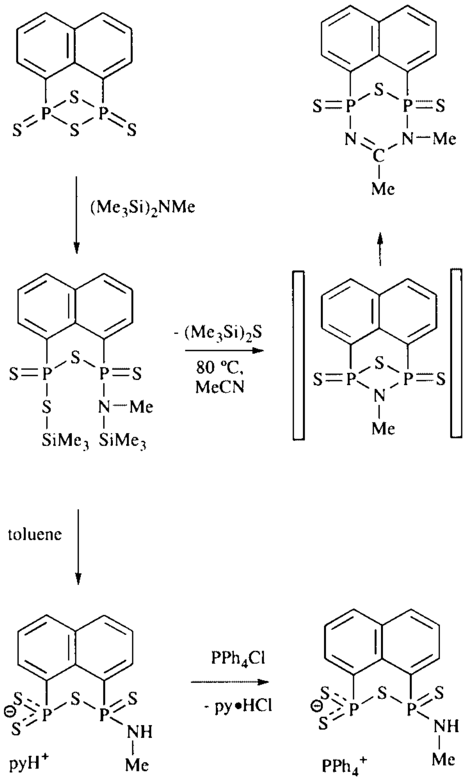
(50)



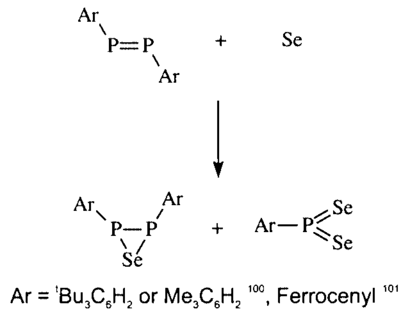
and $[K^+]_2[C_{10}H_6PS_2(\mu\text{-}S)POS^{2-}]\cdot H_2O$ **5** both containing the C_3P_2S ring were prepared in high yields[86] by the reaction of $\mathbf{NpP_2S_4}$ with NaHS and PPh_4Cl, or KOH, respectively, in water (Scheme 8). Salt **5**, containing a P=O terminal bond as well as a P–S–P bridge, undergoes, under acid conditions, a rearrangement reaction leading to the O,S-symmetrically substituted derivative $[K^+]_2[C_{10}H_6PS_2(\mu\text{-}O)PS_2^{2-}]$ **6**, containing a C_3P_2O heterocycle. Dipotassium salt **6** was converted into bis(tetraphenylphosphonium) salt **7** by treatment with PPh_4Cl. Hydrolysis of $[Hpy^+]_2[C_{10}H_6P(S)(NHMe)(\mu\text{-}S)PS_2^-]$ led to $[CH_3NH_3^+][Hpy^+][C_{10}H_6POS(\mu\text{-}O)POS^{2-}]\cdot 1.5$ py.[86]

The bridge cleavage reactions of $\mathbf{NpP_2S_4}$ with nitrogen containing bases have also been studied in some detail. Variation of the amine and the molar ratio used can enable the outcome of the reactions to be controlled quite well. Thus the reaction with methylbis(trimethylsilyl)amine in dichloromethane gives a product of P_2S_2 ring cleavage, $C_{10}H_6P(S)(SSiMe_3)(\mu\text{-}S)P(S)(NMeSiMe_3)$ (Scheme 9). Its subsequent reaction with pyridine (py) gives the desilylated ionic product $[Hpy^+][C_{10}H_6P(S)(NHMe)(\mu\text{-}S)PS_2^-]$, which reacts with tetraphenylphosphonium chloride to give $[PPh_4^+][C_{10}H_6P(S)(NHMe)(\mu\text{-}S)PS_2^-]$. When acetonitrile was used as a solvent, a cage compound 3,4-dimethyl 2,6-(naphthalene-1,8-diyl)-1,3,5,2λ^5,6λ^5-thiadiazadiphosphinine 2,6-disulfide containing the six-membered CN_2P_2S heterocycle was obtained.[87–90]

