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[2+2] Cyclo-addition reactions of bis-pentamethylcyclopentadienyl zirconium metal complexes containing terminal chalcogenide ligands with the phospha-alkyne PC^tBu. Syntheses, crystal and molecular structures of the four complexes $[Zr(\eta^5\text{-}(C_5Me_5)_2(SC(^tBu){=}P))]$, $[Zr(\eta^5\text{-}(C_5Me_5)_2(SeC(^tBu){=}P))]$, $[Zr(\eta^5\text{-}(C_5Me_5)_2(SC(^tBu){=}PSe))]$ and $[Zr(\eta^5\text{-}(C_5Me_5)_2(SC(^tBu){=}PC(Ph){=}N))]$

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Abstract

The chalcogenide complexes $[Zr(\eta^5\text{-}(C_5Me_5)_2({=}E))]$ (E = S, Se), (generated in situ from the corresponding pyridine adducts), undergo [2+2] cyclo-addition reactions with the phospha-alkyne ^tBuCP to afford the structurally characterised complexes $[Zr(\eta^5\text{-}(C_5Me_5)_2(SC(^tBu){=}P))]$ and $[Zr(\eta^5\text{-}(C_5Me_5)_2(SeC(^tBu){=}P))]$. The former complex undergoes ring expansion reactions with either selenium to afford $[Zr(\eta^5\text{-}(C_5Me_5)_2(SC(^tBu){=}PSe))]$ or with PhCN to give $[Zr(\eta^5(C_5Me_5)_2(SC(^tBu){=}PC(Ph){=}N))]$ which have also been characterised structurally.

Keywords: Phospha-alkyne; Cyclo-addition; Chalcogenide; Zirconium; Ring expansion

1. Introduction

There is considerable current interest in the study of metal sulphides [1,2]. The reactivity of certain transition metal sulphides towards alkenes [3] and alkynes [4,5], has been discussed. Recent reports by Goodman and Rauchfuss [6] describe the addition of nitriles to the tetrasulphido anion $[ReS_4]^-$, and we have previously discussed the ready [3+2] cyclo-addition of alkynes and the phospha-alkyne, PC^tBu, to the anionic mononuclear trisulphido complex $[PPh_4][W(\eta^5\text{-}(C_5Me_5)(S)_3)]$, containing three terminal W=S bonds [7,8].

Thus, treatment of $[PPh_4][W(\eta^5\text{-}C_5Me_5)S_3]$ with one equivalent of PC^tBu at room temperature afforded $[PPh_4][W(\eta^5(C_5Me_5)(S)(S_2PC^tBu))]$, which reacts with dry O_2 to give $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2PC^tBu))]_2$ [8] (Scheme 1)

Although a variety of [2 +1], [3+2] and [4+2] cyclo-addition reactions of the phosphaalkyne PC^tBu have also been described, [2+2] cyclo-additions have not been as widely developed [9,10]. When PC^tBu is heated, in the absence of solvent, [11] forming the remarkable tetraphosphacubane, $P_4C_4^tBu_4$, the likely first step involves a [2+2] self cyclo-addition to give the 1,3-diphosphacyclobutadiene $P_2C_2^tBu_2$, followed by a head to tail dimerisation and a further [2+2] cycloaddition step. Supporting evidence [12–14] came from a subsequent study of the reaction of the zirconium complex $[Zr(\eta^5\text{-}C_5H_5)_2P_2C_2^tBu_2]$ with C_2Cl_6 also leading to the tetraphosphacubane, however in this case the tricyclic

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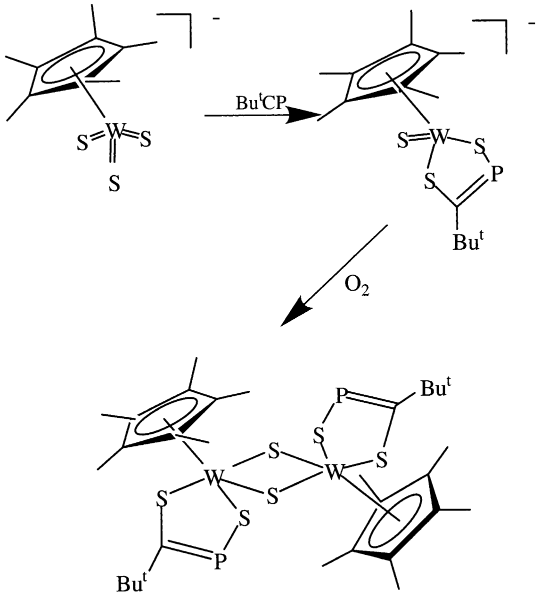
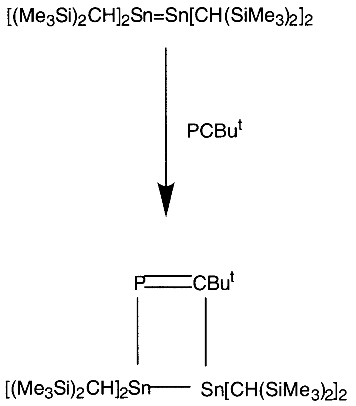


Scheme 1.

tetraphosphatricyclo-octadiene was also observed, which must have been formed by a head to head dimerisation of the key 1,3-diphosphacyclobutadiene intermediate.

A further example of a [2+2] cycloaddition reaction of PC^{t}Bu involves its reaction with the stable distannene $R_2Sn=SnR_2$, (R = $(Me_3Si)_2CH-$), (in equilibrium with the corresponding stannylene) to give the structurally characterised phosphadistannacyclobutene [15]. (Scheme 2)

We now describe our studies on some further [2+2] cyclo-addition reactions of the phospha-alkyne, PC^{t}Bu, with compounds containing zirconium(IV) chalcogenide double bonds, which are generated in situ, in view of our ongoing interest in the similar insertion reactions with stable Ti(IV) and Zr(IV) imides [16–18].



Scheme 2.

