dynamic stability of **1**, implied by eq 1, is not mirrored by a corresponding increase in kinetic stability. Indeed, because tetrahedrane itself is predicted to be a minimum,[10] substitution of lithium for hydrogen results in a dramatic kinetic destabilization of the tetrahedral framework.

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A Simple One-Step Route to a Transition-Metal Complex Containing a Phosphorus–Phosphorus Double Bond. Synthesis and X-ray Crystal Structure of {*trans*-Bis[bis(trimethylsilyl)methyl]diphosphene}bis[tetracarbonyliron(0)]‡

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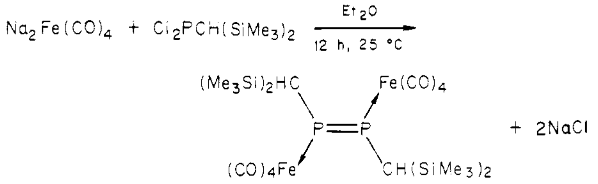
Multiple bonding between the heavier main-group elements has long been thought unlikely for a variety of reasons, which usually involve orbital overlap and thermodynamic considerations.[1] Recently, a number of publications have shown that, by using suitable ligands, compounds containing Si–Si,[2] P–P,[3,4] As–As,[5,6] and Sb–Sb[7] multiple bonds can be stabilized under ambient conditions. However, structural reports in which the multiple bond is unbridged by other species remain quite rare.[3] Here we report (a) a simple one-step, moderate yield (50%) synthesis of a transition-metal complex of the phosphene $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ in which both phosphorus centers behave as simple two electron donors and (b) its spectroscopic (NMR, UV–vis, and IR) and X-ray crystallographic characterization.

The synthesis of the title compound was via the route shown in eq 1. {*trans*-Bis[bis(trimethylsilyl)methyl]diphosphene}bis-



(1)

1, 50%

[tetracarbonyliron(0)], [*trans*-{$[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2$}] (**1**)], was isolated by slow addition of $Na_2Fe(CO)_4{\cdot}1.5$-dioxane (1.29 g, 3.8 mmol) to a stirred solution of dichlorobis(trimethylsilyl)methylphosphine (1 g, 3.8 mmol) in diethyl ether (30 mL) at 0 °C. The solution gradually became red and was allowed to warm to room temperature. Stirring was continued for 12 h, and the volatiles were removed in vacuo. The residue was redissolved in *n*-hexane (20 mL) to give a deep red solution. Filtration and subsequent cooling to −20 °C gave the product as dark red-brown crystals (1.4 g, 50%, mp 145–147 °C).

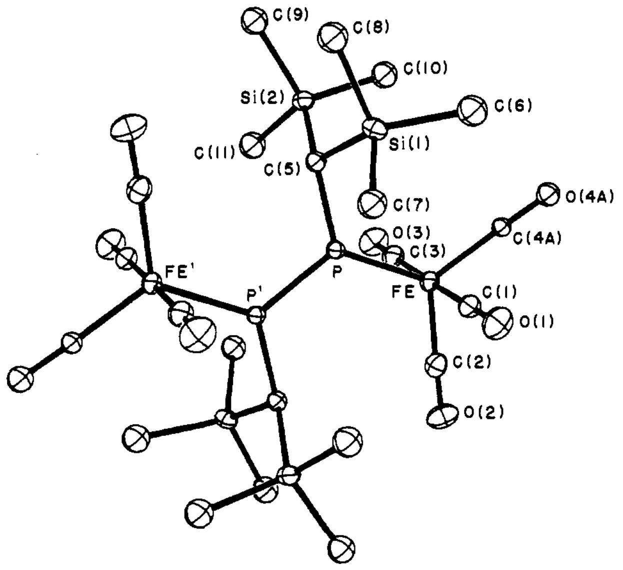


Figure 1. Computer-generated representative diagram of $[Fe(CO)_4]_2$-$[PCH(SiMe_3)_2]_2$. Important bond distances (Å) and angles (deg) are P–P′ = 2.039 (1), P–C(5) = 1.821 (2), Fe–P = 2.226 (1), C(5)PP′ = 107.1 (1), FePC(5) = 125.8 (1), FePP′ = 126.6 (1).

The complex can be handled in air and shows no apparent decomposition after several days exposure to the atmosphere. It is soluble in hydrocarbon solvents, affording solutions that are also air-stable. The complex is thermally stable, melting at 145–147 °C and not decomposing until >200 °C.

