important for ^{13}C NMR, can lead to line broadening, even for fairly dilute proton samples, because of the high-Q and large filling factors of probe coils in modern high field NMR spectrometers. Additionally, even a small amount of radiation damping, which leads to only a slight line broadening, can give rise to major spacing and intensity artifacts in *partially overlapped resonances*. This second effect of radiation damping is not removed by line narrowing techniques, and it is strongly pulse angle dependent. Analogous effects have been investigated previously in sweep NMR with a special feedback spectrometer,[12] but the "multiplet" effect in radiation damping does not seem to have been described previously in ordinary FT NMR. Radiation damping can be reduced by decreasing the filling factor (e.g., by using a smaller diameter tube for a given coil), by decreasing the concentration of the compound, or by detuning the probe. Multiplets whose partially overlapped lines are independent of the pulse angle are free from radiation damping effects.[13]

We plan to investigate other heavy-atom isotope effects on protons by ultrahigh resolution ^1H NMR. Such data are of value in understanding vibrational effects on chemical shifts and to provide comparisons with quantum mechanical calculations.[2]

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(13) We plan to investigate further the radiation damping effects in overlapped multiplets. In CH_3Cl, radiation damping can change the 3:1 doublet into, for example, an apparent 1:1 doublet.

Carbon–Hydrogen Bond Activation and Carbon–Carbon Bond Formation in the Reaction between Ethylene and Hexaisopropoxyditungsten

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Ethylene reacts with certain metal surfaces to give a capping (μ_3) ethylidyne ligand.[1] In triosmium carbonyl chemistry ethylene has been shown to undergo successive C–H activation to give a μ-σ,π-vinyl and a μ-vinylidene ligand.[2] A similar reaction sequence has been reported by Puddephatt and co-workers in the addition of ethyne to a hydrido triangulo platinum complex.[3] We have repeatedly emphasized the relationships, both structural and chemical, between reduced metal oxides of molybdenum and tungsten and smaller alkoxide clusters and their larger (closo) counterparts.[4] For example, the square-$Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ and butterfly-$Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ molecules[5] are *arachno* subunits of the $M_6(\mu_3\text{-}X)_8$ cluster unit, and $W_4(O\text{-}i\text{-}Pr)_{12}$[6] represents a fragment of the $M_6(\mu_2\text{-}X)_{12}$ unit.[7] Furthermore the M_4–alkoxide clusters are formed from the coupling of M_2 alkoxides by steric control in the choice of the OR group. Indeed we have established that an equilibrium exists between $W_4(O\text{-}i\text{-}Pr)_{12}$ and $W_2(O\text{-}i\text{-}Pr)_6$.[6,8] One of our hypotheses is that these small unsaturated alkoxide cluster units may provide models for active sites on reduced metal oxide surfaces. We describe here the observation of the activation of ethylene by $W_2(O\text{-}i\text{-}Pr)_6$ under extremely mild conditions.

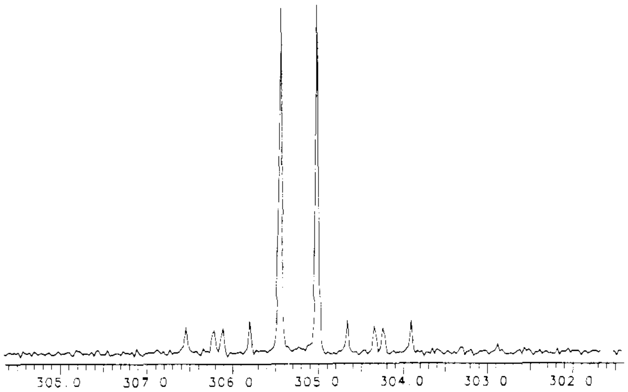

Figure 1. $^{13}C\{^1H\}$ spectrum of the alkylidyne carbon in the ^{13}C labeled compound $W_2(\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2})(O\text{-}i\text{-}Pr)_6$ where *C represents 99 mol % ^{13}C. The spectrum is interpretable in terms of $^1J_{CC} = 30$ Hz and a satellite spectrum arising from coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance $^1J_{WC} = 117$ and 165 Hz. The proton-coupled spectrum reveals that the alkylidyne carbon is coupled to two equivalent hydrogen atoms, consistent with the connectivity $\mu\text{-}{*C}{*CH_2}$, $^2J_{CH} = 6$ Hz. The spectrum was recorded at 22 °C, 75.4 MHz in benzene-d_6. Chemical shifts were referenced to the central carbon signal of benzene-d_6 at 128.0 ppm.

