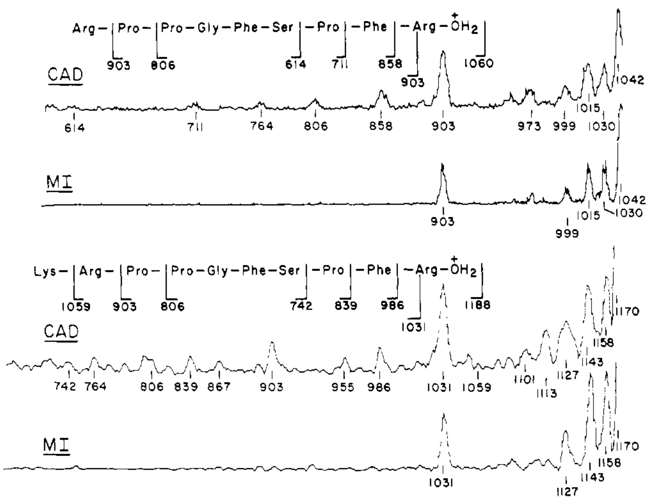

Figure 3. CAD and MI spectra of bradykinin and Lys-bradykinin (~ 5-μg samples); those of Met-Lys-bradykinin are similar (*m/z* 1162 is abundant).

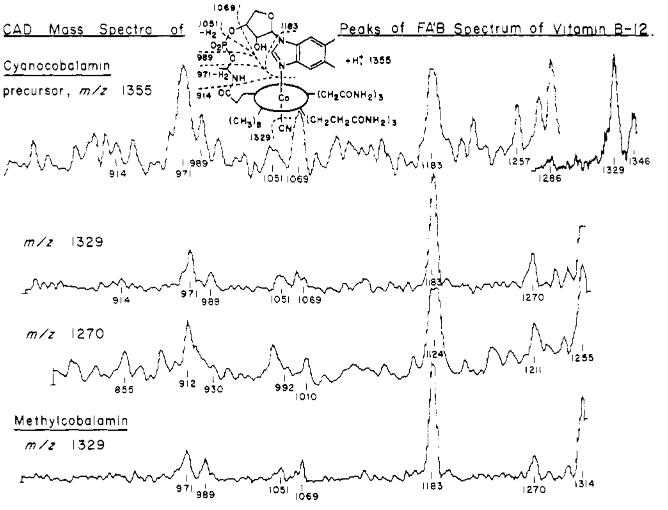

Figure 4. CAD spectra (top three) from *m/z* 1355, 1329, and 1270 of cyanocobalamin; (bottom) *m/z* 1329 of methylcobalamin (~5-μg samples).

and 1329 CAD spectra. (Even the CAD spectrum *m/z* 1386 is strikingly similar to these; its structure could be that of *m/z* 1329 with CH_3 replaced by $CH_2CH_2CONH_2$ or H by CH_2CONH_2.)[15] The sequential losses from the axial chain of 146 (dimethylbenzimidazole + H), 114 and 132 (sugar), 80 (HPO_3), and 57 mass units ($CH(CH_3)CH_2NH$) produce the significant peak groups at *m/z* 1183, 1069, 1051, 989, 971, and 914 in the FAB spectrum.[6a] However, if this were a real unknown this structural assignment would be compromised by the problem of distinguishing peaks due to such sequential loss from the equal number in this region of the FAB spectrum resulting from fragmentations in other parts of the molecule. The CAD spectra of these FAB peaks can resolve this problem by delineating the fragmentation pathways;[16] for example, that of *m/z* 1270 shows the axial chain peaks shifted by 59 mass units vs. the mass 1329 CAD spectrum, demonstrating that the 59 mass units comes from a different part of the molecule. However, the CAD spectra of the FAB peaks centered on *m/z* 1183, 1069, 1051, 989, and 971 show lower mass peaks at these same values; for example, *m/z* 914 is the most abundant high-mass peak in the CAD spectrum of the FAB mass 971 peak. The cobalamin assignement for *m/z* 1329 can be confirmed with reference CAD spectra;[9,16] those from methylcobalamin (Figure 4), hydroxycobalamin, and coenzyme B-12 (not shown) are closely similar. Thus for an unknown these CAD data should provide significant additional evidence of the structure.