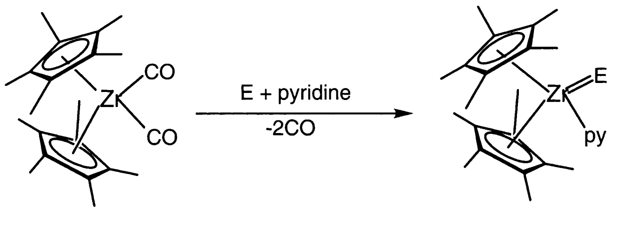
2. Results and discussion

In order to avoid the possibility of competing [2+3] cyclo-addition reactions referred to in the Introduction, mono-terminally bonded chalcogen containing complexes considered for the study were [M(η^5-$(C_5Me_5)_2$(=E))] (M = Ti, Zr; E = O, S, Se). Anderson and co-workers [19] synthesised [Ti(η^5-$C_5Me_5)_2$(py)(=O)] (py=NC_5H_5), from [Ti(η^5-$C_5Me_5)_2$] and N_2O, in the presence of pyridine, in order to stabilise the oxo-titanocene moiety. Likewise, Bergman and co-workers [20] obtained the analogous terminal sulphido complex [Ti(η^5-$C_5Me_5)_2$(py)(=S)] by treating [Ti(η^5-$C_5Me_5)_2$(py)(S)(η^2-C_2H_4)] with S_8. Terminal zirconium oxo complexes have been isolated only recently by Bergman and co-workers [21,22] from a reaction in which [Zr(η^5-$C_5Me_5)_2$(=O)] (generated as a reactive intermediate by the thermal elimination of benzene from [Zr(η^5-$C_5Me_5)_2$(OH)(Ph)], or by deprotonation of [Zr(η^5-$C_5Me_5)_2$(OH)(OSO_2CF_3)] with $KN(SiMe_3)_2$) which was subsequently trapped by both nitriles and alkynes. Parkin and co-workers [23] isolated the terminal zirconium(IV) oxo complex, [Zr(η^5-$C_5Me_5)_2$(py)(=O)] in an analogous manner to that described for the titanium(IV) systems and the corresponding terminal zirconium sulphido, selenido and tellurido complexes, **1**–**3**, [21,23] have been synthesised as shown in Scheme 3. Although addition reactions involving alkynes and nitriles have been carried out with **1** no work has been carried out as yet between the terminal selenido and tellurido complexes **2** and **3**.

2.1. *Synthesis and characterisation of [Zr(η^5-$C_5Me_5)_2$(SC^{t}Bu)P] (4)*

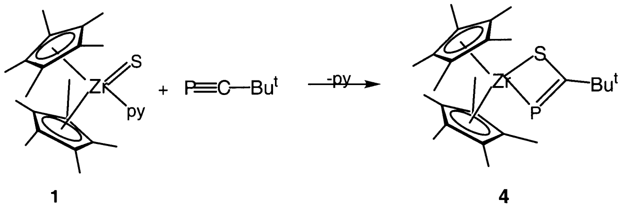
Treatment of [Zr(η^5-$C_5Me_5)_2$(py)(=S)] (**1**) with one equivalent of PC^{t}Bu, in toluene, leads to the ready elimination of pyridine, affording the [2+2] cycloaddition product [Zr(η^5-$C_5Me_5)_2$(SC^{t}Bu)P] (**4**) (Scheme 4).

Compound **4** was fully characterised by $^{31}P\{^1H\}$-, ^1H-, $^{13}C\{^1H\}$-NMR spectroscopy, mass spectroscopy and elemental analysis and its molecular structure was established by a single crystal X-ray diffraction study. The $^{31}P\{^1H\}$-NMR spectrum showed a single lowfield P resonance (δ 380 ppm) which is typical of a C=P double



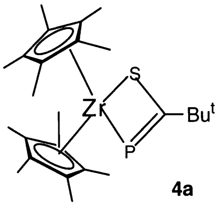
1 E=S; **2** E=Se; **3** E=Te

Scheme 3.

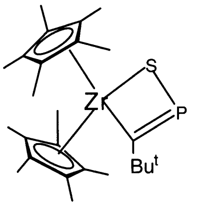


Scheme 4.

bond. The ^{1}H-NMR spectrum shows both the signals for the ^{t}Bu group (relative intensity 3) and a single resonance due to the two magnetically equivalent C_5Me_5 ligands (relative intensity 10). The $^{13}C\{^{1}H\}$-NMR spectrum clearly shows, as well



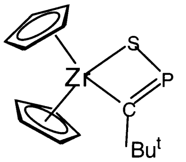
4a



4b

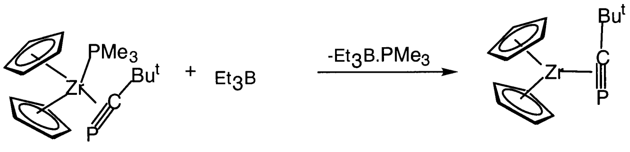
as the resonances for the ^{t}Bu and Cp* groups, a doublet at 191 ppm ($^{1}J_{(CP)}$ 104 Hz), which can be assigned to the unsaturated carbon within the four-membered Zr–S–C–P ring. The mass spectrum shows a parent ion (*m*/*z* 492). The above data are consistent with the two possible isomeric structures, **4a** and **4b**.

Interestingly, the ^{31}P-NMR spectroscopic data are very different from the unpublished data of Binger and co-workers [24,25] for the corresponding bis-cyclopentadienyl complex, **5**, synthesised by a completely different route shown in Schemes 5 and 6, which has a structure analogous to **4b**. Compound **5** (and its Ti analogue) were synthesised

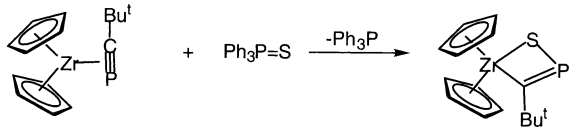


5

from the precursors $[M(\eta^5\text{-}C_5H_5)_2(PC^{t}Bu)(PMe_3)]$ (M = Ti, Zr) which on treatment with BEt_3, leads to the elimination of PMe_3, creating a vacant site and giving the unstable unsaturated η^2-ligated phosphaalkyne–metallocene complex. These complexes are known to usually oligomerise easily to the dimer, (M = Zr) or the trimer, (M = Ti), however, in the presence of $Ph_3P{=}S$ at 0 °C, insertion of a sulphur atom into the



Scheme 5.



Scheme 6.

three membered M–P–C ring occurs, leading to complexes containing the M–S–P–C fragment (see Schemes 5 and 6 for the Zr compound).

