$\Delta H_f(\mathbf{2a})$, is 50.7 ± 4.7 kcal/mol.[18] Support for the observed heat deposition $\Delta H(2)$ corresponding to the H rearrangement is given by (a) product studies,[5,12] (b) the $\Delta H_f(\mathbf{2a})$ value is in good agreement with that obtained by PAC using the experimental heat of reaction for either the insertion of **2a** into the O–H bond of methanol[8d,19a] or the cycloaddition of **2a** with 2,3-dimethyl-2-butene,[19b] and (c) the overall heat of reaction of **1a** → **3a**, $\Delta H(1) + \Delta H(2)$, is similar to that observed for **1b** and **1c** and in reasonable agreement with thermochemical estimates.[19c,20] Irradiation of either **1b** or **1c** in heptane results in only one heat deposition, $\Delta H(1)$, which reflects both the formation and the rearrangement of the carbene. This suggests the rate constants for rearrangement of **2b** and **2c** are $\geq 1 \times 10^8$ s^{-1}.[20b]

The temperature dependence (11.5–61.0 °C) of the rate constant for the rearrangement of **2a** in heptane fits to a single exponential ($R = 0.98$) and yields Arrhenius parameters $E_a = 4.9 \pm 0.5$ kcal/mol and log $(A/\text{s}^{-1}) = 9.7 \pm 0.3$.[11,21,22] The calculated E_a for rearrangement of **2b** and **2c** is ≤2.4 kcal/mol, assuming similar preexponential factors as for **2a** and rate constants for rearrangement of $\geq 1 \times 10^8$ s^{-1} at 295 K.

The presence of a significant activation energy for rearrangement of **2a** (4.9 kcal/mol) relative to methylcarbene (~0 kcal/mol) may result from the stabilization of the carbene **2a** by Cl substitution. This is reflected in the lower reaction exothermicity of **2a** → **3a**, −42.1 kcal/mol, compared to that of methylcarbene to ethylene, −76.9 kcal/mol.[2a] Alternatively, stabilization of **2a** by the solvent, relative to the gas phase, may contribute, in part, to the observed activation energy.[23] The significantly larger rate constant for the rearrangement of **2b** and **2c** relative to **2a** is consistent with a hydride shift process where the α C–H bond being broken is highly polarized in the transition state. The incipient positive charge is stabilized by methyl substitution at the migration center on **2b** and **2c**. A similar rate enhancement is also found for the rearrangement of benzylchlorocarbene to chlorostyrene (5×10^7 s^{-1} at 298 K), presumably due to aromatic stabilization of the transition state.[24]

The low preexponential factor for the rearrangement of **2a** suggests a highly ordered transition state which supports a highly coupled or "concerted" hydride shift and π-bond formation mechanism.[1,4a] Alternatively, quantum mechanical tunneling could be responsible for the observed A factor. However, kinetic analysis of the rate constant for rearrangement of **2a** and **2a**-d_3[11] gives an intermolecular kinetic isotope effect, k_H/k_D, of ≤1.3 at 22 °C.[25] This value is similar to those measured by product competition studies for other singlet carbenes ($k_H/k_D \cong 1.1$–1.5)[2,4] and probably reflects the predicted reactant-like, nonlinear transition state for the hydride migration.[1,2]

The application of PAC to the 1,2-hydrogen-shift rearrangement of alkylchlorocarbenes demonstrates its utility in the study of "invisible" or nonspectroscopic reactive intermediates in solution. However, PAC provides no structural information about the reactive intermediates so care must be exercised in relating a given heat deposition to a specific chemical reaction. Further experiments will examine the effect of carbenic substitution and solvent on the kinetics and energetics of the 1,2-hydrogen-shift rearrangement of alkylhalocarbenes.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8713720), the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(12) (a) The experimental enthalpic fitting parameter, α_n, is the fraction of incident photon energy released in a given heat deposition. The corresponding heat of reaction is $\Delta H(1) = (1 - \alpha_1)E_{h\nu}/\Phi$ or $\Delta H(2) = \alpha_2 E_{h\nu}/\Phi$, where Φ is the reaction quantum yield and $E_{h\nu}$ is the incident laser energy. (b) The values in Table I assume a quantum yield of 1 for each process, i.e., **1a–c** → **2a–c** and **2a–c** → **3a–c**. The quantum yield for the disappearance of **1a** in hexane is 1.00 ± 0.08 as determined by phenylglyoxylic acid actinometry[15] and UV–vis spectroscopy ($\epsilon_{337}(\mathbf{1a}) = 48.6$). This value is similar to gas-phase measurements, 0.95.[7a] A medium-pressure Hg lamp with bandpass filters to isolate the appropriate wavelengths is used. By ^{1}H NMR, the only product observed (>90% yield) after photolysis of **1a** in toluene-d_8 is **3a**. A quantum yield of 1 is assumed for both **1b** and **1c**. This is supported by previous studies,[5] ^{1}H NMR studies which show only alkenyl chloride products (**3b–c**), and the overall reaction thermodynamics.

