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The first 2,3-dihydro-1*H*-[1,2,4] triphosphole

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Abstract

Protonation of the lithium triphospha-cyclopentenyl salt Li ($P_3C_2Bu^t_2RR'$) (R = $(Me_3Si)_2CH$-, R′ = Bu^n) with HCl affords the new 2,3-dihydro-1*H*-[1,2,4] triphosphole $P_3C_2Bu^t_2$(H) (Bu^n)CH$(SiMe_3)_2$ which has been structurally characterised as its $[W(CO)_5]$ complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Triphosphole; Lithium triphospha-cyclopentenyl; Complexes

1. Introduction

Compounds containing P–C multiple bonds are of considerable current interest both on account of their organic reactivity and ligating properties [1–3]. Recently we reported [4] the synthesis of the first 1,2,4-triphosphole ring $P_3C_2Bu^t_2CH(SiMe_3)_2$ (**1**) via alkylation of the corresponding aromatic $P_3C_2Bu^t_2$ ring anion **2**. Unlike other phospholes, **1** was shown to exhibit a pronounced flattening of the formally sp^3 hybridised phosphorus and the ability to act as either a 2e, 4e, or 6e donor [4,5].

We subsequently prepared the triphosphole $P_3C_2(SiMe_3)_2CH(SiMe_3)_2$ in which, remarkably, the saturated phosphorus atom is actually completely planar [6].

Unlike the corresponding aromatic cyclopentadienyl ring systems the triphosphorus rings can be readily transformed into other novel pseudo-aromatic species. Thus, hydride ion transfer to **1**, affords the ring system $P_3C_2Bu^t_2CH(SiMe_3)_2H^-$, (**3**), whose ligating properties are very similar those of an η^5-cyclopentadienyl ligand anion, for example it readily acts as a four-centre 5e donor in both $[Ru(\eta^5\text{-}C_8H_{11})(\eta^4\text{-}P_3C_2Bu^t_2H(CH(SiMe_3)_2]$ and $[Co(CO)_2(\eta^4\text{-}P_3C_2Bu^t_2H(CH(SiMe_3)_2]$ [7,8].

Other members of the triphosphole family result from the reaction of **1** with alkyl lithium reagents, yielding the lithium salt of the triphosphacyclopentenyl anion $P_3C_2Bu^t_2(R)CH(SiMe_3)_2^-$, (**4**) (R = Me, Bu^n) [9]. Remarkably, **4** (R = Me) showed an unprecedented edge ligating mode in the nickel (II) compound $[Ni(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^2\text{-}\{P_3C_2Bu^t_2(Me)CH(SiMe_3)_2\}]$, (**5**) where the triphosphacyclopentenyl ring is unexpectedly bonded via the two saturated phosphorus atoms, rather than by the unsaturated η^3-ligated (CPC) allylic fragment [9].

2. Results and discussion

We now report that controlled protonation of **4** (R = Bu^n) can readily be achieved by treatment with an equimolar amount of HCl to give the first example of a 2,3-dihydro-1*H*-[1,2,4]triphosphole ring system, $P_3C_2Bu^t_2$(H)(Bu^n)CH$(SiMe_3)_2$, **6**. Compound **6** was identified by its $^{31}P\{^1H\}$-NMR spectrum, which shows the expected three doublets of doublets. Two of the resonances lie in the region expected for sp^3 hybridised phosphorus atoms (42.0 and 20.1 ppm, respectively), whereas the other resonance at 345.6 ppm is in the range typical for an sp^2 hybridised phosphorus atom. The two directly bonded sp^3 hybridised phosphorus atoms show the expected large one bond coupling ($^1J_{PP'}$ = 256.4 Hz). The formulation of **6** was further supported by its ^{1}H-

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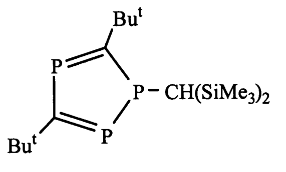