Complex **5** was fully characterised by NMR spectroscopy (δ_P 50.7 ppm), mass spectroscopy and by single crystal X-ray diffraction studies, the latter confirming that the unsaturated ring carbon atom, rather than the phosphorus atom, is σ bonded to the metal centre.

In the present work, the molecular structure of **4** in the solid state was confirmed to be that of **4a** by a single crystal X-ray diffraction study (see Fig. 1). establishing the presence of the Zr–S–C–P four-membered ring system, in which phosphorus is attached to the metal centre and the C-*tert*-buyl group is located as far as possible from the sterically demanding Cp* ligands. Unfortunately, because of some disorder in the ^{t}Bu fragment, bond lengths and angles can only be approximately determined. Since the nucleophilic sulphur would probably preferentially bind to the positively charged P in the polar phospha-alkyne suggesting the [2+2] cycloaddition step to afford **4** might be controlled by the bulky Cp* groups. On the other hand, different behaviour has been found [21,22,26–29] in a series of cycloaddition reactions involving the intermediates $[Zr(\eta^5\text{-}C_5Me_5)_2({=}X)]$ (X = O,S) with the alkyne MeC≡CPh containing one bulky substituent, where in the resulting products **7** and **8** the bulkier organic group is located in the position α to the metal. (Scheme 7).

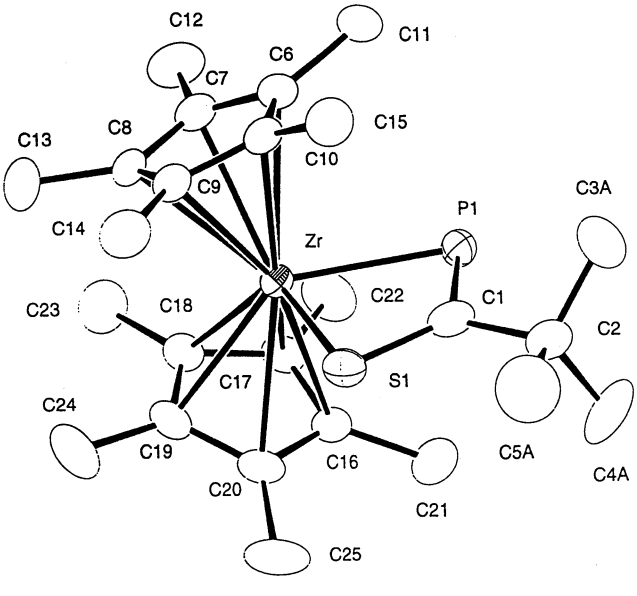
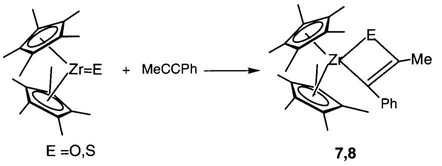


Fig. 1. Molecular structure of **4**.



Scheme 7.

Likewise in similar titanium systems the regiochemistry of the alkyne additions is opposite to that observed for zirconium and the bulky substituent is found in the β-position, possibly due to the more crowded titanium centre.

2.2. Synthesis and characterisation of $[Zr(\eta^5\text{-}C_5Me_5)_2(SeC(^tBu)P)]$ (**9**)

In order to examine the generality of [2+2] cycloaddition reactions of metal chalcogenides with the phosphaalkyne, PC^tBu, reactions were also carried out with analogous terminal selenido and tellurido complexes of zirconium. Thus, treatment of **2**, with PC^tBu in toluene, under ambient conditions, led to the formation of $[(\eta^5\text{-}C_5Me_5)_2(SeC(^tBu)P)]$ (**9**) as shown in Scheme 8. The $^{31}P\{^1H\}$-NMR spectrum of **9** shows a singlet (δ 388 ppm) exhibiting ^{77}Se satellites, with a coupling constant ($^2J_{(PSe)}$ 88 Hz) whose magnitude is typical for a two-bond phosphorus–selenium coupling suggesting a similar structure to **4**. The $^{77}Se\{^1H\}$-NMR spectrum displays a doublet (δ 689 ppm), also with the same coupling constant ($^2J_{(PSe)}$ 88 Hz) and the ^1H- and $^{13}C\{^1H\}$-NMR spectra are similar in pattern to those observed for **4**. The mass spectrum shows a parent ion (m/z 539). The molecular structure was confirmed by a single crystal X-ray diffraction study and is shown in Fig. 2.

The structure is in accord with the above spectroscopic data and establishes the formation of the Zr–Se–C–P ring. It is clear that the phosphorus is coordinated to the metal centre and the C–^{t}Bu is located away from the Cp* groups, as in **4**. However, again as in the case of **4**, there was some disorder around the P, Se and C atoms of the ^{t}Bu, which precludes any detailed discussion of bond lengths and angles.

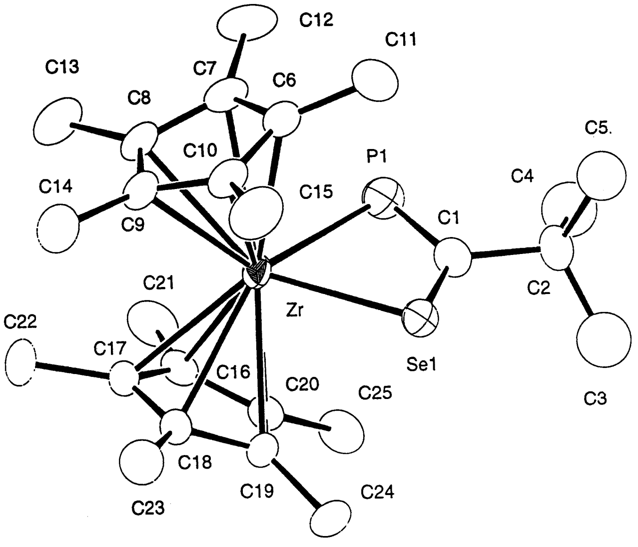
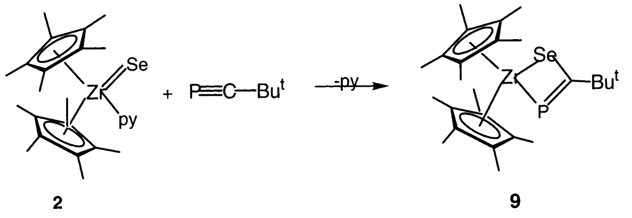


Fig. 2. Molecular structure of **9**.

