The scrambling observed in reaction 4 may proceed by either reversible insertion of an olefin into a metal–hydrogen bond, process 1, or by reversible insertion into vinylic C–H bonds of ethene, process 2. Labeling studies clearly cannot distinguish these two processes in this case. A single vinylic insertion/deinsertion (process 2) or ethene insertion (process 1) would result in exchange rates of 50% of 67%, respectively, of the collision rate with complete scrambling by multiple insertions yielding an exchange efficiency of 80% (assuming no isotope effects). The observed exchange efficiency of 8% for process 4 implies that a maximum of 16% of the collisions result in reaction. This slow rate of exchange is indicative of substantial barriers for both processes 1 and 2.[10]

Reaction with propene is quite different with facile dehydrogenation, process 5, and substantial scrambling is observed with Fe_2D^+, processes 6 and 7. If facile, reversible vinylic insertions were responsible for the scrambling in processes 6 and 7, then reaction of Fe_2H^+ with propene-2-d_1 should yield a 1:1 ratio of H_2 vs HD elimination whereas facile, reversible alkene insertion, process 1, should scramble all hydrogens yielding an H_2:HD elimination ratio of 71%:29%. Both processes 1 and 2 would result in scrambling of the C2 hydrogen on propene. Absence of HD elimination for reaction of Fe_2H^+ with propene-2-d_1 reveals that the C2 hydrogen on propene is not scrambled; therefore, neither process 1 nor process 2 can account for these results. These results, however, can be rationalized by invoking rapid interconversion of a hydrido propene complex with a dihydrido allyl species by reversible insertion across allylic C–H bonds, process 3. Such a scrambling process would render the C2 hydrogen unexchangeable as observed in reaction 8. Complete scrambling of the five terminal hydrogens of propene in reactions 6 and 7 would yield a dehydrogenation distribution consisting of 33% HD and 67% H_2 elimination which is observed. This suggests that the barrier for the reversible insertion of Fe_2H^+ into an allylic C–H bond of propene is very small since it must be traversed several times prior to dehydrogenation.

Additional aspects of the dehydrogenation process 5 can be investigated by monitoring H/D exchange of $Fe_2C_3H_5^+$ with D_2 where *only* four hydrogens are exchangeable, process 9. This exchange is slow with a rate constant for

$$Fe_2(CH_2CHCH_2)^+ \xrightarrow[-4HD]{4D_2} Fe_2(CD_2CHCD_2)^+ \quad (9)$$
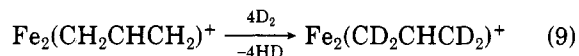
the first exchange roughly 1/10 of the Langevin collision rate.[18] These exchanges can again be rationalized by invoking initial addition of deuterium to the metal centers followed by reversible conversion of the dideuterioallyl species with a deuteriopropene complex resulting in elimination of HD. This scrambling accounts for the four exchangeable hydrogens in $Fe_2C_3H_5^+$ where the C2 hydrogen remains unexchanged as has previously been observed for CpRh(allyl)$^+$.[19] This was substantiated by monitoring H/D exchange of $Fe_2C_3H_4D^+$, formed in reaction 8, with D_2 where *all* four hydrogens undergo exchange, indicating the C2 hydrogen is clearly the unique, unexchangeable hydrogen.

These results demonstrate that the dynamics of hydrogen migrations on small transition-metal centers can be probed by using gas-phase ion techniques. The origin

of the barriers to ethene insertion into an Fe–H bond or insertion into a vinylic C–H bond is unclear for these systems at this time, however, they may be simply due to spin multiplicity restrictions.[20] Such an argument has been used to account for the stability of $Cp_2Mo(H)(C_2H_4)^+$ which does not undergo unimolecular ethene insertion into the M–H bond forming an alkyl species.[21] Additional work in this area concerning these very fundamental and important hydrogen migrations as a function of cluster size and ligand environment should yield important insights into the the factors affecting these arrangements and is currently being pursued in our laboratory.

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Molecular Structure of {Cp₂Ti(PMe₃)}₂(μ-N₂), a Titanocene Dinitrogen Complex

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Summary: Treatment of benzene solutions of bis(trimethylphosphine)titanocene, Cp₂Ti(PMe₃)₂ (1), with 1 atm of N₂ results in formation of an equilibrium mixture containing ca. 30% of {Cp₂Ti(PMe₃)}₂(μ-N₂) (2), a bridging dinitrogen complex of titanocene. Compound 2 can be isolated in 56% yield by stirring a petroleum ether slurry of 1 under N₂ and filtering. The solid-state structure of 2, as determined by single-crystal X-ray diffraction methods, exhibits a relatively long N–N bond and short Ti–N bonds, consistent with substantial back-bonding from the titanium centers to the coordinated dinitrogen.

