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Heterometathesis of diphosphanes (R_2P-PR_2) with dichalcogenides (R'E-ER', E = O, S, Se, Te)†

The reactions of R₂P-PR₂ with R'E-ER', (where E = Se, S, O, Te) to give R₂P-ER' have been explored experimentally and computationally. The reaction of Ph_2P-PPh_2 with PhSe-SePh gives $Ph_2P-SePh$ (1) rapidly and quantitatively. The P-P/Se-Se reaction is inhibited by the addition of the radical scavenger TEMPO which is consistent with a radical mechanism for the heterometathesis reaction. Compound ${\bf 1}$ has been fully characterised, including by X-ray crystallography. A range of other Ar_2P -SeR (R = Ph, n Bu or CH_2CO_2H) have also been prepared and characterised. The reaction of **1** with [Mo(CO)₄(nbd)] (nbd = norbornadiene) gives two products which, from their characteristic ³¹P NMR data, have been identified as cis-[Mo(CO)₄(Ph₂PSePh-P)₂] (8) and the mixed-donor complex cis-[Mo(CO)₄(Ph₂P-SePh-P)(Ph₂P-SePh-Se)] (9). It is deduced that the P and Se atoms in ligand $\mathbf{1}$ have comparable capacity to coordinate to Mo(0). The reaction of Ph₂P-PPh₂ with PhS-SPh gives Ph₂P-SPh (2) quantitatively but no reaction was observed between Ph₂P-PPh₂ and PhTe-TePh. Heterometathesis between Ph₂P-PPh₂ and ^tBuO-O^tBu does not occur thermally but has been observed under UV irradiation to give Ph₂P-O^tBu along with P(v) oxidation by-products. DFT calculations have been carried out to illuminate why heterometatheses with dichalcogenides R'E-ER' occur readily when E = S and Se but not when E = O and Te. The calculations show that heterometathesis is predicted to be thermodynamically favourable for E = O, S and Se and unfavourable for E = Te. The fact that a metathesis reaction between Ph₂P-PPh₂ with ^tBuO-O^tBu is not observed in the absence of UV radiation, is therefore due to kinetics.

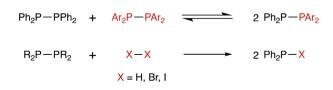
Introduction

The chemistry of diphosphanes (R_2P-PR_2) has attracted considerable attention, and the high reactivity of the P-P bond has been exploited for the diphosphination of a wide range of unsaturated substrates, including alkenes, ¹⁻⁴ alkynes, ⁴⁻⁸ 1,3-dienes, ⁹ arynes, ¹⁰ CO_2 and CS_2 . ¹¹ We recently reported that tetra-aryldiphosphanes readily undergo homometathesis reactions (Scheme 1) under ambient conditions, most likely *via* homolysis of the P-P bond and the generation of Ar_2P^* radicals. ¹² Also shown in Scheme 1 are diphosphane reactions with diatomic X_2 that could be classed as examples of diphosphane heterometathesis reactions. ^{13,14}

Here, we report our experimental and computational investigations of the heterometatheses shown in Scheme 2 15

Compounds containing P–S or P–Se bonds have been widely applied in organic synthesis as reagents for S or Se transfer (Lawesson's reagent¹⁶ and Woollins' reagent¹⁷ respectively). Furthermore, P/S and P/Se compounds are of interest in their own right^{18–20} with potential applications ranging from semi-conductors to pesticides.²¹ However, to date, little attention has been given to compounds of the type R₂P–SR or R₂P–SeR which are amongst the simplest organophosphorus(III) compounds containing S or Se. Arbuzov reported the first examples of Ph₂P–SR (R = alkyl) compounds over a century ago.²² In the 1960s, McLean reported the synthesis of Ph₂P–SePh (1) and Ph₂P–SPh (2) from Ph₂PCl by the routes shown in

[†] Electronic supplementary information (ESI) available. CCDC 2162103. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2dt01093c



Scheme 1 Metathesis reactions of diphosphanes.

and show that this is an effective route for the synthesis of compounds of the type Ph₂P-SeR.

