Synthesis, crystal structure and theoretical studies of the first *endo*:*endo*-2,4-diphosphabicyclo[1.1.0]butane†

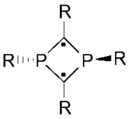
Cameron Jones,* Jamie A. Platts* and Anne F. Richards

Department of Chemistry, University of Wales, Cardiff, PO Box 912, Park Place, Cardiff, UK CF10 3TB.
E-mail: jonesca6@cardiff.ac.uk

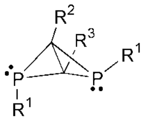
Received (in Cambridge, UK) 29th January 2001, Accepted 27th February 2001
First published as an Advance Article on the web 16th March 2001

The reaction of $PbCl_2$ with *Z*-[CyP=C(Bu^t)MgCl(OEt_2)] (Cy = cyclohexyl) affords the first example of an *endo*:*endo*-2,4-diphosphabicyclo[1.1.0]butane, $Cy_2P_2C_2Bu^t_2$, which displays unusual spectroscopic and geometric properties, the origins of which have been explored by theoretical calculations.

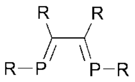
Because of their unusual properties and application to organic transformations, strained hydrocarbon rings and cages have been the subject of intense investigation.[1] In recent years this attention has extended to the phosphorus substituted analogues of these systems, often with remarkable results.[2] For example, Niecke *et al.* have succeeded in preparing several stable, crystalline, diradical 1,3-diphosphacyclobutanediyls **I**.[3] Thermal valence isomerisations of these have yielded 1,2-dihydro-1,2-diphosphetes **IV**[4] whilst a photolytic isomerisation has yielded the only example of a 2,4-disphosphabicyclo[1.1.0]butane **II** (R^1 = Mes* ($C_6H_2Bu^t_3$-2,4,6), R^2 = $SiMe_3$, R^3 = H, **1**) which has *exo*:*endo*-phosphorus substituents.[3] Indeed, compound **1** can itself thermally valence isomerise to the corresponding 1,4-diphosphabutadiene **III**. The relative stabilities of these isomers have been calculated to be in the order **I** < **II** < **III** < **IV**.[3–5] Compounds of the general type **III** and **IV** are now relatively common and have found a number of applications as building blocks in organophosphorus and organometallic chemistry, and as ligands in the formation of novel coordination compounds.[2,6] Despite this, examples of **I** and **II** are very rare and their preparation can be challenging. We have developed a high yielding stereospecific route to a range of phosphavinyl Grignard reagents, *e.g.* *Z*-[CyP=C(Bu^t)MgCl(OEt_2)] (Cy = cyclohexyl) **2**,[7] which we saw as potential precursors to $P_2C_2R_4$ heterocycles such as **I** and **II** *via* oxidative coupling reactions. The results of our endeavours in this area are reported herein.



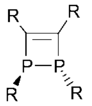
I



II



III

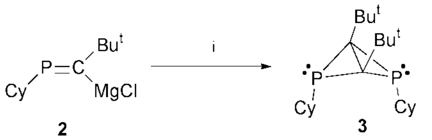


IV

Treatment of an ethereal solution of $PbCl_2$ with 2 equivalents of **2** at −78 °C led to the deposition of lead metal and the stereoselective formation of the diphosphabicyclo[1.1.0]butane **3** in 60% yield (Scheme 1). The reaction also occurs with $SnCl_2$ though in lower (30%) yield. The mechanism of this reaction presumably involves an organolead intermediate, *Z,Z*-[Pb{C(Bu^t)=PCy}$_2$], though this could not be detected when the reaction was followed by ^{31}P NMR spectroscopy. The formation of **3** contrasts with the reaction between **2** and Me_2SnCl_2 which does not lead to an oxidative coupling but to *Z,Z*-[Me_2Sn{C(Bu^t)=PCy}$_2$] as the major product.[8] Interestingly, **3** was found to be remarkably stable (mp 118 °C) and did not valence isomerise in refluxing toluene over 10 h or when treated with UV light (*cf.* the facile thermal isomerisation of **1**).

Most of the spectroscopic data‡ for **3** are consistent with its proposed structure. However, its $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ 12 ppm which is far removed from the expected region (upfield of δ −80 ppm, *e.g.* δ −83 and −84 ppm for **1**) for three-membered phosphirane rings[2,9] but close to values normally observed for examples of **I**.[3,4] In addition, the signal for the framework carbon atoms appears as a triplet at δ 60.3 ppm, $^1J_{PC}$ 52 Hz, which is significantly downfield of the values for **1**, δ 28.3 ppm, and phosphirane rings in general.[9] We hoped to shed light on these apparent inconsistencies by carrying out density functional studies[10] on the three possible stereoisomers of tetramethyl-2,4-disphosphabicyclo[1.1.0]butane. A summary of the results of this preliminary investigation is shown in Table 1.

