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Synthetic, structural and theoretical studies on the new 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes, $P_2EC_2Bu^t_2(H)Me$, ($E =$ S, Se, Te) and their $[M(CO)_5]$ complexes ($M =$ Cr, Mo, W)

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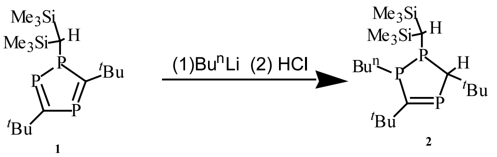
Abstract

Methylation of the 1,2,4-thia-, selena- and tellura-diphospholes $P_2EC_2Bu^t_2$ ($E = $ S, Se, Te) with MeLi, followed by protonation with HCl, affords the new 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes. Further treatment with $[M(CO)_5(THF)]$ ($M =$ Cr, Mo, W) yields the corresponding η^1-metal pentacarbonyl complexes, of which $[M(CO)_5\{\eta^1\text{-}P_2EC_2Bu^t_2(H)Me\}]$, ($E = $ S, $M = $ W; $E = $ Se, $M = $ Cr, $M = $ Mo, $M = $ W) have been structurally characterised by single crystal X-ray diffraction studies. Theoretical calculations carried out on the different isomers of the 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes, and the 2,3-dihydro-1*H*-1,2,4-triphosphole are also presented and discussed. © 2002 Elsevier Science B.V. All rights reserved.

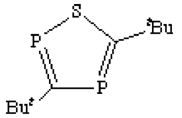
Keywords: Diphospholes; Thia; Selena; Tellura; Methylation; Pentacarbonyl complexes

1. Introduction

A very recent report from our laboratory [1] describes the alkylation of the 1,2,4-triphosphole **1** with Bu^nLi and subsequent protonation of the intermediate lithium triphospha-cyclopentenyl salt, resulting in the first example of the 2,3-dihydro-1*H*-1,2,4-triphosphole **2**.



Current interest in the chemistry of low-coordinate phosphorus compounds [2] and phospholes containing additional heteroatoms [3–21] led us to attempt to extend the chemistry of the 1,2,4-triphosphole to the *iso*-electronic 1,2,4-thia-, selena- and tellura-diphospholes, **3**, **4** and **5**, respectively.



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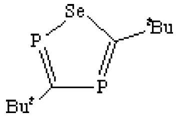

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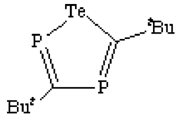

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We now report syntheses of the first examples of 2,3-dihydro-1,2,4-thia-, selena- and tellura-diphospholes and the solid state structures of some of their η^1-$[M(CO)_5]$ complexes ($M =$ Cr, Mo and W). Unexpectedly, the chemistry of the new rings proved to be significantly different than that of the corresponding triphosphole and so quantum mechanical theoretical studies have also been carried out to better understand the differences in their reactivity.

2. Results and discussion

2.1. Synthesis and characterisation of $P_2EC_2Bu^t_2(H)Me$ (**6**, $E = S$; **7**, $E = Se$; **8**, $E = Te$)

Compounds **3**, **4** or **5** in THF, were each treated with one equivalent of MeLi at −78 °C, followed by one

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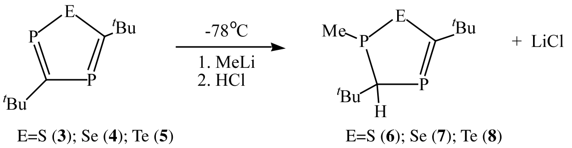
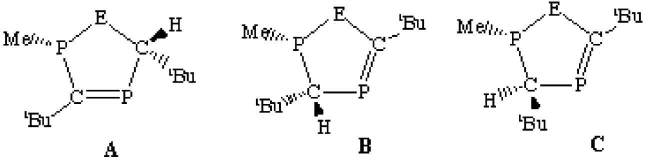


Scheme 1.

equivalent of HCl, resulting in the pale yellow compounds $P_2EC_2Bu^t_2(H)Me$, (E = S, **6**; E = Se, **7**; E = Te, **8**) (Scheme 1).

Although it was expected (and subsequently established, vide infra) that methylation would occur on the phosphorus atom adjacent to the heteroatom in each case, protonation of the intermediate lithium salt could result in isomers of type **A**, **B** or **C**. Isomer **A** would be analogous to compound **2** above. Isolation of a pure sample of **6** was accomplished through column chromatography, whereas compounds **7** and **8** were isolated by high-vacuum sublimation.

1



Interestingly, the $^{31}P\{^1H\}$-NMR of the reaction products in all cases showed the presence of only one major product. The $^{31}P\{^1H\}$-NMR spectra of **6**, **7** and **8** exhibit a pattern of lines typical for an [AX] spin system, with one resonance lying in the range expected for an sp^2-hybridised P(A) phosphorus atom, and the other in the range typical for an sp^3-hybridised P(X) phosphorus centre. In **7** an additional large coupling constant (244 Hz) to the ^{77}Se nucleus ($I = 1/2$, 7.6%) is observed in the resonance for the sp^3-hybridised P(X) phosphorus atom, whereas only an additional small coupling (42 Hz) is observed in the chemical shift attributed to the sp^2-hybridised P(A) phosphorus, confirming that the phosphorus atom next to the selenium is the one that has been methylated. The ^1H-NMR spectra of all the three compounds **6**–**8** show the expected resonances corresponding to the two types of Bu^t groups, the Me group and the ring hydrogen, but did not provide conclusive evidence as to which of the isomers **A**–**C** was formed. Chemical shift and coupling constant data for **6**–**8** are listed in the Section 3.

