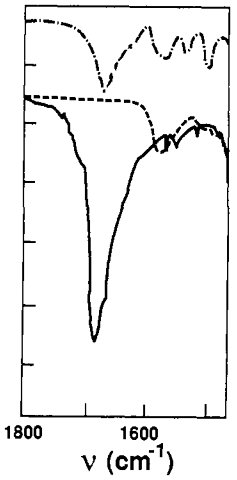

Figure 2. IR of $\mathbf{4}^{\bullet-}$ (—■—), $\mathbf{4}^{2-}$ (- -), and **4** (—) formed sequentially from reduction of **4** and reoxidation to **4** in DMF,$Bu_4N(BF_4)$. The spectrum of $\mathbf{4}^{\bullet-}$ is offset for clarity.

mixed-valence structure which tends to temporarily localize the anion radical charge on one quinone moiety.

This structural hypothesis is supported by comparison of the IR spectrum of $\mathbf{4}^{\bullet-}$ (Figure 2) with the spectra of the delocalized $\mathbf{3}^{\bullet-}$ and the localized[8] $\mathbf{6}^{\bullet-}$. In DMSO $\mathbf{3}^{\bullet-}$ has a C=O band[9] at 1581 cm^{-1} as expected[10] if both quinones share the extra electron, while $\mathbf{6}^{\bullet-}$ has both a quinone C=O at 1650 and semiquinone C=O at 1505 cm^{-1}. In contrast to both, $\mathbf{4}^{\bullet-}$ has no clearly recognizable band in the C=O region (1700–1450 cm^{-1}). This is similar to the spectrum of the anion radical of an unconjugated bis-indanone anion radical studied by Mazur and Schroeder and precociously explained in terms of a mixed-valence structure.[11]

Also in agreement with this hypothesis are the $E^{\circ\prime}$ values (Table I). Since the anion of $\mathbf{4}^{\bullet-}$ is largely localized, it is relatively easy to add a second electron, and the separation (ΔE) between the first and second peaks is small. For comparison, consider the localized **6** (ΔE = 230 mV) and the delocalized **3** (ΔE = 480 mV) along with **4** (ΔE = 250 mV). It is also notable that the first $E^{\circ\prime}$ for **5** is essentially the same as that for the model monoquinone **1**.

The hypothesis of charge localization in the larger ions was tested with ab initio, restricted Hartree–Fock level calculations using both single- and double-ζ basis sets.[12] Such calculations showed that because the longer ions are extraordinarily polarizable, extremely small perturbations lead to substantial localization of the odd electron on one quinone moiety. A localized ion necessarily has a nonsymmetric charge distribution relative to the center of mass, giving rise to a dipole moment. Therefore, as a measure of localization we have subjected the ions to small perturbations and calculated the dipole moments of these perturbed ions. For comparison, we also calculated the dipole moments of hypothetical, completely localized ions, which have one-half of a negative charge on each oxygen of one quinone moiety. For example, a calculation using a geometry with the two C–O distances on one end lengthened by 0.01 Å and the two on the other end shortened by 0.01 Å (corresponding to a B_{1u} vibrational distortion) gave large dipole moments for $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ (Table I). These dipole moments were about 70% as large as the moments calculated using the completely localized models. Calculations including a small electrostatic field (like a solvent field) along the long molecular axis gave similar results. Thus, the calculations show $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ are different from $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ and that small perturbations lead to localization of the odd electron for $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$.

The surprising conclusion of this study is that at least on the IR time scale the extra electron of $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ is largely localized on one quinone unit. This is in spite of the fact that the two quinones are connected by what is considered an excellent π delocalizing, conjugated framework.

Acknowledgment. This work was supported by NSF, SDIO/NRL, and the Minnesota Supercomputer Institute, We thank Professor Adrian Docken for the sample of **6**.