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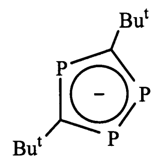

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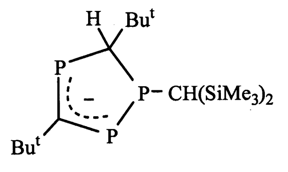

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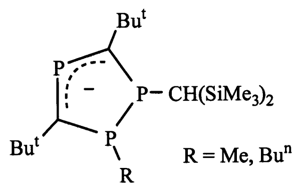

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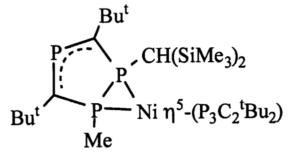

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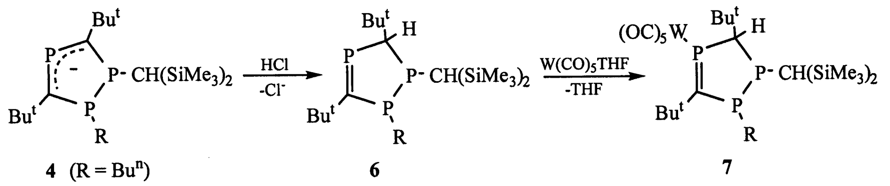

Scheme 1.

NMR and mass spectra and by its ready conversion to the pentacarbonyl tungsten complex [W(CO)$_5$(P$_3$C$_2$-Bu$^t_2$(H)(Bu^n)CH(SiMe$_3$)$_2$], **7** (see Scheme 1).

The ^{31}P{^{1}H}-NMR spectrum of **7** showed clearly that the mode of attachment of the [W(CO)$_5$] fragment was via the sp^2 hybridised phosphorus, since only this resonance (at 323.4 ppm) exhibits ^{183}W satellites ($^1J_{WP(X)} = 132.1$ Hz). The two remaining resonances at 55.3 and 35.1 ppm, can be attributed to the two saturated P atoms. Interestingly, when the parent triphosphole, **1**, acts as a 2e donor towards a platinum (II) centre, it also undergoes preferential co-ordination via the unique sp^2 hybridised phosphorus atom [5].

Full structural characterisation of **7** was by a single crystal X-ray diffraction study and its molecular structure is shown in Fig. 1, together with selected bond lengths and angles. As expected, the tungsten is bonded to the ring via the sp^2 hybridised phosphorus atom P(3). The sum of the bond angles around P(1), P(2) and C(6), clearly shows that these atoms are sp^3 hybridised, whereas the sum of the angles at both P(3) and C(7) are typical for sp^2 hybridisation. Furthermore, the shortest intra-cyclic P–C distance is that for the P(3)–C(7) double bond (1.700 Å), the remaining P–C bonds being much longer (P(3)–C(6) = 1.846, P(1)–C(6) = 1.875 and P(2)–C(7) = 1.803 Å, respectively), as expected for P–C single bonds [10–12].

It was anticipated that deprotonation of **6** might offer a useful route to regenerate **4**, but surprisingly it did not react at all with strong bases such as DBU or MeLi. Furthermore, **4** (R = Me), formed by treatment of **1** with MeLi, reacts with HCl to give several uncharacterised compounds, but no evidence for the formation of **6** (R = Me), so presumably the presence of the larger butyl group in **6** (R = Bu^n), provides the necessary stabilising effect.

3. Experimental

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. Column chromatography was carried out under an inert atmosphere.