^aSchool of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK. E-mail: paul.pringle@bristol.ac.uk

^bChemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, UK ^cCardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT 11K

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$$Ph_2P-PPh_2$$
 + RE-ER 2 Ph_2P -ER E = O, S, Se, Te

Scheme 2

Scheme 3 Previously reported Ar₂P-ER compounds.^{23,24}

Scheme 3, although no NMR spectroscopic data for these compounds were reported.²³ More recently, Cui *et al.*²⁴ prepared thioaniline derivative 3 similarly (Scheme 3).

Results and discussion

Diphosphane-diselenide metathesis

The reaction between equimolar quantities of tetraphenyldiphosphane and diphenyldiselenide in THF (Scheme 4) was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 10 min, the signal for Ph₂P–PPh₂ at $\delta(\text{P})$ –15.0 ppm had been replaced by a singlet at $\delta(\text{P})$ +29.4 ppm with ^{77}Se satellites ($^1\!J_{\text{PSe}}$ = 229 Hz); the $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum is a doublet at $\delta(\text{Se})$ 307.5 ppm ($^1\!J_{\text{PSe}}$ = 229 Hz), consistent with the formation of the selanyl-phosphane, Ph₂P–SePh (1). The product was isolated in 92% yield and further characterised by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, and

mass spectrometry (see ESI† for the data).²⁵ Crystals of **1** were grown from CH₂Cl₂/*n*-hexane *via* vapour diffusion and its X-ray crystal structure determined (see Fig. 1).

The P–Se bond length in 1 of 2.2620(5) Å is close to the mean average of 2.217 Å obtained from the 686 single crystal X-ray structures that feature a P–Se bond in the Cambridge Structural Database (CSD). There are no crystal structures in the CSD of compounds of the type Ar_2P –SeAr' (or Ar_2P –SAr') with which to compare 1, but the pyramidal geometry at P and bent geometry at Se are as expected.

The P_2R_4/Se_2R_2 heterometathesis reaction has been extended to the preparation of the new selanylphosphanes 4–7 (Scheme 4) by combination of the appropriate diphosphane and diselenide. Each of these compounds was isolated in good yield (quantitative yields observed by *in situ* $^{31}P\{^1H\}$ NMR spectroscopy) as an oil or oily solid and then fully characterised by $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$, ^{11}H , $^{13}C\{^1H\}$ and APCI mass spectrometry (see ESI† for the data). The modest isolated yields of 4 and 7

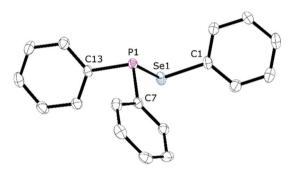


Fig. 1 Thermal ellipsoid (50% probability) representation of the crystal structure of diphenyl(phenylselanyl)phosphane (1), hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–Se1 2.2620(5), P1–C7 1.8421(18), P1–C13 1.8343(18), Se1–C1 1.9316(18); C7–P1–Se1 103.62(6), C7–P1–C13 100.15(8), C13–P1–Se1 96.38(6), P1–Se1–C1 98.66(5).

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(shown in Scheme 4) are due to losses during work-up, since the NMR yields were quantitative. These reactions were carried out in THF, CH2Cl2 or toluene and in no case was the solvent observed to affect the rate or outcome of the reaction, which in all cases had proceeded to completion within the time required (ca. 30 s) to obtain a ³¹P{¹H} NMR spectrum of the reaction mixture. Of particular note is the carboxylic acid 7, which shows that the P-Se bond is tolerant of reactive functional groups. The synthesis of 1 in CDCl₃ was repeated in an amberised NMR tube (to reduce the effect of photolysis) but again, complete conversion to 1 was observed within 30 s.

When the reaction of Ph2P-PPh2 with PhSe-SePh was carried out in the presence of 4 equiv. of TEMPO in THF, the heterometathesis reaction was inhibited: in the absence of TEMPO, complete conversion was observed within 1 min, while in the presence of TEMPO, the reaction proceeded to 54% conversion after 90 min. Other products are detected associated with the formation of Ph2P-TEMPO species (see ESI†). This is consistent with radicals being involved in the reaction, as we previously demonstrated in the homometathesis of diphosphanes.12 As a result, the radical chain mechanism shown in Scheme 5 is proposed. Diselenides are wellknown to form RSe' radicals by photolytic cleavage of the weak Se-Se bond (BDE 41 kcal mol⁻¹). ²⁶⁻³² It is therefore plausible that RSe-SeR cleavage to produce RSe' radicals initiates the radical chain process shown in Scheme 5.33