The wide range of reactivity for P–S heterocycles immediately encourages investigation into P–Se chemistry. We have conducted some preliminary experiments in this area. A number of groups have investigated the synthesis of $(RP)_xSe_y$ rings[91–98] which are accessible by a variety of routes, including simple reaction of $(PhP)_5$ with grey selenium in toluene. Apart from the simple five-membered rings which are structurally related to $(PPh)_5$ by substitution of PPh groups by selenium atoms, it is also possible to synthesize analogues of Lawesson's reagent. The ^{t}Bu sulfur and selenium analogues of **LR** were compared structurally a number of years ago.[99] Yoshifuji *et al.* and Weber *et al.* have used an addition reaction (eqn. 51) to prepare both cyclic ArP_2Se and noncyclic $ArPSe_2$.[100,101] Yoshifuji prepared larger rings using the Mes* ($^tBu_3C_6H_2$) group[102] and carried out some simple selenation reactions on amides, although the conditions needed are rather vigorous.



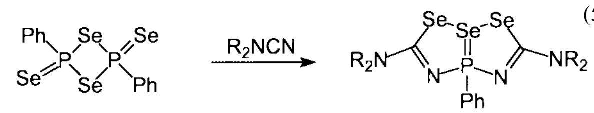
Scheme 9



(51)

Several years ago we found that $(PhP)_xSe_y$ rings may undergo insertion reactions with multiple bonded organics such as acetone and CS_2[103] (Scheme 10). Hill and Malget[104] used **LR** to convert a ketenyl into a thioketenyl and subsequently made use of a heterocycle, which they described as 'Woollins' reagent' to prepare the selenoketenyl.[105]

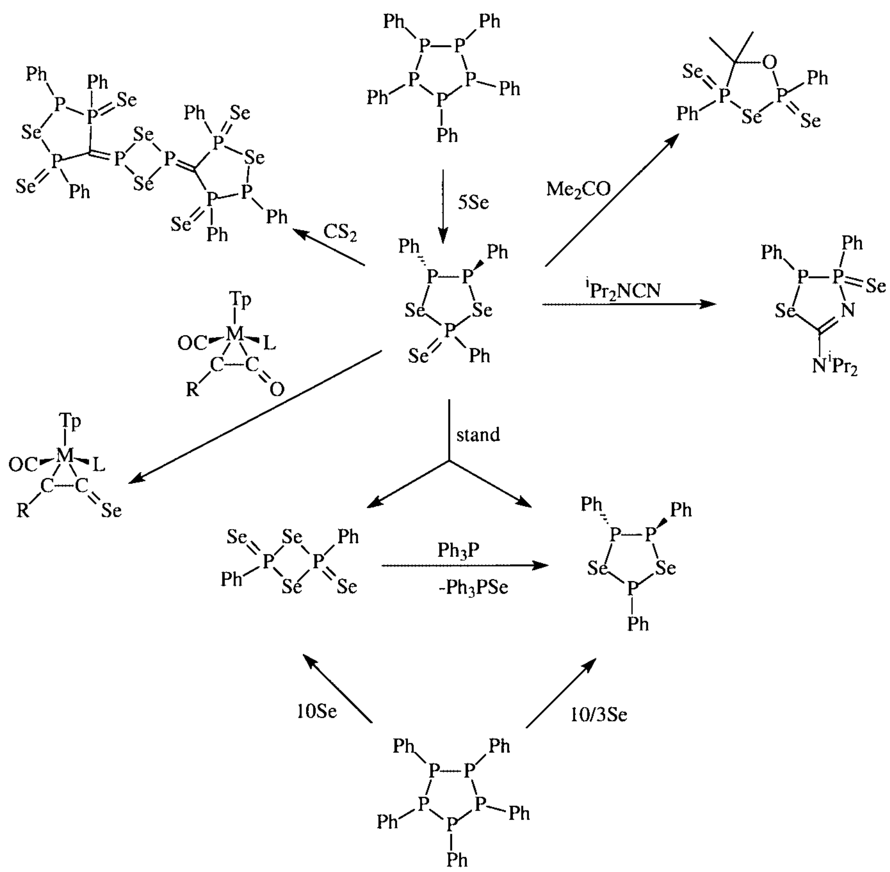
In other studies we have found the outcome of the insertion reactions is dependent on the type of P–Se heterocycle used[106,107] and that it is possible to isolate a triselenaphosphetane according to eqn. (52). Interestingly, this new



(52)

triselenaphosphapentalene presents bonding questions that await answers. Although shown with a central P=Se group at *ca.* 2.22 Å it has to be considered a very long P=Se double bond or a short P–Se single bond, a point further accentuated by the intermediate nature of the $J\{P–Se\}$ coupling at *ca.* 320 Hz.