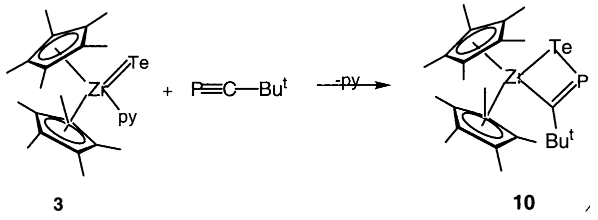
2.3. Synthesis and characterisation of $[Zr(\eta^5\text{-}C_5Me_5)_2(TeC(^tBu)P)]$ (**10**)

When a similar reaction is carried out between PC^tBu and the resulting red–brown tellurido complex **3**, surprisingly, on the basis of NMR studies the resulting red–brown complex $[Zr(\eta^5\text{-}C_5Me_5)_2(TeC(^tBu)P)]$ (**10**), appears to have a different structure to **4** and **9** and is actually similar to **4b** (see Scheme 9). The compound was characterised solely by NMR and mass spectroscopy.

The $^{31}P\{^1H\}$ spectrum for **10** exhibits a singlet (δ 95 ppm), with ^{127}Te satellites ($^1J_{(PTe)}$ 626 Hz), which is considerably shifted upfield when compared with that observed in both **4** (δ 380 ppm) and **9** (δ 388 ppm). The large coupling constant is also much more typical of a one bond than a two bond phosphorus–tellurium coupling when compared to the values obtained for the corresponding 1,2,4- ($^1J_{(PTe)}$ 1021; $^2J_{(PTe)}$ 158 Hz) and 1,3,4-telluradiphosphole ring systems ($^2J_{(PTe)}$ 148 Hz). The $^{127}Te\{^1H\}$-NMR spectrum was also recorded confirms this, displaying a doublet (δ 664 ppm) with a large coupling constant of 626 Hz. This information leads to the conclusion that in **10** the isomeric complex has been formed, where the unsaturated phosphorus is coordinated to the tellurium and not to the Zr centre. In



Scheme 8.



Scheme 9.

order to provide further confirmation, the $^{13}C\{^{1}H\}$-NMR spectrum was obtained. This shows the similar resonances for the carbons of the ^{t}Bu and Cp* groups as those observed for complex **4**, however a new doublet at an unusually low field shift (δ 303 ppm, $^{1}J_{(PC)}$ 105 Hz), is clearly visible and can be assigned to the unsaturated ring carbon. This downfield shift compared with the shift for the ring carbon in **4** (δ −191 ppm) may be attributed to the carbon which is now bonded directly to the metal centre. The doublet also exhibits ^{127}Te satellites ($^{2}J_{(TeC)}$ 45 Hz) which lie in the expected range for a two bond carbon–tellurium coupling [20,21] ($^{1}J_{(CTe)}$ 317 Hz, $^{2}J_{(CTe)}$ 39 Hz). The mass spectrum of **10** shows a parent ion (m/z 587). A possible reason why the phosphaalkyne fragment has added in the opposite manner to that observed for the zirconium sulphide and selenide systems may be due to the longer Zr–Te bond distance in **10** when compared to the Zr–S and Zr–Se bond lengths in **4** and **9**, thus leading to the expansion of the four membered metallacycle, allowing the approach of the ^{t}Bu groups. Unfortunately, it did not prove possible to grow crystals of **10** suitable for X-ray crystallography.

2.4. Further reactions of [Zr(η^5-C_5Me_5)$_2$(SC(^{t}Bu)P)] (4) with chalcogenides, nitriles and isonitriles

Further ring expansion reactions of the four-membered zirconium–phosphaalkyne ring complex **4**, with other chalcogenides, nitriles and isonitriles were carried out.

2.5. Synthesis and characterisation of [Zr(η^5-C_5Me_5)$_2$(SPC(^{t}Bu)Se)] (11)

Thus, a solution of **4** and one equivalent of elemental selenium was stirred overnight to afford [Zr(η^5-C_5Me_5)$_2$(SPC(^{t}Bu)Se)] (**11**) as a red solid (see Scheme 10). The product was fully characterised by $^{31}P\{^{1}H\}$-, $^{77}Se\{^{1}H\}$-, ^{1}H-, $^{13}C\{^{1}H\}$-NMR spectroscopy, mass spectroscopy and elemental analysis. The $^{31}P\{^{1}H\}$-NMR spectrum of **11** shows a singlet (δ −273 ppm), shifted significantly upfield when compared with **4**. The phosphorus resonance exhibits ^{77}Se satellites, ($^{1}J_{(PSe)}$ 361 Hz), indicative of a one bond coupling. Interestingly, in the ^{1}H-NMR spectrum of complex **11**, the resonances of the Cp* protons unexpectedly are observed as a singlet, indicating that the complex is fluxional in solution at room temperature. A single crystal X-ray diffraction study was performed on **11** and the molecular structure is shown in Fig. 3 together with selected bond lengths and angles.

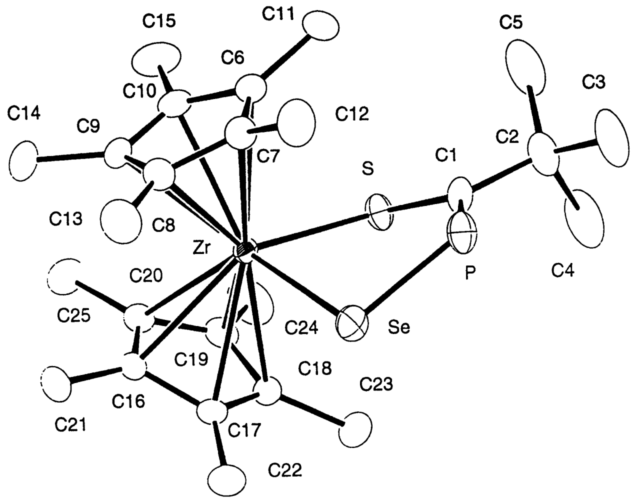
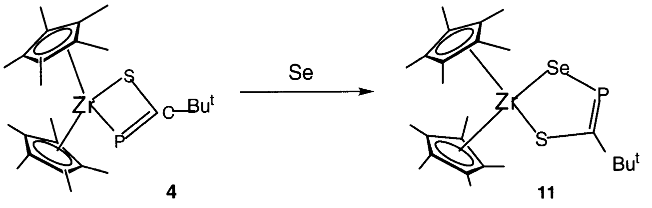
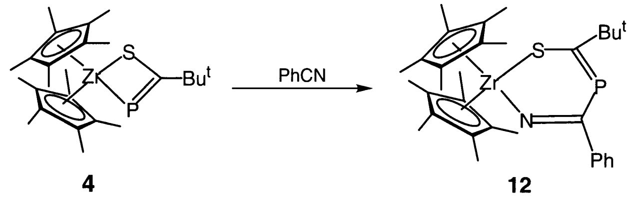


