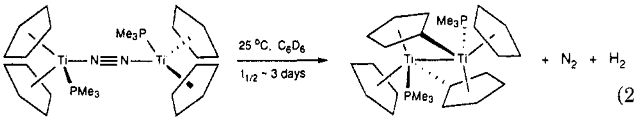
Other aspects of the structure of 2 are unremarkable; the average centroid–Ti–centroid angle (132.1°) and average N–Ti–P angle (83.0°) are typical of Cp_2TiLL' complexes. Complete tables of bond distances and angles are included in the supplementary material.

The infrared spectrum of 2 (Nujol) shows two bands at 1423 and 1279 cm^{-1}. Although 2 is noncentrosymmetric in the solid state, neither band appears to arise from the N–N stretch, as 1 exhibits a virtually identical spectrum. The two bands, therefore, are most likely due to Cp and PMe_3 vibrational modes in both 1 and 2. The absence of an observable μ-N_2 stretch in 2 is consistent with a suggestion by Bercaw[10] that the intensity of $\nu(\mu\text{-}N_2)$ in $\{Cp^*_2Zr(N_2)\}_2(\mu\text{-}N_2)$ is dependent upon vibrational coupling with the symmetric stretching modes of the terminal nitrogen ligands. It is observed that strong oscillators (L = N_2 or CO) in $\{Cp^*_2Zr(L)\}_2(\mu\text{-}N_2)$ lead to $\nu(\mu\text{-}N_2)$ of medium intensity, whereas only a very weak band is observed for L = PF_3.[3b]

Pure 2 in benzene-d_6 exhibits doublets at δ 5.18 (J_{PH} = 2.1 Hz) and 0.82 (J_{PH} = 5.7 Hz) in the ^1H NMR spectrum, due to the Cp and PMe_3 ligands, and a singlet at δ 23.4 in the $^{31}P\ \{^1H\}$ spectrum.

The dinitrogen ligand in 2 is fairly labile and can be displaced in benzene solution under 1 atm of carbon monoxide to yield $Cp_2Ti(CO)_2$. Treatment with excess PMe_3 under vacuum produces 1 and liberates 1.03 ± 0.05 equiv of N_2 per equiv of 2, as collected and measured by Toepler pump.

Shilov et al. have reported that reduction of Cp_2TiCl_2 in the presence of PPh_3 under a nitrogen atmosphere produces a complex containing coordinated phosphine and dinitrogen.[13] Subsequently, careful studies by Brintzinger and co-workers indicated that the unusual titanocene phosphine dimer $\{Cp_2Ti(PPh_3)\}_2$ absorbs nitrogen to produce a dimeric nitrogen complex.[2c] In light of the structure of 2, it seems likely that the analogous triphenylphosphine complex $\{Cp_2Ti(PPh_3)\}_2(\mu\text{-}N_2)$ is formed in the above-mentioned reactions. Not surprisingly, 2 does not react with excess PPh_3 in solution, presumably due to a preference for the smaller PMe_3. It is interesting, however, that both reports of the PPh_3 complex suggest it does not easily lose N_2, whereas decomposition of 2 occurs upon standing in benzene solution under 1 atm of N_2 over a period of days at 25 °C, cleanly producing $\{(\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4))(Cp)Ti(PMe_3)\}_2$[14] and presumably H_2 (eq 2).



(2)

Further studies of the reactivity of 2, including reactions which may liberate nitrogen reduction products, are currently in progress and will be reported separately.

Acknowledgment. We wish to thank the Research Corp. for an Exxon Education Foundation grant and the University of Pennsylvania Research Fund for support of this research. L.J.P. also wishes to thank the University of Pennsylvania College of Arts and Sciences for a Dean's Fellowship.

Registry No. 1, 95936-00-8; 2, 112320-19-1; $Cp_2Ti(CO)_2$, 12129-51-0.

Supplementary Material Available: Description of X-ray data collection and refinement and tables of positional parameters, anisotropic thermal parameters, and intramolecular bond distances and angles for 2 (12 pages); a listing of final structure factor amplitudes for 2 (13 pages). Ordering information is given on any current masthead page.

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[14] Identified by comparison of the ^1H NMR spectrum with that of a sample prepared from Cp_2TiCl_2 by the literature method. ^1H NMR (C_6D_6, 25 °C): δ 5.45 (1 H), 5.09 (5 H), 5.03 (1 H), 4.94 (1 H), 4.43 (1 H), 0.90 (d, 9 H). The chemical shifts differ somewhat from those reported previously, obtained in toluene-d_8 at −20 °C: Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27.