This area promises many interesting (and potentially useful) new heterocycles.



Scheme 10

References

1 M. P. Cava and M. I. Levinson, *Tetrahedron*, 1985, **41**, 5061.
2 R. A. Cherkasov, G. A. Kutyrev and A. N. Pudovik, *Tetrahedron*, 1985, **41**, 2567.
3 H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse and T. H. Chao, *J. Am. Chem. Soc.*, 1956, **78**, 5018.
4 B. R. Belleau and C. Franchini, *US Pat.*, 4,428,889, 1984 (*Chem. Abstr.*, **100**, 192077h).
5 P. Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, 1952, **74**, 4933.
6 N. M. Yousif, U. Pedersen, B. Yde and S. O. Lawesson, *Tetrahedron*, 1984, **40**, 2663.
7 H. Hirai and H. Yoshioka (Sumitomo Chemical Co. Ltd.), *Ger. Offen.*, 1806105, 1969 (West German Patent) (*Chem. Abstr.*, **71**, 50213h).
8 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *Heteroatom Chem.*, 1999, **10**, 651.
9 M. R. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 3653.
10 A. M. Z. Slawin, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1987, 1741.
11 M. R. St. J. Foreman, J. Novosad, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1997, 1347.
12 J. T. Shore, W. T. Pennington, M. C. Noble and A. W. Cordes, *Phosphorus Sulfur Relat. Elem.*, 1988, **39**, 153.
13 P. E. Newallis, J. P. Chupp and L. C. D. Groenweghe, *J. Org. Chem.*, 1962, **27**, 3829.
14 M. Yokoyama, Y. Hasegawa, H. Hatanaka, Y. Kawazoe and T. Imamoto, *Synthesis*, 1984, 827.
15 C. Lensch and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 2855.
16 A. Zul-Qarnain Khan and J. Sandström, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2085.
17 Y. Takaguchi and N. Furukawa, *Chem. Lett.*, 1996, 859.
18 J. Roffey, Ph.D. Thesis, Loughborough University, 1996.
19 S. Buscemi and N. Vivona, *Heterocycles*, 1994, **38**, 2423.
20 T. Nishio, N. Okuda and C. Kashima, *J. Chem. Soc., Perkin Trans. 1*, 1992, 899.
21 F. Z. Basha and J. F. DeBernardis, *J. Heterocycl. Chem.*, 1987, **24**, 789.
22 D. Konwar, R. C. Boruah, J. S. Sandhu and J. N. Baruah, *Indian J. Chem., Sect. B*, 1982, **21**, 899.
23 T. Nishio, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1113.
24 R. Shabana, A. A. El-Barbary, N. M. Yousif and S. O. Lawesson, *Sulfur Lett.*, 1984, **2**, 203.
25 M. Shimagaki, Y. Fujieda, T. Kimura and T. Nakata, *Tetrahedron Lett.*, 1995, **36**, 719.
26 T. Mukaiyama, K. Watanabe and I. Shiina, *Chem. Lett.*, 1995, 1.
27 N. Shimomura and T. Mukaiyama, *Chem. Lett.*, 1993, 1941.
28 M. I. Levinson and M. P. Cava, *Heterocycles*, 1982, **19**, 241.
29 M. Caron, *J. Org. Chem.*, 1986, **51**, 4075.
30 D. R. Shridhar, M. Jogibhukta, P. Shanthan Rao and V. K. Handa, *Synthesis*, 1982, 1061.
31 F. Freeman, D. S. H. L. Kim and E. Rodriguez, *J. Org. Chem.*, 1992, **57**, 1722.
32 A. Merz and F. Ellinger, *Synthesis*, 1991, 462.
33 D. R. Shridhar, M. Jogibhukta, P. Shanthan Rao and V. K. Handa, *Indian J. Chem., Sect. B*, 1983, **22**, 1187.
34 T. Nishhio, N. Okuda and C. Kashima, *J. Heterocycl. Chem.*, 1988, **25**, 1437.
35 F. Hadj-Abo, S. Bienz and M. Hesse, *Tetrahedron*, 1994, **50**, 8665.
36 K. Tae and J. S. Urden, *Synth. Commun.*, 1995, **25**, 2647.
37 T. Nishio, *Helv. Chim. Acta.*, 1998, **81**, 1207.
38 O. Uchikawa, K. Fukatatsu and T. Aono, *J. Heterocycl. Chem.*, 1994, **31**, 877.
39 T. Ozturk, *Tetrahedron Lett.*, 1996, **37**, 2821.
40 C. W. Ong, C. M. Chen and Long Fu Wang, *Tetrahedron Lett.*, 1998, **39**, 9191.
41 P. T. Wood and J. D. Woollins, *Transition Met. Chem.*, 1987, **12**, 403.
42 R. Jones, D.J. Williams, P. T. Wood and J. D. Woollins, *Polyhedron*, 1987, **6**, 539.
43 G. A. Zank and T. B. Rauchfuss, *Organometallics*, 1984, **3**, 1191.
44 J. P. Fackler, Jr., A. M. Mazany, D. Seyferth, H. P. Withers, Jr., T. G. Wood and C. F. Campana, *Inorg. Chim. Acta*, 1984, **82**, 31.
45 C. J. Carmalt, J. A. C. Clyburne, A. H. Cowley, V. Lomeli and B. G. McBurnett, *Chem. Commun.*, 1998, 243.
46 J. Barrau, M. El Amine, G. Rima and J. Satgé, *Can. J. Chem.*, 1986, **64**, 615.
