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Chemistry and ligating properties of the 1,2,4-thiadiphosphole $P_2SC_2Bu^t_2$

Sarah E. d'Arbeloff-Wilson [a], Peter B. Hitchcock [a], John F. Nixon [a,*], László Nyulászi [b]

[a] *School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, UK*
[b] *Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest Gellért tér 4, Hungary*

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Abstract

New synthetic routes to the 1,2,4- and 1,3,4-thiadiphospholes, $P_2SC_2Bu^t_2$, are presented. Both η^1-$W(CO)_5$ and η^5-$M(CO)_3$ complexes (M = Mo, W) of the 1,2,4-thiadiphosphole ring are described and the molecular structure of the former determined by a single crystal X-ray study is in good agreement with theoretical calculations. The thermal conversion of the η^1-$M(CO)_5$ complex to the η^5-$M(CO)_3$ complex is attributable to the entropy change in the reaction. A sequence of [4+2] and [2+2+2] cyclo-addition reactions of the 1,2,4-thiadiphosphole, $P_2SC_2Bu^t_2$, with the phosphaalkyne, $P{\equiv}CBu^t$, affords the tetracyclic cage compound $P_4SC_4Bu^t_4$ which has also been structurally characterised. © 2002 Published by Elsevier Science B.V.

Keywords: Thiadiphosphole; Phosphaalkyne; Carbonyl complexes

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1. Introduction

Only very few 1,2,4- and 1,3,4-thiadiphospholes, $P_2SC_2R_2$, have been reported and there is only a single report of a 1,2,5-thiadiphosphole ($R = CF_3$). The first known 1,2,4-thiadiphosphole $P_2S(CSiMe_3)C(SSiMe_3)$ (**1**) reported by Appel et al. [1] was synthesised by the reaction of carbon disulphide with lithium *bis*-trimethylsilyl phosphide and chlorotrimethylsilane (Fig. 1).

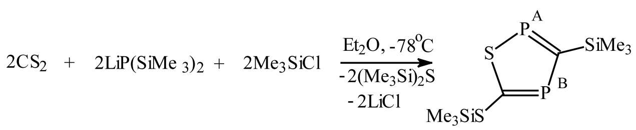

Fig. 1.

Characterisation of **1** was solely by elemental analysis and NMR spectroscopic data, the $^{31}P\{^1H\}$-NMR spectrum showing an [AB] system consisting of two doublets at 309 (P^A) and 304 (P^B) ppm in the unsaturated region with a characteristic two bond coupling constant ($^2J_{P(A)P(B)}$) 59 Hz). Märkl et al. [2] found that the 1,2,4-thiadiphosphole $P_2SC_2Ph_2$ (**2**) was formed, albeit in low yield, among a mixture of other cyclic products from the reaction between a 1,3,4-oxa-thia-azole and the chlorophosphaalkene $Ph(SiMe_3)C{=}PCl$.

The oily 3,5-di-*tert*-butyl-1,2, 4-thiadiphosphole (**3**) was first reported by Lindner et al. [3] via an unusual synthetic route involving insertion of $P{\equiv}CBu^t$ into the P=S bond of the η^2-thiophosphinito manganese complex $[Mn(CO)_4(PPh_3)(PCy_2S)]$. The resulting intermediate is kinetically unstable and undergoes a [2+2] cyclo-addition with a second molecule of phosphaalkyne to give **3** with elimination of $[Mn(CO)_4(PPh_3)(PCy_2)]$. The orientation of the inserted phosphaalkyne is both electronically and sterically controlled [4], thereby resulting specifically in the 1,2,4-isomer. The same authors [5] subsequently reported that **3** could also be synthesised using $[Co(PEt_2S)(CO)_2(PPh_3)]$ and were able to structurally characterise the crystalline 1,2,4-thiadiphosphole, $P_2SC_2R_2$ (**4**) (R = adamantyl) and establish that the ring is planar [6].

In seeking alternative synthetic approaches to this type of ring system, we took advantage of the reactivity of the P≡C triple bond in cycloaddition reactions [7] and its remarkable similarity with the C≡C triple bond [8]. Phospha-alkyne cycloaddition reactions afford a variety

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* Corresponding author. Fax: +44-1273-677196.
E-mail address: j.nixon@sussex.ac.uk (J.F. Nixon).

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of five-membered heterophospholes [7,9] and thiadiphospholes have been considered as possible [3+2] products from cycloadditions between $P\equiv CBu^t$ and a PC(H)S intermediate [10].

Very recently we showed in a collaboration with the Regitz group, [11] that the phosphalkyne, $P\equiv CBu^t$, readily reacts with CS_2 (or its complexes) to produce an isomeric mixture of the 1,2,4- and 1,3,4-thiadiphosphole rings **3** and **5** (Fig. 2) and provided a detailed theoretical explanation of the reaction pathways. We also structurally characterised some η^1-Pt(II) complexes of both ring systems.

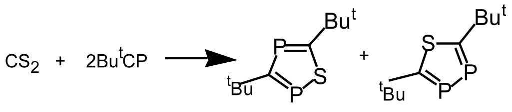
Ruf [12] and Grobe et al. [13] have independently described a similar reaction of $P\equiv CBu^t$ with CS_2 but only identified **3**. Regitz and coworkers [14], in unpublished work, have very recently developed an alternative synthetic route to **3** utilising $P\equiv CBu^t$ and $TaSCl_3$.We present here new studies on other preparative routes to the 1,2,4- and 1,3,4-thiadiphospholes **3** and **5** and the reactivity and ligating behaviour of the former.