The mass spectra of **6**–**8** each exhibited the expected parent ions and the proposed structures of **6** and **7** were subsequently confirmed by single crystal X-ray diffraction studies of their η^1-metal pentacarbonyl complexes (vide infra). Confirmation of the structure of **8** comes through comparison of its spectroscopic data with those of **6** and **7**.

2.2. *Synthesis and characterisation of the [$M(CO)_5(\eta^1$-$P_2EC_2Bu^t_2(H)Me)$] complexes (M = Cr, Mo, W; E = S, Se, Te)*

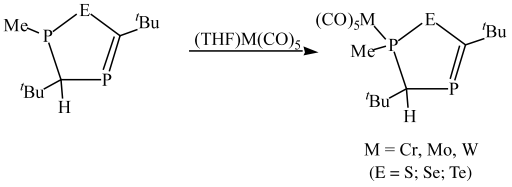
Treatment of THF solutions of **6**–**8** with a selection of [$M(CO)_5(THF)$] complexes, (M = Cr, Mo or W), followed by high-vacuum sublimation of the resulting products, gave the pale-yellow complexes [$M(CO)_5P_2EC_2Bu^t_2(H)Me$], (E = S, M = W **9**; E = Se, M = Cr **10**, M = Mo **11**, M = W **12**; E = Te, M = W **13**) (Scheme 2)

The η^1-mode of attachment of the [$M(CO)_5$] fragment to the rings was established as being in all cases via the sp^3 hybridised P(X) phosphorus atom bonded directly to the chalcogenide. The $^{31}P\{^1H\}$-NMR spectra of compounds **9**–**13** also clearly exhibit the expected tungsten satellites (^{183}W, $I = 1/2$, 14.4%) around the resonance of P(X) and the magnitude of the $^1J_{P(A)W}$ coupling constants are typical for η^1-ligated [$W(CO)_5$]–phosphine complexes.

The $^{31}P\{^1H\}$-NMR chemical shifts (Table 1) of **10**–**12** are in line with the expected trends previously established for δ P(X) within Group 6 metal carbonyl–phosphine complexes [21]. Their mass spectra all showed the expected parent ions, as well as peaks corresponding to successive loss of the five CO groups.

Suitable crystals of compounds **9**–**12** were grown from hexane solutions, and single crystal X-ray diffraction studies established their molecular structures (see Figs. 1–4). The data clearly show that protonation of the initially generated methylated chalcogenadiphosphaallyl anion had occurred on the carbon atom which lies between the two phosphorus atoms, thereby confirming the previously proposed structures for **6** and **7**. Furthermore, all four structures show only the presence of one isomer resulting from protonation being exclusively in a *trans*-position relative to the methyl group (e.g. type **B** structure).

In all four complexes **9**–**12** the bond distances between ring positions P(2) and C(2) are typical for a P=C double bond lying in the range 1.669–1.697 Å, whereas, the corresponding distances between positions P(1) and C(1) are more typical for P–C single bonds (1.878–1.888 Å). Likewise, the sum of the bond angles around the carbon atom adjacent to the chalcogenide is in all cases 360°, clearly indicating a sp^2-hybridised



9-13

Scheme 2.

Table 1
$^{31}P\{^1H\}$-NMR data for **10**–**12** (δ in ppm, J in Hz)

Compound, metal	$\delta_{P(A)}$	$\delta_{P(X)}$	$^2J_{P(A)P(X)}$
10, Cr	249.8	105.2	23.8
11, Mo	249.9	75.4	23.9
12, W	245.3	47.5	25.0

carbon atom. It is interesting to note that in the previously reported η^1-$W(CO)_5$ complexes of the parent 1,2,4-chalcogeno-diphospholes **3**, **4** and **5** metal pentacarbonyl coordination also occurs via the phosphorus atom which is adjacent to the chalcogenide.

Although X-ray diffraction data for tellurium compound **13** were not obtained, comparison of spectroscopic data indicates its structure to be similar with that of **9** and **12**. All three compounds show similar magnitudes of the two-bond ^{31}P–^{31}P and one-bond ^{31}P–^{183}W coupling constants, as well as the expected trend in ^{31}P chemical shifts [22]. Theoretical calculations carried out on a model compound of **8**, to be described later in Section 2.4, also support a structure similar to those of the analogous model compounds of **6** and **7**.

2.3. *Comparison of the reactivity of the chalcogena-diphospholes with the structurally related 1,2,4-triphosphole*

The above results clearly show that whereas in compounds **6**–**8** the double bond occupies a position adjacent to the chalcogenide, the recently reported isoelectronic 2,3-dihydro-1*H*-1,2,4-triphosphole **2** has the double bond in a different position [1]. Although the initial alkylation step occurs at the same phosphorus atom position in both types of ring system, the subsequent protonation step of the intermediate phospha-allylic salt occurs on a different ring carbon atom.

2.4. *Theoretical calculations*

In an attempt to better understand the origin of the differences in reactivity of these isoelectronic alkylated ring anions towards protonation, theoretical calculations were carried out for a series of heterodiphosphole derivatives $C_2H_4P_2E$ (E = O, S, Se, Te, NH and PH). Two isomeric products **A** and **B** were considered. Each of them is protonated at the phosphorus in the α-position from the heteroatom (E), while the second proton is positioned at the carbon (i) in the β-position from E (structure **A**) or (ii) in the α-position from E (structure **B**).