The coordination and reduction of molecular nitrogen by group 4 metallocenes has been the subject of intense study and some controversy.[1] Much of the ambiguity surrounding this chemistry stems from the instability and resulting complexity of the parent "titanocene". Three research groups have reported the preparation of unstable dimeric nitrogen complexes of composition {Cp₂Ti}₂N₂ (Cp ≡ η^5-C₅H₅), however, the properties of the compounds vary and their relationship is not clear.[2] Although the work

(1) (a) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* 1981, *19*, 1. (b) Bercaw, J. E. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ugo, R., Eds.; Plenum: New York, 1977; Vol. 1, p 129.
(2) (a) Van Tamelen, E. E.; Cretney, W.; Klaentschi, N.; Miller, J. S. *J. Chem. Soc., Chem. Commun.* 1972, 481. (b) Borodko, Yu. G.; Ivleva, I. N.; Kachapina, L. M.; Salienko, S. I.; Shilova, A. K.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.* 1972, 1178. (c) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* 1972, *94*, 1219.

(18) It was impossible to accurately measure the H/D exchange rate; however, it clearly is quite slow and was estimated to proceed at 1/10 the Langevin collision frequency.
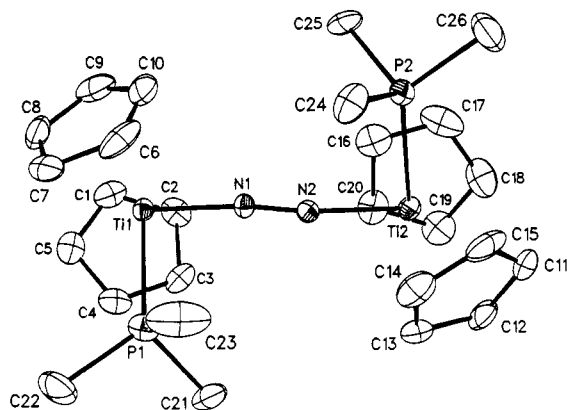(19) Beauchamp, J. L.; Stevens, A. E., Corderman, R. R. *Pure Appl. Chem.* 1979, *51*, 967.
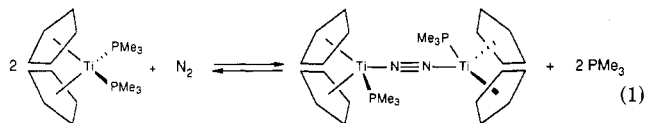
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Figure 1. ORTEP drawing of **2** showing the non-hydrogen atoms.

Table I. Selected Bond Lengths and Angles for Compound 2

Bond Lengths (Å)			
Ti1–P1	2.538 (2)	Ti2–P2	2.525 (2)
Ti1–N1	1.920 (6)	Ti2–N2	1.921 (5)
Ti1–$\bar{C}_{ring1}{}^a$	2.411	Ti2–$\bar{C}_{ring3}{}^a$	2.408
Ti1–$\bar{C}_{ring2}{}^a$	2.430	Ti2–$\bar{C}_{ring4}{}^a$	2.414
N1–N2	1.191 (8)		
Bond Angles (deg)			
P1–Ti1–N1	84.9 (2)	Ti1–N1–N2	169.0 (5)
P2–Ti2–N2	81.0 (2)	Ti2–N2–N1	172.6 (5)
R1–Ti1–R2[b]	131.7	R3–Ti2–R4[b]	132.4

^{a} Ti–$\bar{C}_{ring}$ values refer to the average Ti–C distance of the Cp rings. ^{b} R1–4 are the centroids of the Cp rings.

of Bercaw and co-workers with pentamethylcyclopentadienyl analogues[3] and by Teuben and co-workers on titanium(III) dinitrogen complexes[4] has clarified many aspects of titanium dinitrogen chemistry, no simple bridging dinitrogen complex of $Cp_2Ti(II)$ has previously been structurally characterized.[5] We now report the preparation and molecular structure of {$Cp_2Ti(PMe_3)$}$_2$(μ-N_2), a phosphine-substituted titanocene dinitrogen complex.