Addition of ethylene (2 equiv) to a hydrocarbon solution of $W_2(O\text{-}i\text{-}Pr)_6$ leads to a reaction at −20 °C. The initially formed complex is possibly a dissociatively labile adduct $W_2(O\text{-}i\text{-}Pr)_6(C_2H_4)_x$ which reacts at 22 °C, $t_\infty = 24$ h, to give a new compound both quantitatively and irreversibly.[9] The new compound is highly fluxional on the NMR time scale, and even at −90 °C the alkoxide signals are not completely frozen out in toluene-d_8. However, it appears that the alkoxide methyne signals fall into a 3:2:1 integral ratio. Thoughout the temperature range +22 °C to −90 °C the ^1H signals derived from ethylene appear as triplets $\delta = 4.70$ and 2.75 ppm and a quintet $\delta = 3.58$ with $J_{HH} = 6.0$ and 6.5 Hz, respectively. On single frequency decoupling the quintet resonance at 3.58 ppm, *both* triplets collapse to singlets, which establishes the connectivity $X\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Y$ (the apparent quintet is really a triplet of triplets). In the ^{13}C spectrum there are resonances at δ 56.3 with $J_{^{183}W-^{13}C} = 99$ Hz and $\delta = 42.6$ and 54.2. There is no discernible coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance to the latter two resonances, but in the proton-coupled ^{13}C spectrum all of the above carbon signals show one bond coupling to two hydrogen atoms. This reliably establishes the connectivity $WCH_2CH_2CH_2Y$. There is in addition a fourth carbon resonance at δ 305.3. Reactions employing $*C_2H_4$, where *C respresents 99 mol % ^{13}C identify the connectivity depicted diagrammatically in I below, in which the alkylidyne carbon bridges two inequivalent W atoms. The proton-decoupled spectrum of the alkylidyne carbon δ 305.3 ppm is shown in Figure 1 for the product derived from the use of $*C_2H_4$. Note the appearance of two significantly different couplings to ^{183}W, 117

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(1) (a) Eg. on Pt surfaces, see: Somorjai, G. A. In *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: 1981; p 278. (b) See, also for μ-vinylidyne and μ-ethylidyne interconversions: Hills, M. M.; Parmeter, J. E. Weinberger, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597. Hatzikus, G. H.; Loxton, C. M.; Masel, R. I. *J. Vac. Sci. Technol.*, in press (Proc. 1986 Am. Vac. Soc. Natnl. Symp.).

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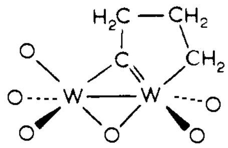
(7) For drawings of the so-called 6–8 and 6–12 clusters, see the following: Raithby, P. R. in ref 2., Chapter 1, pp 118–121, Figures 2, 3, 5, and 6 or Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 4th eds; Wiley: 1980; p 57.

(8) For $W_4(O\text{-}i\text{-}Pr)_{12} \rightarrow 2W_2(O\text{-}i\text{-}Pr)_6$, $\Delta H° = +23$ kcal mol^{-1} and $\Delta S° = +61$ eu. Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. *J. Am. Chem. Soc.*, submitted for publication.