2. Results and discussion

2.1. Alternative syntheses of the thiadiphospholes $P_2SC_2Bu^t_2$

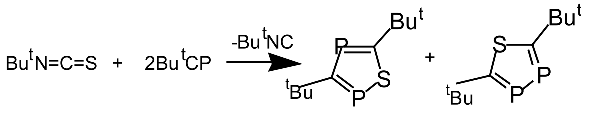
In the light of our previous results, in which one S atom is effectively removed from CS_2, in its reaction with two phosphaalkynes, it was decided to extend this chemistry to include other possible sources of sulphur. It was anticipated that reactions of other heterocumulenes such as isothiocyanides, RN=C=S, with $P\equiv CBu^t$ might offer an alternative route to that using CS_2 with the elimination of the isocyanide $C\equiv NR$ and these expectations were fully borne out. Thus, treatment of $S=C=NBu^t$, with an excess of $PC\equiv Bu^t$, under gentle heat for half an hour, led to the expected formation of **3** and **5** (ratio 4:1) as evidenced by their characteristic $^{31}P\{^1H\}$-NMR spectra, with simultaneous elimination of $C\equiv NBu^t$ (Fig. 3).

The formation of the isonitrile was confirmed by its subsequent treatment with [Mo(norbornadiene)(CO)$_4$] to afford the red crystalline product *cis*-[Mo(CN-Bu^t)$_2$(CO)$_4$] (**6**) which was structurally characterised by a single crystal X-ray diffraction study to be published elsewhere [15].



3 **5**

Fig. 2.



3 **5**

Fig. 3.

Other possible synthetic routes were investigated to see if alternative sources of reactive sulphur could be found to combine with the two phosphaalkyne units. One of the more simple and convenient routes involved the UV irradiation of 2-methyl-thiacyclopropane in the presence of $P\equiv CBu^t$, which readily led to a mixture of both thiadiphospholes **3** and **5** in the ratio of 8:1, albeit in overall poor yield, with propene presumed to be the other product (Fig. 4).

Interestingly, Lawesson's reagent $(PhP(=S)S)_2$ did not prove to be a source of sulphur in its reaction with $P\equiv CBu^t$, although there are reports of its use as a 1,3-dipolarophile [16]. However, the more reactive dimeric ferrocene derivative $[Fe_2(C_5H_4Me)_2(C_5H_3MeP(S)S)_2]$, treated with $P\equiv CBu^t$ (Fig. 5) did prove to be a mild method of synthesis of the rings **3** and **5** in the ratio of 6:1

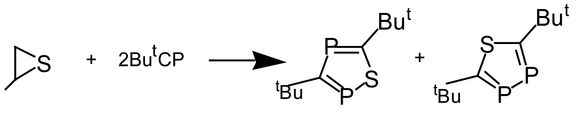
Unexpectedly, the direct reaction between $P\equiv CBu^t$ and elemental sulphur was unsuccessful, unlike the analogous reactions with the other chalcogenides Se and Te, which afford mixtures of the selena- and telluradiphospholes [17]. Likewise, treatment of $P\equiv CBu^t$ with the phosphine sulphide, $Ph_3P=S$, also proved unsuccessful, leading instead to the formation of several uncharacterised products.

2.2. Ligating properties of the 1,2,4-thiadiphosphole 3

2.2.1. Synthesis and characterisation of $[W(CO)_5\eta^1\text{-}P_2SC_2Bu^t_2]$ (7)

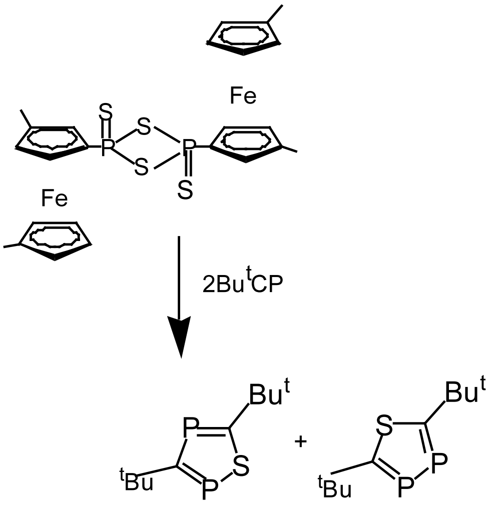
Treatment of the 1,2,4-thiadiphosphole **3** with [W(CO)$_5$THF] in THF at ambient temperature afforded the yellow complex $[W(CO)_5(\eta^1\text{-}P_2SC_2Bu^t_2)]$ (**7**) which was found to involve η^1-coordination of the ring phosphorus adjacent to sulphur (Fig. 6).

The $^{31}P\{^1H\}$-NMR spectrum of a solution of **7** showed an [AB] spin system, with chemical shifts (δ 259.2 P(B), 210.1 P(A) ppm). Since the corresponding values for uncoordinated **3** are (δ 266.1 P(B), 254.4 P(A) ppm), the data strongly suggest that P(A) is the donor



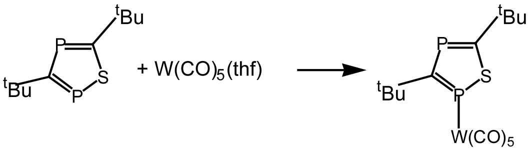
3 **5**

Fig. 4.



3 **5**

Fig. 5.



3 **7**

Fig. 6.

centre and this was confirmed by the magnitude of the one bond $^{183}W-^{31}P$ coupling constant, measured from the satellites around the resonance of P(A), ($^1J_{(P(A)W)}$ 250 Hz) which lies in the expected range for tertiary phosphine complexes containing an η^1-ligated [W(CO)$_5$] fragment.