As described by Alt and Rausch,[6] bis(trimethylphosphine)titanocene, $Cp_2Ti(PMe_3)_2$ (**1**), is a convenient precursor to low-valent titanocene complexes. Exposure of **1** in benzene-d_6 to 1 atm of nitrogen results in an equilibrium mixture of **1** and ca. 30% of a new complex exhibiting a doublet at δ 5.18 (J = 2.1 Hz), attributable to the Cp of a monophosphine species. The Cp resonance of **1** in this mixture is broadened considerably, and all of the phosphine resonances are observed as one broad signal at δ 0.83. The $^{31}P\{^1H\}$ NMR spectrum shows a very broad peak at δ 40.5 due to **1**[7] and a sharp singlet at δ 23.4. Addition of 3 equiv of PMe_3 to this mixture results in the loss of the signals associated with the new species and a sharpening of the ^{31}P resonance of **1**.

The new complex can be isolated by exploiting the greater solubility of **1**. Thus stirring a slurry of **1** in petroleum ether overnight under 1 atm of nitrogen yields a reddish brown solid, which on the basis of NMR, Toepler pump analysis of displaced dinitrogen, and single crystal X-ray structure determination is confirmed as {$Cp_2Ti(PMe_3)$}$_2$(μ-N_2) (**2**, eq 1).[8,9]

The molecular structure of **2** is shown in Figure 1, and selected bond distances and angles are listed in Table I. The structure consists of two $Cp_2Ti(PMe_3)$ fragments connected by a nearly linear dinitrogen bridge, an arrangement similar to those found in the structures of {$Cp*_2Zr(N_2)$}$_2$(μ-N_2)[10] (**3**; $Cp*$ = η^5-C_5Me_5), {$Cp*_2Ti$}$_2$(μ-N_2)[3a] (**4**), and {$Cp_2Ti(p$-tolyl)}$_2$(μ-N_2)[4a] (**5**). The N–N bond in **2** (1.191 (8) Å) is longer than in **3** (1.182 (3) Å), **4** (1.165 (14) Å), and **5** (1.162 (12) Å), although the differences are within the statistical error limits. However, the Ti–N bonds are significantly shorter than in **4** and **5** (mean values 1.921 (6) vs 2.010 (10) and 1.962 (6) Å). These values are consistent with a greater degree of π-backbonding to the dinitrogen ligand in **2** than in either **4** or **5**, although the Ti–N–N–Ti linkage in **4** may also reflect the greater steric demands of the $Cp*$ rings. The titanium(II) centers in **2**, containing electron-donating phosphines, are expected to be more electron rich than the titanium centers in **4** or **5**. Although significantly longer than that in free N_2 (1.0976 Å), the N–N bond in **2** falls short of a typical N–N double bond (1.24 Å).

The titanocene fragments in **2** are twisted with respect to one another such that each phosphine is nearly eclipsed with a ring on the adjacent metal. The P1–Ti1–Ti2–P2 torsion angle is 109°. The Cp rings are planar and are symmetrically bound at average Ti–C distances of 2.411, 2.43, 2.408, and 2.414 Å, somewhat longer than the average in $Cp_2Ti(CO)_2$[11] (2.347 Å) and $Cp_2Ti(CO)(PMe_3)$[12] (2.357 Å).

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(5) Pez and co-workers have reported the molecular structure of (μ_3-N_2){(η^5:η^5-$C_{10}H_8$)(η^5-C_5H_5)$_2$Ti$_2$}{(η^1:η^5-C_5H_4)(η^5-C_5H_5)$_3$Ti$_2$}, an unusual tetranuclear complex in which a dinitrogen ligand bridges three metals. Although formally divalent, the titanium centers are not simple (η^5-C_5H_5)$_2$Ti^{II} units: Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482.

(6) Kool, L. R.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(7) Compound **1** exhibits a sharp ^{31}P resonance at δ 40.5 under vacuum in benzene-d_6 at 25 °C.

(8) Preparation of **2**. A slurry of **1** (752 mg, 2.279 mmol) in 20 mL of dry petroleum ether was stirred under N_2 for 16 h. After the solution was cooled to –40 °C, the reddish brown solid was filtered and dried in vacuo. A small amount of **1** remaining was removed by repeating this procedure and filtering at 25 °C to yield 340 mg (56%) of **2**. ^1H NMR (C_6D_6, 25 °C): δ 5.18 (d, J_{PH} = 2.1 Hz, 20 H, C_5H_5), 0.82 (d, J_{PH} = 5.7 Hz, 18 H, P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (81.015 MHz, C_6D_6, 25 °C): δ 23.4 (s). Repeated attempts to obtain an accurate elemental analysis of **2** (multiple analyses by two commercial laboratories) were unsuccessful; the compound was reportedly "oxidized during handling", despite handling under an "inert" atmosphere. Combustion analysis performed by a colleague at the University of Pennsylvania yielded a value low in carbon. Anal. Calcd for $C_{26}H_{38}N_2P_2Ti_2$: C, 58.22; H, 7.14; N, 5.22. Found: C, 56.75; H, 7.41; N, 5.36. Nitrogen analysis was obtained from Toepler pump measurements.