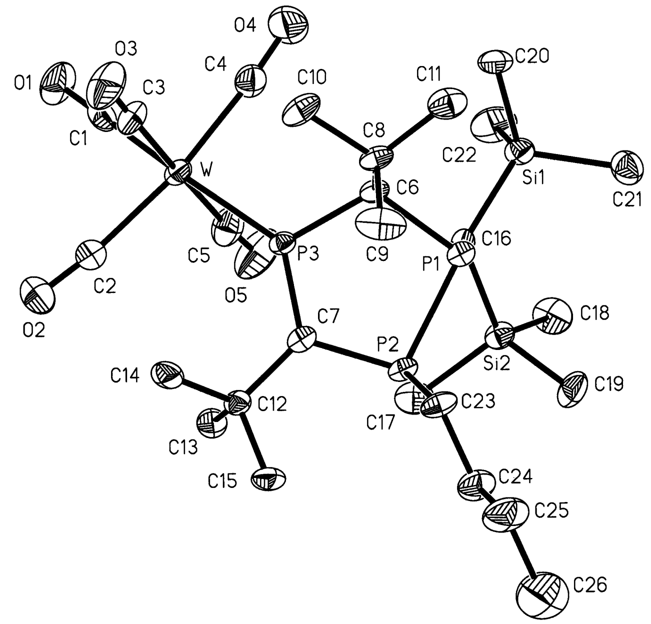

Fig. 1. Molecular structure of **7**. Selected bond lengths (Å) and angles (°): W–P(3) = 2.531(2), P(1)–C(6) = 1.875(7), P(1)–P(2) = 2.215(3), P(2)–C(7) = 1.803(8), P(3)–C(7) = 1.700(7), P(3)–C(6) = 1.846(7), P(1)–C(16) = 1.866(7), P(2)–C(23) = 1.875(7), C(1)–W–P(3) = 175.3(2), C(2)–W–P(3) = 98.8(2), C(3)–W–P(3) = 92.9(2), C(4)–W–P(3) = 89.9(2), C(5)–W–P(3) = 85.4(2), C(16)–P(1)–P(2) = 102.2(2), C(6)–P(1)–P(2) = 97.4(2), C(16)–P(1)–C(6) = 101.2(3), C(7)–P(2)–C(23) = 111.2(3), C(7)–P(2)–P(1) = 104.4(3), C(23)–P(2)–P(1) = 104.0(3), C(7)–P(3)–P(6) = 105.0(3), C(7)–P(3)–W = 133.4(3), C(6)–P(3)–W = 119.0(2), C(8)–C(6)–P(3) = 112.8(5), C(8)–C(6)–P(1) = 114.2(5), P(3)–C(6)–P(1) = 110.2(4), C(12)–C(7)–P(3) = 122.8(5), C(12)–C(7)–P(2) = 119,0(5), P(3)–C(7)–P(2) = 116.9(4).

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.

3.1. Preparation of $P_3C_2Bu^t_2(H)(Bu^n)CH(SiMe_3)_2$ (**6**)

Exactly 0.41 ml of Bu^nLi (standardised 2.46 M in hexanes, 1.0 mmol) was added dropwise to a solution of $P_3C_2Bu^t_2CH(SiMe_3)_2$ (**1**) (0.45 g, 1.0 mmol) in THF (10 ml) previously cooled to −78 °C. The resulting deep red solution was stirred for 10 min after which 0.99 ml of HCl (1.00 M in Et_2O, 0.99 mmol) was added dropwise. The solution, which turned pale yellow, was then allowed to warm to room temperature (r.t.). Solvents were removed in vacuo and the residual oil was purified by column chromatography using hexane as the eluting solvent, yielding **6** (0.32 g, 72% yield) but a satisfactory elemental analysis was not possible.