As expected, the ^{1}H-NMR spectrum of **7** shows two distinct resonances corresponding to the different types of Bu^t groups. Further evidence supporting the characterisation of **3** results from the mass spectrum which exhibits the expected parent ion at *m*/*z* 556 and peaks corresponding to the stepwise loss of all five CO groups (*m*/*z* 528, 500, 472, 444, 416, respectively) and a single crystal X-ray structure determination.

2.2.2. Crystal and molecular structure of [W(CO)$_5\eta^1$-$P_2SC_2Bu^t_2$] (7)

Suitable single crystals of **7** were grown from a hexane solution and a single crystal X-ray diffraction study was performed. The molecular structure which is shown in Fig. 7, together with selected bond lengths and angles, confirms the η^1-ligation mode via P(A) and is similar to those we published previously [18] for the analogous 1,2,4-selena and tellura-diphosphole complexes. A noteworthy structural feature of **7** is the planarity of the ring The ring angles at carbon lie close to 120° while those at P or S are closer to 100°. The two P=C bond distances (1.695(11), 1.690(11) Å) lie in the expected range for P=C double bonds and the structure is in good agreement with that obtained from theoretical calculations [23], on the complex **7** and on the free ring **3** (vide infra). The B3LYP/LANL2DZ* calculated geometry of **7** is in reasonably good agreement with that of the X-ray structure and also with that of the free ring (with the real *tert*-Bu substituents) calculated at the same level of the theory (See Table 1). Structural data are also similar to those observed previously [6] for the thiadiphosphole $P_2SC_2Ad_2$ **4**.

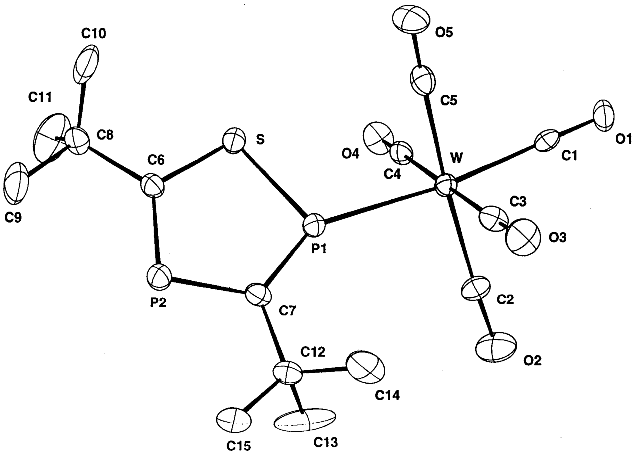


Fig. 7. Molecular structure of [W(CO)$_5$η^1-$P_2SC_2Bu^t_2$] (**7**) together with the atomic numbering scheme and some selected bond lengths (Å) and bond angles (°) P(1)–S = 2.045(4), S–C(6) = 1.726(10), C(6)–P(2) = 1.690(11), P(2)–C(7) = 1.763(11), P(1)–C(7) = 1.695(11), P(1)–W = 2.483(3), W–C(1) = 2.014(11), P(1)–S–C(6) = 100.3(4), C(6)–P(2)–C7) = 101.8(5), P(2)–C(7)–P(1) = 117.8(6), S–P(1)–W = 113.04(14), P(1)–W–C(1) = 173.2(3).

2.2.3. Synthesis and characterisation of [Mo(CO)$_3$(η^5-$P_2SC_2Bu^t_2$)] (8) and [W(CO)$_3$(η^5-$P_2SC_2Bu^t_2$)] (9)

In view of the known exclusive η^5-ligating properties of the isoelectronic aromatic 1,2,4-triphosphole $P_3RC_2Bu^t_2$ (R = (Me$_3$Si)$_2$CH–) towards a variety of transitions metal, [19–22], reactions were also carried out with the 1,2,4-thiadiphosphole **3** to see if it would also prove possible to synthesise analogous η^5-metal complexes. Theoretical calculations concerning the 'aromaticity' of **3** suggested that it ought to behave as a 6e-

Table 1
Experimental and calculated bond length data (Å) for **3** and **7**

	7: X-ray	**7**: Calculated	**3**: Calculated
P1S	2.045(4)	2.07(2)	2.08(9)
P1C7	1.695(11)	1.69(3)	1.71(7)
P2C7	1.736(11)	1.76(5)	1.78(0)
P2C6	1.690(11)	1.71(1)	1.72(0)
SC6	1.726(10)	1.72(4)	1.73(7)
P1W	2.483(3)	2.31(1)	

donor in view of the comparability of the magnitude of the BDSHRT, BI and NICS parameters (53, 56 and −12.4, respectively) with those for thiophene (57, 68 and −13.2, respectively) [24].

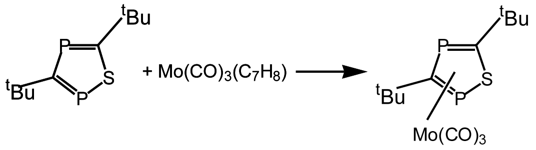
Thus, treatment of the 1,2,4-thiadiphosphole **3** with [Mo(cycloheptatriene)(CO)$_3$] in THF readily afforded [Mo(CO)$_3$(η^5-P$_2$SC$_2$Bu$^t_2$)] (**8**) in good yield (Fig. 8).

It was also possible to thermally convert the η^1-complex [{W(CO)$_5$}(η^1-P$_2$SC$_2$Bu$^t_2$)] (**7**) on heating in boiling THF, to the η^5 product [W(CO)$_3$(η^5-P$_2$SC$_2$Bu$^t_2$)] (**9**) in moderate yield, with evolution of CO (Fig. 9).

