

Synthesis and coordination chemistry of 1,3,5-triphosphabicyclo[2.1.0]-pent-2-ene

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Room temperature electrocycloislation of the 1,2,4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ affords the new 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene which undergoes a very rapid [1,3]-phosphorus migration which can be stopped by coordination of $[W(CO)_5]$; the two isomeric phosphorus compounds react differently with $[PtCl_2(PEt_3)_2]$, the latter *via* an insertion of the metal into the P–P bond and a chlorine migration reaction to afford *trans*- $[PtCl(PEt_3)_2P_2C_2-Bu^t_2PClCH(SiMe_3)_2]$, the molecular structure of which has been determined by a single crystal X-ray diffraction study.

We recently showed¹ that the activation barrier for the [1,3]-phosphorus migration in the hypothetical 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene $P_3C_2H_3$ **1** is estimated (MP4SDTQ/6-31G*/MP2/6-31G*+ZPE) to be only 11.62 kcal mol⁻¹, which is considerably smaller than the barrier (31.13 kcal mol⁻¹) for the corresponding [1,3]-carbon migration in the structurally related hydrocarbon C_5H_6 **2**. We attributed the much more facile migration within the phosphorus system to favourable cleavage of the weak P–P bond in **1** compared to the strong C–C bond in **2** and to the suprafacial pathway in both systems, which requires the migrating atom to become planar, and is therefore much more favourable for phosphorus than carbon (see Scheme 1). We now present the first experimental support for these proposals with the synthesis of 1-bis-(trimethylsilylmethyl)-1,3,5-triphosphabicyclo[2.1.0]pent-2-ene **3** and a study of its dynamic behaviour and ligating properties.

The recently described² 1,2,4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ **4** readily undergoes a slow electrocycloislation reaction on long standing in sunlight at room temperature, to afford the new isomeric 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene **3** (Fig. 1). The reaction, which is accelerated by irradiation with a tungsten lamp (100 W), is about 60% complete after one week.

When the electrocycloislation reaction is monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the original three doublet-of-

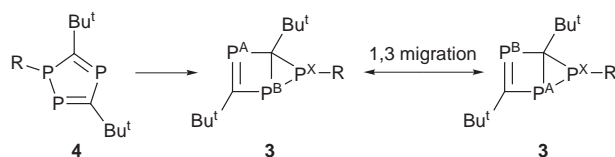
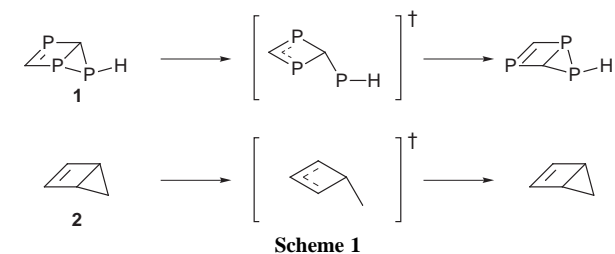
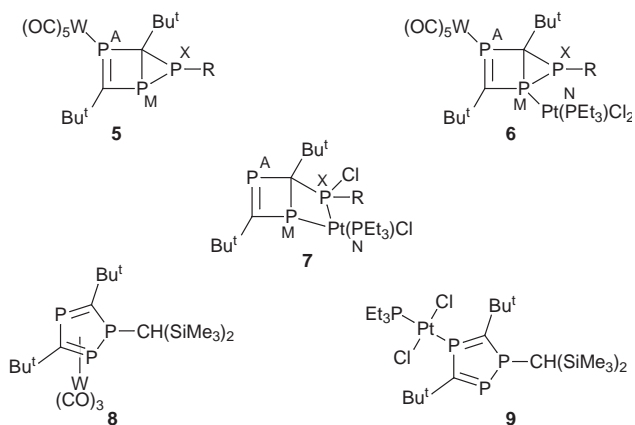


Fig. 1 R = CH(SiMe₃)₂

doublets resonances (δ_P 244.4 P_(A), 180.0 P_(B) and 112.0 P_(X)) of **4** steadily disappear and are replaced by two new resonances attributed to **3** (a doublet δ_P 166.6 and a triplet δ_P 24.1). The simplicity of the $^{31}P\{^1H\}$ NMR spectrum of **3** shows that two phosphorus atoms P_(A) and P_(B) become magnetically equivalent because of the fast [1,3]-sigmatropic rearrangement of **3**. On cooling the sample the doublet resonance broadens but the dynamic process is still evident even at -110 °C.