(13) PAC measures the total volume change of the associated reaction. This includes volume changes from thermal, ΔV_{th}, and reaction volume, ΔV_{rx}, changes. The reaction volume contribution has previously been neglected,[8a–d,9,10] but it can be significant.[8e] We are presently investigating the magnitude of such changes. In both **1a** → **2a** and **1b–c** → **3b–c**, the reaction volume change should be positive which would give an erroneously large value for $\Delta H(1)$. However, the reaction volume change for **2a** → **3a** should be small so both $\Delta H(2)$ and $\Delta H_f(2)$ should accurately reflect the thermal volume change.

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(18) The PAC $\Delta H_f(\mathbf{2a})$ value includes the differential heat of solvation between **2a** and **3a**. Although the heat of solvation of **3a** is probably small, the stabilization of **2a** by solvent may be quite significant. Consequently, the $\Delta H_f(\mathbf{2a})$ value may be lower than that obtained in the gas phase.

(19) (a) Using $\Delta H_f(\text{CH}_3\text{CH(OCH}_3\text{)Cl}) = -64.8$ kcal/mol,[16b] $\Delta H_f(\text{CH}_3\text{OH}) = -48.1$ kcal/mol,[16a] and the heat of reaction, −65.8 kcal/mol, $\Delta H_f(\mathbf{2a}) = 49.1$ kcal/mol. (b) Using $\Delta H_f(\text{C}_8\text{H}_{15}\text{Cl}) = -7.7$ kcal/mol,[17b] $\Delta H_f(\text{C}_6\text{H}_{12}) = -16.4$ kcal/mol,[16a] and the heat of reaction, −38.6 kcal/mol, $\Delta H_f(\mathbf{2a}) = 47.3$ kcal/mol. (c) $\Delta H(1) + \Delta H(2) = -62.6$ kcal/mol using $\Delta H_f(\mathbf{1a}) = 71.2$ kcal/mol.[17c]

(20) (a) Compounds **1a–c** can potentially rearrange to their corresponding diazo compounds. Although this process has not yet been observed in solution for alkylchlorodiazirines, it potentially occurs in the gas phase.[7] This pathway would potentially complicate the PAC thermodynamic results, depending on the quantum efficiency and the rate constant for the decomposition of the diazo compound. However, on the basis of the evidence cited above, it appears unlikely that the PAC intermediate is the diazo compound and not the carbene **2a**, i.e., the PAC kinetic results are unaffected. (b) Quenching experiments suggest that some **3a** may be formed directly from **1a**, ≤10 ns, possibly via the diazo compound but presumably not via the ground-state carbene. The observed $\Delta H(2)$ would have to be corrected by dividing by the quantum yield for the reaction which does proceed via the carbene **2a**.[12] Consequently, $\Delta H_f(\mathbf{2a}) = 50.7$ kcal/mol would be a lower limit. Similarly, the large $\Delta H(1)$ value and the lack of a second heat deposition for both **1b** and **1c** could potentially be explained by the direct formation of **3b** and **3c** from **1b** and **1c**, without the intermediacy of carbenes **2b** and **2c**. In this regard, the PAC experiment would yield no information about the lifetime of carbenes **2b** and **2c**.

(21) Activation parameters are obtained from a nonlinear least-squares fit of the rate constants (5 determinations, 5 temperatures) to the Arrhenius equation.

(22) For comparison, the Arrhenius parameters for the related 1,2-hydrogen shift in benzylchlorocarbene to chlorostyrene obtained by indirect competition experiments are estimated to be $E_a = 6.4$ kcal/mol and log $(A/\text{s}^{-1}) = 12.2$.[3a]

(23) The rearrangement of **2a** is not observed by PAC in the more polar solvent CH$_3$CN at 22 °C, suggesting the lifetime of **2a**, ≥2 μs, is significantly longer than that in heptane. Irradiation of **1a** in CH$_3$CN produces only one heat deposition, ≤10 ns. The $\Delta H(1)$ value, −40.5 kcal/mol, indicates significant stabilization by the solvent, ~13 kcal/mol relative to heptane, presumably by formation of the acetonitrile ylide.