Unfortunately, despite many attempts, it did not prove possible to obtain crystals of either **8** or **9** suitable for an X-ray diffraction study; however, the correct formulation can be readily deduced from spectroscopic data. The mass spectra of both η^5-metal tricarbonyl complexes were very similar, showing the expected parent ions (*m*/*z* 412 (**8**), 500 (**9**)) and peaks corresponding to stepwise loss of the three CO groups. The ^{31}P{^{1}H}-NMR spectra for **8** and **9** are also both distinctly different from those of the corresponding η^1-pentacarbonyl complex **7** consisting of two resonances, each of which appears as a doublet resulting from the two bond $^2J_{(P(A)P(B))}$ coupling (32 Hz). The resonances for both P(A) and P(B) in **8** and **9** have shifted significantly to high field compared with those in both the free ring **3** and the complex [W(CO)$_5$(η^1-P$_2$SC$_2$Bu$^t_2$)] (**7**) (Table 2). It can also be seen that the $^2J_{(P(A)P(B))}$ coupling constant increases in the η^1-complex **7** and significantly decreases in the η^5-complexes **8** and **9**, in comparison to the $^2J_{(PP)}$ found in the free thiadiphosphole **3** reflecting the strong interaction of the whole of the ring system with the [M(CO)$_3$] fragments.

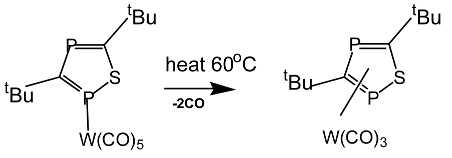
3. Theoretical aspects of 1,2,4-thiadiphosphole complexation

The relative stabilities of the different complexation modes of the 1,2,4-thiadiphosphole **3** were studied computationally [23]. As model compounds, the computationally amenable chromium complexes of the parent 1,2,4-thia-diphosphole ring (C$_2$H$_2$P$_2$S) have been investigated. The three possible coordination compounds **10**, **11** and **12** are shown in Fig. 10.



3 **8**

Fig. 8.

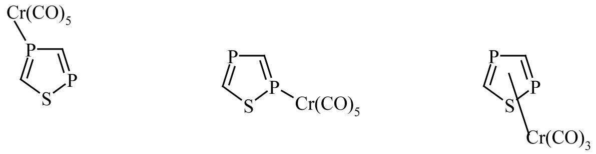


7 **9**

Fig. 9.

Table 2
^{31}P{^{1}H}-NMR data for **3**, **7**, **8** and **9** (δ in ppm, J in Hz)

Compound	δ P(A)	δ P(B)	$^2J_{(P(A)P(B))}$
3	266.1	254.4	49.8
7	259.2	210.1	62.5
8	79.2	48.5	32.6
9	51.7	34.3	33.2



10 **11** **12**

Fig. 10.

Table 3
Relative energies of **10**, **11** and **12**+2CO in terms of ZPE corrected total energy (ΔE+ZPE), enthalpy (ΔH) and Gibbs free energy (ΔG)

	ΔE+ZPE	$\Delta H_{298\ K}$	$\Delta G_{298\ K}$	$\Delta G_{500\ K}$
10	0.0	0.0	0.7	3.0
11	2.0	2.7	0.0	0.0
12+2CO	35.0	36.3	16.2	4.6

All data are in kcal mol^{-1} at the B3LYP/6-311+G* level of the theory.

The relative stabilities of **10**, **11** and **12**+2 CO in terms of total energy, enthalpy (298 K) and Gibbs free energy are presented in Table 3. The most stable structure according to the calculations is **10**, for which the analogous complexation mode has not been observed for the 1,2,4-thiadiphosphole ring having the real (^{t}Bu) substituents.

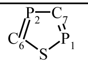
In terms of Gibbs free energy, however, **11** is slightly more stable than **10**.

The complexation mode analogous to **10** has been determined computationally [18] to be the most stable one for the 1,2,4-selenadiphosphole (C$_2$H$_2$P$_2$Se) (by 1.6 kcal mol^{-1} B3LYP/3-21G(*)), while the observed coordination site for the *tert*-butyl substituted ring was also at the 4-position. Apparently, the bulky *tert*-butyl groups at the 3- and 5-position destabilise the complex at the 4-position. Indeed, calculating the relative stabilities of the two possible η^1-complexes, the 2-[$Cr(CO)_5C_2Bu^t_2P_2Se$] compound, turned out to be more stable by 6.5 kcal mol^{-1} (B3LYP/3-21G*) than the corresponding 4-[$Cr(CO)_5C_2Bu^t_2P_2Se$] complex [18].

We, therefore, considered the relative stabilities of the η^1-complex **11** and the η^5-complex **12** (+2CO). The latter is far less stable than **11** and cannot be stabilised by kinetic factors. To understand the formation of **12** from **11** on heating, the entropy factor should be considered. Whereas the enthalpy function is nearly unchanged by varying the temperature (not shown in Table 3), the relative Gibbs free energies show a strong variance, as expected since three particles are formed from one in the **11** → **12** + 2CO reaction. At about 570 K the calculated Gibbs free energies of **11** and **12** + 2CO are equal. Considering that the calculations refer to the unsubstituted systems and the *tert*-Bu substituent must have a larger steric repulsive effect on **11** (since both the *tert*-Bu and $Cr(CO)_5$ groups are in plane) than on **12**, it is understandable that **7** rearranges to **9** at 66 °C (i.e. at much lower temperature than the calculated change in the Gibbs free energies of the model compounds **11** and **12**). Further to the understanding of the **7**–**9** conversion, the effect of the gaseous CO should be considered, which on leaving the reaction mixture, will shift the equilibrium further towards **12**.