The structure of the complex has been solved by single-crystal X-ray diffraction and is illustrated in Figure 1.[8] It consists of isolated neutral molecules with no short intermolecular contacts. The molecule has a center of inversion as crystallographically required. Each iron atom exhibits trigonal-bipyramidal coordination to four carbonyl ligands and one (equatorial) phosphorus atom with Fe–P of 2.226 (1) Å. Compound **1** is the first reported example of a complex in which the group 5b multiple bond is unbridged by a transition-metal atom. The geometry at each phosphorus atom is planar, and this planarity extends to include the two $Fe(CO)_2$(equatorial) moieties. The angles at phosphorus (figure) are distorted from the pure trigonal values with the C(5)PP′ angle = 107.1 (1)°; this is wider than the 102.8 (1)° found in bis(2,4,6-tri-*tert*-butyldiphosphene) (**2**), the only other structurally characterized compound containing an unbridged P–P double bond.[3] The P–P′ distance in **1**, 2.039 (1) Å, is ca. 0.2 Å shorter than single P–P bond lengths and very close to the value of 2.034 (2) Å found in **2**.[10] The phosphorus lone-pair involvement

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†No reprints available.

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[8] A red-brown prism of **1** was cut to the dimensions 0.25 × 0.50 × 0.37 mm and mounted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator. With Mo Kα radiation (λ 0.710 69 Å) and crystal cooled to 140 K, crystal data were as follows: triclinic, space group $P\bar{1}$ (No. 2); a = 9.090 (2) Å, b = 9.551 (3) Å, c = 11.830 (4) Å; α = 109.74 (2)°, β = 91.73 (2)°, γ = 115.52 (2)°; Z = 1; μ = 10.45 cm^{-1} (range of absorption correction factors 1.1–1.2). Data were collected to $2\theta_{max}$ of 55° with an ω-scan technique. A total of 3922 unique data were collected, of which 3493 had $I > 3\sigma(I)$. No absorption or extinction corrections were performed. Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. Computer programs were those of SHELXTL, version 3, July 1981 package. The structure was solved by direct methods. The hydrogen bonded to C(5) was located on a difference Fourier map and allowed to refine isotropically. With anisotropic thermal parameters for non-hydrogen atoms and with the methyl hydrogen atoms riding on the bonded carbon, R = 0.035 and R_w = 0.035. One of the equatorial carbonyl groups, C(4)–O(4), had three-fold disorder and was refined with occupancies as least-squares parameters C(4A)–O(4A) 36%, C(4B)–O(4B) 34% and C(4C)–O(4C) 30%. Only one of these carbonyl groups, C(4A)–O(4A), is shown in Figure 1. Atomic coordinates, thermal parameters, and tables of bond lengths and angles are available as supplementary material.

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in donor bonding to iron therefore leaves the P–P distance essentially unchanged, which suggests that the lone-pair involvement in P–P bonding is minimal. The remaining interatomic distances and angles within the molecule are normal.

NMR data are as follows: ^{31}P NMR ($CDCl_3$) δ 384.55 (s from 21 to −60 °C (relative to external 85% H_3PO_4)); ^{13}C NMR ($CDCl_3$) SiC_3 (s, δ 1.72), $CHSi_2$ (t, δ 32.1, $J_{N(PC)} = 19.5$ Hz), CO (s, δ 214.8); ^{1}H NMR ($CDCl_3$) $SiMe_3$ (s, δ 0.28), CH (br s, δ 3.5); ^{13}C and ^{1}H NMR shifts are relative to Me_4Si. Both the ^{31}P and ^{13}C NMR spectra are consistent with the structure established by X-ray diffraction. The triplet seen at 32.1 ppm in the ^{13}C NMR for $CHSi_2$ appears to be characteristic of a P–P-containing system and is similar to that observed by Cowley and co-workers for CSi_3 in $(Me_3Si)_3CPPC(SiMe_3)_3$[4] and by others in alkylated diphosphines.[9] In the case of the ^{1}H NMR, studies are still in progress owing to the unusual behavior of the hydrogen attached to the α-carbon atom. The resonance position is very solvent dependent, and the broad pattern seen at 21 °C is split into a multiplet at low temperature. Clearly the proton is showing dynamic behavior, and variable-temperature NMR (both ^{1}H and ^{13}C) may explain the unusual behavior; UV–vis ($CDCl_3$) λ_{max} 382 and 287 (sh) nm; IR ν_{CO}(Nujol) 2053 (sh, m), 1988 (sh, m), 1962 cm^{-1}; IR ν_{CO}(CH_2Cl_2) 2026 (m), 1985 (m), 1953 cm^{-1}.