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(25) The rate constants for rearrangement of **2a** and **2a**–d_3 are equal within the error limits of the photoacoustic experiment. We are examining the temperature dependence on the rate constant for rearrangement of **2a**–d_3.

Divalent Vanadium and Dinitrogen Fixation: The Preparation and X-ray Structure of $(\mu\text{-N}_2)\{[(o\text{-Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{V(Py)}\}_2(\text{THF})_2$

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Since the initial discovery by Shilov that a V(OH)$_2$/Mg(OH)$_2$ system acts as a 1-electron reductant for the transformation of dinitrogen to N$_2$H$_4$ and NH$_3$,[1] the fixation of dinitrogen by divalent

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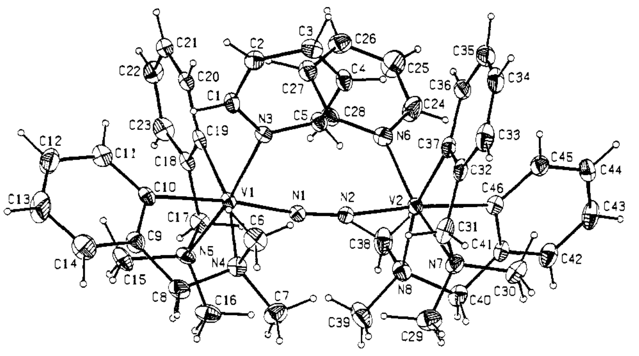
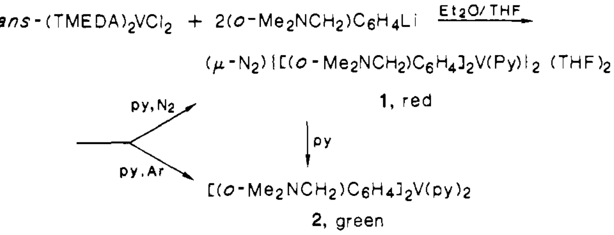


Figure 1. ORTEP drawing of 1 showing the labeling scheme. Selected bond distances (Å) and angles (deg): V1–N1 = 1.833 (3); N1–N2 = 1.228 (4); V1–N3 = 2.195 (3); V1–N4 = 2.322 (3); V1–N5 = 2.316 (3); V1–C10 = 2.204 (4); V1–C19 = 2.125 (4); N1–V1–N3 = 90.5 (1); N3–V1–C19 = 90.4 (1); C10–V1–C19 = 90.1 (1); N1–V1–N5 = 90.7 (1); V1–N1–N2 = 171.6 (3).

vanadium systems has received considerable attention.[2] In spite of these efforts and the possible relevance for vanadium nitrogenase modeling studies,[3] there are no examples reported up to date of characterized dinitrogen complexes. Possible reason for this lacuna in the literature is the extreme paucity of V(II) chemistry, limited exclusively to few diversified cases.[4] Information is so far available only on cyclopentadienyl[5] and related systems.[6] Undoubtedly, the limiting step in the development of this chemistry has been the absence of suitable V(II) starting materials.[7] We recently found that an unexpectedly high affinity of divalent vanadium for ligands containing nitrogen as donor atom allows the mild-condition and large-scale preparation of a class of monomeric and octahedral V(II) complexes *trans*-$Cl_2V(L)_4$ [L = pyridine, pyrrolidine, $^1/_2$*N,N,N′,N′*-tetramethylethylenediamine (TMEDA)].[8]

The reaction of *trans*-$Cl_2V(TMEDA)_2$ with 2 equiv of (*o*-$Me_2NCH_2)C_6H_4Li$ in THF/Et_2O proceeds at room temperature, forming brown-reddish solutions (eq 1). Addition of a small excess of pyridine slowly turns the color to emerald-green and precipitation of deep-red crystals of (μ-N_2){[(*o*-$Me_2NCH_2)C_6H_4]_2V$(Py)}$_2$(THF)$_2$ (**1**) were observed.[9] The molecular geometry of