The migration process of P_(X) from P_(A) to P_(B) can however be stopped completely by ligation of a $[W(CO)_5]$ fragment to **3**. Thus $[W(CO)_5(THF)]$ readily reacts with **3** in THF at room temperature to afford the red η^1 -complex $[W(CO)_5P_3C_2-Bu^t_2CH(SiMe_3)_2]$ **5** in 70% yield. The mode of attachment of



the $[W(CO)_5]$ fragment was established as being *via* the unique sp²-hybridised phosphorus P_(A), by its $^{1}P\{^1H\}$ NMR spectrum which shows three resonances (δ_P 270.7 P_(A), 33.8 P_(M) and -78.8 P_(X)), each occurring as a doublet of doublets. The high field shifts of P_(M) and P_(X) are typical for sp³-hybridised phosphorus atoms and each exhibits the expected large direct one-bond coupling ($^1J_{P(M)P(X)} = 151.3$ Hz). The low field P_(A) resonance, which is typical of an sp²-hybridised phosphorus, also shows two additional two-bond couplings ($^2J_{P(A)P(M)} = 83.8$ Hz and $^2J_{P(A)P(X)} = 21.7$ Hz) and the characteristic ^{183}W satellites ($^1J_{PW} = 229.3$ Hz). Isomers **3** and **4** thus behave quite differently towards zerovalent tungsten, the latter giving only the η^5 -complex $[W(CO)_3P_3C_2Bu^t_2CH(SiMe_3)_2]$ **8** under a variety of reaction conditions.³

$[PtCl_2(PEt_3)_2]$ reacts with **5** in THF at room temperature to afford the yellow bimetallic complex *trans*- $[PtCl_2(PEt_3)_2W(CO)_5P_3C_2Bu^t_2CH(SiMe_3)_2]$ **6** (79% yield) with a similar structure to **5**, in which the additional $[PtCl_2(PEt_3)_2]$ fragment becomes attached to the sp³-hybridised phosphorus at the junction of the 3- and 4-membered rings, as was established spectroscopically.[‡]

The identity of the 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene, **3**, was confirmed by its unusual reaction with $[PtCl_2(PEt_3)_2]$ at room temperature, to give the yellow air-stable complex *trans*- $[PtCl(PEt_3)_2P_2C_2Bu^t_2PClCH(SiMe_3)_2]$ **7** (77% yield), the molecular structure of which was confirmed spectroscopically[‡] and by a single crystal X-ray diffraction study. The reaction