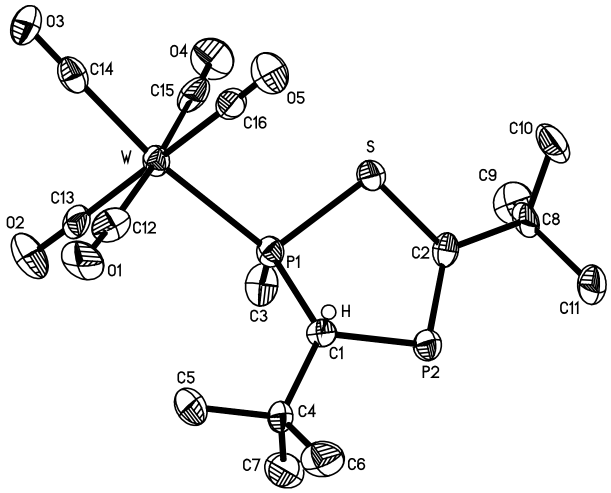
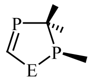


Fig. 1. Molecular structure of **9**. Selected bond lengths (Å) and angles (°): S–C(2) 1.759(12); C(2)–P(2) 1.677(13); P(2)–C(1) 1.888(11); C(1)–P(1) 1.843(12); P(1)–S 2.106(4); C(2)–C(8) 1.533(15); C(1)–C(4) 1.569(16); P(1)–C(3) 1.819(12); P(1)–W 2.520(3); P(1)–S–C(2) 97.9(4); S–C(2)–P(2) 121.4(7); S–C(2)–C(8) 114.1(9); C(8)–C(2)–P(2) 124.4(9); C(2)–P(2)–C(1) 99.2(5); P(2)–C(1)–P(1) 109.8(5); P(2)–C(1)–C(4) 110.8(8); C(4)–C(1)–P(1) 120.9(9); C(1)–P(1)–C(3) 106.2(6); C(1)–P(1)–S 95.2(4); C(3)–P(1)–S 102.5(5); W–P(1)–C(1) 131.0(4); W–P(1)–C(3) 112.6(4); W–P(1)–S 104.21(15); C(14)–W–P(1) 169.7(3); C(15)–W–P(1) 82.9(3); C(16)–W–P(1) 90.0(3); C(12)–W–P(1) 100.1(4); C(13)–W–P(1) 91.9(3).



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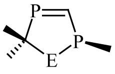


B

While in case of E=PH structures **A** and **B** are of course identical, for the other systems where E = O, S, Se, Te, or NH, the **A**-type structure is more stable, as can be seen from the data collected in Table 2. Apparently, the conjugation between the hetero-element lone pair and the π-system of the double bond contributes to the stabilisation of structure **A**. In case of structure **B**, the phosphorus lone pair, which has considerable s-character, is unable to overlap with the π-system [23]. The lack of conjugation has also been shown in case of vinyl phosphine [24–26].

Table 2
B3LYP/6-311+G** (B3LYP/3-21G(*) data in parenthesis) ΔE (**A**–**B**) relative energies (in kcal mol^{-1}) of the **A** and **B** type heterodiphosphole derivatives $C_2H_4P_2E$ and E_{stab} energies (in kcal mol^{-1}) of the (1) isodesmic reaction for different E

E	ΔE (**A**–**B**)	E_{stab}	ΔE_{stab}
O	6.4 (6.9)	13.3	8.3
S	5.2 (5.2)	8.5	3.5
Se	3.8 (3.9)	6.5	1.5
NH	13.7 (17.7)	17.1	12.1
PH	0.0	5.0	

ΔE_{stab} denotes the energy of the isodesmic reaction (2).

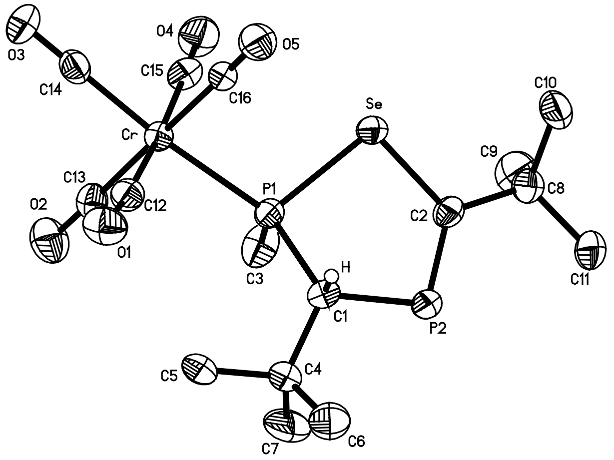


Fig. 2. Molecular structure of **10**. Selected bond lengths (Å) and angles (°): Se–C(2) 1.914(4); C(2)–P(2) 1.669(5); P(2)–C(1) 1.883(4); C(1)–P(1) 1.853(5); P(1)–Se 2.2449(13); C(2)–C(8) 1.535(6); C(1)–C(4) 1.557(6); P(1)–C(3) 1.828(5); P(1)–Cr 2.3896(13); P(1)–Se–C(2) 94.04(14); Se–C(2)–P(2) 120.4(2); Se–C(2)–C(8) 115.1(3); C(8)–C(2)–P(2) 124.5(3); C(2)–P(2)–C(1) 102.3(2); P(2)–C(1)–P(1) 111.4(2); P(2)–C(1)–C(4) 110.2(3); C(4)–C(1)–P(1) 120.5(4); C(1)–P(1)–C(3) 104.2(2); C(1)–P(1)–Se 95.57(15); C(3)–P(1)–Se 102.94(18); Cr–P(1)–C(1) 131.77(15); Cr–P(1)–C(3) 112.01(16); Cr–P(1)–Se 105.77(5); C(14)–Cr–P(1) 170.31(15); C(12)–Cr–P(1) 99.46(14); C(16)–Cr–P(1) 91.62(12); C(15)–Cr–P(1) 83.87(14); C(13)–Cr–P(1) 89.50(13).