Synthesis and Metal Carbonyl Complexes of a Stable 1-Phosphadiene

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Summary: Dehydrohalogenation of the chlorophosphine, $R_2NP(Cl)CHRCH{=}CHR$ (**1**, R = Me_3Si), with DBU affords the stable 1-phosphadiene, $R_2NP{=}CRCH{=}CHR$ (**2**), which, under some conditions, is formed together with the isomeric phosphacyclobutene **3**. Reactions of the phosphadiene **2** with $Fe_2(CO)_9$ or $Mo(CO)_6$ give the η^1-complexes, **2**$\cdot M(CO)_n$ (**4**, M = Fe, n = 4; **5**, M = Mo, n = 5). The molecular structure of **5** is confirmed by an X-ray crystallographic analysis.

There has been considerable recent interest in the synthesis and structures of phosphadienes, the acyclic, conjugated butadiene analogues, in which one or more of the carbon atoms are replaced by 2-coordinate phosphorus centers. The reported compounds of this type include a few 2-phosphadienes,[1,2] several 2,3-diphosphadienes,[3] unique examples of a 1,3-diphosphadiene,[4] a 1,2,4-triphosphadiene,[5] and two 1,4-diphosphadienes.[6] In addition, there appears to be only one report of a stable 1-phosphadiene[1] which is sterically protected (to the point of being completely unreactive) by a 2,4,6-$(t\text{-}Bu)_3C_6H_2$ substituent on phosphorus. The 1-phosphadienes should be particularly versatile ligands, having a variety of po-

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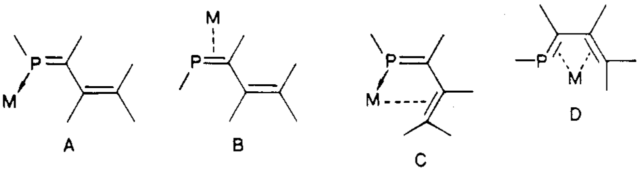
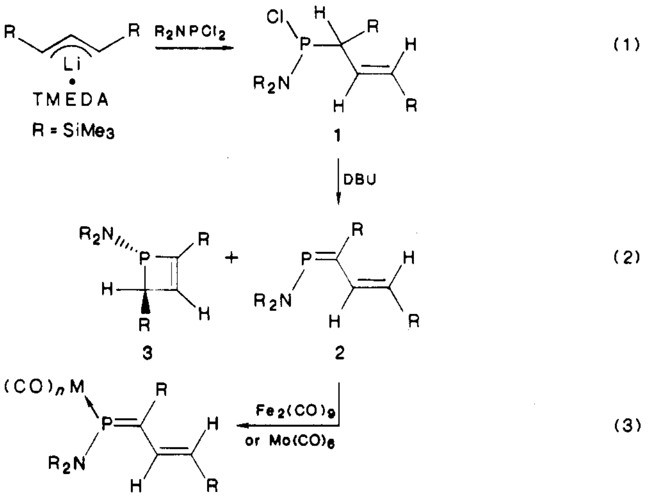
tential coordination modes ranging from η^1 (A) to η^4 (D). Many more possibilities exist if bimetallic complexes are considered. Among these systems, the first example is of the η^4 (D) type, as recently reported by Mathey.[7]



We report here the synthesis and two metal carbonyl complexes of a new, thermally stable 1-phosphadiene, [bis(trimethylsilyl)amino][1,3-bis(trimethylsilyl)-2-propenyl]phosphine (2)[8] (eq 1–3). This diene is similar



4: M = Fe, n = 4
5: M = Mo, n = 5

to the simple (methylene)phosphines $(Me_3Si)_2NP{=}C(SiMe_3)R$ (R = H, $SiMe_3$), the derivative chemistry and structures of which have been previously studied.[9-13] The introduction of a C=C double bond in conjugation with the P=C bond in the 1-phosphadiene **2**, however, leads to some markedly different chemistry. For example, oxidation reactions of **2** with Me_3SiN_3 or sulfur are accompanied by ring closure to yield novel phosphacyclobutene products.[14]