The calculated structural parameters (Table 4) of the 1,2,4-thiadiphosphole ring upon complexation are also of interest. Whereas η^1-complexation hardly effects the geometry of the ring, as shown above, η^5-coordination results in significant equalisation of the bond lengths, indicating an increased delocalisation and aromaticity. It is also worthwhile mentioning that similar structural changes were observed when comparing the molecular structure of 1-(bis-trimethylsilyl-methyl)-2,4-di-*tert*-butyl-1,2,4-triphosphole [19] with those of its [$M(CO)_3$] complexes (M = Cr, Mo, W) [21]. An increase of the bond angle sum about the tri-coordinate phosphorus was also observed on complexation, indicating that the lone pair of the tri-coordinate phosphorus is somewhat more involved in the formation of the delocalised π-system than in the parent uncomplexed system.

Table 4
Calculated (B3LYP/6-311+G*) bond lengths (Å) of **10**, **11** and **12**

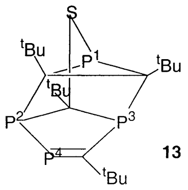
	**10**	**11**	**12**
SP_1	2.119	2.103	2.187
P_1C_7	1.706	1.696	1.745
C_7P_2	1.751	1.766	1.770
P_2C_6	1.706	1.713	1.760
C_6S	1.713	1.721	1.761
CrS	-	-	2.472
CrP_1	-	2.369	2.458
CrC_7	-	-	2.258
CrP_2	2.382	-	2.508
CrC_6	-	-	2.143

The numbering of the ring atoms is identical to those used for the X-ray structure.

4. Cyclo-addition reactions

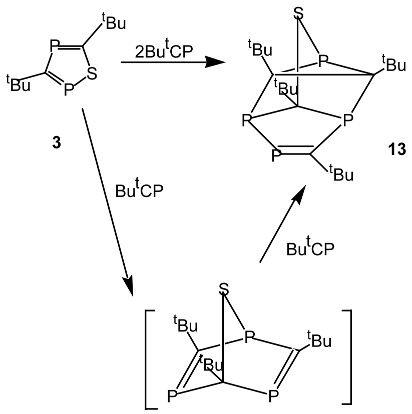
4.1. Synthesis and characterisation of $P_4SC_4Bu^t_4$ (13)

Although the above discussion indicates that the 1,2,4-thiadiphosphole **3** exhibits some aromatic character, it was also found that it would undergo [4+2] cycloaddition reactions with P≡CBu^t and in this respect it differs from the isoelectronic triphosphole $P_3RC_2Bu^t_2$ (R = $HC(SiMe_3)_2$) which shows no such behaviour. Thus, treatment of a solution of **3** in toluene with two equivalents of P≡CBu^t and heating at 80 °C for 8 h, led to the formation of the tetracyclic product, 2,3,6,9-tetrat-butyl-5-thia-1,4,7, 8-tetraphosphatetracyclo[4.3.0.0^{2,4}0^{3,7}]non-8-ene, $P_4SC_4Bu^t_4$ (**13**) (see Scheme 1 below).



13

Compound **13** was fully characterised by $^{31}P\{^1H\}$-, ^1H-NMR spectroscopy, mass spectroscopy, elemental analysis and its molecular structure established by a single crystal X-ray crystallographic determination. The $^{31}P\{^1H\}$-NMR spectrum for **13** clearly shows the addition of two equivalents of P≡CBu^t to the thiadiphosphole **3**, as four signals are clearly visible. The high field resonance at $\delta = -98$ ppm (P1) consists of a triplet ($^2J_{(P(1)P(2))}$ 7 Hz), resulting from the equal two bond



Scheme 1.

couplings to P2 and P3, and lies in the region typical for a phosphirane system [25]. The low field doublet of doublets resonance ($\delta = 406$ ppm (P4)) clearly indicates the presence of a phosphaalkene fragment. This signal shows direct bonding to P2 ($\delta = 125$ ppm) by a large $^{1}J_{(P(4)P(2))}$ coupling constant of 286 Hz and is further split by a typical $^{2}J_{(P(4)P(3))}$ coupling of 18 Hz to P3 ($\delta =$ 116 ppm) and also shows a small $^{3}J_{(P(4)P(1))}$ coupling constant (6 Hz) to P1. Both chemical shifts of P2 and P3 are in good agreement with those of $\lambda^3\sigma^3$-phosphorus atoms in comparable compounds [26,27]. The P3 signal has a multiplet structure resulting from $^{2}J_{(P(3)P(1))}$ couplings to P1 and P4 (16 Hz each) as well as to P2 (33 Hz). The ^{1}H-NMR spectrum of **9** shows the presence of four different Bu^t groups and the mass spectrum exhibits the expected parent ion (*m*/*z* 432). Although no intermediates can be detected in the ^{31}P{^{1}H}-NMR spectrum, the mechanism of formation is assumed to involve an initial [4+2] cycloaddition reaction between **3** and one equivalent of P≡CBu^t to afford an intermediate shown in Scheme 1, which then undergoes a homo Diels–Alder reaction with a further equivalent of P≡CBu^t to give **13**.

4.2. Crystal and molecular structure of $P_4SC_4Bu^t_4$ (13)

A single crystal X-ray crystallographic analysis confirmed the structure of **13** which is shown in Fig. 11, together with selected bond lengths and angles. The phosphaalkene unit in the structure is characterised by a typical P=C bond length of 1.692(3) Å, the P2–P4 bond length is 2.2133(11) Å and the phosphorus–carbon bond lengths lie between 1.857(3) and 1.905(3) Å and are thus in the usual range for phosphorus–carbon single bonds. The three-membered ring contains two almost identical bond lengths (1.861(3) Å P1/C1, 1.857(3) Å P1/C2) while the internal angle at P1 of 49.93° is similar to those found in the literature [25] for these types of compounds. It should be mentioned here that analogous products have recently been reported by Regitz and coworkers, [17,26–28], from the reaction between the 1,2,4-oxa and selena-diphospholes and several phosphaalkynes which led to the formation of both possible regioisomers.