Fig. 3. Molecular structure of **11** together with selected bond lengths (Å) and bond angles (°): Zr–S 2.5440(6), Zr–Se 2.6385(3), S–C(1) 1.740(3), P–C(1) 1.709(3), Se–P(1) 2.2284(8), C(1)–C(2) 1.534(4), Zr–C(7) 2.584(2); Se–Zr–S 86.16(2), Zr–S–C(1) 105.97(9), S–C(1)–P 126.3(2), C(1)–P–Se 108.86(9), P–Se–Zr 97.66(2), P–C(1)–C(2) 117.6(2), C(8)–Zr–C(16) 94.47(8).

As suggested by the NMR data, the selenium atom has clearly inserted into the Zr–P bond, forming a five-membered (ZrSPCSe) metallacycle whose P=C fragment is twisted above the plane formed by the Zr, S and Se atoms by an angle of 10°. The dihedral angle between the planes formed by the two Cp* rings is 45.6°. The P–C(1) bond length (1.709 Å) which is typical for a P=C double bond, is also indicated by the wide P–C(1)–C(2) bond angle (117.6°). The Zr–S distance (2.544 Å) lies within the typical Zr–S single bond range (2.42–2.55 Å) [30–33] and has been lengthened considerably from that observed in the starting material, **2** (2.334 Å) [34], which is consistent with the change in Zr–S bond order from 2 to 1. The Zr–Se bond length (2.638 Å) lies in the expected range for a Zr–Se single bond (typically 2.658 Å) [34] (Zr=Se bond length in **3** (2.480 Å)).



Scheme 10.



Scheme 11.

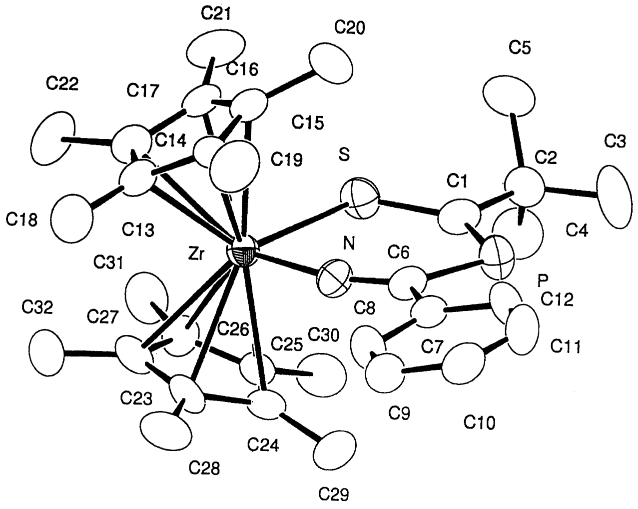


Fig. 4. Molecular structure of **12** together with selected bond lengths (Å) and bond angles (°): Zr–N 1.988(10), Zr–S 2.585(3), N–C(6) 1.28(1), P–C(6) 1.85(1), P–C(1) 1.70(1), S–C(1) 1.75(1), C(1)–C(2) 1.55(2), Zr–C(25) 2.58(1); S–Zr–N 82.3(3), S–C(1)–P 132.9(8), P–C(6)–N 123.1(9), P–C(6)–C(7) 115.1(9).

*2.6. Synthesis and characterisation of [Zr(η^5C$_5$Me$_5$)$_2$(SC(^{t}Bu)PC(Ph)N)] (**12**)*

Complex **4** was reacted with one equivalent of PhCN in toluene at room temperature resulting in the formation of the six-membered ring complex [Zr(η^5-C$_5$Me$_5$)$_2$(SC(^{t}Bu)PC(Ph)N)] (**12**) (Scheme 11).

The ^{31}P{^{1}H}-NMR spectrum of **12** shows a singlet at 137 ppm and its mass spectrum exhibits a parent ion (*m*/*z* 595). Its molecular structure, which was confirmed by a single crystal X-ray diffraction study, is shown in Fig. 4, together with selected bond lengths and angles.

The structure clearly shows that the nitrogen is attached to the metal centre and the aryl group occupies the β-position to zirconium, lying away from the bulky Cp* substituents, inferring that steric factors must be the dominant influence. The N–C bond length (1.28 Å) is within the expected value for a N–C double bond and the six-membered ring formed by Zr–S–C–P–C–N is almost planar ($\Sigma_{(\text{internal angles})} = 718°$). It is interesting to note that Bergman and co-workers [20,29] have reported syntheses of the reactive intermediates [Zr(η^5-C$_5$Me$_5$)$_2$(=X)] (X = O,S) **1** and **2**.

In the presence of benzonitrile the sulphido complex **2** cleanly afforded the corresponding six-membered metallacycle shown in Scheme 12 which arises from a via a [2+2 +2] cycloaddition reaction.

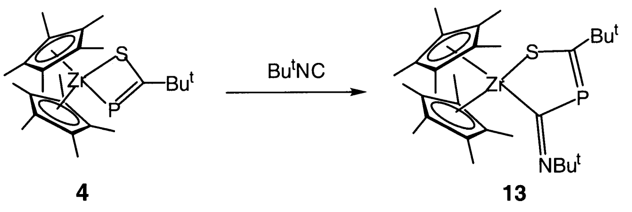
It was also noted that in the case of similar reactions with an excess of an alkyne, the insertion of a second molecule of the alkyne, to give a six-membered ring, does not occur. A similar reaction involving the titanium systemswith an excess of various nitriles resulted only in the formation of four membered (TiSCN) metallacycles.