McLean reported²³ that Ph₂P-SePh (1) is unstable with respect to isomerisation to Ph₃P=Se at 100 °C, over a period of 3-4 h. We have found that 1 is relatively stable under ambient conditions, which makes it easy to handle. Thus solid samples of 1 can be stored under argon at room temperature with <10% degradation observed (traces of Ph₂PH detected) even after 4 months. When water was added to a solution of 1

Initiation Propagation Termination

Scheme 5 Radical chain mechanism proposed dichalcogenide metathesis

in CDCl3 and the emulsion shaken under nitrogen, only very slow hydrolysis to Ph2P(O)H was observed: after 2 days, the hydrolysis mixture contained unreacted 1 (ca. 60%) along with a prominent signal (22%) at +32.5 ppm, consistent with the formation of Ph₂P(O)OH;³⁴ crystals that grew from this solution were shown to match the structure of Ph₂P(O)OH, 'DPPHIN' in the CSD.

The observed kinetic stability of selanylphosphane 1 prompted us to explore its coordination chemistry with Mo(0). To the best of our knowledge, selanylphosphanes have not previously been used as ligands for transition metals. It was of interest to investigate which of the two potential donor atoms (P and Se) would bind to the metal in the complexes, since both are known to bind to metals in mixed P,Se ligands such as Ph₂PCH₂CH₂SePh.³⁵⁻³⁷ Treatment of [Mo(CO)₄(nbd)] (nbd = norbornadiene) with 2 equiv. of 1 in CD₂Cl₂, gave a mixture of two products in the ratio of ca. 4:1 according to ${}^{31}P{}^{1}H$ NMR spectroscopy (see Fig. 2), which have been assigned to the isomers of cis- $[Mo(CO)_4(1)_2]$ (8 and 9 in Scheme 6) on the basis of their characteristic ³¹P NMR parameters.

The major product is a singlet at $\delta(P)$ +59.7 ppm with outer ⁷⁷Se satellites (${}^{1}J_{PSe}$ = 333 Hz) that are themselves split into doublets (${}^{2}J_{PP}$ = 25 Hz) and inner 77 Se satellites (${}^{3}J_{PSe}$ = 40 Hz). This product is assigned the structure 8 where both ligands are P-bound cis on the Mo; this is supported by the large coordination chemical shift ($\Delta \delta_{\rm P}$ = +29.2) and the small $^2J_{\rm PP}$. The inequivalence observed in the satellites is a result of the loss of symmetry in the ⁷⁷Se isotopologue (see Fig. 2).

The second product is assigned structure 9, containing one P-bound and one Se-bound ligand 1, on the basis of the 31P NMR data. Two doublets are observed at $\delta(P^1)$ +62.4 ppm and $\delta(P^2)$ +17.8 ppm (${}^3J_{PP}$ = 22 Hz). The $\Delta\delta_P$ of +31.2 for P^1 in 9 is similar to the $\Delta \delta_{\rm P}$ of the P in 8 and is therefore consistent with P^1 being directly bound to Mo. The $\Delta \delta_P$ of -12.7 ppm for P^2 is assigned to the Se-bound ligand in 9. After the mixture of products was heated to 60 °C in CDCl3 for 3.5 h, complex 9 was the dominant species (ratio of complexes 9:8 was 5:1 according to ³¹P NMR spectroscopy, see ESI†). In the IR spectrum of the mixtures of 8 and 9, several absorptions in the range 1892–2027 cm⁻¹ were evident, as expected for the ν (CO) bands for these cis complexes present. Solutions of the molybdenum complexes 8 and 9 in a CH2Cl2/water emulsion did not undergo any changes after 17 h, indicating good water tolerance.

The analogous complexation reaction of selanylphosphane 7 with [Mo(CO)₄(nbd)] in CH₂Cl₂ produced a similar pattern of products according to ³¹P NMR spectroscopy (see ESI†): two products in the ratio 4:1, with a singlet at +50.8 ppm (with ⁷⁷Se satellites) and two doublets at +54.0 and 17.7 ppm (${}^{3}J_{PP}$ = 21 Hz) consistent with the formation of analogues of 8 and 9.