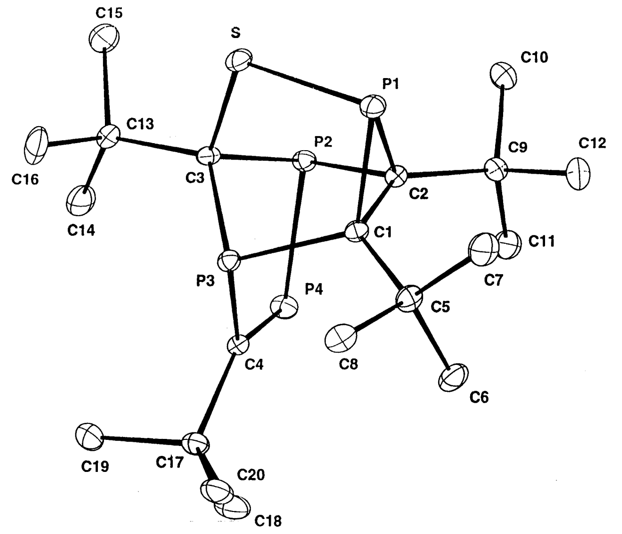


Fig. 11. Molecular structure of $P_4SC_4Bu^t_4$ (**13**) together with the atomic numbering scheme and some selected bond lengths (Å) and bond angles (°). S–C(3) = 1.836(3), S–P(1) = 2.0939(13), P(1)–C(2) = 1.857(3), P(1)–C(1) = 1.861(3), P(2)–C(3) = 1.866(3), P(2)–C(2) = 1.875(3), P(2)–P(4) = 2.2133(11), P(3)–C(4) = 1.851(3), P(3)–C(3) = 1.877(3), P(3)–C(1) = 1.905(3), P(4)–C(4) = 1.692(3), C(1)–C(2) = 1.569(4), C(3)–S–P(1) = 95.71(9), C(2)–P(1)–C(1) = 49.93(11), C(2)–P(1)–S = 100.12(9), C(3)–P(2)–C(2) = 93.34(12), C(3)–P(2)–P(4) = 96.77(9), C(4)–P(3)–C(3) = 97.78(12), C(4)–P(4)–P(2) = 98.16(10), P(4)–C(4)–P(3) = 117.63(15).

5. Experimental

All manipulations were carried out using conventional high vacuum and Schlenk line techniques, under an atmosphere of dry argon, or dinitrogen in an MBraun or Miller–Howe glove box. Solvents were refluxed over suitable drying agents, and distilled and degassed prior to use. Toluene and C_6H_6 were refluxed over sodium, THF was refluxed over potassium. Petroleum ether (40–60 °C b.p.) and pentane were refluxed over sodium–potassium alloy. Calcium hydride was used as a drying agent for MeCN. NMR solvents were dried over potassium (d_6-benzene), sodium (d_8-toluene) or CaH_2 (d_2-dichloromethane), then vacuum transferred into ampoules and stored under dinitrogen prior to use.

NMR spectra were recorded on Bruker DPX 300 or AMX 500 spectrometers. Chemical shifts reported in ppm (δ) are relative to the residual proton chemical shift of the deuterated solvent (^{1}H), the carbon chemical shift of the deuterated solvent (^{13}C) and external H_3PO_4 (^{31}P). Mass spectra were recorded on a VG autospec Fisons instrument (Electron ionisation at 70 eV) by Dr. A. Abdul-Sada. Elemental analyses were performed by Micro Analytisches Labor Paschen (Germany) or A.T. Stones of the Department of Chemistry, University College, London.

Both P≡CBu^t and [Mo(cycloheptatriene)(CO)$_3$] were synthesised according to standard literature methods [29,30] and [W(CO)$_5$THF] was made by UV irradiation of [W(CO)$_6$] in THF for 6 h. CS$_2$, Bu^{t}NCS and CH$_3$CH$_2$CHS were purchased from Sigma Aldrich and used without further purification. The ferrocene [Fe$_2$(C$_5$H$_4$Me)$_2$(C$_5$H$_3$MeP(S)S)$_2$] was a gift from Professor D.J. Woollins, University of St. Andrews, UK.

5.1. Reaction of Bu^{t}N=C=S with P≡CBu^t

P≡CBu^t (2.608 g, 26.08 mmol) was added to a solution of Bu^{t}NCS (1.5 g, 13.04 mmol) in ether (10 ml) and the reaction mixture was heated to 35 °C for 1/2 h and then stirred for a further 3 h. The solvents were removed in vacuo and the resulting yellow solution was purified by column chromatography (kieselgel–hexane) to give a yellow oil (yield 1.138 g, 37.6%) which was found to be the products **3** and **5** in the approximate ratio of 4:1.

5.2. Reaction of CH_3CH_2CHS with $P{\equiv}CBu^t$

$P{\equiv}CBu^t$ (0.81 g, 8.1 mmol) was added to a solution of CH_3CH_2CHS (0.4 g, 5.4 mmol) in toluene (5 ml) and the reaction mixture was irradiated with a UV lamp for 4 h. The solvents were removed in vacuo and the resulting yellow solution was purified by column chromatography (kieselgel–hexane) to give a yellow oil (yield 0.355 g, 28.4%) which was found to be a roughly 8:1 mixture of **3** and **5**.