1 has been demonstrated by X-ray analysis and is shown in Figure 1. The molecule is binuclear with no crystallographically imposed symmetry[10] and is composed of two almost identical fragments linked by a bridging dinitrogen moiety. As a probably minimization of steric hindrance, the two vanadium fragments are staggered by almost 90° [torsion angle N3–V1–V2–N6 = 84.2 (1)°]. Each vanadium atom has an octahedral coordination environment with a molecule of pyridine placed cis to the (μ-N_2) ligand. The remaining four coordination sites are occupied by the two chelating (*o*-$Me_2NCH_2)C_6H_4$– groups. The octahedral geometry of each vanadium atom is slightly distorted, probably as an effect of the steric interaction between the two vanadium units [C19–V1–N4 = 165.7 (1)°, C10–V1–N1 = 171.8 (1)°, N5–V1–N3 = 168.1 (1)°]. The vanadium–carbon bonds trans to the (μ-N_2) ligand are significantly longer than those in the cis positions [V1–C10 = 2.204 (4) Å and V1–C19 = 2.125 (4) Å, respectively]. This might be due to a trans effect of the partial π character of the vanadium–dinitrogen bond. In fact, the V–N distances (V1–N1 = 1.833 (3) Å, V2–N2 = 1.832 (3) Å] are quite short, suggesting a significant extent of double bond character.[11] In agreement with these considerations, the V–(μ-N_2)–V unit is close to linear [V1–N1–N2 = 171.6 (3)°, V2–N2–N1 = 171.3 (3)°] with a quite elongated N–N distance [N1–N2 = 1.228 (4) Å]. Therefore, the bonding mode of (μ-N_2) is somewhere between those observed in the cases of group IV metal compounds (Zr, Ti)[12,13] and the neopentylidene Ta complex,[14] which represent the two extreme cases of dinitrogen fixation and 2-electron reduction. However, the value of the magnetic moment of **1** [$\mu_{eff} = 3.47\mu_B$ per vanadium atom; calculated spin only for d^3 V(II) $\mu_{eff} = 3.87\mu_B$] although significantly lower than expected for a V(II) species, does not substantiate the point of view that (μ-N_2) has undergone a significant extent of reduction.

The IR spectrum of **1** differs for only three bands at 1597, 1487, and 785 cm^{-1} from that of $[(o\text{-}Me_2NCH_2)C_6H_4]_2V(Py)_2$[9] (**2**) prepared following the same procedure under exclusion of nitrogen (argon atmosphere). Although **1** is not centrosymmetric in the

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(10) Monoclinic crystals, space group $P2_1/n$, with a = 15.032 (3) Å, b = 19.014 (2) Å, c = 17.895 (2) Å, β = 93.78 (2)°, V = 5103.6 (1) Å^3, Z = 4. Diffraction data [1.07° < θ < 26.00°] were collected at 130 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Data were corrected for the scale variation, Lorentz and polarization effects but not for absorption. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86). All the atoms were located, including those of the two partially disordered molecules of THF, and refined anisotropically. Hydrogen atoms were located by using difference Fourier techniques and isotropically refined. Block-diagonal least-squares refinement converged to R_F = 0.060 (R_w = 0.059).

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solid state, none of these resonances appears to arise from the N–N stretching as **1**-^{15}N exhibits a virtually identical spectrum.

The coordination of N_2 is quite robust and only traces of nitrogen were pumped-off from a solution of **1** in THF, during several evacuation cycles carried out in a high-vacuum line equipped with a Toepler pump. However, complex **1** exhibited a quite promising chemical reactivity because replacement of (μ-N_2) can be achieved with a number of reagents including CO, acetylenes, and other unsaturated organic substrates. An extensive study to delineate the chemistry of this complex is in progress at the moment,

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and an extensive list of bond distances, angles, and torsion angles (19 pages); tables of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

Formation of NH_x(a) Species by Hydrogenation of c(2×2)-N on Pd(100)

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Neither dissociative adsorption of N_2 on palladium metal surface nor formation of bulk nitride of palladium has been observed, So far, only adsorption of nitrogen stimulated by electron bombardment on polycrystalline Pd,[1] Pd(331),[2] Pd(110),[3] or enrichment or accumulation of nitrogen through dissociative adsorption of NO on Pd(331)[2] or during reaction of NO with CO or H_2 nitrogen on polycrystalline Pd[4] has been reported in the literature. The catalytic reduction of NO with hydrogen or carbon monoxide, NO + H_2 or CO → N(a) + H_2O or CO_2, on a Pd(100) surface yielded the ordered adsorption of N in a c(2×2) structure.[5] In this paper, NH_x intermediates were detected during hydrogenation of N(a) on a Pd(100) surface by high-resolution electron energy loss spectroscopy (HREELS).

