www.rsc.org/chemcomm

ChemComm

Development of a new sterically protecting auxiliary of the metacyclophane type and application to unsymmetrical diphosphenes, 1,3-diphosphaallene and 1,4-diphosphabutatriene⁺

Kozo Toyota, Akitake Nakamura and Masaaki Yoshifuji*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan. E-mail: voshifi@mail.cc.tohoku.ac.jp; Fax: +81-22-217-6562; Tel: +81-22-217-6558

Received (in Cambridge, UK) 3rd October 2002, Accepted 31st October 2002 First published as an Advance Article on the web 15th November 2002

A new bulky bromobenzene of the metacyclophane type was converted to an unsymmetrically substituted 1,4-diphosphabutatriene whose spin-spin coupling constant $({}^{3}J_{PP})$ turned out to be larger, for the first time, than the ${}^{2}J_{PP}$ value of the corresponding 1,3-diphosphaallene.

Sterically protected heterocumulenes¹⁻⁶ containing multiple bonds of the heavier main-group elements, such as silaallenes² and phosphaallenes⁴ attract current attention. Heterocumulenes containing two or three heavy atoms7-11 have also been of interest. Utilizing an extremely bulky 2,4,6-tri-tert-butylphenyl (Mes*) group as a sterically protecting auxiliary,¹² we have reported the preparation of the first 1-phosphaallenes,^{4a} as well as the first symmetrical^{7a} and unsymmetrical 1,3-diphosphaallenes.^{7e} Although Märkl and Kreitmeier prepared the first symmetrically substituted 1,4-diphosphabutatriene,^{10a} we have reported an alternative synthesis of the diphosphabutatriene^{10b,c} as well as the preparation of tungsten complexes of the diphosphabutatriene.^{10c} However, preparation of an unsymmetrically substituted and metal-free 1,4-diphosphabutatriene remained unexplored.

In the course of our study of new sterically demanding groups and systematic modification of the Mes* group, we have prepared various bulky bromobenzenes containing the Mes* framework.^{13,14} We now report utilization of new bulky arenes of the metacyclophane type as a sterically protecting auxiliary and the preparation of unsymmetrically substituted 1,4-diphosphabutatrienes for the first time as well as unsymmetrical diphosphene and 1,3-diphosphaallene.

Preparation of 7a starting from 2-bromo-1,3-bis(bromomethyl)benzene (1)15 is shown in Scheme 1. The bis-Wittig



reaction of 4a using ylide 5 [Ph₃P=CH(CH₂)₅CH=PPh₃] gave a mixture of (Z,Z)-6a and (E,Z)-6a [(Z,Z)-6a : (E,Z)-6a = 9:16]. Catalytic hydrogenation of the mixture afforded a met-

† Electronic supplementary information (ESI) available: Physical data. See http://www.rsc.org/suppdata/cc/b2/b209666h/



Scheme 1 Reagents and vield: i. KCN, 18-crown-6, MeCN, H₂O, 96%; ii. MeI, KOH, DMSO, H₂O, 60%; iii, DIBAL-H, hexane, C₆H₆, 81%; iv, 5, THF, 58% (isomeric mixture); v, H₂, PtO₂, EtOH, 97%; vi, n-BuLi, THF then PCl₃; vii, Mes*P(H)Li, THF, then DBU, 50% based on 7a; viii, CCl₄, n-BuLi, THF, 20% [64% of (E)-9 was recovered]; ix, t-BuLi, THF, 77%; x, Mes*P=C=C(Li)Tms, THF; xi, KF, 18-crown-6, toluene, 12% for (E)-12 (based on 7a).

acyclophane derivative 7a. Similarly, 4b¹⁴ was converted to 7b, *via* **6b** [(Z,Z)-6b:(E,Z)-6b = 11:9], in 87% overall yield.[‡]

Then preparations of low coordinated phosphorus compounds bearing the new sterically protecting group were examined, as follows. Lithiation of 7a with butyllithium followed by reaction with PCl₃ afforded the corresponding phosphonous dichloride 8 [³¹P NMR (162 MHz, C₆D₆) $\delta_{\rm P}$ = 152.4]. Reaction of 8 with Mes*P(H)Li¹⁶ followed by dehydrochlorination using DBU afforded an unsymmetrical diphosphene (E)-9.