Treatment of $(Me_3Si)_2NPCl_2$[15] (350 mmol) with 1 equiv of [1,3-bis(trimethylsilyl)propenyl]lithium[16] [prepared from $Me_3SiCH{=}CHCH_2SiMe_3$ and n-BuLi in Et_2O (600 mL) and TMEDA (56 mL)] affords the chlorophosphine **1** (eq 1) as a distillable, yellow liquid (bp 108–110 °C (0.06 mm); 79% yield).[17] Dehydrohalogenation of the chlorophosphine **1** is best achieved by using DBU {1,8-diazabicyclo[5.4.0]undec-7-ene} as the base (eq 2) and generally results in the formation of a mixture of the 1-phosphadiene **2** and its structural isomer, the phosphacyclobutene **3**.[18] The selective formation of the 1-phosphadiene **2**, however, is observed when a deficiency of the base is employed. Thus, treatment of the chlorophosphine **1** (270 mmol) with *0.5* equiv of DBU [in hexane (500 mL), at reflux for 10–12 h], followed by filtration and vacuum distillation (twice through a 10-cm column), affords the diene **2** as a light yellow liquid (bp 82–89 °C (0.07 mm); 61% yield based on **1**).[19]

Table I. NMR Spectroscopic Data[a]

	diene **2**	complex **5**
$\delta(^{31}P)$	317.6	280.6
$\delta(^{1}H)$ (J_{PH}, J_{HH})		
HC=	7.40 (12.3, 19.5)	7.09 (22.1, 19.5)
H(Si)C=	5.67 (2.9, 19.5)	5.40 (6.0, 19.5)
$\delta(^{13}C)$(J_{PC})		
P=C	187.93 (84.0)	187.62 (21.6)
HC=	142.25 (13.7)	145.30 (19.9)
H(Si)C=	128.06 (24.2)	128.54 (25.2)
CO (trans)		210.22 (34.6)
CO (cis)		204.84 (12.1)
$\delta(^{29}Si)$ (J_{PSi})		
SiN	3.33 (3.8)	6.90 (8.5)
SiC=P	−6.27 (42.4)	−3.93 (29.0)
H(Si)C=	−6.36 (4.1)	−6.08 (4.8)

[a] Chemical shifts downfield from Me_4Si for ^1H, ^{13}C, and ^{29}Si spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ for ^1H, ^{13}C, and ^{29}Si spectra (all recorded on a Varian XL 300 spectrometer); CH_2Cl_2 for ^{3}P spectra (recorded on a JEOL FX-60 instrument).

The NMR spectroscopic data (Table I) readily confirms the molecular structure of the diene **2**, including the stereochemistry about the double bonds. Noteworthy are the downfield ^{31}P and ^{13}C chemical shifts of the P=C moiety that are consistent with sp^2 hybridization and typical of silylated (methylene)phosphines.[9,13] The large $^3J_{HH}$ coupling of 19.5 Hz indicates a trans geometry about the C=C double bond, while the large $^2J_{PSi}$ coupling of 42.4 Hz indicates a cis relationship[10a,20] between the phosphorus lone pair and the Me_3Si group on the adjacent carbon atom.

The reactions of the phosphadiene **2** (5 mmol) with 1 equiv of either $Fe_2(CO)_9$ [in pentane (25 mL), stirred overnight] or $Mo(CO)_6$ [in heptane (40 mL), refluxed for 3 h] occur readily to yield the metal carbonyl complexes **4** and **5** (eq 3), respectively. After solvent removal, the iron

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(8) Compound **2**, as an impure mixture with its cyclic isomer **3** and without experimental details, has been mentioned previously. Neilson, R. H. *Phosphorus Sulfur* **1983**, *18*, 43. See also: Thoma, R. J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.

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(17) Characterization data for **1**: $^{31}P\{^1H\}$ NMR δ 149.3 (major diastereomer), 165.0 (minor); $^{13}C\{^1H\}$ NMR δ 50.20 (d, $^1J_{PC}$ = 62.5 Hz, PC), 141.92 (d, $^2J_{PC}$ = 13.1 Hz, HC=), 131.56 [d, $^3J_{PC}$ = 10.1 Hz, Si(H)C=]; $^{29}Si\{^1H\}$ NMR δ 10.98 (d, $^2J_{PSi}$ = 11.9 Hz, NSi), 0.32 (d, $^2J_{PSi}$ = 27.1 Hz, PCSi), −7.69 [d, $^4J_{PSi}$ = 2.8 Hz, Si(H)C=]. Anal. Calcd: C, 43.70; H, 9.54. Found: C, 43.51; H, 9.46.