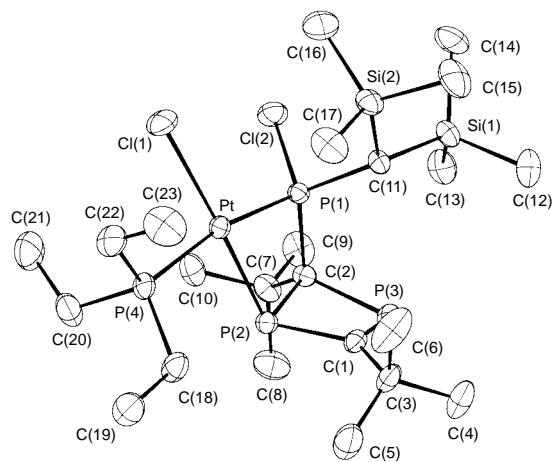


Fig. 2 Molecular structure of *trans*-[PtCl(PEt₃)P₂C₂Bu₂PClCH(SiMe₃)₂] **7** together with the atomic numbering scheme and some selected bond lengths (Å) and angles (°): Pt–P(1) 2.263(1), Pt–P(2) 2.299(1), Pt–P(4) 2.322(2), Pt–Cl(1) 2.381(2), P(1)–C(11) 1.826(5), P(1)–C(2) 1.877(5), P(1)–Cl(2) 2.062(2), P(2)–C(1) 1.820(5), P(2)–C(2) 1.907(5), P(3)–C(1) 1.698(5), P(3)–C(2) 1.876(5), P(1)–Pt–P(2) 71.90(5), P(1)–Pt–P(4) 167.25(5), P(2)–Pt–P(4) 95.42(5), P(1)–Pt–Cl(1) 100.38(6), P(2)–Pt–Cl(1) 164.50(6), P(4)–Pt–Cl(1) 91.63(6)

involves both an insertion of the metal–ligand fragment into the weak P–P bond of the three-membered ring of **3** and a chlorine migration from platinum to phosphorus. Clearly the dynamic behaviour of **3**, involving rapid breaking and remaking of the P–P bond, facilitates the insertion step.

We previously reported⁴ a similar ring opening and chlorine transfer from Pt^{II} to phosphorus in the reaction of [PtCl₂(CNR)₂] (R = Bu^t, *p*-MeOC₆H₄) with the three-membered phosphirene ring PPhCPh=CPh to form the dimeric chlorophosphane complex [PtCl(PClPhCPh=CPh)(CNBu^t)₂].

The mass spectrum of compound **7** exhibits a molecular ion peak at *m/z* 774 and the expected fragmentation pattern and the ³¹P{¹H} NMR spectrum exhibits the anticipated pattern of lines arising from an [AMNX] spin system. § The molecular structure of **7**, shown in Fig. 2, was established by a single crystal X-ray diffraction study¶ and is in full accord with the NMR spectroscopic data. The symmetry around the Pt^{II} atom is close to idealised square planar geometry, and the Pt–P distances and the P=C double bond length [P(3)–C(1) 1.698(5) Å] are typical.^{5,6} Isomers **3** and **4** thus also behave quite differently towards divalent platinum, the latter giving the η¹-complex *trans*-[PtCl₂(PEt₃)P₃C₂Bu₂CH(SiMe₃)₂] **9** in which the platinum is attached to the unsaturated phosphorus lying between the two ring carbon atoms.⁷

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Notes and References

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‡ *Synthesis*. *trans*-[PtCl₂(PEt₃)(W(CO)₅)P₃C₂Bu₂CH(SiMe₃)₂] **6**: to a solution of [{W(CO)₅}P₃C₂Bu₂CH(SiMe₃)₂] **5** (120 mg, 0.195 mmol) in chloroform (5 ml), at room temperature, was slowly added a solution of [PtCl₂(PEt₃)₂] (75.0 mg, 0.097 mmol) dissolved in chloroform (10 ml). The resulting mixture was stirred for 8 h and the solvent removed *in vacuo*. The yellow solid was washed with light petroleum (bp 60–80 °C; 5 ml) to give **6** (155 mg, 79%). ³¹P{¹H} NMR data (101.3 MHz, CDCl₃, 25 °C): δ_p 304.6 (dd, P_(A), ¹J_{P(A)W} = 251.2, ²J_{P(A)P(M)}} = 65.1, ²J_{P(A)P(X)}} = 26.8 Hz); 82.9 (ddd, P_{(M)}}, ¹J_{P(M)Pt}} = 2422, ²J_{P(M)P(N)}} = 529.1, ¹J_{P(M)P(X)}} = 200.3, ²J_{P(M)P(A)}} = 65.1 Hz); 11.1 (dd, P_{(N)}}, ¹J_{P(N)Pt}} = 2767, ²J_{P(N)P(M)}} = 529.1 Hz); –99.4 (dd, P_{(X)}}, ¹J_{P(X)P(M)}} = 200.3, ²J_{P(X)P(A)}} = 26.8 Hz).