The structures of 7a and (E)-9 were unambiguously determined by X-ray crystallography (Figs. 1 and 2).¹⁷ The -P=P- moiety in (E)-9 is distorted from planarity: the torsion angle C(1)-P(1)-P(2)-C(22) is 167.7(2)° whereas in Mes*P=P-Mes*, 12a the corresponding torsion angle is $172.2(1)^{\circ}$. This may be attributable to molecular packing in the crystal, because the large methylene bridge pushes the aryl substituent of the neighboring molecules. Interplanar angles between the average plane of C(1)-P(1)-P(2)-C(22) and average aromatic ring planes [C(1)-C(6) and C(22)-C(27)] are 73.4(1)° and 68.96(10)°, respectively.

When (E)-9 was treated with carbon tetrachloride and butyllithium,7d 3,3-dichloro-1,2-diphosphirane 10 was obtained in 20% yield [$\delta_P(C_6D_6) = -65.3$ and -63.4, AB, ${}^1J_{PP} = 136.1$ Hz], and 64% of (E)-9 was recovered. Reaction of 10 with tertbutyllithium afforded stable 1,3-diphosphaallene 11: [MS m/z604 (M⁺) and 548 (M⁺- *t*-Bu + 1)]. Contrary to the case of **11**, attempted synthesis of 1-(2,4,6-tri-tert-butylphenyl)-



Fig. 1 Molecular structure of 7a, showing the atomic labelling scheme with thermal ellipsoids (30% probability).

10.1039/b209666h



Fig. 2 Molecular structure of (*E*)-**9**, showing the atomic labelling scheme with thermal ellipsoids (30% probability). Some selected bond lengths (Å) and angles (°): P(1)-P(2), 2.039(2); P(1)-C(1), 1.861(4); P(2)-C(22), 1.861(4); P(2)-P(1)-C(1), 101.4(1); P(1)-P(2)-C(22), 97.9(1).

3-(2,4,6-triisopropylphenyl)-1,3-diphosphaallene resulted in formation of the corresponding dimer.¹⁸

Finally, **8** was converted to the first unsymmetrically substituted metal-free 1,4-diphosphabutatriene, in a similar manner to that reported by Märkl and Kreitmeier.^{10a} Reaction of Mes*P=C=C(Li)Tms with **8** in THF followed by treatment with KF and 18-crown-6 under refluxing toluene gave a mixture of (*E*)-**12** and (*Z*)-**12** [4:1 ratio]. After column chromatographic treatment (SiO₂-hexane), (*E*)-**12** was isolated in 12% yield as yellow solid [MS m/z 616 (M⁺)]. ¹³C{¹H} NMR (100 MHz) spectrum of (*E*)-**12** in CDCl₃ showed signals at δ = 192.1 (dd, ¹J_{PC} = 40.5 Hz and ²J_{PC} = 24.4 Hz) and 192.5 (dd, ¹J_{PC} = 40.6 Hz and ²J_{PC} = 22.5 Hz), due to the cumulene carbons. Table 1 shows ³¹P NMR chemical shifts and spin–spin

Table 1 shows ³¹P NMR chemical shifts and spin-spin coupling constants (J_{PP}) for **9**, **11**, **12** together with those for Mes*P=(C)_n=P[W(CO)₅]Mes* (**13**: n = 0, ¹⁹ **14**: n = 1, ²⁰ **15**: $n = 2^{10c}$), and Mes*P=CH–CH=PMes* (**16**). ²¹ The ³ J_{PP} for (*E*)-and (*Z*)-**12** are larger than the ² J_{PP} value for **11**, due to the π -conjugation of the two phosphorus–carbon double bonds in the –P=C=C=P– array of **12**, while the π systems in the –P=C=P– moiety of **11** is perpendicular. These ³ J_{PP} values in **12** are even larger than ³ J_{PP} for a 1,4-diphosphabutadiene **16**. Coupling constants for the tungsten complexes **14** and **15** are larger than those for the compounds **11** and **12**, respectively. In contrast, the ¹ J_{PP} value for the tungsten complexes **13** is smaller than that for the diphosphene (*E*)-**9**, probably because the extreme steric congestion in **13** might affect the conformation.