5.3. Reaction of $[Fe_2(C_5H_4Me)_2(C_5H_3MeP(S)S)_2]$ with $P{\equiv}CBu^t$

$P{\equiv}CBu^t$ (0.048 g, 0.485 mmol) was added to a solution of the ferrocene $[(Fe_2(C_5H_4Me)_2(C_5H_3MeP(S)S)_2]$ (0.1 g, 0.16 mmol) in toluene (5 ml) and the dark brown reaction mixture was stirred for 48 h. The solvents were removed in vacuo and the resulting brown solution was purified by column chromatography (kieselgel–hexane) to give a yellow oil (yield 0.011 g, 29.3%) which was found to be a 6:1 mixture of **3** and **5**.

5.4. Synthesis of $[W(CO)_5\eta^1\text{-}P_2SC_2Bu^t_2]$ (7)

A solution of $[W(CO)_5THF]$ (0.35 g, 0.86 mmol) in THF (5 ml) was added to a solution of $P_2SC_2Bu^t_2$ **3** (0.1 g, 0.43 mmol) (containing about 10% of the isomeric **5**) in THF (5 ml) and the yellow resulting mixture stirred for 48 h. Removal of the solvent in vacuo produced an oily yellow residue which was purified by column chromatography (kieselgel–hexane) to give a yellow solid identified as $[W(CO)_5\eta^1\text{-}P_2SC_2Bu^t_2]$ (yield 0.146 g, 61.3%). Found: C, 32.3; H, 3.2; $C_{15}H_{18}P_2SO_5W$ requires: C, 32.37; H, 3.23%. Crystals suitable for an X-ray diffraction study were grown from a cooled and concentrated hexane solution (−38 °C) $^{31}P\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 259.2 (d, P(A), $^2J_{(P(A)P(B))}$ 62.5 Hz, $^1J_{P(A)W}$ 250.5 Hz) 210.1 (d, P(B), $^2J_{P(A)P(B)}$ 62.4 Hz) ppm.

^1H-NMR data (d_6-benzene, 295 K): δ 1.53 (d, 9H, $C(CH_3)_3$ $^4J_{HP}$ 1.7 Hz) 1.1 (d, 9H, $C(CH_3)_3$ $^4J_{HP}$ 1.3 Hz) ppm.

$^{13}C\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 222.4 [d, 1C, $P\underline{C}P$, $^1J_{(PC)}$ 79 Hz], 216.2 [d, 1C, $P\underline{C}S$, $^1J_{(PC)}$ 76 Hz], 41.6 [d, 1C, $PC\underline{C}(CH_3)_3P$, $^2J_{(PC)}$ 18.2 Hz], 40.1 [d, 1C, $PC\underline{C}(CH_3)_3S$, $^2J_{(PC)}$ 17.9 Hz], 36.9 [dd, 3C, $PCC(\underline{C}H_3)_3P$, $^3J_{(PC)}$ 8.9 Hz, $^3J_{(PC)}$ 7.9 Hz], 31.2 [d, 3C, $PCC(\underline{C}H_3)_3S$, $^3J_{(PC)}$ 8.8 Hz] ppm.

EIMS *m/z* (%):556 (36) [M], 528 (42) [M−CO], 500 (38) [M−2(CO)], 472 (71) [M−3(CO)], 444 (52) [M−4(CO)], 416 (29) [M−5(CO)] 232 (100) [M−5(CO)−W].

Crystal data for **7**: $C_{15}H_{18}P_2SW$, $M = 556.1$, monoclinic $P2_1/n$ (No. 14), $a = 6.345(2)$, $b = 30.209(4)$, $c = 10.651(2)$ Å, $\beta = 92.07(2)°$, $V = 2040.2(14)$ Å^3, $T = 173(2)$ K, $Z = 4$, D_{calc} 1.81 mg m^{-3}, $\mu = 5.94$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000)$ 1072, crystal size $0.3 \times 0.1 \times 0.1$ mm^3 3939 measured reflections, 3606 independent reflections ($R_{int} = 0.0925$), 2759 reflections with $I > 2\sigma(I)$, Final indices $R_1 = 0.047$, $wR_2 = 0.111$ for $I > 2\sigma(I)$, $R_1 = 0.072$, $wR_2 = 0.131$ for all data. Data collection: Enraf–Nonius CAD4 Program package WINGX-97. Structure was refined using full-matrix least-squares on F^2 with SHELXL-97.

*5.5. Synthesis of $[Mo(CO)_3\eta^5\text{-}P_2SC_2Bu^t_2]$ (**8**)*

Similarly $[Mo(C_7H_8)(CO)_3]$ (0.15 g, 0.54 mmol) was added as a solid to a solution of $P_2SC_2Bu^t_2$ **3** (0.1 g, 0.43 mmol) in THF (8 ml) and the resulting mixture stirred for 48 h at room temperature (r.t.). Removal of the solvent in vacuo produced an oily red residue which was purified by column chromatography (kieselgel–hexane) to give a red solid which was identified as $[\{Mo(CO)_3\}\eta^5\text{-}P_2SC_2Bu^t_2]$ (**7**) (yield 0.121 g, 68.4%).

$^{31}P\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 79.2 (d, P(A), $^2J_{P(A)P(B)}$ 32.6 Hz) 48.5 (d, P(B), $^2J_{P(A)P(B)}$ 32.1 Hz) ppm. ^1H-NMR data (d_6-benzene, 295 K): δ 1.42 (d, 9H, $C(CH_3)_3$ $^4J_{(HP)}$ 1.6 Hz) 1.2 (d, 9H, $C(CH_3)_3$ $^4J_{(HP)}$ 1.1 Hz) ppm.