Furthermore, the energy of the isodesmic reaction (1) (E_{stab} in Table 2) with E=PH is indeed the smallest among the different heteroatom units (E = O, S, Se, NH and PH). By substracting the stabilisation energy (E_{stab}) of vinyl phosphine from the E_{stab} values of the other vinyl compounds we can obtain ΔE_{stab}, which is the energy of reaction (2). This models the difference of the conjugation between the PH unit and the other heteroatom units (E), namely the energy difference between the **A** and **B** structures. It can be clearly seen that the relative stabilities of the **A** and **B** type structures in Table 2 exhibit similar values and show the same trends as the energies of the isodesmic reaction (2).

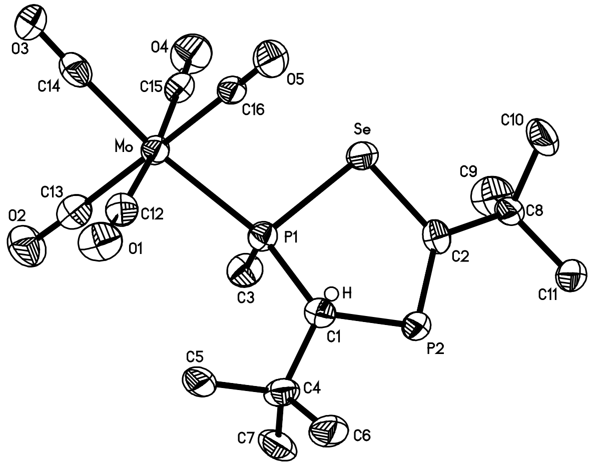


Fig. 3. Molecular structure of **11**. Selected bond lengths (Å) and angles (°): Se–C(2) 1.931(6); C(2)–P(2) 1.671(7); P(2)–C(1) 1.878(7); C(1)–P(1) 1.850(7); P(1)–Se 2.242(2); C(2)–C(8) 1.513(9); C(1)–C(4) 1.569(9); P(1)–C(3) 1.830(7); P(1)–Mo 2.5405(18); P(1)–Se–C(2) 94.3(2); Se–C(2)–P(2) 119.9(4); Se–C(2)–C(8) 114.1(5); C(8)–C(2)–P(2) 126.0(5); C(2)–P(2)–C(1) 101.8(3); P(2)–C(1)–P(1) 112.1(4); P(2)–C(1)–C(12) 110.9(4); C(12)–C(1)–P(1) 119.6(5); C(1)–P(1)–C(3) 105.2(3); C(1)–P(1)–Se 94.8(2); C(3)–P(1)–Se 103.3(2); Mo–P(1)–C(1) 132.6(2); Mo–P(1)–C(3) 112.2(2); Mo–P(1)–Se 103.58(7); C(14)–Mo–P(1) 169.6(2); C(15)–Mo–P(1) 83.61(18); C(16)–Mo–P(1) 90.97(18); C(12)–Mo–P(1) 100.30(19); C(13)–Mo–P(1) 91.8(2).

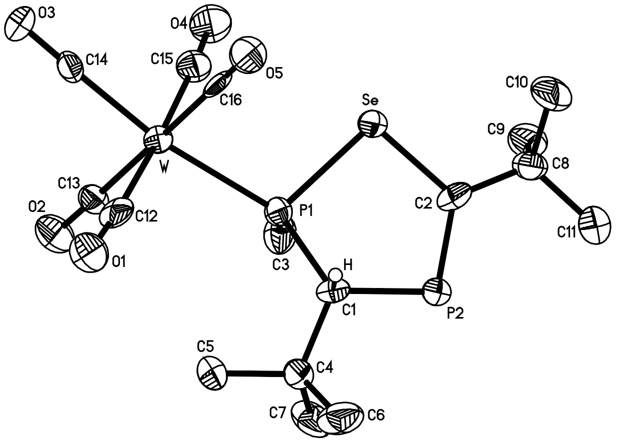


Fig. 4. Molecular structure of **12**. Selected bond lengths (Å) and angles (°): Se–C(2) 1.906(11); C(2)–P(2) 1.697(12); P(2)–C(1) 1.882(12); C(1)–P(1) 1.859(11); P(1)–Se 2.242(3); C(2)–C(8) 1.478(17); C(1)–C(4) 1.567(15); P(1)–C(3) 1.812(13); P(1)–W 2.525(3); P(1)–Se–C(2) 94.9(4); Se–C(2)–P(2) 119.7(7); Se–C(2)–C(8) 116.7(8); C(8)–C(2)–P(2) 123.6(9); C(2)–P(2)–C(1) 101.7(5); P(2)–C(1)–P(1) 111.3(5); P(2)–C(1)–C(4) 110.8(7); C(4)–C(1)–P(1) 118.9(8); C(1)–P(1)–C(3) 105.8(6); C(1)–P(1)–Se 94.9(4); C(3)–P(1)–Se 102.7(4); W–P(1)–C(1) 131.7(4); W–P(1)–C(3) 112.5(5); W–P(1)–Se 103.99(12); C(14)–W–P(1) 168.7(3); C(15)–W–P(1) 82.2(4); C(16)–W–P(1) 90.6(3); C(12)–W–P(1) 100.1(1); C(13)–W–P(1) 91.5(3).

$$\text{HE–CH=PH} + \text{CH}_4 \Rightarrow \text{HE–CH}_3 + \text{H}_2\text{C=PH} \qquad (1)$$

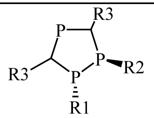
$$\text{HE–CH=PH} + \text{PH}_3 \Rightarrow \text{H}_2\text{P} - \text{C=PH} + \text{H}_2\text{E} \qquad (2)$$

where E = O, S, Se, Te, NH, PH.