We are investigating sensitivity and resolution improvements using ion-counting detection, increased number of collisions and collision energies (post-MS-I acceleration),[2] other collision gases, double-focusing MS-II,[2] alternative ionization methods, and further computer automation.

Acknowledgment. We thank S. L. Cohen, P. L. Danis, and F. Turecek for assistance and the National Institutes of Health and the Army Research Office for financial support.

Registry No. Cesium iodide, 7789-17-5; gastrin, 9002-76-0; bradykinin, 58-82-2; cyanocobalamin, 68-19-9.

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(15) FAB of cyanocobalamin gives *m/z* 1329, 1355, and 1386 peak abundances of 10:3:1 initially but 10:1.5:2.5 after 10 min, consistent with at least part of the 1386^+ precursor being formed by the FAB process.

(16) Cheng, M. T.; Barbalas, M. P.; Pegues, R. F.; McLafferty, F. W. *J. Am. Chem. Soc.*, in press.

An Unsymmetrically Substituted Diphosphene: NMR Spectroscopic Data Pertinent to the Phosphorus-Phosphorus Double Bond[1]

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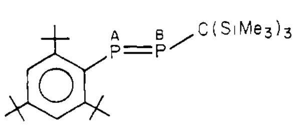
Received December 21, 1982

The use of appropirate steric blockades has permitted the recent isolation of symmetrically substituted compounds featuring silicon–silicon,[2] germanium–germanium,[3] and phosphorus–phosphorus[4] double bonds. We now report the first unsymmetrically substituted compound featuring multiple bonding between heavier main-group elements. The isolation of this unsymmetrical diphosphene (RP═PR′) has led to new NMR spectroscopic data pertinent to the phosphorus–phosphorus double bond.

A mixture of 0.97 g (2.9 mmol) of $(Me_3Si)_3CPCl_2$ and 0.5 g (1.45 mmol) of $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)PCl_2$ in 50 mL of THF was treated with 176 mL of 0.49 M sodium naphthelenide in 50 mL of THF at −78 °C. After evacuation of the solvent and naphthalene, the resulting red-brown solid was dissolved in hexane and separated by column chromatography on silica gel. The first and third fractions were identified as the symmetrical diphosphenes $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**1**)[4b,f] and $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)P{=}P\text{-}(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**2**),[4b,c,e] respectively, on the basis of NMR data.[4] Evaporation of solvent from the second fraction resulted in the unsymmetrical diphosphene **3**. The high-resolution mass spectrum (HRMS) for the parent peak of **3** showed the following:



3

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(1) Presented at the 38th Southwest and 6th Rocky Mountain Combined Regional ACS Meeting, El Paso, TX, Dec 1982, Abstr 154.

(2) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343–1344. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150–1152.

(3) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136–6137.

(4) (a) Yoshifuji, M.; Shima, I.; Inamoto, N. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589. (b) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *Ibid.* **1982**, *104*, 5820–5821. (c) Bertrand, G.; Couret, C.; Escudie, J.; Majid, S.; Majoral, J.-P. *Tetrahedron Lett.* **1982**, *23*, 3567–3570. (d) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609–610. (e) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *Ibid.* **1982**, *691*–693. (f) Couret, C.; Escudie, J.; Satge, J. *Tetrahedron Lett.* **1982**, *23*, 4941–4942.