$^{13}C\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 183.4 [d, 1C, $P\underline{C}P$, $^1J_{(PC)}$ 100.3 Hz], 159.2 [d, 1C, $P\underline{C}S$, $^1J_{(PC)}$ 94.3 Hz], 32.6 [d, 1C, $PC\underline{C}(CH_3)_3P$, $^2J_{(PC)}$ 15.2 Hz], 38.1 [d, 1C, $PC\underline{C}(CH_3)_3S$, $^2J_{(PC)}$ 12.9 Hz], 36.9 [dd, 3C, $PCC(\underline{C}H_3)_3P$, $^3J_{(PC)}$ 7.6 Hz, $^3J_{(PC)}$ 7.1 Hz], 30.2 [d, 3C, $PCC(\underline{C}H_3)_3S$, $^3J_{(PC)}$ 11.3 Hz] ppm.

EIMS *m/z* (%): 412 (30) [M], 384 (32) [M−CO], 356 (38) [M−2(CO)], 328 (51) [M−3(CO)], 232 (100) [M−3(CO)−Mo].

*5.6. Synthesis of $[W(CO)_3\eta^5\text{-}P_2SC_2Bu^t_2]$ (**9**)*

$[W(CO)_5(\eta^1\text{-}P_2SC_2Bu^t_2)]$ (0.15 g, 0.26 mmol) was heated in THF (10 ml) at 66 °C for 2 h. Removal of the solvent in vacuo produced an oily yellow residue which was purified by column chromatography (kieselgel–hexane) to give a yellow solid which was identified as $[W(CO)_3\eta^5\text{-}P_2SC_2Bu^t_2]$ (yield 0.073 g, 54.2%).

$^{31}P\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 51.7 (d, P(A), $^2J_{P(A)P(B)}$ 33.2 Hz) 34.3 (d, P(B), $^2J_{P(A)P(B)}$ 33.2 Hz) ppm.

^{1}H-NMR data (d_6-benzene, 295 K): δ 1.33 (d, 9H, $C(CH_3)_3$ $^4J_{(HP)}$ 1.8 Hz). 1.09 (d, 9H, $C(CH_3)_3$ $^4J_{(HP)}$ 1.2 Hz) ppm.

EIMS *m*/*z* (%): 500 (31) [M], 472 (42) [M–CO], 444 (24) [M–2(CO)], 416 (40) [M–3(CO)], 232 (100) [M–3(CO)–W].

5.7. Synthesis of $P_4SC_4Bu^t_4$ (**13**)

$P_2SC_2Bu^t_2$ **3** (0.2 g, 0.86 mmol) (containing ca. 10% of **5**) was dissolved in toluene (10 ml) and to this was added $P{\equiv}CBu^t$ (0.17 g, 1.7 mmol). The pale yellow reaction mixture was stirred and heated to 80 °C for 8 h, during which time the solution turned deep yellow in colour. The solvents were then removed in vacuo and the remaining yellow product was purified by column chromatography (kieselgel–hexane) to give a yellow solid, which was identified as $P_4SC_4Bu^t_4$ (yield 0.35 g). Found: C, 55.6; H, 8.1; $C_{20}H_{36}P_4S$ requires: C, 55.55; H, 8.13%. Crystals suitable for an X-ray diffraction study were grown from a cooled hexane solution (−38 °C).

$^{31}P\{^1H\}$-NMR data (d_6-benzene, 295 K): δ 406.2 (ddd, P(4), $^1J_{P(4)P(2)}$ 286.3 Hz, $^2J_{P(4)P(3)}$ 18.1 Hz, $^3J_{P(4)P(1)}$ 6.1 Hz), 125.2 (ddd, P(2), $^1J_{P(2)P(4)}$ 285.3 Hz, $^2J_{P(2)P(3)}$ 15.2 Hz, $^2J_{P(2)P(1)}$ 17.4 Hz), 116.4 (ddd, P(3), $^2J_{P(3)P(1)}$ 16.3 Hz, $^2J_{P(3)P(4)}$ 16.1 Hz, $^2J_{P(3)P(2)}$ 15.2 Hz), −98.5 (t, P(1), $^2J_{P(1)P(2)} = {}^2J_{P(1)P(3)} = 17.1$ Hz) ppm.

^{1}H-NMR data (d_6-benzene, 295 K): δ 1.57 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.32 (d, 9H, $C(CH_3)_3$ $^4J_{(HP)}$ 2.1 Hz) 1.27 (s, 9H, $C(CH_3)_3$) ppm.

EIMS *m*/*z* (%): 432 (100) [M], 417 (12) [M–CH_3], 231 (32) [M–CH_3–$P_2C_2Bu^t_2CC_2H_6$] 200 (35) [[M–CH_3–$P_2C_2Bu^t_2CC_2H_6$–S].

Crystal data for **13**: $C_{20}H_{36}P_4S$, $M = 432.43$, monoclinic $P2_1/c$ (No. 14), $a = 16.417(9)$, $b = 9.762(3)$, $c = 15.917(4)$ Å, $\beta = 118.08(2)°$, $V = 2250.8(14)$ Å^3, $T = 173(2)$ K, $Z = 4$, D_{calc} 1.28 mg m^{-3}, $\mu = 0.43$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000)$ 928, crystal size $0.2 \times 0.2 \times 0.05$ mm^3 4090 measured reflections, 3950 independent reflections ($R_{int} = 0.029$), 3160 reflections with $I > 2\sigma(I)$, Final indices $R_1 = 0.040$, $wR_2 = 0.090$ for $I > 2\sigma(I)$, $R_1 = 0.057$, $wR_2 = 0.092$ for all data, Data collection: Enraf–Nonius CAD4 Program package WINGX-97. Structure was solved by direct methods and refined using full-matrix least-squares on F^2 with SHELXL-97.

6. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre.

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