The notable conclusion from the Mo coordination chemistry is that, for Ph2P-SeR, the PPh2 and SeR groups have comparable donor ability. The fine balance between the linkage isomers with P or Se coordination is likely a consequence of the donor atoms both being soft and the steric hindrance around the SeR being less than around the PPh₂.

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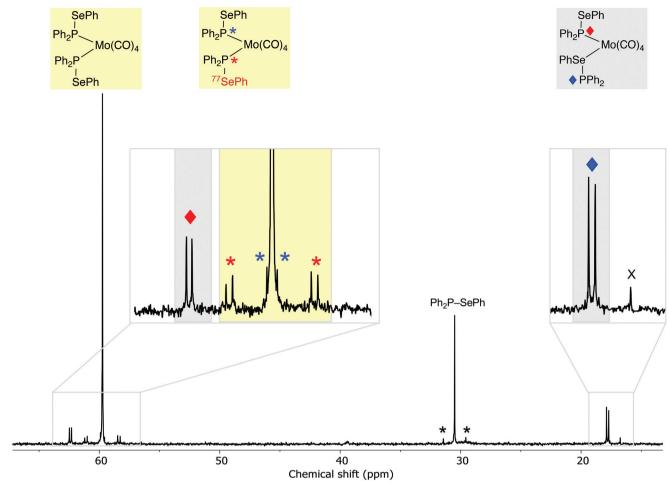


Fig. 2 31P{1H} NMR spectrum of the product mixture obtained from the reaction of Ph₂P-SePh with [Mo(CO)₄(nbd)]. The large singlet at ca. 60 ppm is assigned to the symmetrical P,P-complex 8 and the expansion shows the signals associated with the 77 Se isotopologue of 8, which show satellite signals due to ${}^{1}J_{PSe}$ (*) and ${}^{3}J_{PSe}$ (*). The doublets at ca. +62 (\spadesuit) and +18 (\spadesuit) are assigned to 9, the P,Se-linkage isomer of 8 (${}^{77}Se$ satellites obscured by the noise). The signal at ca. 31 ppm is for unreacted ligand 1 with ⁷⁷Se satellites (*). The minor signal labelled X at ca. +17 ppm is unassigned.

Diphosphane-disulfide metathesis

The reaction of tetraphenyldiphosphane with diphenyl disulfide or 4-aminophenyl disulfide gave the previously reported sulfanylphosphanes 2 and 3 respectively (see Scheme 7). 23,24,38 Compared with the rapid diselenide reactions (Scheme 4), the disulfide analogues are sluggish, requiring up to 20 h to reach completion in an unagitated NMR tube. The reactions were significantly more rapid when they were stirred and were most rapid in chloroform (as with the diphosphane homometathesis).12 The conversions to 2 and 3 were apparently quantitative in the reactions monitored by ³¹P{¹H} NMR spectroscopy but the isolated yields were modest (see Scheme 7); there were significant losses on the

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short alumina column used to purify the crude products (see ESI†).

The diphosphane-disulfide metathesis was inhibited by the presence of TEMPO (4 equiv.), consistent with the reaction following the radical chain mechanism shown in Scheme 5, as for the diphosphane-diselenide process. The reaction of Ph₂P-PPh2 with PhS-SPh in CDCl3 was followed by 31P{1H} NMR spectroscopy and 2 was formed in 34% yield after 1 h of reaction. When the same reaction was performed in the presence of 4 equivalents of TEMPO, 8% conversion to 2 was observed after 1 h (see ESI†). The higher rate observed with the diselenide than with the disulfide reflects the ease with which homolysis of the weak Se-Se bond takes place compared to the homolysis of either the S-S or P-P bonds. 39-41

Attempted diphosphane-ditelluride and diphosphaneperoxide metatheses

When Ph₂P-PPh₂ and PhTe-TePh were mixed in C₆D₆, no heterometathesis reaction (Scheme 2) was observed even after 12 days. The compound Ph₂P-TePh has not been previously reported, although its P(v) isomer Ph3P=Te is readily prepared.42