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Surface Methylene, Hydrogen, and C_xH Species from the Dissociative Adsorption of Diazirine on W(100) at 100 K

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Diazirine is found to be a suitable precursor for the isolation of C_1 fragments on W(100). The catalytic transformation or synthesis of hydrocarbon molecules on surfaces may often involve the formation of adsorbed C_1 intermediates. A knowledge of the identity and the chemistry of such species is crucial to the determination of surface reaction mechanisms as well as the factors which govern selectivity in heterogeneous catalysis. Vibrational spectroscopy in the form of electron energy loss spectroscopy (EELS), and more recently FT-IRAS, has led to the detection of adsorbed CH, CH_2, CCH, CCH_2, CCH_3, and $CHCH_2$ on single crystal metal surfaces following the decomposition of adsorbed parent molecules such as ethylene or acetylene.[1a–d] However, as yet, there is no clear evidence that the decomposition of these molecules on metal surfaces leads to adsorbed methylene.[2] Interest in adsorbed CH_2 stems from the role it is proposed to play in a variety of surface reactions such as methanation, metathesis, homologation, and Fischer–Tropsch reactions.[3] The chemistry and structure of the CH_2 ligand has been explored in detail by inorganic chemists. Among the many fascinating results of the latter studies is the observation that ethylene reacts with methylene bridged dinuclear complexes to yield propene.[4] The conversion of the μ-CH_2 ligand to μ-CH_2CO and μ-C_3H_6 ligands has also been reported.[5,6] Clearly there is a need for a parallel exploration of CH_2 chemistry on metal surfaces. A delineation of the similarities and the differences in the chemistry of such a reactive

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species would possibly reveal additional insight on the extent to which metal complexes may serve as models for extended metal surfaces.

Since typical simple hydrocarbons do not decompose on most metals to yield adsorbed methylene, special preparation schemes are necessary. George et al.[7] used diazomethane adsorption to isolate CH_2 on Ru(001). Ketene was used by McBreen et al.[8] to generate methylene on Fe(110). Extensive spectroscopic studies of the interaction of ketene with Pt(111) and with Ru(100) have been performed by White et al.[9,10] It appears possible to use a halocarbon such as dichloromethane to generate adsorbed CH_2,[11] but the resulting coadsorbed halogen would be expected to greatly influence any ensuing surface chemistry of the hydrocarbon fragment. More subtle, though nevertheless significant, interactions may occur between coadsorbed CO and CH_2 derived from ketene.[12] The ideal approach is to use CH_2N_2, since for most metals nitrogen should desorb leaving a pure hydrocarbon surface layer. However, the experimental problem with diazomethane, in addition to the well-known difficulty in handling and storing it, is that since it is very reactive it may decompose during introduction to the vacuum chamber. In this way, as has been pointed out by Hills et al.,[13] one may inadvertently expose the sample to ethylene formed from CH_2N_2 in the doser. In this letter we wish to report on the feasibility of using diazirine, which is a cyclic isomer of diazomethane, as a precursor for adsorbed methylene. The unreactive nature of diazirine[14] makes it promising for UHV studies in that it may largely preclude unwanted interactions with the chamber walls or the gas doser, and thus the molecule may remain intact until it encounters the highly reactive clean surface of the sample under study. Paulett and Graham[15] observed, in an early mass spectrometric study, that diazomethane decomposed in the metal gas handling line, whereas diazirine remained stable.

The experiments were performed in a stainless steel UHV chamber equipped with a 127° cylindrical deflector EELS instrument and a mass spectrometer. The W(100) surface was cleaned by oxygen treatment followed by electron bombardment heating. The base pressure of the system was in the 10^{-11} Torr range. The EELS measurements were made at 60° angle of incidence and with an electron impact energy of 1.8 eV. The acceptance angle of the analyzer is ±0.5°. Off-specular measurements were made by rotating the analyzer by 6°. Diazirine was prepared following the procedure of Ohme and Schmitz,[16] in a turbomolecular pumped gas handling line which was attached directly to the UHV leak valve. A detailed account of the apparatus and the preparation will be given elsewhere. The purity of the diazirine following introduction into the vacuum chamber was checked using a quadrupole mass spectrometer. Typical relative mass spectral abundances as observed by us compare well with data reported by Paulett and Ettinger.[15]

Spectra were recorded in-specular and off-specular for various exposures of W(100) to diazirine at 100 K. Representative spectra are shown in Figure 1. The in-specular spectrum for an exposure of approximately 0.4 L of diazirine (a) displays well-resolved intense losses at 780, 1030, and 1440 cm^{-1} and a double peak at 2950 and 3050 cm^{-1}. Higher exposures lead to the further growth of the feature at 2950 cm^{-1} and little change in the other losses. The growth with increasing exposure of the loss at 2950 cm^{-1} obscures the feature at 3050 cm^{-1}. However, the presence of the latter peak at higher exposures is evident from the asymmetry of the CH stretching loss. The loss at 3050 cm^{-1} is more clearly resolved in off-specular spectra due to the relative decrease in the intensity of the peak at 2950 cm^{-1}. Two less intense losses at 570 and 1230 cm^{-1} are resolved in the in-specular spectra. The loss at 780 cm^{-1} is strongly attenuated in off-specular spectra indicating that it is a dipole-enhanced mode. Adsorption at room temperature leads to a loss at 600 cm^{-1}, which may be attributed to surface carbon.