It should be noted that Bergman and co-workers [26] have previously reported the formation of reactive intermediates (η^5-C$_5$Me$_5$)$_2$Zr=O and (η^5-C$_5$Me$_5$)$_2$Zr=S and the sulfur compound underwent [2+2+2] cycloaddition with PhCN to generate a six-membered metallacycle. Likewise, a metallacycle containing the six-membered Ti–P=CR–C(O)–CR=P (R = ^{t}Bu) Ti ring system was proposed by Cowley et al. [35], as a possible intermediate in the reaction between [Ti(η^5–C$_5$H$_5$)$_2$(CO)$_2$] and PC^{t}Bu to form the heterocycle, P$_2$C$_2^t$Bu$_2$CO.

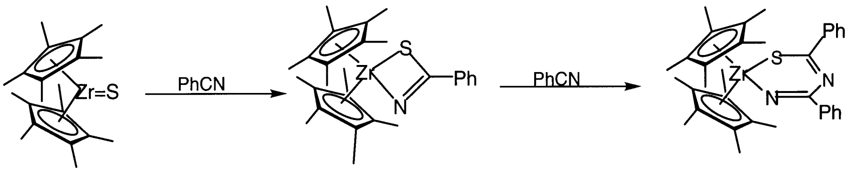
*2.7. Synthesis and characterisation of [Zr(η^5-C$_5$Me$_5$)$_2${SC(^{t}Bu)PC(=N^{t}Bu)}] (**13**)*

Finally, the reaction between **4** and the isonitrile, ^{t}BuNC was carried out to afford [Zr(η^5-C$_5$Me$_5$)$_2${SC(^{t}Bu)PC(=N^{t}Bu)}] (**13**), containing a five-membered ZrSCPC ring system (Scheme 13).

Unfortunately, although it proved difficult to grow suitable crystals suitable for crystallography, the product was characterised by NMR and mass spectroscopy. The ^{31}P{^{1}H}-NMR spectrum shows a singlet (δ 162 ppm) and in the ^{1}H-NMR spectrum, the resonances for the two ^{t}Bu groups (δ 1.4, 1.7 ppm) as well as those for the Cp* ligands can be seen, in the ratio of 3:3:10. The ^{13}C{^{1}H}-NMR spectrum is the most indicative in helping to determine the structure. It exhibits the required



Scheme 13.



Scheme 12.

resonances for the ^{t}Bu group attached to the P=C fragment, as well as additional doublets for the second ^{t}Bu group, of the isonitrile moiety. The doublets for the two ring carbons are also clearly visible. The signal for the unsaturated ring C (δ 248 ppm), lying between the P and S, has been shifted downfield when compared to the equivalent carbon in **4** (δ 191 ppm, $^1J_{(CP)}$ 68 Hz) and the new C (of the ^{t}BuNC fragment) appears at 270 ppm ($^1J_{(CP)}$ 80 Hz) which is in a similar region to that observed for the unsaturated carbon in **10** (δ 303 ppm), used as a drying agent for acetonitrile. NMR solvents were dried over potassium (benzene-d_6), sodium (toluene-d_8) or calcium hydride (dichloromethane-d_2), then vacuum transferred into ampoules and stored under dinitrogen prior to use.

3. Experimental

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

NMR spectra were recorded on a Bruker DPX 300 or a Bruker AMX 500 spectrometer at the operating frequencies shown below in Table 1. 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 Pascher (Germany) or A.T. Stones of the Department of Chemistry, University College London.

3.1. *[Zr(η^5-C_5Me_5)$_2$(SC(^{t}Bu)P)] (**4**)*

PC^{t}Bu (0.021 g, 0.210 mmol) was added to a stirred suspension of [Zr(η^5-C_5Me_5)$_2$(=S)(py)] (**1**) (0.100 g, 0.212 mmol) in toluene (10 ml). The reaction mixture

Table 1
Crystallographic data for [Zr(η^5-C_5Me_5)$_2$(SC(^{t}Bu)P)] (**4**), [Zr(η^5-C_5Me_5)$_2$(SeC(^{t}Bu)P)] (**9**), [Zr(η^5-C_5Me_5)$_2$(SC(^{t}Bu)PSe)] (**11**) and [Zr(η^5-C_5Me_5)$_2${SC(^{t}Bu)PC(Ph)N}] (**12**)

	4	**9**	**11**	**12**
Formula	$C_{25}H_{39}PSZr$	$C_{25}H_{39}PSeZr$	$C_{25}H_{39}PSSeZr$	$C_{32}H_{44}PSNZr$
Mol. wt. (g mol^{-1})	493.84	540.74	572.80	596.96
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)
Color of crystal	Brown	Brown	Brown	Red
Crystal size (mm^3)	0.20 × 0.15 × 0.04	0.14 × 0.10 × 0.02	0.30 × 0.40 × 0.02	0.25 × 0.14 × 0.02
Unit cell dimensions				
a (Å)	14.5948(8)	9.810(1)	10.2410(7)	9.6038(4)
b (Å)	11.9668(3)	9.8946(7	18.6038(5)	9.8590(2)
c (Å)	15.0620(2)	13.708(1)	14.4626(3)	31.740(2)
α (°)		76.938(1)		
β (°)	109.0125(7)	84.8979(9)	105.8013(6)	
γ (°)		74.7278(9)		
V (Å^3)	2487.1(1)	1249.8(2)	2651.3(2)	3005.3(2)
Z	4	2	4	4
ρ_{calc} (g cm^{-3})	1.319	1.437	1.435	1.319
μ(Mo–K$_\alpha$) (cm^{-1})	5.99	19.69	19.36	5.09
Absorption range	0.84–0.99	0.68–0.96	0.63–0.96	0.36–0.99
$2\theta_{max}$ (°)	55	55	55	55
No. of measured reflections	5538	5242	6027	3876
No. observed reflections	5534 [a]	5238 [a]	6024 [a]	3225 [b]
No. parameters	298	248	262	326
R [c]	0.054	0.061	0.043	0.092
R_w [d]	0.054	0.065	0.053	0.093
GOF [e]	1.61	2.17	1.97	2.03

[a] All reflections used.

[b] Observation criterion $I > 1\sigma(I)$.