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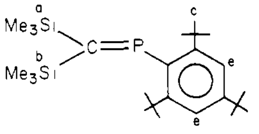
calcd, 538.3164; found, 538.3172. On the basis of ^{31}P NMR spectroscopy, the yields of **1**–**3** were 20%, 60%, and 20%, respectively. The 81.03-MHz $^{31}P\{^1H\}$ NMR spectrum of **3** consists of an AB pattern with δ_A +533.1,[5] δ_B +530, and J_{PP} = 619.7 Hz. For single-bonded trivalent phosphorus compounds, J_{PP} falls in the range 200–300 Hz.[6] We attribute the significantly larger magnitude of J_{PP} in **3** to shortening of the phosphorus–phosphorus bond length and to π-bond formation rather than to changes in P(3s) character because the P–P–C bond angle in **2** is approximately the same as that in the diphosphines $(Mes)_4P_2$[7] and $(Cy)_4P_2)$[8] (Mes = mesityl, Cy = cyclohexyl). The ^{31}P chemical shift of **3** is also of interest. While the average chemical shift of **3** (+531.5 ppm) falls between those of the symmetrically substituted diphosphenes **1** (+599.6 ppm) and **2** (+494.0 ppm), the chemical shift difference between the A and B nuclei in **3** is only 3 ppm, thus suggesting extensive charge delocalization in the phosphorus–phosphorus double bond. Unlike the symmetrical diphosphenes **1** and **2**, which exhibit "deceptively simple" triplet $^{13}C\{^1H\}$ patterns for the ortho (2,4,6-$(t\text{-}Bu)_3C_6H_2$) and $(Me_3Si)_3C$ carbons,[4b] the corresponding resonances for unsymmetrical phosphene **3** comprise doublets of doublets. $^{13}C\{^1H\}$ NMR (22.615 MHz, Me_4Si) for **3**: δ 33.9 ($o\text{-}Me_3C$, dd, J_{PCCCC} = 5.5, J_{PPCCCC} $\sim$ 1.0 Hz), 35.5 ($(Me_3Si)_3C$, dd, J_{PC} = 116.2, J_{PPC} = 11.8 Hz), 4.5 ($(Me_3Si)_3C$, dd, j_{PCSiC} = 4.3, J_{PPCSiC} $\sim$ 1.0 Hz). The four-bond coupling between P and the Me carbons of the ortho-*t*-Bu groups is quite large (5.5 Hz) and suggestive of a through-space interaction. Compound **3** is not as stable as its symmetrical counterparts **1** and **2**, undergoing decomposition in ~2 days at ambient temperature to produce (2,4,6-$(t\text{-}Bu)_3C_6H_2)PH_2$ as the major product.

Since we have shown[4b] that **1** can be prepared in high yield by treating $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$, we examined the reaction of this lithium reagent with $(Me_3Si)_3CPCl_2$/(2,4,6-$(t\text{-}Bu)_3C_6H_2)PCl_2$ mixtures in THF solution. This reaction produced small quantities of **1** and **2**; however, the major product exhibited a ^{31}P NMR singlet at 393 ppm. Identification of this material as the new phosphaalkene **4** is based on its independent synthesis by the following two-step procedure: (i) dehydrochlorination of $(Me_3Si)_2CHPCl_2$ with 1,4-diazabicyclo[2.2.2]octane (Dabco) to form $(Me_3Si)_2C{=}PCl$;[9] (ii) treatment of $(Me_3Si)_2C{=}PCl$ with 2,4,6-$(t\text{-}Bu)_2C_6H_2Li$ in hexane/THF solution. **4**: HRMS calcd 434.2953, found 434.2961; ^1H NMR (90 MHz) δ 0.2 (Me_3Si(a), d, 9 H, J_{PCSiCH} = 1.5 Hz), –0.4 (Me_3Si(b), s, 9 H), 1.45 (*t*-Bu(c), s, 18 H), 1.25 (*t*-Bu(d), s, 9 H), 7.35 (CH(e), s, 2 H). Compound **4** is the exclusive product of the reaction of (2,4,6-$(t\text{-}Bu)_3C_6H_2)PCl_2$ with $(Me_3Si)_3CLi$, a process that proceeds presumably via Me_3SiCl elimination from **5**. Finally, it is of interest to note that the reaction of $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$ does not result in detectable quantities of the phosphaalkene $(Me_3Si)_2C{=}PC(SiMe_3)_3$ (**6**).[10]



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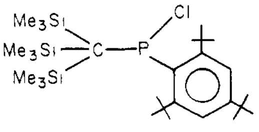

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Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation for generous financial support.