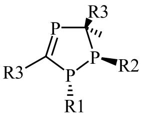
It is also worth noting that the analogous isodesmic reaction for the substituted alkenes also showed a similar trend, e.g. the conjugation stabilisation in the case of $HS{-}CH{=}CH_2$ was shown to be smaller than for $HO{-}CH{=}CH_2$ [27].

The relative energies of the **A** and **B** type structures for the heterodiphospholes are governed by the conjugative stabilisation, in case of the 1,2,4-triphospholes the decisive factor in the product stability is the difference between the substituents at the two neighbouring phosphorus atoms. We have considered the 2,3-dihydro-1*H*-[1,2,4] triphosphole derivatives, containing different substituent patterns (R_1, R_2, R_3) and the results are summarised in Table 3.

Table 3
Relative energies of the **A** and **B** type 1,2,4-triphosphole derivatives $C_2HP_3(R_1)(R_2)(R_3)_2$ in kcal mol^{-1} at the B3LYP/3-21G(*) level

	
$R_1=R_2=R_3=H$	0.0
$R_1=CH(SiMe_3)_2;R_2=R_3=H$	-0.4
$R_1=CH(SiMe_3)_2;R_2=R_3=Me$	-0.3
$R_1=CH(SiMe_3)_2;R_2=nBu;R_3={}^tBu$	3.0

The substituent pattern is shown in the table on the schematic ring.



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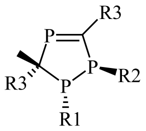

B

Whereas the relative stabilities of the **A** and **B** type structures are similar with the smaller substituents, for the bulkier alkyl groups the **B** type structure is preferred, in agreement with the observed product [1].

To understand the formation of the *trans*-protonated products **9**–**12**, additional calculations were carried out for the **A** type thiadiphosphole. According to the calculations with the methyl substituent at the phosphorus and the Bu^t group at the α-carbon atom, the *cis* structure turned out to be more stable than the *trans* by 3.0 kcal mol^{-1}. Since the formation of the $[W(CO)_5]$ complex is unlikely to alter the configuration, the most likely explanation is that the protonation of the initially formed methylated product is controlled by kinetic effects.

A theoretical study of the hypothetical $Li^+(THF)_3$ salt of the $C_2P_2SHMe_2$ ring anion, at the B3LYP/3-21G* level, shows that the structure in which $Li^+(THF)_3$ is in a *trans*-position with respect to the methyl group attached to the phosphorus is found to be 4.1 kcal mol^{-1} more stable than the corresponding *cis*-structure (Fig. 5). Thus, subsequent protonation should occur with retention of configuration. Interestingly, retention of the configuration in case of methylation (by MeI) of lithiated phenylalanine is known, whereas methylation of a potassium salt resulted in inversion of the configuration [28].

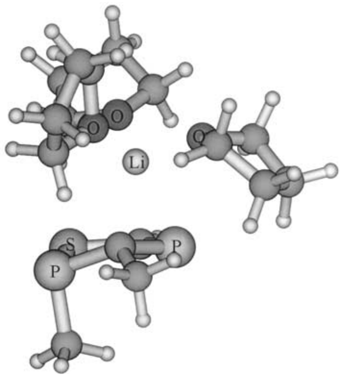

Fig. 5. Calculated structure of the hypothetical $Li^+(THF)_3\cdot P_2C_2S(H)Me_2$.

3. Experimental

3.1. Standard procedures

Standard procedures for the manipulation of air-sensitive materials were employed. Unless otherwise stated, all manipulations were carried out at ambient temperature under an atmosphere of dry argon gas using standard Schlenk, syringe and high-vacuum-line techniques. Solvents were dried, freshly distilled under nitrogen and degassed prior to use. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Mass spectra were recorded by Dr A. Abdul-Sada using a Fison Instruments-VG Autospec. Compounds **3**–**5** were made according to literature procedures.

3.2. Preparation of $P_2SC_2Bu^t_2(H)Me$ (6)

Exactly 0.32 ml of standardised MeLi (1.56 M in Et_2O, 0.50 mmol) was added dropwise to a solution of **3** (0.50 mmol) in THF (5 ml) cooled to −78 °C. The resulting deep red solution was stirred for 10 min after which 0.50 ml of standardised HCl (1.00 M in Et_2O, 0.50 mmol) was added dropwise upon which the solution turned pale yellow. After warming to room temperature (r.t.), solvents were removed in vacuo. Chromatography (silica-gel–hexane) afforded **6** as a yellow oil (0.110 g, 89%).

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 218.5 (d, P(A), $^2J_{P(A)P(X)}=12.6$ Hz); δ 69.4 (d, P(X), $^2J_{P(A)P(X)}=12.6$ Hz). ^1H: δ 1.03 (d, 3H, CH_3, $^2J_{HP}=7.07$ Hz); δ 1.10 (s, 9H, $C(CH_3)_3$); δ 1.44 (s, 9H, $C(CH_3)_3$); δ 2.56 (d of d, 1H, CH, $^2J_{HP}=19.6$ Hz, $^3J_{HP}=10.5$ Hz). $^{13}C\{^1H\}$: δ 215.3 (d of d, C, $^1J_{CP}=58.3$, $^2J_{CP}=4.9$); δ 71.4 (d of d, C, $^1J_{CP}=51.0$ Hz, $^1J_{CP}=38.6$ Hz); δ 33.4 (d, $C(CH_3)_3$, $^2J_{CP}=13.2$ Hz); δ 32.0 (s, $C(CH_3)_3$); δ 30.3 (s, $C(CH_3)_3$); δ 29.7 (d of d, $C(CH_3)_3$, $^2J_{CP}=9.9$ Hz, $^2J_{CP}=7.2$ Hz); δ 13.8 (d, CH_3, $^1J_{CP}=27.9$ Hz).