[c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[d] $R_w = [\{\Sigma\, w(|F_o| - |F_c|)^2\}/\Sigma w\, F_o^2]^{1/2}$.

[e] $GOF = [\{\Sigma\, w(|F_o| - |F_c|)^2\}/(N_o - N_p)]^{1/2}$, where N_o and N_p denote the number of data and parameters.

was stirred for 24 h, during which time the solution colour changed from yellow to red. Volatiles were removed in vacuo and the resulting red residue extracted with hexane (15 ml). Slow evaporation of the hexane solution led to the formation of red crystals of **4** (yield 0.064 g, 61%). Crystals suitable for X-ray analysis were grown from a slowly cooled and concentrated hexane solution (−45 °C).

NMR data (all in benzene-d_6, 295 K).

$^{31}P\{^1H\}$: δ 380.2 ppm, ^1H; δ 1.68 [s, 30H, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 1.65 [s, 9H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ δ 191.4 [d, 1C, P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 104 Hz], 119.3 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 45.8 [d, 1C, PC*C*(CH$_3$)$_3$, $^2J_{(PC)}$ 7 Hz], 34.5 [d, 3C, PCC(*C*H$_3$)$_3$, $^3J_{(PC)}$ 10 Hz], 11.7 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$] ppm. EIMS *m/z* (%): 492 (24) [M$^+$], 392 [M−(PC^{t}Bu)]$^+$. Anal. Found C, 59.61; H, 7.99; S, 6.21. Calc. for $ZrC_{25}H_{39}SP$: C, 59.83; H, 8.16; S, 6.65%.

3.2. *[Zr(η^5-C$_5$Me$_5$)$_2$(SeC(^{t}Bu)P)]* (**9**)

PC^{t}Bu (0.028 g, 0.280 mmol) was added to a stirred suspension of [Zr(η^5-C$_5$Me$_5$)$_2$(=Se)(py)] (**2**) (0.150 g, 0.289 mmol) in toluene (12 ml). The reaction mixture was stirred for 24 h, during which time the solution colour changed from green/brown to red. The volatiles were removed in vacuo and the resulting red residue was extracted with hexane (15 ml). Slow evaporation of the hexane solution led to the formation of red crystals of **9** (yield 0.073 g, 47%). Crystals suitable for X-ray analysis were grown by slowly cooling a concentrated hexane solution (−45 °C).

NMR data (all in benzene-d_6, 295 K).

$^{31}P\{^1H\}$: δ 388.1 [s, $^2J_{(PSe)}$ 89 Hz] ppm; $^{77}Se\{^1H\}$ δ 608.0 [d, $^2J_{(SeP)}$ 89 Hz] ppm; ^1H: δ 1.74 [s, 30H, $2\{C_5(CH_3)_5\}$], 1.79 [s, 9H, ^1H δ 1.74 [s, 30H, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 1.79 [s, 9H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$: δ 184.3 [d, 1C, P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 110 Hz], 120.2 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 43.2 [d, 1C, PC*C*(CH$_3$)$_3$, $^2J_{(PC)}$ 8 Hz], 30.5 [d, 3C, PCC(*C*H$_3$)$_3$, $^3J_{(PC)}$ 12 Hz], 10.5 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$] ppm. EIMS *m/z* (%): 539 (32) [M$^+$], 439 [M−(PC^{t}Bu)]$^+$. Anal. Found C, 54.23; H, 7.40. Calc. for $ZrC_{25}H_{39}SeP$: C, 54.52; H, 7.43%.

3.3. *[Zr(η^5-C$_5$Me$_5$)$_2$(TeC(^{t}Bu)P)]* (**10**)

PC^{t}Bu (0.022 g, 0.220 mmol) was added to a stirred suspension of [Zr(η^5-C$_5$Me$_5$)$_2$(=Te)(py)] (**3**) (0.125 g, 0.220 mmol) in toluene (15 ml). The reaction mixture was stirred for a further 24 h, during which time the solution colour changed from red to green. Volatiles were removed in vacuo and the resulting green residue was extracted with hexane (20 ml). This solution was concentrated again and dried under vacuo, yielding **10** as a green solid (yield 0.084 g, 65%).

NMR data (all in benzene-d_6, 295 K).

$^{31}P\{^1H\}$: δ 93.3 [s, $^1J_{(PTe)}$ 625 Hz] ppm; $^{125}Te\{^1H\}$: δ 661.4 [d, $^1J_{(TeP)}$ 625 Hz] ppm; ^1H: δ 1.76 [s, 30H, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 1.57 [s, 9H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$-NMR data (benzene-d_6, 295 K): δ 304.0 [d, 1C, P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 105 Hz, $^1J_{(CTe)}$ 45 Hz], 118.3 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 51.4 [d, 1C, PC*C*(CH$_3$)$_3$, $^2J_{(PC)}$ 25 Hz], 37.9 [d, 3C, PCC(*C*H$_3$)$_3$, $^3J_{(PC)}$ 15 Hz], 14.4 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$] ppm. EIMS *m/z* (%): 587 (24) [M$^+$], 487 [M−(PC^{t}Bu)]$^+$.

3.4. *[Zr(η^5-C$_5$Me$_5$)$_2$(SC(^{t}Bu)PSe)]* (**11**)

[Zr(η^5-C$_5$Me$_5$)$_2$(SC(^{t}Bu)P)] (**4**) prepared as stated above (0.100 g, 0.203 mmol) was then dissolved in toluene (10 ml) and elemental Se (0.024 g, 0.304 mmol) was added. The solution turned dark red rapidly and the reaction mixture was stirred for 24 h. The solution was filtered to remove any excess Se and the volatiles were removed in vacuo. Recrystallisation of the resulting red residue with hexanes (5 ml) yielded dark red crystals of **11** (yield 0.092 g, 79%). Crystals suitable for X-ray analysis were grown from a slowly cooled hexane solution (−45 °C).

NMR data (all in benzene-d_6, 295 K).