Table 1 $^{31}\mathrm{P}\,\mathrm{NMR}$ data of some unsymmetrical low-coordinated phosphorus compounds

Compound	$\delta(\mathbf{P}^{\mathbf{A}})^{a}$	$\delta(P^B)^a$	$J_{ m PP}$ /Hz
(E)- 9	487.4	497.7	581.3
11	140.8	145.5	23.5
(E)- 12	174.6	182.8	257.1
(Z)-12	168.5	173.9	294.3
13 ^b	375.4	486.3	561.5
14 ^c	132.8	151.9	39
15^{d}	105.3	181.5	315.1
$(E,Z)-16^{e}$	243.1	284.5	188

^{*a*} In CDCl₃, relative to external 85% H₃PO₄. ^{*b*} Data taken from Ref. 19. ^{*c*} Data taken from Ref. 20b. ^{*d*} Data taken from Ref. 10c. ^{*e*} Data taken from Ref. 21.

This work was supported in part by the Grants-in-Aid for Scientific Research (Nos. 13304049, 14044012, and 13640522) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

[‡] The geometries were determined based on vicinal spin–spin coupling constants between the vinyl protons: in (Z,Z)-**6a**, ³J = 11.2 Hz, whereas in (E,Z)-**6a**, ³J = 16.0 Hz (E) and 11.2 Hz (Z).

§ Crystal data for **7a**: $C_{21}H_{33}$ Br, monoclinic, space group $P2_1/n$ (#14), *a* = 11.387(2), *b* = 10.989(3), *c* = 15.757(5) Å, β = 103.25(3)°, *V* =

1919.2(9) Å³, Z = 4, $D_{calc} = 1.265 \text{ g cm}^{-1}$, $\mu(MoK\alpha) = 21.45 \text{ cm}^{-1}$. 3091 Unique reflections with $2\theta \le 50.0^{\circ}$ were collected at 170 K. Of these 2939 with $I > 2.0\sigma(I)$ were used for R1 calculation. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. R1 = 0.064, R = 0.133, $R_w = 0.170$. CCDC 193389.

Crystal data for (*E*)-**9**: $C_{39}H_{62}P_2$, orthorhombic, space group $P_{2,2,2_1}$ (#19), a = 15.398(2), b = 23.597(5), c = 10.236(2) Å, V = 3719(1) Å³, Z = 4, $D_{calc} = 1.059$ g cm⁻¹, μ (MoK α) = 1.40 cm⁻¹. 3205 Unique reflections with $2\theta \le 50.0^{\circ}$ were collected at 173 K. Of these 2997 with $I > 2.0\sigma(I)$ were used for *R*1 calculation. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. R1 = 0.062, R = 0.134, $R_w = 0.139$. CCDC 193025.

See http://www.rsc.org/suppdata/cc/b2/b209666h/ for crystallographic data in CIF or other electronic format.