Experiments were performed in an ultrahigh vacuum chamber attached with a small-volume, high-pressure reactor of which details were reported elsewhere.[6] A clean surface was obtained by Ar ion bombardment and oxidation at a 10^{-7} Torr of O_2 at 700–900 K followed by annealing in vacuum. The clean Pd(100) surface was exposed to a 1:1 mixture of NO and H_2 or NO and CO at a total pressure of 2–4 Torr and 550–600 K for 5 min. The gas phase was evacuated, and the crystal was rapidly cooled to room temperature. The crystal was then heated to 450 K for a few seconds to remove molecularly adsorbed species, By this procedure, a clean Pd(100) surface only with adsorbed nitrogen in a relatively large amount, N(KLL)/Pd(MNN) = 0.02, was obtained.[5]

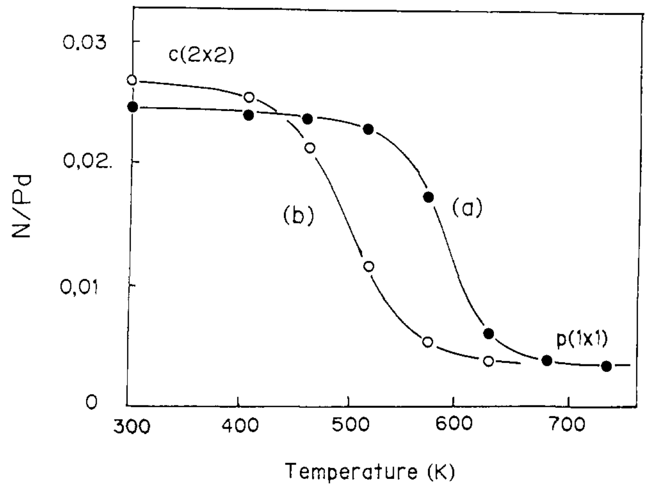

Figure 1. Change of N(KLL)/Pd(MNN) AES ratio when c(2×2)-N on the Pd(100) surface was heated in vacuum (curve a) and in H_2 of 1 × 10^{-6} Torr (curve b).

Figure 1 shows the change of the N/Pd Auger peak ratio when the c(2×2)-N on the Pd(100) surface was heated up step by step in vacuum (curve a) and in 1 × 10^{-6} Torr of H_2 (curve b). It is clear that the N/Pd ratio started to decrease at about 550 K in vacuum but at 430 K in H_2. HREELS was used to follow the surface reaction of c(2×2)-N with hydrogen. A c(2×2)-N overlayer was prepared on the Pd(100) surface and was examined by in situ HREELS experiments while exposing the surface to 1 × 10^{-7} Torr of H_2 at 400 K for 50 min. The N–H stretching vibration was seen at 3190 cm^{-1}. The deformation frequencies of the NH_x (x = 1, 2, 3) species were observed between 1140 and 1600 cm^{-1} for NH_3(a),[7] 1560 cm^{-1} for NH_2 in an amido(NH_2) complex of Co,[8] and 1414 cm^{-1} for NH in a imido(NH) complex of Os.[9] Our spectra do not have sufficient resolution (about 20 meV during this experiment) to identify the specific value of x, and a very weak band which might correspond to Pd–N was recognized in some cases at 720 cm^{-1}. Figure 2 shows the time dependent change of the HREELS spectra of the c(2×2)-N Pd(100) surface in the presence of 10^{-7} Torr of H_2 at 375 K. The heating current through the sample during measurement of the energy loss spectrum may be responsible for the poor S/N ratio of the spectrum. The loss peak for the NH_x species grew for 16 min (spectrum 2). When the H_2 was replaced with D_2 at 19 min, the peak for ND_x appeared immediately (spectrum 4) and became the major peak at 41 min (spectrum 5). A large inverse isotope effect in the synthesis of ammonia on a doubly promoted Fe catalyst[10] and a large normal isotope effect in the decomposition of ammonia on W-filament, powder, and polycrystalline foil[11] have been observed. In the case of the hydrogenation reaction of c(2×2)-N on the Pd(100) surface, when the ambient gas was replaced with a 1:1 mixture of H_2 and D_2 (1 × 10^{-7} Torr) at 53 min, peaks for NH_x and ND_x were observed simultaneously (spectra 6 and 7). The S/N ratio was rather poor, but no appreciable isotope effect was observed for the equilibrium amounts of the NH_x species on the Pd(100) surface. The LEED pattern of c(2×2) did not change when the surface was exposed to H_2 at around 400 K, and there was no great difference from the c(2×2) of pure N(a) by visual observation of the "I-V" function. When the surface with NH_x was heated up to 450 K in vacuum, the peak at 3190 cm^{-1} disappeared, but no appreciable decrease of N(a) by AES was observed. It is therefore likely that N(a) is still the dominant species and NH_x is a small part on the surface,

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