47 I. S. Nizamov, V. A. Kuznetzov and E. S. Batyeva, *Heteroatom Chem.*, 1997, **8**, 323.
48 I. S. Nizamov, A. V. Matseevskii, E. S. Batyeva, B. E. Abalonin, I. I. Vandyukova and R. R. Shagidullin, *Heteroatom Chem.*, 1997, **8**, 329.
49 F. Bigoli, P. Deplano, F. A. Devillanova, J. R. Ferraro, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli, E. F. Trogu and J. M. Williams, *Inorg. Chem.*, 1997, **36**, 1218.
50 P. Cadot, V. Bereau and F. Secheresse, *Inorg. Chim. Acta.*, 1995, **239**, 39.
51 K. Diemert, P. Haas and W. Kuchen, *Chem. Ber.*, 1978, **111**, 629.
52 W. Kuchen and H. Keck, *Z. Naturforsch., Teil B*, 1976, **31**, 437.
53 W. Kuchen, R. Uppenkamp and K. Diemert, *Z. Naturforsch., Teil B*, 1979, **34**, 1398.
54 A. F. Hill and J. M. Malget, *Chem. Commun.*, 1996, 1177.
55 R. Shabana, F. H. Osman and S. S. Atrees, *Tetrahedron*, 1993, **49**, 1271.
56 R. Shabana, F. H. Osman and S. S. Atrees, *Tetrahedron*, 1994, **50**, 6975.
57 L.-N. He, R.-X. Zhuo, R.-Y. Chen and J. Zhou, *Synth. Commun.*, 1997, **27**, 2853.
58 E. Flunk and H. Binder, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 260.
59 S. J. Brois (On behalf of Exxon Research and Engineering Co.), *US Pat.*, 4,042,523, 1977 (*Chem. Abstr.*, **87**, 204150e).
60 N. Schindler and W. Ploger, *Synthesis*, 1972, 421.
61 N. Schindler (On behalf of Henkel and Cie GmbH), *West German Pat.*, 2133329, 1971 (*Chem. Abstr.*, **78**, 111507).
62 T. Sasaki, K. Shimizu and M. Ohno, *Chem. Pharm. Bull.*, 1984, **32**, 1433.
63 A. Ecker, I. Boie and U. Schmidt, *Monatsh. Chem.*, 1973, **104**, 503.
64 A. Ecker, I. Boie and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 191.
65 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1999, 1175.
66 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 1997, 855.
67 E. H. Uhing, *US Pat.*, 4,231,970, 1980 (*Chem. Abstr.*, **94**, 84303).
68 T. Selzer and Z. Rappoport, *J. Org. Chem.*, 1996, **61**, 5462.
69 J. Hasserodt, H. Pritzkow and W. Sundermeyer, *Chem. Ber.*, 1993, **126**, 1701.
70 N. Dubau-Assibat, A. Baceiredo and G. Bertrand, *J. Org. Chem.*, 1995, **60**, 3904.
71 W. Zeiss and A. Schmidpeter, *Z. Naturforsch., Teil B*, 1979, **34**, 1042.
72 R. N. Butler, E. C. McKenna and D. C. Grogan, *Chem. Commun.*, 1997, 2149.
73 H. W. Roesky and M. Diet, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 425.
74 W. Zeiss and H. Henjes, *Z. Naturforsch., Teil B,* 1979, **34**, 1334.
75 A. A. El-Barbary and S. O. Lawesson, *Indian J. Chem., Sect. B*, 1984, **23**, 655.
76 M. St. J. Foreman, A. M. Z. Slawin and J. D Woollins, *J. Chem. Soc., Dalton Trans.*, 1999, 3419.
77 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 1997, 1269.
78 A. Schmidpeter and N. Schindler, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 943.
79 Farbenfabriken Bayer AG, *West German Pat.*, 1911329, 1969 (*Chem. Abstr.*, **74**, 42394).
80 R. Shabana and S. S. Atrees, *Phosphorus Sulfur Silicon Relat. Elem.*, 1995, **102**, 9.
81 R. Shabana, M. R. Mahran and T. S. Hafez, *Phosphorus Sulfur Relat. Elem.*, 1987, **31**, 1.
82 V. Piquet, A. Baceirredo, H. Gornitzka, F. Dahan and G. Bertrand, *Chem. Eur. J.*, 1997, **3**, 1757.
83 M.-E. Eleftheriou, J. Novosad, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1991, 116.
84 P. Kilian, J. Touzin, J. Marek, J. D. Woollins and J. Novosad, *Main Group Chem.*, 1996, **1**, 425.
85 M. St. J. Foreman, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1995, 2217.
86 P. Kilian, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.*, 1999, 2327.
87 J. Brinek, J. Touzin, M. Alberti and J. Marek, *Chem. Listy*, 1997, **91**, 627.
88 P. Kilian, P. Pazdera, J. Marek, J. Novosad and J. Touzin, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1497.
89 P. Kilian, J. Marek, R. Marek, J. Touzin, O. Humpa, J. Novosad and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1998, 1176.
90 P. Kilian, J. Marek, R. Marek, J. Tousek, O. Humpa, A. M. Z.