(18) For example, treatment of **1** with an excess of DBU (2–3 equiv) affords a distillable (bp 63–68 °C (0.01 mm),; 40% yield), but inseparable, mixture of **2** and **3** in a 2.5:1 ratio (by NMR integration). See ref 8. Anal. Calcd: C, 47.94; H, 10.19. Found: C, 47.58; H, 10.20. Spectroscopic data for **3** (obtained from mixture): $^{31}P\{^1H\}$ NMR δ 51.2; $^{13}C\{^1H\}$ δ 47.92 [d, $^1J_{PC}$ = 16.1 Hz, Si(H)CP], 145.70 (d, $^2J_{PC}$ = 6.8 Hz, HC=), 168.60 (d, $^1J_{PC}$ = 36.1 Hz, SiC=); ^1H NMR δ 2.74 [d of d, $^2J_{PH}$ = 6.0 Hz, $^3J_{HH}$ = 1.2 Hz, Si(H)C], 6.38 (d of d, $^3J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 1.2 Hz, HC=).

(19) Anal. Calcd for pure **2**: C, 47.94; H, 10.19. Found: C, 47.67; H, 10.13. See Table I for NMR data.

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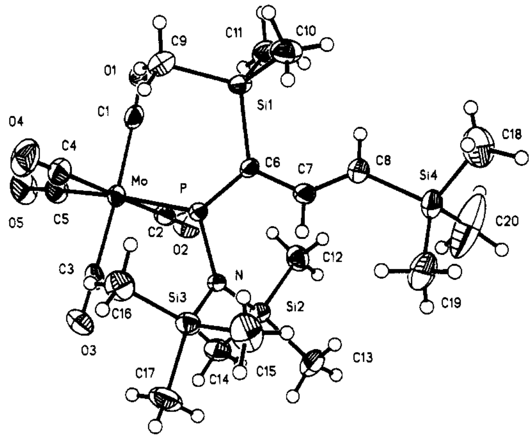

Figure 1. ORTEP drawing of **5**. Thermal elipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo–P = 2.518 (2); Mo–C(1) = 2.019 (5); Mo–C(2) = 2.043 (5); Mo–C(3) = 2.027 (2); Mo–C(4) = 2.053 (5); Mo–C(5) = 1.985 (6); P═C(6) = 1.677 (5); P–N = 1.699 (4); C(6)–C(7) = 1.467 (7); C(6)–Si(1) = 1.900 (5); C(7)–C(8) = 1.334 (8); C(8)–Si(4) = 1.849 (6); N–Si(2) = 1.760 (4); N–Si(3) = 1.769(3); Mo–P–C(6) = 134.4 (2); Mo–P–N = 114.5 (1); C(6)–P–N = 110.2 (2); P–C(6)–Si(1) = 123.0 (3); P–C(6)–C(7) = 119.7 (4); C(7)–C(6)–S(1) = 117.3 (4); C(6)–C(7)–C(8) = 126.6 (5); C(7)–C(8)–Si(4) = 127.1 (4).

derivative is isolated as a viscous, orange liquid[21] that decomposes, with loss of CO, on standing at room temperature. The molybdenum complex **5**, however, is much more stable and can be purified by recrystallization from pentane.[22] The NMR spectra (e.g., ^1H and ^{13}C) of **5** (Table I) exhibit signals for of the P═CC═C linkage that are quite similar to those of the uncomplexed diene. When combined with the relatively small upfield shift of the ^{31}P signal, these data are indicative of η^1-complexation of the phosphorus lone pair to the metal center.[11,13]

The X-ray crystallographic analysis[23] of **5** (Figure 1) is completely consistent with the NMR spectroscopic data and confirms the η^1-coordination mode as well as the basic structure of the 1-phosphadiene ligand. In **5**, there are numerous intramolecular contacts of 2.30–2.65 Å involving the methyl groups of the Me_3Si moieties. Many of these are associated with the π-system and with some of the carbonyl groups. Thus, the molecular geometry is a steric compromise with the π-system being significantly nonplanar [e.g., the P–C(6)–C(7)–C(8) torsion angle is 142.0 (2)°]. The geometry about the P═C double bond itself, however, is essentially planar [with deviations of less than 0.05 Å in the PC(6)C(7)NSi(1) plane]. The Mo atom lies 0.610 (1) Å out of this plane due to a close interaction between CO groups on the metal and the $Me_3Si(1)$ moiety. The planar P═C double bond of **5** contrasts markedly with the severely twisted [by 30.3 (6)°] P═C linkage in the related (methylene)phosphine complex $(CO)_4Fe\cdot[(Me_3Si)_2NP{=}C(SiMe_3)_2]$.[13] Apparently, the -HC═CH- moiety (intervening between the P═C bond and the terminal silyl group) reduces the steric congestion sufficiently to permit a nearly coplanar geometry about the double bond in this case. Finally, we note that the P═C bond length of 1.677 (4) Å in **5** is statistically longer than the 1.657 (5) Å value observed for the latter complex.