(9) We have recently characterized the bisethylene adduct $W_2(ONp)_6(C_2H_4)_2$ formed by the addition of ethylene to hydrocarbon solutions of $W_2(ONp)_6$ where Np = neopentyl.



and 165 Hz, implying a gross asymmetry in the alkylidyne bridge, which may formally be assigned to W–C single and double bonds, respectively, as shown in I above. It should be noted that we can find no evidence for the presence of W–H moieties from either ^{1}H NMR spectra or ^{13}C proton-coupled spectra. Thus we believe that the new compound is formed with the liberation of dihydrogen according to eq 1.[10]

$$W_2(O\text{-}i\text{-}Pr)_6 + 2C_2H_4 \rightarrow W_2(\mu\text{-}CCH_2CH_2CH_2)(O\text{-}i\text{-}Pr)_6 + H_2 \quad (1)$$

The new compound has a structural analogy with the previously fully characterized compound $W_2(\mu\text{-}NC(Ph)CHCH)(O\text{-}i\text{-}Pr)_6$ formed by the coupling of C≡C and C≡N ligands at the dinulcear center.[11] A plausible reaction pathway leading to the $W_2(\mu\text{-}CCH_2CH_2CH_2)$ moiety involves (i) C–H activation to generate a hydrido σ,π-vinyl, (ii) conversion to a μ-vinylidene ligand with elimination of H_2 and (iii) coupling of the $\mu\text{-}C{=}CH_2$ ligand with ethylene.

To our knowledge the $W_2(\mu\text{-}CCH_2CH_2CH_2)$ dimetallacycle has not been seen before in organometallic chemistry though there is clearly some analogy with proposed mechanisms for hydrocarbon chain grown on metal surfaces.

Further studies are in progress.[12]

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[10] In the presence of excess ethylene, ethane is formed as evidenced by ^{13}C and ^{1}H NMR spectroscopy employing sealed NMR tubes.

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Preparation, Characterization, and X-ray Crystal Structure of an Acetonitrile-Complexed Ruthenium Silylene

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Silylene complexes ($L_nM{=}SiR_2$) are postulated intermediates in a number of transition-metal-mediated transformations, including Rochow's direct process,[1] catalytic redistribution of silanes,[2] and various silylene-transfer reactions.[3] Unfortunately, such species have been synthetically elusive, despite the well-established existence of congeneric carbene,[4] germylene,[5,6] stannylene,[5,7] and plumbylene[5,6b,c,8] complexes. Although numerous examples of silylene-bridged bimetallic species exist,[9] there are no well-characterized examples of compounds possessing a formal metal–silicon double bond, despite numerous attempts to prepare them.[10] To investigate the chemistry of transition-metal–silicon double bonds, we are attempting to develop synthetic routes to such terminal silylene complexes. Here we report the first synthesis and complete structural characterization of a base-stabilized transition-metal silylene complex.

The synthetic approach described here involves removal of a group bound to silicon with an electrophilic reagent, E^+ (eq 1, $Cp^* = \eta^5\text{-}C_5Me_5$, L = PMe_3). This technique has been quite

$$Cp^*L_2Ru{-}SiXR_2 + E^+Y^- \rightarrow [Cp^*L_2Ru{=}SiR_2]^+Y^- + E^+X^- \quad (1)$$

useful in syntheses of carbene complexes[4,11] but has thus far failed to afford the analogous silylenes. In particular, where fluorinated anions (BF_4^-, PF_6^-) have been employed, fluorination of the silyl ligand results.[9b,10a,g] For this reason our efforts have focused on the less-coordinating tetraphenylborate anion. Our choice of an electron-rich metal center should further stabilize an electron-deficient silicon center.

The starting ruthenium silyl complex **2** is prepared by reaction of excess $HSiPh_2Cl$ with the alkyl $Cp^*L_2RuCH_2SiMe_3$[12] (**1**) in toluene at 100 °C (eq 2). This reaction produces mostly the pale

$$\underset{\mathbf{1}}{Cp^*L_2RuCH_2SiMe_3} + (x + 2y)HSiPh_2Cl \xrightarrow[-yPMe_3]{-SiMe_4} x\underset{\mathbf{2}}{Cp^*L_2RuSiPh_2Cl} + y\underset{\mathbf{3}}{Cp^*LRu(SiPh_2Cl)_2H} \quad (2)$$

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