Mass spectrum (EI): m/z: 248 $[P_2SC_2Bu^t_2(H)Me]^+$; 233 $[P_2SC_2Bu^t_2(H)]^+$; 191 $[P_2SC_2Bu^t(H)Me]^+$.

3.3. Preparation of $P_2SeC_2Bu^t_2(H)Me$ (7)

In a similar fashion to the above, exactly 0.63 ml of standardised MeLi (1.56 M in Et_2O, 0.99 mmol) was added dropwise to a solution of **4** (0.99 mmol) in THF (10 ml) cooled to −78 °C. The resulting deep red solution was stirred for 10 min after which 0.99 ml of standardised HCl (1.00 M in Et_2O, 0.99 mmol) was added dropwise upon which the solution turned pale yellow. After warming to r.t. solvents were removed in vacuo and the yellow oil was sublimed at 1×10^{-5} mbar and 80 °C affording **7** (0.236 g, 80%).

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 230.0 (d, P(A), $^2J_{P(A)P(X)} = 12.5$ Hz, $^2J_{SeP(A)} = 42.4$ Hz); δ 63.7 (d, P(X), $^1J_{SeP(X)} = 244.2$ Hz). $^{77}Se\{^1H\}$: δ 1050.9 (d of d, Se_1, $^1J_{SeP(A)} = 244$ Hz, $^2J_{SeP(X)} = 42.4$ Hz). ^1H: δ 1.13 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.32$ Hz); δ 1.38 (d, 3H, CH_3, $^2J_{HP} = 4.65$ Hz); δ 1.42 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.58$); δ 2.97 (d of d, 1H, CH, $^2J_{HP} = 10.39$ Hz, $^3J_{HP} = 2.24$ Hz). $^{13}C\{^1H\}$: δ 207.4 (d of d, C, $^1J_{CP} = 56.4$, $^1J_{CP} = 5.9$); δ 73.1 (d of d, C, $^1J_{CP} = 55.0$ Hz, $^2J_{CP} = 33.6$ Hz); δ 35.4 (d of d, $C(CH_3)_3$, $^3J_{CP} = 14.4$ Hz, $^3J_{CP} = 6.6$ Hz); δ 34.5 (d of d, $C(CH_3)_3$, $^2J_{CP} = 15.4$ Hz, $^3J_{CP} = 8.1$ Hz); δ 33.6 (d, $C(CH_3)_3$, $^3J_{CP} = 13.3$ Hz); δ 32.3 (pseudo t, $C(CH_3)_3$, $^3J_{CP} = 8.9$ Hz, $^3J_{CP} = 8.9$ Hz); δ 10.3 (d of d, CH_3, $^1J_{CP} = 34.0$ Hz, $^3J_{CP} = 4.5$ Hz).

Mass spectrum (EI): m/z: 296 $[P_2SeC_2Bu^t_2(H)Me]^+$; 281 $[P_2SeC_2Bu^t_2(H)]^+$; 239 $[P_2SeC_2Bu^t(H)Me]^+$.

3.4. Preparation of $P_2TeC_2Bu^t_2(H)Me$ (**8**)

To a solution of **5** (0.25 mmol) in THF (8 ml), cooled to −78 °C, 0.16 ml of standardised MeLi (1.56 M in Et_2O, 0.25 mmol) was added dropwise resulting in a deep red solution. After stirring for 10 m 0.25 ml of standardised HCl (1.00 M in Et_2O, 0.25 mmol) was added dropwise upon which the solution turned pale yellow. Solvents were removed in vacuo and sublimation (1×10^{-5} mbar, 90 °C) afforded **8** (0.077 g, 89%).

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 269.4 (d, P(A), $^2J_{P(A)P(X)} = 14.5$ Hz); δ 38.5 (d, P(X), $^2J_{P(A)P(X)} = 14.5$ Hz). ^1H: δ 1.12 (s, 9H, $C(CH_3)_3$); δ 1.25 (d, 3H, CH_3, $^2J_{HP} = 5.94$ Hz); δ 1.51 (s, 9H, $C(CH_3)_3$); δ 3.02 (d of d, 1H, CH, $^2J_{HP} = 15.71$ Hz, $^3J_{HP} = 4.32$ Hz). $^{13}C\{^1H\}$: δ 198.3 (d of d, C, $^1J_{CP} = 54.2$, $^1J_{CP} = 4.8$); δ 75.5 (d of d, C, $^1J_{CP} = 54.7$ Hz, $^2J_{CP} = 31.3$ Hz); δ 34.3 (d of d, $C(CH_3)_3$, $^3J_{CP} = 13.4$ Hz, $^3J_{CP} = 7.5$ Hz); δ 33.2 (d of d, $C(CH_3)_3$, $^2J_{CP} = 17.3$ Hz, $^3J_{CP} = 9.2$ Hz); δ 32.1 (d, $C(CH_3)_3$, $^3J_{CP} = 12.4$ Hz); δ 30.5 (d of d, $C(CH_3)_3$, $^3J_{CP} = 11.1$ Hz, $^3J_{CP} = 7.9$ Hz); δ 12.3 (d of d, CH_3, $^1J_{CP} = 32.5$ Hz, $^3J_{CP} = 6.1$ Hz).

Mass spectrum (EI): m/z: 346 $[P_2TeC_2Bu^t_2(H)Me]^+$; 331 $[P_2TeC_2Bu^t_2(H)]^+$; 289 $[P_2TeC_2Bu^t(H)Me]^+$.