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(5) Positive ^{31}P chemical shifts are downfield form external 85% H_3PO_4 and vice versa.

(6) Harris, R. K.; Norval, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1979**, 826–831.

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(9) This compound was described first by Appel and Westerhaus: Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

(10) We have prepared phosphaalkene **6** via the reaction of $(Me_3Si)_2C{=}PCl$ with $(Me_3Si)_3CLi$; HRMS calcd 420.2104, found 420.2117; $^{31}P\{^1H\}$ NMR (36.43 MHz) δ 422 (s).

Toward Tricyclo[2.2.2.2]decane. 1. [*n*.2.2.2]Paddlane Systems, *n* = 10–14

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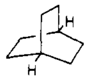
Received December 17, 1982

Consider bicyclo[2.2.2]octane (**1**). The molecule is stable and only slightly strained. The same would be true were the bridgehead hydrogens of **1** replaced by a long enough chain of *n* methylene groups (**2**, the [*n*.2.2.2]paddlanes[1]). Were *n* made smaller, the strain would increase; the geometry about the bridgehead atoms would certainly change. At the symmetrical extreme, when *n* is 2, there would probably be a coplanar (**3a**) or pyramidal (**3b**) arrangement of substituents about these bridgeheads.[2] The associated strain energy is then calculated to be well above 300 kcal/mol.[2b] Thus, between *n* is large and *n* is small the bridgehead atoms of the [*n*.2.2.2]paddlanes must undergo gross rehybridization. We have set out to explore this systematically.[3] Here we report our first finds.



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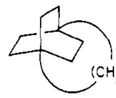

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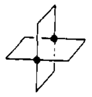
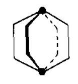
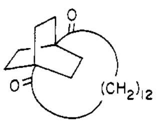


3a



3b

Reaction of bicyclo[2.2.2]octane-1,4-dialdehyde[4] with lithium metal and 1,12-dibromododecane under specially developed conditions[4] gave [14.2.2.2]paddlanedione **4**, mp 98–99 °C, and the "double" paddlane **5**, mp 125–126 °C. Although the yield of paddlane **4** is not good (15%), the starting materials are readily available, and it is easy enough to accumulate substantial quantities of the compound.



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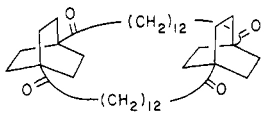

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The [14.2.2.2]paddlane **4** is the first of this dimension with all ethano bridges unsubstituted. Its ^1H NMR spectrum (Figure 1a) is interesting; the 12 protons on the three ethano bridges appear magnetically equivalent at 1.83 ppm even at 500 MHz. Thus, on this NMR time scale, their environment is being averaged by rotation of the bicyclooctane subunit through the large loop of the fourth paddlane bridge. Molecular mechanics calculations (MM2)[5] indicate that this bridging of the 1,4-bicyclooctane

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(1) This nomenclature is due to J. J. Bloomfield: Hahn, E. H.; Bohm, H.; Ginsburg, D. *Tetrahedron Lett.* **1973**, 507.

(2) (a) See the discussion in the following: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; Chapter 6. (b) Würthwein, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 843. (c) Wiberg, K. B.; O'Donnell, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6660.

(3) For earlier, relevant work see ref 2c and the following: Vogtle, F.; Mew, P. K. T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 60.

(4) See Supplementary material.

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