The extension of this work to other transition metals with a variety of substituents and group 5b metal centers is in progress.

Acknowledgment. We are grateful to the Research Corp. and the NSF (CHE-8116355) for generous financial support. We thank B. Murray and Dr. G. B. Matson for experimental assistance.

Supplementary Material Available: Listing of atom coordinates, temperature factors, bond distances and angles (2 pages). Ordering information is given on any current masthead page.

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(10) **Note Added in Proof:** Professor Cowley has informed us that the structure of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ consists of two crystallographically independent molecules with P–P distances of 2.014 (6) and 2.004 (6) Å.

Synthesis of (±)-Kopsanone and (±)-10,22-Dioxokopsane, Heptacyclic Indole Alkaloids

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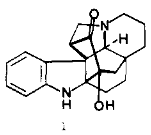
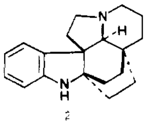
The first documented isolation of a member of the heptacyclic *Aspidofractinine* indole alkaloids was kopsine **1**, in 1890.[1] It was



1



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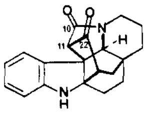
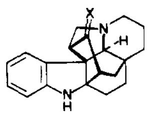


3

not until the early 1960s that the extraordinary complex cage structure of the kopsane alkaloids was elucidated.[2] It is historically interesting to note that the more famous heptacyclic indole alkaloid strychnine eventually submitted to classical structure elucidation by chemical degradation, whereas the kopsanes did not. Their structures were deduced by mass spectrometry,[3] and subsequently (−)-kopsanone methiodide was confirmed by single-crystal X-ray crystallography.[4] While the hexacyclic indole alkaloid aspidofractinine **2** has been synthesized,[5] there is no literature that describes any synthetic approaches to the more condensed kopsane alkaloids.

The complete synthesis of both 10,22-dioxokopsane **3** and kopsanone **4**, central members of this group of alkaloids, is described in Scheme I. Conversion of the aldehyde **6** into the sulfoxide **10** proceeded by using our previously described methodology.[6] Treatment of **10** with TFAA/0–130 °C gave directly the required homoannular diene **11**.

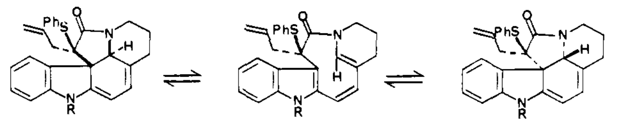


4 (X = O), 5 (X = H,OH)

The formation of the C_{11}–C_{12} bond (**10** → **11**) must procede the elimination of HCl, since we know that the 1,4-dihydrocarbazole that would result from prior elimination of HCl aromatizes (1,4-elimination) to a carbazole under the conditions of this reaction.[7] Consequently, **10** must, via a sulfonium ion (Pummerer reaction), give **10a**, which places the equatorial Cl atom allylic to the newly formed *N-p*-methoxyphenylsulfonyl enamine, thus facilitating its elimination, followed by proton loss to give the homoannular diene **11**.

The crucial allylation at C_{11} was conducted by treatment of **11** with $KN(SiMe_3)_2$/THF/0 °C/allyl bromide, to give *exclusively* **12** (91%), with the stereochemistry shown.

The stereochemical analysis of the alkylation of **11**, at C_{11}, would predict that the incoming electrophile should approach the C-11 carbanion from the convex face to give **12a**. This would place the allyl group (dienophile) on the wrong face of **11** to undergo [2 + 4] cycloaddition to the ring-C diene. Fortunately, this would not be incompatible with the synthetic plan, since thermal equilibriation (diene ⇄ triene, **12a**/**12b**) provides a pathway to **12c** (mirror image of **12**), which can now cyclize to the heptacyclic kopsane structure **13**. Alternatively the carbanion at C_{11} is pyramidally stable and not delocalized into the amide carbonyl group. Delocalization of negative charge into the amide carbonyl group destroys the amide resonance (ca. 12 kcal mol^{-1}) and may not be necessary since the inductive effect of both the SPh and $CONR_2$ groups is sufficient to stabilize the C_{11} carbanion.



12a 12b 12c

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