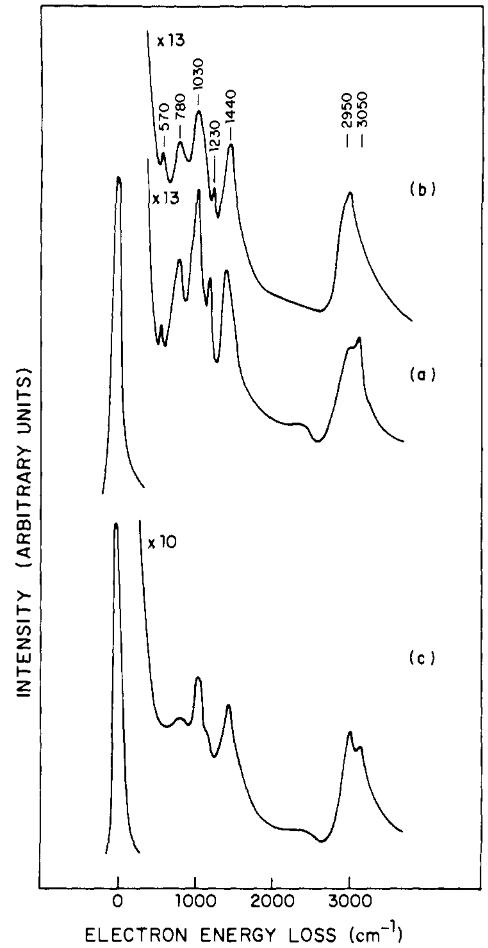

Figure 1. EELS spectra for the adsorption of diazirine on clean W(100) at 100 K: (a) 0.4 L CH_2N_2 and (b) 9 L CH_2N_2. Both spectra were measured in-specular. Spectrum (c) is for a 9 L exposure of CH_2N_2 and was taken 6° off-specular.

The loss at 1030 cm^{-1} which is resolved in all of the spectra in Figure 1 may be assigned to a metal-hydrogen stretching mode, characteristic of β_1-H. This species is observed at high coverage on clean unreconstructed W(100)[17] and at lower coverages on W(100) in the presence of coadsorbed oxygen.[18] Adsorbed hydrogen resulting from the decomposition of both C_2H_2 and C_2H_4 on W(100) displays an intense loss at 1020 cm^{-1}.[19] The loss at 580 cm^{-1} may be assigned to a metal-carbon stretching mode, as the corresponding mode for C_2H_4 on W(100) appears at 600 cm^{-1}.[19] The absence of a loss at approximately 2100 cm^{-1} indicates that there is negligible adsorption of molecular nitrogen on the CH_2N_2 exposed surface.

A great deal of data has been accumulated in the literature on the surface species which appear during the thermally induced decomposition of alkenes and alkynes on metal surfaces.[1a-d] EELS spectra repeatedly show the existence of a species, characterized by a loss in the 760-880-cm^{-1} region and a loss in the 2990-3050-cm^{-1} region, immediately prior to complete decomposition.

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Through correlation with hydrogen desorption measurements and comparison with IR spectra of organometallic complexes, this species is usually attributed to surface methylidyne or to an acetylide species in the case where a ν(CC) mode at approximately 1300 cm^{-1} is detected. For the system Ru(001), for example, CH is characterized by a stretching mode at 3010–3030 cm^{-1} and a bending mode at 800–840 cm^{-1}.[1a] The corresponding modes for $(CO)_4Co_3$–(μ_3-CH)[20] appear at 3041 and 850 cm^{-1}, respectively. The ν(CC) mode for acetylide on Ru(001) appears at 1290 cm^{-1}.[1a] On the basis of the above fingerprinting considerations we assign the observed losses at 780, 1230, and 3050 cm^{-1} to a mixture of adsorbed CH and C_2H. Adsorbed acetylide is a common decomposition product of C_2 molecules, such as ethylene or acetylene, on metal surfaces. However, if acetylide is indeed present on the W(100) surface, following CH_2N_2 adsorption, then it most likely results from the coupling of C_1 species. Another possible route to CCH is the interaction of an adsorbed C_1 unit with a molecule of CH_2N_2. The remaining two losses at 2950 and 1440 cm^{-1} are typical for a CH_2 species. The δ (CH_2) and the ν_5 (CH_2) modes for CH_2 on Fe(110) appear at 1420 and 2970 cm^{-1}, respectively.[8] The corresponding modes for $Fe_2(CO)_6(\mu\text{-}CO_2)(\mu\text{-}CH_2)$ appear at 1379 and 2910 cm^{-1}, respectively.[21] The interpretation of the interaction of diazirine with W(100) at 100 K, as given above, leads to the following simple decomposition scheme:

$$CH_2N_2(g) + W(100) \rightarrow CH_2ads + C_xHads + Hads + N_2(g)$$

We anticipate that on less reactive metals than tungsten we may be able to use diazirine to vary the surface concentration of selected C_1 units. With this in mind, we are in the process of studying the interaction of diazirine-d_2 and diazirine with the Pd(110) surface as a function of temperature.

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Organolanthanide-Catalyzed Hydroamination. Facile, Regiospecific Cyclization of Unprotected Amino Olefins

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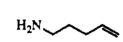
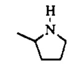
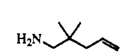
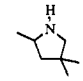
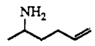
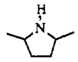
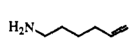
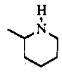
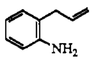
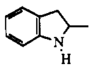
The remarkable facility with which early lanthanide–alkyl bonds undergo olefin insertion within bis(pentamethylcyclopentadienyl)metal coordination spheres[1] (e.g., eq 1; N_t (1 atm ethylene; 25 °C) $\gtrsim$ 1800 s^{-1} when X = primary alkyl or hydride and Ln = La[1a]) suggests that, in this environment, thermodynamically feasible but normally unobserved insertion processes involving other metal–X bonds may also be rapid. Coupling to proton-transfer processes (e.g., eq 2) would then constitute a

$$Cp'_2Ln\text{—}X + H_2C{=}CH_2 \rightarrow Cp'_2Ln\text{—}CH_2CH_2X \quad (1)$$

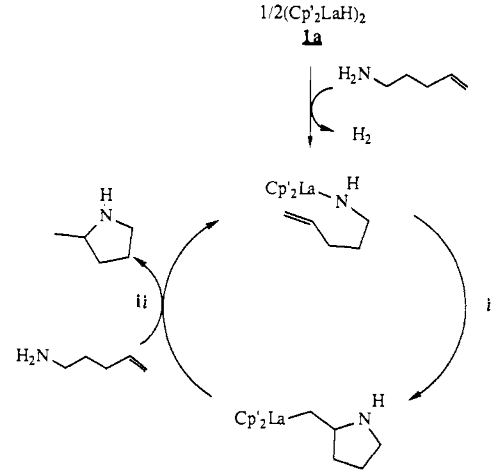
$$Cp'_2Ln\text{—}CH_2CH_2X + HX \rightarrow Cp'_2Ln\text{—}X + CH_3CH_2X \quad (2)$$

catalytic cycle for HX addition to olefins. For lanthanide amides (X = NR_2), we estimate eq 1 to be approximately thermoneutral,[2,3] while eq 2 should be both rapid[4a] and exothermic.[2a–d,4b,c] As the first embodiment of such a strategy, we report here the facile and regiospecific organolanthanide-catalyzed hydroamination/cyclization of N-unprotected amino olefins,[5] heretofore difficult homogeneous transformations proceeding (e.g., with Pd^{2+} catalysts) via distinctly different mechanistic pathways.[6–8]

Table I

entry	substrate (ref)		product (ref)		N_t (h^{-1}, °C)	catalyst
1		**2**[9]		**7**[9]	13 (25) 140 (60)	**1a** **1a**
2		**3**[6a]		**8**[9]	125 (25) 75 (80) <1 (80)	**1a** **1b** **1c**
3		**4**[9]		**9**[9,13]	84 (25)	**1a**
4		**5**[9]		**10**[9,13]	5 (60)	**1a**
5		**6**[14]		**11**[13]	13 (80)	**1a**

Scheme I



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