3.5. Preparation of $[W(CO)_5P_2SC_2Bu^t_2(H)Me]$ (**9**)

To $P_2SC_2Bu^t_2(H)Me$ (0.25 g, 1.0 mmol) in THF (5 ml), a solution of $[W(CO)_5(THF)]$ (1.5 mmol) in THF (15 ml) was added. After stirring for 12 h the solvent was removed in vacuo and the yellow oil was sublimed (1×10^{-5}, 80 °C) affording **9** (0.31 g, 52%). Recrystallisation from hexane afforded single crystals for the X-ray diffraction study.

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 233.9 (d, P(A) $^2J_{P(A)P(X)} = 24.1$ Hz); δ 67.1 (d, P(X), $^2J_{P(A)P(X)} = 24.1$ Hz, $^1J_{WP(X)} = 118.2$).

Mass spectrum (EI): m/z: 572 $[P_2SC_2Bu^t_2(H)Me\{W(CO_5)\}^+]$, 559 $[P_2SC_2Bu^t_2(H)\{W(CO_5)\}^+]$, 516 $[P_2SC_2Bu^t_2(H)Me\{W(CO_3)\}^+]$, 460 $[P_2SC_2Bu^t_2(H)Me\{W(CO)\}^+]$, 432 $[P_2SC_2Bu^t_2(H)Me\{W\}^+]$.

3.5.1. X-ray cystallographic data for **9**

Empirical formula: $C_{16}H_{22}O_5P_2SW$; $M = 572.19$; $T = 173(2)$ K; Monoclinic $P2_1/c$ (number 14), $a = 10.9025(6)$, $b = 6.6148(2)$, $c = 29.3773(15)$ Å; $\beta = 92.023(16)°$; $V = 2117.3(2)$ Å^3; $Z = 4$; $D_{calc} = 1.80$ mg m^{-3}; $F(000) = 1112$. Data were collected on a crystal of size $0.20 \times 0.20 \times 0.10$ mm using KappaCCD diffractometer, $\lambda = 0.71073$ Å. A total of 3631 independent reflections were collected, 3211 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The final R indices were $R_1 = 0.058$, $wR_2 = 0.139$ for $I > 2\sigma I$ and $R_1 = 0.066$, $wR_2 = 0.142$ for all data.

3.6. Preparation of $[Cr(CO)_5P_2SeC_2Bu^t_2(H)Me]$ (**10**)

To $P_2SeC_2Bu^t_2(H)Me$ (0.30 g, 1.0 mmol) in THF (5 ml) a solution of $[Cr(CO)_5(THF)]$ (1.5 mmol) in THF (15 ml) was added. After stirring for 16 h the solvent was removed in vacuo and the yellow oil was sublimed (1×10^{-5}, 85 °C) resulting in **10** (0.20 g, 42%). Recrystallisation from hexane afforded single crystals for the X-ray diffraction study.

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 249.8 (d, P(A) $^2J_{P(A)P(X)} = 23.8$ Hz); δ 105.2 (d, P(X), $^2J_{P(A)P(X)} = 23.8$ Hz, $^1J_{SeP(X)} = 101.1$ Hz).

Mass spectrum (EI): m/z: 488 $[P_2SeC_2Bu^t_2(H)Me\{Cr(CO_5)\}^+]$, 460 $[P_2SeC_2Bu^t_2(H)Me\{Cr(CO_4)\}^+]$, 432 $[P_2SeC_2Bu^t_2(H)Me\{Cr(CO)_3\}^+]$, 404 $[P_2SeC_2Bu^t_2(H)Me\{Cr(CO)_2\}^+]$, 376 $[P_2SeC_2Bu^t_2(H)Me\{Cr(CO)\}^+]$, 296 $[P_2SeC_2Bu^t_2(H)Me^+]$.

3.6.1. X-ray crystallographic data for **10**

Empirical formula: $C_{16}H_{22}CrO_5P_2Se$; $M = 487.24$; $T = 173(2)$ K; Orthorhombic $Pna2_1$ (no. 33), $a = 29.3219(14)$, $b = 11.1265(5)$, $c = 6.4617(2)$ Å; $V = 2111.39(15)$ Å^3; $Z = 4$; $D_{calc} = 1.533$ mg m^{-3}; $F(000) = 984$. Data were collected on a crystal of size $0.40 \times 0.20 \times 0.20$ mm using KappaCCD diffractometer, $\lambda = 0.71073$ Å. A total of 3466 independent reflections were collected, 3086 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The final R indices were $R_1 = 0.035$, $wR_2 = 0.072$ for $I > 2\sigma I$ and $R_1 = 0.044$, $wR_2 = 0.075$ for all data.

3.7. *Preparation of* $[Mo(CO)_5P_2SeC_2Bu^t_2(H)Me]$ (**11**)

To $P_2SeC_2Bu^t_2(H)Me$ (0.30 g, 1.0 mmol) in THF (5 ml) a solution of $[Mo(CO)_5(THF)]$ (1.5 mmol) in THF (15 ml) was added. After stirring for 16 h the solvent was removed in vacuo and the yellow oil was sublimed (1×10^{-5}, 90 °C) resulting in **11** (0.19 g, 35%). Recrystallization from hexane afforded single crystals for the X-ray diffraction study.

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 249.8 (d, P(A) $^2J_{P(A)P(X)} = 23.9$ Hz); δ 75.4 (d, P(X) $^2J_{P(A)P(X)} = 23.9$ Hz, $^1J_{SeP(X)} = 101.3$ Hz).

Mass spectrum (EI): *m/z*: 532 $[P_2SeC_2Bu^t_2(H)Me\{Mo(CO_5)\}^+]$, 504 $[P_2SeC_2Bu^t_2(H)Me\{Mo(CO_4)\}^+]$, 476 $[P_2SeC_2Bu^t_2(H)Me\{Mo(CO)_3\}^+]$, 448 $[P_2SeC_2Bu^t_2(H)Me\{Mo(CO)_2\}^+]$, 420 $[P_2SeC_2Bu^t_2(H)Me\{Mo(CO)\}^+]$, 296 $[P_2SeC_2Bu^t_2(H)Me^+]$.