(9) A crystal of **2** ($C_{26}H_{38}N_2P_2Ti_2$, fw 536.35) measuring 0.35 × 0.20 × 0.10 mm enclosed in a 0.5-mm glass capillary was mounted on an Enraf-Nonius CAD4 diffractometer and cell parameters determined: triclinic space group $P\bar{1}$ (Z = 2) with a = 8.313 (2) Å, b = 11.990 (2) Å, c = 14.263 (3) Å, α = 83.57 (2)°, β = 87.65 (2)°, and γ = 71.18 (2)°. A total of 5401 unique reflections were measured, of which 1869 with I > 3σ were used in the refinement (289 parameters). After refinement, final agreement factors were determined as R_1 = 0.047 and R_2 = 0.050, and the final goodness-of-fit was 1.069. Full details of data collection and refinement are included in the supplementary material.

(10) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8351.

(11) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367.

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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 Cp₂TiLL' 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 PMe₃ vibrational modes in both **1** and **2**. The absence of an observable μ-N₂ stretch in **2** is consistent with a suggestion by Bercaw[10] that the intensity of $\nu(\mu$-N₂) in {Cp*₂Zr(N₂)}₂(μ-N₂) is dependent upon vibrational coupling with the symmetric stretching modes of the terminal nitrogen ligands. It is observed that strong oscillators (L = N₂ or CO) in {Cp*₂Zr(L)}₂(μ-N₂) lead to $\nu(\mu$-N₂) of medium intensity, whereas only a very weak band is observed for L = PF₃.[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 PMe₃ ligands, and a singlet at δ 23.4 in the ³¹P {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 Cp₂Ti(CO)₂. Treatment with excess PMe₃ under vacuum produces **1** and liberates 1.03 ± 0.05 equiv of N₂ per equiv of **2**, as collected and measured by Toepler pump.

Shilov et al. have reported that reduction of Cp₂TiCl₂ in the presence of PPh₃ 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 {Cp₂Ti(PPh₃)}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 {Cp₂Ti(PPh₃)}₂(μ-N₂) is formed in the above-mentioned reactions. Not surprisingly, **2** does not react with excess PPh₃ in solution, presumably due to a preference for the smaller PMe₃. It is interesting, however, that both reports of the PPh₃ complex suggest it does not easily lose N₂, whereas decomposition of **2** occurs upon standing in benzene solution under 1 atm of N₂ over a period of days at 25 °C, cleanly producing {(μ-(η^1:η^5-C₅H₄))(Cp)Ti(PMe₃)}₂[14] and presumably H₂ (eq 2).

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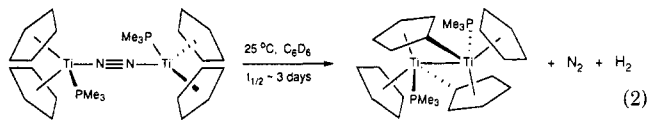
Further studies of the reactivity of **2**, including reactions which may liberate nitrogen reduction products, are currently in progress and will be reported separately.

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.

Synthesis and Metal Carbonyl Complexes of a Stable 1-Phosphadiene

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Summary: Dehydrohalogenation of the chlorophosphine, R₂NP(Cl)CHRCH=CHR (**1**, R = Me₃Si), with DBU affords the stable 1-phosphadiene, R₂NP=CRCH=CHR (**2**), which, under some conditions, is formed together with the isomeric phosphacyclobutene **3**. Reactions of the phosphadiene **2** with Fe₂(CO)₉ or Mo(CO)₆ give the η^1-complexes, **2**·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-Bu)₃C₆H₂ substituent on phosphorus. The 1-phosphadienes should be particularly versatile ligands, having a variety of po-

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(14) Identified by comparison of the ¹H NMR spectrum with that of a sample prepared from Cp₂TiCl₂ by the literature method. ¹H NMR (C₆D₆, 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.

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