Slawin, J. Touzin, J. Novosad and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1999, 2231.
91 P. T. Wood and J. D. Woollins, *Chem. Commun.*, 1988, 1190.
92 P. T. Wood and J. D. Woollins, *Phosphorus Sulfur Silicon Relat. Elem.*, 1989, **41**, 51.
93 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Phosphorus Sulfur Silicon Relat. Elem.*, 1992, **65**, 111.
94 S. W. Hall, M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1991, **10**, 261.
95 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams, P. T. Wood and J. D. Woollins, *Heteroatom Chem.*, 1990, **1**, 351.
96 M. Baudler, H. Suchomel, G. Furstenberg and U. Schings, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1044.
97 M. Yoshifugi, K. Shivayama and N. Inomoto, *Chem. Lett.*, 1984, 6036.
98 K. Karaghiosoff and G. Jochem, *Phosphorus Sulfur Silicon Relat. Elem.*, 1989, **41**, 460.
99 J. T. Shore, W. T. Pennnington, M. C. Noble and A. W. Cordes, *Phosphorus Sulfur Relat. Elem.*, 1988, **39**, 153.
100 M. Yoshifuji, K. Shitsayamo and N. Inamoto, *Chem. Lett.*, 1984, 603.
101 L. Weber, G. Meine, N. Niederprum and R. Boese, *Organometallics*, 1989, **6**, 87.
102 D. L. An, K. Toyota, M. Yasunami and M. Yoshifuji, *Chem Lett.*, 1995, 199.
103 J. C. Fitzmaurice, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1988, 741.
104 A. F. Hill and J. M. Malget, *Chem. Commun.*, 1996, 1177.
105 I. Baxter, A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1997, 2049.
106 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem.*, 2000, in press.
107 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, unpublished work.