$^{31}P\{^1H\}$: δ −273.4 [s, $^1J_{(PSe)}$ 360 Hz] ppm; $^{77}Se\{^1H\}$: δ 568.7 [d, $^1J_{(SeP)}$ 360 Hz] ppm; ^1H: δ 1.71 [s, 30H, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 1.42 [s, 9H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$: δ 239.4 [d, 1C, P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 101 Hz], 118.4 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 49.2 [d, 1C, PC*C*(CH$_3$)$_3$, $^2J_{(PC)}$ 18 Hz], 37.8 [d, 3C, PCC(*C*H$_3$)$_3$, $^3J_{(PC)}$ 12 Hz], 12.6 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$] ppm. EIMS *m/z* (%): 571 (41) [M$^+$], 392 [M-(SePC^{t}Bu)]$^+$. Anal. Found C, 51.17; H, 7.12; S, 5.64. Calc. for $ZrC_{25}H_{39}SPSe$: C, 51.40; H, 7.01; S, 5.72%.

3.5. *[Zr(η^5-C$_5$Me$_5$)$_2${SC(^{t}Bu)PC(Ph)N}]* (**12**)

[Zr(η^5-C$_5$Me$_5$)$_2$(SC(^{t}Bu)P)] (**4**) (0.200 g, 0.405 mmol) was then dissolved in toluene (10 ml) and PhCN (0.083 g, 0.811 mmol) was added dropwise. The reaction mixture was stirred for 48 h, during which time the solution turned from light to dark red. The volatiles were removed in vacuo and the residue was extracted with hexane (15 ml), giving red crystals of **12** (yield 0.102 g, 42%). Crystals suitable for X-ray analysis were grown from a cooled toluene solution (−30°C).

NMR data (all in benzene-d_6, 295 K).

$^{31}P\{^1H\}$: δ 136.8 ppm; ^1H: δ 8.39 [m, 2H, $C(C_6H_5)$], 7.03 [m, 2H, $C(C_6H_5)$], 7.20 [m, 1H, $C(C_6H_5)$], 1.94 [s, 9H, $C(CH_3)_3$], 1.79 [s, 30H, $2\{\eta^5\text{-}C_5(CH_3)_5\}$] ppm. $^{13}C\{^1H\}$: δ 220.4 [d, 1C, P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 103 Hz], 189.6 [d, 1C, N*C*(C$_6$H$_5$), $^1J_{(PC)}$ 98 Hz] 133.5 [s, 1C, NC(*C*$_6$H$_5$)], 127.2 [s, 2C, NC(*C*$_6$H$_5$)], 126.6 [d, 1C, NC(C$_6$H$_5$), $^2J_{(PC)}$ 7 Hz] 125.8 [d, 2C, NC(C$_6$H$_5$), $^3J_{(PC)}$ 4 Hz], 118.9 [s, 10C, $2\{\eta^5\text{-}C_5(CH_3)_5\}$], 47.2 [d, 1C, PCC(CH$_3$)$_3$, $^2J_{(PC)}$ 19 Hz], 34.8 [d, 3C, PCC(CH$_3$)$_3$,

$^3J_{(PC)}$ 11 Hz], 11.5 [s, 10C, 2{η^5-C$_5$(CH$_3$)$_5$}] ppm. EIMS *m/z* (%): 595 (22) [M$^+$], 492 [M−(PhCN)]$^+$, 392 [M−(PhCN)−(PC^{t}Bu)]$^+$. Anal. Found C, 63.83; H, 7.34; N, 2.52; S, 5.11. Calc. for ZrC$_{32}$H$_{44}$SPN: C, 63.65; H, 7.58; N, 2.39; S, 6.65%.

3.6. *[Zr(η^5-C$_5$Me$_5$)$_2${SC(^{t}Bu)PC(N^{t}Bu)}] (**13**)*

[Zr(η^5-C$_5$Me$_5$)$_2$(SC(^{t}Bu)P)] (**4**) (0.275 g, 0.557 mmol) was then dissolved in toluene (12 ml) and ^{t}BuNC (0.051 g, 0.613 mmol) was added dropwise. The reaction mixture was allowed to stir for 24 h, during which time the solution turned from light to dark red. The volatiles were removed in vacuo and the residue was extracted with hexane (15 ml), giving **13** as a red solid (yield 0.253g, 79%).

NMR data (all in benzene-*d*$_6$, 295 K).

^{31}P{^{1}H}: δ 162.6 ppm; ^{1}H: δ 1.79 [s, 9H, PC(CH$_3$)$_3$], 1.71 [s, 30H, 2{η^5-C$_5$(CH$_3$)$_5$}], 1.42 [s, 9H, NC(CH$_3$)$_3$] ppm. ^{13}C{^{1}H}: δ 270.7 [d, 1C, N*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 80 Hz], 248.8 [d, 1C P*C*C(CH$_3$)$_3$, $^1J_{(PC)}$ 68 Hz] 116.4 [s, 10C,2{η^5-*C*$_5$(CH$_3$)$_5$}], 46.7 [d, 1C, PC*C*(CH$_3$)$_3$, $^2J_{(PC)}$ 23 Hz], 34.9 [d, 3C, NC*C*(CH$_3$)$_3$$^2J_{(PC)}$ 11 Hz], 34.5 [d, 1C, PCC(*C*H$_3$)$_3$, $^3J_{(PC)}$ 13 Hz], 31.2 [d, 1C, NCC(*C*H$_3$)$_3$ $^3J_{(PC)}$ 6 Hz], 12.6 [s, 10C, 2{η^5-C$_5$(*C*H$_3$)$_5$}] ppm. EIMS *m/z* (%): 575 (68) [M$^+$], 492 [M−(^{t}BuNC)]$^+$, 392 [M−(^{t}BuNC)−(PC^{t}Bu)]$^+$.

3.7. *X-ray structure determination of **4**, **9**, **11** and **12***

Intensity data for **4**, **9**, **11** and **12** were collected on a Quantum CCD/Rigaku AFC7 diffractometer at −80 °C using Mo–K$_\alpha$ graphite collimated radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied, and the structures were solved using direct methods and refined by full-matrix least-squares on *F* using the TEXSAN package. Anisotropic refinement was applied to all non-hydrogen atoms, and all hydrogen atoms were put at calculated positions. For **4**, sulfur, phosphorus and carbons of the *tert*-butyl group are disordered with occupancy factors of 55:45. In the case of **5**, selenium, phosphorus, and carbons of the *tert*-butyl group are disordered with occupancy factors of 57:43, and they are isotropically refined. These crystallographic data are summarised in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 174602–174605 for **4**, **9**, **11** and **12**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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