Further studies of the derivative chemistry of the 1-phosphadienes such as **2**, including other possible coordination modes (e.g., B and C) as well as nucleophilic additions to the P═CC═C system, are currently in progress.

Acknowledgment. We thank the U.S. Office of Naval Research and The Robert A. Welch Foundation (Grants P-759 and P-074) for financial support. The experimental assistance of Dr. Donn DuBois is also acknowledged.

Registry No. 1, 112044-08-3; 2, 89982-69-4; 3, 112044-09-4; 4, 112044-10-7; 5, 112044-11-8; $(Me_3Si)_2NPCl_2$, 54036-90-7; $Me_3SiCH{=}CHCH_2SiMe_3$, 17891-78-0; $Fe_2(CO)_9$, 15321-51-4; $Mo(CO)_6$, 13939-06-5; [1,3-bis(trimethylsilyl)propenyl]lithium, 61518-50-1.

Supplementary Material Available: Tables of atomic positional parameters and U_{eq} values, hydrogen atom positions and isotropic U values, anisotropic thermal parameters, interatomic distances, and valence angles (5 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[21] Characterization data for **4**: $^{31}P\{^1H\}$ NMR δ 280.2; $^{13}C\{^1H\}$ NMR δ 173.90 (br, s, $^1J_{PC} \approx 0$ Hz, P═C), 145.10 (d, $^2J_{PC} = 19.1$ Hz, HC═), 127.30 [d, $^3J_{PC} = 27.3$ Hz, Si(H)C═], 213.90 (d, $^2J_{PC} = 22.5$ Hz, CO); ^1H NMR: δ 5.59 [d of d, $^4J_{PH} = 6.0$ Hz, $^3J_{HH} = 19.5$ Hz, Si(H)C═], 7.50 (d of d, $^3J_{PH} = 24.0$ Hz, $^3J_{HH} = 19.5$ Hz, HC═). Elemental analysis not obtained due to thermal instability.

[22] Anal. Calcd for **5**: C, 39.26; H, 6.26. Found: C, 39.02; H, 6.28. See table I for NMR data.

[23] **5**: crystal of dimensions 0.2 × 0.5 × 0.5 mm; triclinic space group $P\bar{1}$, with $a = 11.569$ (9), $b = 12.454$ (9), $c = 12.641$ (9) Å; $\alpha = 103.75$ (9), $\beta = 104.89$ (8), $\gamma = 104.34$ (9)°; $V = 1614$ (2) Å^3; $Z = 2$; D(calcd for $MoC_{20}H_{38}Si_4PO_5N$) = 1.258 g cm^{-3}; $F(000) = 636$; λ(Mo Kα) = 0.710 73 Å; $\mu = 6.15$ cm^{-1}. A total of 2906 independent reflections ($3 \leq 2\theta \leq 40°$) were collected on a Nicolet R3m/μ update of a P2$_1$ diffractometer using the Wyckoff mode (2θ fixed, ω varied) and graphite-monochromated Mo Kα radiation: 2501 reflections collected, 2501 $\geq 3\sigma(I)$, Lorentz and polarization corrections applied, Ψ-scan empirical absorption correction (transmission factors 0.730–0.851, $R_{merge} = 0.016$). Anisotropic block-cascade, least-squares refinement (H atoms allowed to ride at fixed distance on carbon atoms with one isotropic thermal parameter refined for all H atoms) led to a final $R = 0.0350$, $wR = 0.0436$, $S = 1.75$, and $(\Delta/\sigma)_{max} = 0.10$, with $w = [\sigma^2(F_o) + 0.000\,133F_o^2]^{-1}$. Computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration: Nicolet PN-269-1040340 (1986). Atomic scattering factors and anomalous dispersion corrections from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. Atomic coordinates, bond lengths, valence angles, anisotropic thermal parameters, and H atom coordinates are listed in supplementary Tables 1–5. Lists of structure factors are also available.