Similarly, when Ph₂P-PPh₂ and ^tBuO-O^tBu were mixed in toluene, no heterometathesis reaction (Scheme 8) to give the known¹⁷ compound Ph₂P-O^tBu was observed after 72 h. The only products detected by $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectroscopy were the monoxide Ph₂P(O)-PPh₂ (12%: 2 doublets at +32.7 and -24.7, $J_{PP} = 218 \text{ Hz})^{43}$ and Ph₂PH (12%, -40.2 ppm). ¹² Even when a large excess (~15-fold) of ^tBuO-O^tBu was used and the reaction mixture was heated to 60 °C, only oxidation products were observed and no heterometathesis product. However, when this reaction was repeated in C₆D₆ and irradiated with near-UV

light, gradual formation of a new species was observed by ³¹P{¹H} NMR spectroscopy characterised by a singlet at +87.1 ppm and assigned to the phosphinite Ph₂P-O^tBu on the basis of the chemical shift being consistent with the reported value.44 After the irradiation was continued for a further 1 h, a significant quantity of the phosphinate Ph₂P(O)-O^tBu (47% of the total ³¹P integral, see ESI†) was identified by a singlet at +25.7 ppm, in good agreement with literature data. 45 The formation of this P(v) species was further supported by the detection of the phosphinate [M + Na]⁺ ion by mass spectrometry (297.1 m/z observed, 297.1 theoretical). In summary, there is evidence that under UV irradiation, the diphosphane/peroxide heterometathesis does indeed occur but that by-products associated with oxidation by 'BuO-O'Bu contaminate the product (see Scheme 8).

DFT study of heterometathesis reactions of diphosphanes

The general reaction that has been calculated is shown in Scheme 9 and the results are given in Table 1. It was anticipated that the results for the diphosphane metatheses with diatomic molecules Z₂ would be the simplest to interpret. The DFT-calculated ΔE values for the addition of diatomic Z_2 to R_2P-PR_2 , where R = Ph (A), or Me (B), are presented as entries 1-10 of Table 1. The values of ΔH estimated using the mean bond strengths for P-P (51 kcal mol⁻¹), ⁴⁶ Z-Z, and P-Z are also given in Table 1 and there is good agreement between ΔE and ΔH for Z = H, F, Cl, Br and I. The two consistent trends in the heterometathesis equilibria are: (i) ΔE becomes increasingly more favourable with increasing electronegativity of Z; (ii) Me₂P-PMe₂ metatheses are more favourable (by 6-10 kcal mol⁻¹) than the corresponding Ph₂P-PPh₂ metatheses. The position of the equilibrium in Scheme 9 is determined by the relative Z-Z and P-Z bond energies, which in turn will be influenced by a combination of the following factors. (a) The very high H-H and very low F-F bond strengths dominate the

$$R_2P-PR_2$$
 + Z-Z 2 R_2P-Z

A R=Ph
B R=Me

Z = H F Cl Br l
OPh SPh SePh TePh

Scheme 9

Table 1 Calculated ΔE for the heterometatheses shown in Scheme 9^a

Entry	Diphosphane	Z-Z	D(Z-Z)	Product	D(P-Z)	ΔH	ΔE
1	A	H_2	104	Ph ₂ P-H	77	+1	+6.8
2	A	F_2	37	Ph ₂ P-F	117	-146	-131.2
3	A	$\overline{\text{Cl}}_2$	58	Ph ₂ P-Cl	79	-49	-44.1
4	A	Br_2	45	Ph ₂ P-Br	65	-34	-28.9
5	A	I_2	36	Ph ₂ P-I	51	-15	-10.9
6	В	$\overline{\mathrm{H}}_2$	104	Me ₂ P-H	77	+1	+0.7
7	В	F_2	37	Me ₂ P-F	117	-146	-141.3
8	В	$\tilde{\text{Cl}}_2$	58	Me ₂ P-Cl	79	-49	-52.4
9	В	Br_2	45	Me ₂ P-Br	65	-34	-36.6
10	В	I_2	36	Me ₂ P-I	51	-15	-17.9
11	A	t BuO-O t Bu	33	Ph_2P-O^tBu	84	-84	-69.4
12	A	PhO-OPh	33	Ph ₂ P-OPh	84	-84	-71.7
13	A	PhS-SPh	51	Ph ₂ P-SPh	55	-8	-4.2
14	A	PhSe-SePh	41	Ph ₂ P-SePh	_	_	-5.6
15	A	PhTe-TePh	_	Ph ₂ P-TePh	_	_	7.4