3.1.1. Spectroscopic data for 6

Spectroscopic data: for **6**: NMR(C_6D_6, 298K): δ_H(300 MHz) 0.18 (s, 18H, $(Si(CH_3)_3)_2$), 1.55 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.4$ Hz); 1.58 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.5$ Hz), 1.62 (d of t, 3H, CH_3, $^3J_{HH} = 3.8$ Hz $^4J_{HP} = 1.3$ Hz), 1.71–1.76 (m, 6H, $CH_2CH_2CH_2$), 2.12 (d of d, 1H, CH, $^2J_{HP} = 13.3$ Hz, $^3J_{HP} = 8.7$ Hz), 2.89 (dd, 1H, CH (ring), $^2J_{HP} = 14.1$ Hz, $^2J_{HP} = 9.2$ Hz). δ_P(121.7 MHz) 345.6 (d of d, P(X), $^2J_{P(X)P(B)} = 22.7$ Hz, $^2J_{P(X)P(A)} = 17.6$ Hz), 42.0 (d of d, P(B), $^1J_{P(A)P(B)} = 256.4$ Hz, $^2J_{P(B)P(X)} = 22.7$ Hz), 20.1 (d of d, P(A), $^1J_{P(A)P(B)} = 256.4$ Hz, $^2J_{P(A)P(X)} = 17.6$ Hz). MS data (EI): *m/z* 448 (M^+).

3.2. Preparation of $[W(CO)_5(P_3C_2Bu^t_2(H)(Bu^n)CH(SiMe_3)_2]$ (7)

To **6** (0.30 g, 1.0 mmol) in THF (5 ml), was added $[W(CO)_5[(THF)]$ (1.5 mmol) in THF (15 ml) and after stirring the solution for 14 h, the metal complexes in the reaction mixture were identified by their $^{31}P\{^1H\}$-NMR spectral data. Removal of the solvent produced an orange solid, which was purified by column chromatography using hexane as the eluting solvent to give **7** (0.53 g, 68% yield). Recrystallisation from p.e. (60–80 °C) at −10 °C afforded orange crystals of **7** suitable for X-ray diffraction study.

3.2.1. Spectroscopic data for 7

Spectroscopic data: for **7**: NMR(C_6D_6, 298K): δ_H(300 MHz) 0.38 (s, 18H, $(Si(CH_3)_3)_2$), 1.09 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.2$ Hz), 1.29 (d, 9H, $C(CH_3)_3$, $^4J_{HP} = 1.3$ Hz), 1.67 (d of t, 3H, CH_3, $^3J_{HH} = 3.8$ Hz $^4J_{HP} = 1.3$ Hz), 1.75–1.79 (m, 6H, $CH_2CH_2CH_2$), 2.03 (d of d, 1H, CH, $^2J_{HP} = 11.3$ Hz, $^3J_{HP} = 6.9$ Hz), 2.93 (d of d, 1H, CH (ring), $^2J_{HP} = 13.3$ Hz, $^2J_{HP} = 7.8$ Hz). δ_P(121.7 MHz) 323.4 (d of d, P(X), $^1J_{P(X)W} = 132.1$ Hz, $^2J_{P(X)P(B)} = 28.7$ Hz, $^2J_{P(X)P(A)} = 20.3$ Hz), 55.3 (d of d, P(B), $^1J_{P(A)P(B)} = 262.3$ Hz, $^2J_{P(B)P(X)} = 20.3$ Hz), 35.1 (d of d, P(A), $^1J_{P(A)P(B)} = 262.3$ Hz, $^2J_{P(A)P(X)} = 28.7$ Hz). MS data (EI): *m/z* 772 (M^+).

3.2.2. Crystal data for 7

Crystal data: for **7**: $WP_3Si_2O_5C_{26}H_{47}$, $M = 772.58$, monoclinic $P2_1/n$ (non-standard No. 14), $a = 9.554(7)$, $b = 16.909(5)$, $c = 21.728(10)$ Å, $\beta = 94.90(5)$, $V = 3497(3)$ Å^3, $T = 173(2)$, $Z = 4$, $\mu = 3.539$ mm^{-1}, $\lambda = 0.71073$ Å, 6518 reflections collected, 6136 independent ($R_{int} = 0.057$), $R_1 = 0.0457$, $wR_2 = 0.1091$ for $I > 2\sigma I$, $R_1 = 0.0667$, $wR_2 = 0.1228$ for all data. Data collection were carried out using an Enraf-Nonius CAD4 diffractometer.

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