§ *Synthesis*. *trans*-[PtCl(PEt₃)P₂C₂Bu₂PClCH(SiMe₃)₂] **7**: [PtCl₂(PEt₃)₂] (145 mg, 0.19 mmol) was added, as a solid, to a solution of P₃C₂Bu₂CH(SiMe₃)₂ **3** (160 mg, 0.41 mmol) in chloroform (10 ml), and stirred for 8 h. The yellow solid was filtered and washed with light petroleum (bp 60–80 °C; 5 ml) to give **7** (230 mg, 77% yield). Recrystallisation from THF–light petroleum (bp 30–40 °C) gave yellow crystals (mp 186 °C) suitable for the X-ray diffraction study (Found: C, 35.70; H, 6.71; C₂₃H₅₂Cl₂Si₂P₄Pt requires C, 35.66; H, 6.77%). ¹⁹⁵Pt{¹H} NMR data (53.8 MHz, CDCl₃, 25 °C): δ –3974 (dddd, Pt, ¹J_{PtP(X)}} = 2884, ¹J_{PtP(N)}} = 2778, ¹J_{PtP(M)}} = 564.5, ³J_{PtP(A)}} = 216.2 Hz). ³¹P{¹H} NMR data (101.3 MHz, CDCl₃, 25 °C): δ_p 371.0 (dd, P_(A), ³J_{P(A)Pt}} = 216.2, ²J_{P(A)P(M)}} = 59.0, ²J_{P(A)P(X)}} = 11.2 Hz); 117.6 (dd, P_{(X)}}, ¹J_{P(X)Pt}} = 2884, ²J_{P(X)P(N)}} = 540.1, ²J_{P(X)P(A)}} = 11.2 Hz); 10.2 (d, P_{(N)}}, ¹J_{P(N)Pt}} = 2778, ²J_{P(N)P(X)}} = 540.1 Hz); –13.9 (d, P_{(M)}}, ¹J_{P(M)Pt}} = 564.5, ²J_{P(M)P(A)}} = 59.0 Hz). ¹H NMR data (250.2 MHz, CDCl₃, 25 °C): δ 1.94 (d, 1 H, CH, ²J_{HP}} = 6.3 Hz); 1.90 [m, 6 H, 3(CH₂)]; 1.47 [s, 9 H, C(CH₃)₃]; 1.27 [s, 9 H, C(CH₃)₃]; 1.13 [dt, 9 H, 3(CH₃)], ³J_{HP}} = 16.0, ³J_{HH}} = 7.5 Hz); 0.58 [s, 9 H, Si(CH₃)₃]; 0.35 [s, 9 H, Si(CH₃)₃]. Mass spectrum (EI): *m/z* 774 [PtCl(PEt₃)P₂C₂Bu₂PClCH(SiMe₃)₂]⁺ (30%), 674 [PtCl(PEt₃)PCBu^tPClCH(SiMe₃)₂]⁺, 390 [P₂C₂Bu₂PCH(SiMe₃)₂]⁺, 73 [SiMe₃]⁺.

¶ *Crystal data* for **7**, C₂₃H₅₂Cl₂Si₂P₄Pt, *M* = 774.7, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 18.545(2), *b* = 10.943(5), *c* = 16.745(3) Å, β = 95.14(1)°, *U* = 3385(2) Å³, *Z* = 4, *D*_c = 1.52 g cm^{–3}. Crystal size 0.3 × 0.3 × 0.2 mm. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer using Mo–Kα radiation, λ = 0.71073 Å, μ = 45.8 cm^{–1}. A total of 9818 unique reflections were measured, of which 6979 had *I* > 2σ(*I*). Non-H atoms were located by direct methods (SHELXS-86) and the structure was refined by full-matrix least-squares (SHELXL-93), non-H atoms anisotropic. *R*₁ = 0.042, *wR*₂ = 0.117 (all data). CCDC 182/897.

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