It is clear that the *endo*:*endo* isomer is the thermodynamically least favourable of the three isomers but probably forms in the case of **3** due to stereochemical constraints on the coupling reaction. The calculated ^{31}P NMR shift for **4** is close to the experimental value for **3** and more than 100 ppm downfield of the values for **5**, **6** and the experimentally observed compound **1**.[3] Unfortunately there are no known examples of *exo*:*exo* diphosphabicyclobutanes for purpose of comparison. An explanation for the low field ^{31}P and ^{13}C NMR shifts for **3**



2 3

Scheme 1 *Reagents and conditions:* i, 1/2 $PbCl_2$, Et_2O, −78 °C, −$MgCl_2$, − $Pb_{(s)}$

Table 1 Calculations on tetramethyl-2,4-diphosphabicyclo[1.1.0]butane isomers

	Endo:*endo* (C_2) **4**	*Exo*:*exo* (C_{2v}) **5**	*Endo*:*exo* (C_s) **6**
Relative energy/kJ mol^{-1}	25.5	6.5	0.0
^{31}P NMR/ppm	19 (12)[a]	−171	−104, −143 (−83, −84)[b]
Fold angle (PCCP)/°	131.7 (131.6)[a]	109.5	117.5 (117)[a]
C_{ring}–C_{ring}/Å	1.53 (1.54)[a]	1.48	1.50 (1.51)[b]
Σ angles on P/°	275.6 (280.2)[a]	247.3	266.3, 251.0 (257.1, 253.8)[b]

Geom. calculations: B3LYP/6-31 + G(d,p); energy and NMR calculations: B3LYP/6-311++G(d,p).[10] [a] Experimental values for **3**. [b] Experimental values for **1**.[3]

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† Electronic supplementary information (ESI) available: calculation data and atomic coordinates for compounds **4**–**6**. See http://www.rsc.org/suppdata/cc/b1/b100993l/

DOI: 10.1039/b100993l

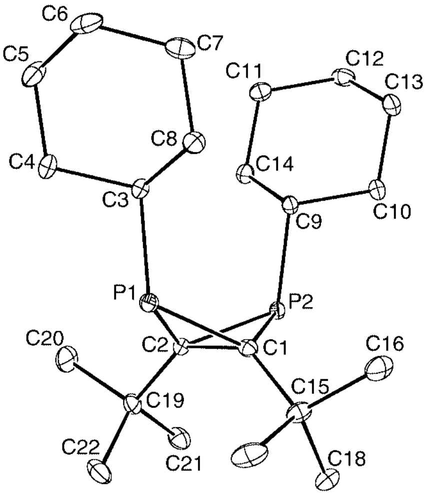

Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.833(3), P(1)–C(2) 1.826(3), P(1)–C(3) 1.875(3), P(2)–C(1) 1.819(3), P(2)–C(2) 1.832(3), P(2)–C(9) 1.859(3), C(1)–C(2) 1.543(4); C(2)–P(1)–C(1) 49.89(13), C(2)–P(1)–C(3) 113.03(13), C(1)–P(1)–C(3) 117.25(13), C(1)–P(2)–C(2) 50.01(13), C(1)–P(2)–C(9) 112.39(13), C(2)–P(2)–C(9) 116.47(13), C(15)–C(1)–C(2) 138.0(3), C(19)–C(2)–C(1) 138.0(3).

may be drawn from its geometry (Fig. 1).§ The fold angle between its two PCC rings is in good agreement with theoretical calculations on **4** and markedly greater than in **1**,[3] **5** and **6**. There is a concomitant loss of pyramidalisation of its P- and framework C-centres relative to **1** and **6** and a lengthening of the transannular bond. Thus it is possible that the bonding in the P_2C_2 frameworks of the *endo*:*endo* isomers, **3** and **4**, lies closer to that reported for partially delocalised 1,3-diphosphacyclobutanediyls than does the bonding in the *endo*:*exo* isomers, **1** and **6**. In this context it is noteworthy that the two general valence isomers **I** and **II** have been described as bond stretch or orbital isomers.[3,4]

We are currently carrying out more extensive calculations to determine the nature of any bonding differences in **4**–**6**. We are also further investigating valence isomerisations of **3** and related compounds, in addition to exploring the versatility of **2** as a synthon in the formation of other strained organophosphorus heterocycles and cages. The results of these studies will appear in forthcoming publications.

We gratefully acknowledge financial support from the EPSRC (studentship for A. F. R) and for access to the UK Computational Chemistry Facility.

Notes and references

‡ *Spectroscopic data* for **3**: $^{31}P\{^1H\}$ NMR (145.8 MHz, C_6D_6) δ 12 (s, PCy); ^1H NMR (400 MHz, C_6D_6) δ 1.17 (s, 18H, Bu^t), 0.80–1.75 (m, 22H, Cy); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K) δ 24.9 (CH_2), 26.1 (CH_2, $^3J_{PC}$ 6 Hz), 30.3 (CH_2, $^2J_{PC}$ 11 Hz), 30.9 ($C(CH_3)_3$, $^3J_{PC}$ 7 Hz), 31.5 (CH, $^1J_{PC}$ 62, $^3J_{PC}$ 11 Hz), 32.5 ($C(CH_3)_3$, $^2J_{PC}$ 14 Hz), 60.3 (PCP, $^1J_{PC}$ 52 Hz); IR ν/cm^{-1} 1458m, 1376m, 1259m, 847m, 802m, 720 m; MS APCI *m*/*z* (%): 366 (M^+, 100); satisfactory elemental analysis obtained.

§ *Crystal data* for **3**: $C_{22}H_{40}P_2$ M = 366.48, orthorhombic, space group $P2_12_12_1$, a = 9.945(2), b = 14.071(3), c = 16.065(3) Å, V = 2248.1(8) Å^3, Z = 4, D_c = 1.083 g cm^{-3}, $F(000)$ = 808, μ(Mo-Kα) = 1.95 cm^{-1}, 150(2) K, 2303 unique reflections, R (on F) 0.0417, wR (on F^2) 0.1223 ($I > 2\sigma I$).

CCDC 157235. See http://www.rsc.org/suppdata/cc/b1/b100993l/ for crystallographic data in .cif or other electronic format.

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10 Full details of calculations have been submitted as supplementary material (ESI).†