3.7.1. *X-ray crystallographic data for* **11**

Empirical formula: $C_{16}H_{22}MoO_5P_2Se$; $M = 531.18$; $T = 173(2)$ K; Monoclinic $P2_1/c$ (no.14), $a = 11.1254(5)$, $b = 6.5845(5)$, $c = 29.4228(16)$ Å; $\beta = 91.094(3)°$; $V = 2155.0(2)$ Å^3; $Z = 4$; $D_{calc} = 1.637$ mg m^{-3}; $F(000) = 1056$.

Data were collected on a crystal of size $0.10 \times 0.05 \times 0.05$ mm using KappaCCD diffractometer, $\lambda = 0.71073$ Å. A total of 3788 independent reflections were collected, 2244 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The final R indices were $R_1 = 0.0571$, $wR_2 = 0.0932$ for $I > 2\sigma I$ and $R_1 = 0.1192$, $wR_2 = 0.1110$ for all data.

3.8. *Preparation of* $[W(CO)_5P_2SeC_2Bu^t_2(H)Me]$ (**12**)

To $P_2SeC_2Bu^t_2(H)Me$ (0.30 g, 1.0 mmol) in THF (5 ml) a solution of $[W(CO)_5(THF)]$ (1.5 mmol) in THF (15 ml) was added. After stirring for 14 h the solvent was removed in vacuo and the yellow oil was sublimed (1×10^{-5}, 95 °C) resulting in **12** (0.17 g, 28%). Recrystallization from hexane afforded single crystals for the X-ray diffraction study.

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 245.3 (d, P(A) $^2J_{P(A)P(X)} = 25.0$ Hz); δ 47.5 (d, P(X), $^2J_{P(A)P(X)} = 25.0$ Hz, $^1J_{SeP(X)} = 102.0$, $^1J_{WP(X)} = 126.4$).

Mass spectrum (EI): *m/z*: 620 $[P_2SeC_2Bu^t_2(H)Me\{W(CO_5)\}^+]$, 592 $[P_2SeC_2Bu^t_2(H)Me\{W(CO_4)\}^+]$, 564 $[P_2SeC_2Bu^t_2(H)Me\{W(CO)_3\}^+]$, 536 $[P_2SeC_2Bu^t_2(H)Me\{W(CO)_2\}^+]$, 508 $[P_2SeC_2Bu^t_2(H)Me\{W(CO)\}^+]$, 296 $[P_2SeC_2Bu^t_2(H)Me^+]$.

3.8.1. *X-ray crystallographic data for* **12**

Empirical formula: $C_{16}H_{22}O_5P_2SeW$; $M = 619.09$; $T = 173(2)$ K; Monoclinic $P2_1/c$ (number 14), $a = 11.1048(7)$, $b = 6.5798(4)$, $c = 29.3570(14)$ Å; $\beta = 91.186(4)°$; $V = 2141.6(2)$ Å^3; $Z = 4$; $D_{calc} = 1.92$ mg m^{-3}; $F(000) = 1184$. Data were collected on a crystal of size $0.20 \times 0.20 \times 0.10$ mm using KappaCCD diffractometer, $\lambda = 0.71073$ Å. A total of 3626 independent reflections were collected, 2786 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The residual peak of 1.7 e Å^{-3} is phantom peak possibly related to the W atom position by pseudo-symmetry. The final R indices were $R_1 = 0.0559$, $wR_2 = 0.0113$ for $I > 2\sigma I$ and $R_1 = 0.085$, $wR_2 = 0.121$ for all data.

3.9. *Preparation of* $[W(CO)_5P_2TeC_2Bu^t_2(H)Me]$ (**13**)

To $P_2TeC_2Bu^t_2(H)Me$ (0.14 g, 0.4 mmol) in THF (5 ml) a solution of $[W(CO)_5(THF)]$ (1.0 mmol) in THF (15 ml) was added. After stirring for 14 h the solvent was removed in vacuo and the yellow oil was sublimed (1×10^{-5}, 90 °C) resulting in **13** (0.11 g, 40%).

NMR data (C_6D_6): $^{31}P\{^1H\}$: δ 285.1 (d, P(A) $^2J_{P(A)P(X)} = 26.7$ Hz); δ 20.3 (d, P(X) $^2J_{P(A)P(X)} = 26.7$ Hz, $^1J_{WP(X)} = 130.2$ Hz).

Mass spectrum (EI): *m/z*: 668 $[P_2SeC_2Bu^t_2(H)Me\{W(CO_5)\}^+]$, 640 $[P_2SeC_2Bu^t_2(H)Me\{W(CO_4)\}^+]$, 612 $[P_2SeC_2Bu^t_2(H)Me\{W(CO)_3\}^+]$, 584 $[P_2SeC_2Bu^t_2(H)Me\{W(CO)_2\}^+]$, 528 $[P_2SeC_2Bu^t_2(H)Me\{W\}^+]$, 346 $[P_2SeC_2Bu^t_2(H)Me^+]$.

3.10. *Theoretical calculations*

Density functional calculations were carried out by using the B3LYP functional as implemented in the GAUSSIAN-98 program package. [29] Optimisations were carried out by using the 3-21G* basis set, followed by calculation of the second derivatives. Since all the calculated harmonic frequencies turned out to be positive, the structures obtained are real minima on the potential energy hypersurface. Further optimisations were carried out at the B3LYP/6-311+G** level, unless otherwise stated. For the Te containing compounds LANL2DZ (+polarization function) calculations were carried out, by using the B3LYP functional.

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