- 1 As a review, see: J. Escudié, H. Ranaivonjatovo and L. Rigon, *Chem. Rev.*, 2000, **100**, 3639.
- 2 G. E. Miracle, J. L. Ball, D. R. Powell and R. West, J. Am. Chem. Soc., 1993, 115, 11598.
- 3 (a) B. E. Eichler, D. R. Powell and R. West, *Organometallics*, 1998, **17**, 2147; (b) N. Tokitoh, K. Kishikawa and R. Okazaki, *Chem. Lett.*, 1998, 811.
- 4 (a) M. Yoshifuji, K. Toyota, K. Shibayama and N. Inamoto, *Tetrahedron Lett.*, 1984, **25**, 1809; (b) M. Yoshifuji, S. Sasaki and N. Inamoto, *Tetrahedron Lett.*, 1989, **30**, 839; (c) M. Yoshifuji, H. Yoshimura and K. Toyota, *Chem. Lett.*, 1990, 827.
- 5 (a) G. Märkl, H. Sejpka, S. Dietl, B. Nuber and M. L. Ziegler, Angew. Chem., Int. Ed. Engl., 1986, 25, 1003; (b) M. Yoshifuji, K. Toyota, H. Yoshimura, K. Hirotsu and A. Okamoto, J. Chem. Soc., Chem. Commun., 1991, 124.
- 6 M. Bouslikhane, H. Gornitzka, H. Ranaivonjatovo and J. Escudié, Organometallics, 2002, 21, 1531.
- 7 (a) M. Yoshifuji, K. Toyota and N. Inamoto, J. Chem. Soc., Chem. Commun., 1984, 689; (b) H. H. Karsch, F. H. Köhler and H.-U. Reisacher, Tetrahedron Lett., 1984, 25, 3687; (c) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus and F. Knoch, Angew. Chem., Int. Ed. Engl., 1984, 23, 619; (d) M. Yoshifuji, S. Sasaki, T. Niitsu and N. Inamoto, Tetrahedron Lett., 1989, 30, 187; (e) M. Yoshifuji, S. Sasaki and N. Inamoto, J. Chem. Soc., Chem. Commun., 1989, 1732; (f) M. Gouygou, C. Tachon, R. El Ouatib, O. Ramarijaona, G. Etemad-Moghadam and M. Koenig, Tetrahedron Lett., 1989, 30, 177.
- 8 (a) O. I. Kolodiazhnyi, *Tetrahedron Lett.*, 1982, **23**, 4933; (b) R. Appel and W. Paulen, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 785; (c) L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg and J.-P. Declercq, *Chem. Eur. J.*, 1999, **5**, 774; (d) H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu and N. Knouzi, *Organometallics*, 1996, **15**, 3070; (e) H. Ranaivonjatovo, H. Ramdane, H. Gornitzka, J. Escudié and J. Satgé, *Organometallics*, 1998, **17**, 1631.
- 9 M. Bouslikhane, H. Gornitzka, J. Escudié, H. Ranaivonjatovo and H. Ramdane, J. Am. Chem. Soc., 2000, 122, 12880.
- 10 (a) G. Märkl and P. Kreitmeier, Angew. Chem., Int. Ed. Engl., 1988, 27, 1360; (b) M. Yoshifuji, K. Toyota and H. Yoshimura, Chem. Lett., 1991, 491; (c) S. Ito, K. Toyota and M. Yoshifuji, J. Organomet. Chem., 1998, 553, 135.
- 11 H. Grützmacher, S. Freitag, R. Herbst-Irmer and G. S. Sheldrick, Angew. Chem., Int. Ed. Engl., 1992, 31, 437.
- 12 (a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc., 1981, **103**, 4587; (b) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc., 1982, **104**, 6167.
- 13 M. Yoshifuji, J. Organomet. Chem., 2000, 611, 210, and references cited therein.
- 14 M. Yoshifuji, M. Nakazawa, T. Sato and K. Toyota, *Tetrahedron*, 2000, 56, 43.
- 15 F. Vögtle, Chem. Ber., 1969, 102, 1784.
- 16 M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita and K. Nishimoto, J. Am. Chem. Soc., 1983, 105, 2495.
- 17 C. K. Johnson, Oak Ridge National Laboratory Report, ORNL-TM-5138, Oak Ridge, TN, 1976.
- 18 R. Appel and F. Knoll, Adv. Inorg. Chem., 1989, 33, 259.
- 19 M. Yoshifuji, K. Toyota, T. Sato and N. Inamoto, *Sci. Rep., Tohoku Univ., Ser. 1*, 1990, **73**, 1.
- 20 (a) M. Yoshifuji, K. Shibayama, T. Hashida, K. Toyota, T. Niitsu, I. Matsuda, T. Sato and N. Inamoto, J. Organomet. Chem., 1986, 311, C63; (b) C. A. Akpan, P. B. Hitchcock, J. F. Nixon, M. Yoshifuji, T. Niitsu and N. Inamoto, J. Organomet. Chem., 1988, 338, C35.
- 21 R. Appel, J. Hünerbein and N. Siabalis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 779.