^a All energies are given in kcal mol^{-1} and are calculated at STP (298 K, 1 atm). D(Z-Z) and D(P-Z) are the average bond dissociation energies given in ref. 46.

explanation of why the metathesis equilibria with H_2 and F_2 are the least and most favourable respectively. (b) The electrostatic stabilising effect of the $P^{\delta+}$ –Z $^{\delta-}$ dipole on the P–Z bond strength will increase with increasing electronegativity of Z. (c) The size of Z increases in the order F < Cl < Br < I and this will contribute to a lower P–Z bond strength (in that same order) due to increasingly poorer orbital overlap and increasing steric congestion. (d) The P–Z bond may be stronger in Me_2P –Z than in Ph_2P –Z, due to the lower steric hindrance of the PMe_2 group and the greater +I inductive effect of the Me substituents stabilising the δ + charge on the PMe_2 .

The calculated thermodynamics of the metathesis reactions of Ph₂P-PPh₂ with PhE-EPh, where E = O, S, Se, or Te are given in Table 1, entries 12-15. These equilibria will depend on the relative PhE-EPh and Ph2P-EPh bond energies with potentially similar factors at play to those labelled (a)-(c) above, used for the diatomic Z₂ reactions. However, in the case of the dichalcogenides, the PhO-OPh equilibrium (entry 12) is exceptional in being extremely favourable (ΔE of -69.4 kcal mol⁻¹) as a consequence of the low O-O bond energy and the high P-O bond energy (due in part to the large $P^{\delta+}$ -Z $\delta^$ dipole). By contrast, for the other dichalcogenides (entries 13-15), the ΔE values are relatively small, reflecting the fact that the P-P, E-E and P-E bond energies are similar due to the similarity of the electronegativities and sizes of P, S, Se and Te. The calculated ΔE for the diselenide and disulfide reactions are both ca. -5 kcal mol⁻¹ and therefore favour the formation of Ph2P-EPh, in agreement with the experimental observations. The calculated ΔE of +7 kcal mol⁻¹ for the ditelluride/ diphosphane metathesis disfavours the formation of Ph₂P-TePh which is consistent with no reaction between Ph₂P-PPh₂ and PhTe-TePh being observed experimentally.

Although the 'BuO-O'Bu/Ph₂P-PPh₂ metathesis (entry 11, Table 1) is very strongly favoured energetically for the formation of Ph₂P-O'Bu, experimentally, the reaction (Scheme 8) only proceeded under UV irradiation and produced oxidation by-products; the lack of thermal reaction is therefore

due to a kinetic barrier, possibly caused by the bulky ^tBu substituents.

Conclusion

The heterometathesis reactions of Ph2P-PPh2 with RE-ER to give Ph_2P -ER proceed smoothly when E = S or Se but not when E = O or Te. We have shown that Ar_2P-PAr_2 with RSe-SeR gives a range of Ar₂P-SeR compounds (1 and 4-7) in quantitative spectroscopic yields and 100% atom-economy. The reaction of Ph₂P-PPh₂ with ArS-SAr produces Ph₂P-SAr, albeit more slowly than with the Se analogues. The inhibition by TEMPO of the heterometatheses of Ph₂P-PPh₂ with RE-ER (E = Se or S) suggests radical processes are involved in the mechanism. DFT calculations have shown that the heterometatheses with RE-ER are thermodynamically favourable when E = S or Se but not when E = Te, which aligns with the experimental observations. However, the calculations also suggest that the heterometathesis of diphosphanes with peroxides (i.e. E = O) would be very strongly favoured thermodynamically. The lack of thermal reaction between Ph₂P-PPh₂ with ^tBuO-O^tBu is therefore due to kinetics. There is evidence of formation of Ph₂P-O^tBu when mixtures of Ph₂P-PPh₂ and ^tBuO-O^tBu are photolysed but the reaction is complicated by the simultaneous formation of oxidation products. The selanylphosphane Ph2P-SePh (1) can be stored for weeks, largely unchanged at ambient temperatures and is only very slowly hydrolysed by water over several days. The ligand properties of 1 are of interest as it coordinates to Mo(0) to give products whose ³¹P parameters are consistent with coordination via the P and Se being competitive. This is an unusual example of linkage isomerism that is worthy of further study.

Conflicts of interest

There are no conflicts to declare.

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Acknowledgements

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