formyl moieties in $[(HCO)_2(Mo_8O_{28})]^{-6}$. The stereochemical positions of the bridging methoxy groups appear to be unique.

The rate-limiting step in the conversion of methanol to formaldehyde over MoO_3 is the breaking of a C–H bond.[1] Presumably, one of the methoxy protons is transferred to a neighboring oxygen atom on the MoO_3 surface. As a model for the methoxy–MoO_3 intermediate in this reaction, the conformations of the methoxy groups in the $Mo_8O_2(OCH_3)_4^{-4}$ anion of the present structure were thus of particular interest; the formation of short C–H--O contacts[15] would obviously indicate possible paths for proton transfers. There are, in fact, three contacts with H--O distances that are less than 2.5 Å.[16] Interestingly, the methoxy groups adopt conformations that allow *one* hydrogen atom of each group to form a short C–H--O intramolecular contact. One intermolecular contact is also found. All three have terminal oxygen atoms (i.e., Mo═O) as receptors. Table III gives the geometrical details of these contacts.

Registry No. $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8CH_3OH$, 86747-45-7; $Na_4[Mo_8O_{24}(OCH_3)_4]$, 86727-42-6; $Mo_2O_5(OCH_3)_2$, 86727-41-5; Na_2MoO_4, 7631-95-0; Mo_4O_{11}, 12033-38-4; MoO_2, 18868-43-4; $Na_4Mo_8O_{26}$, 57455-64-8; MoO_3, 1313-27-5; formaldehyde, 50-00-0; methanol, 67-56-1.

Supplementary Material Available: A listing of positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles, figures of the Na(1) and Na(2) environments, and a table of structure amplitudes (45 pages). Ordering information is given on any current masthead page.

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(15) Taylor, R.; Kennard. O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070.

(16) Typical of (and inherent in) the X-ray diffraction method, the hydrogen atom positions suffer from systematic errors which lead to C–H bond lengths that are considerably shorter than the true internuclear distances. The calculated H--O distances are consequently somewhat longer than their true values.

Detection by ^{13}C CPMAS NMR of Molecules Photochemically Generated in Organic Glasses at Low Temperature

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Detection and characterization of matrix-isolated molecules by UV, IR, and EPR spectroscopy has become a powerful method for the study of reactive species.[1] Although it is the most diagnostic spectroscopic tool for structural analysis, NMR has never been used to detect molecules photochemically generated in the solid state. The reason for this has been lack of sensitivity and resolution in the NMR spectra of solids, but the cross polarization–magic angle spinning (CPMAS) experiment has led to significant improvement in both sensitivity and resolution.[2] Therefore, we have explored the potential of low-temperature CPMAS NMR spectroscopy for studies of photolytically generated species and report here on the development of a technique that permits the detection by NMR of molecules photochemically generated in organic glasses.

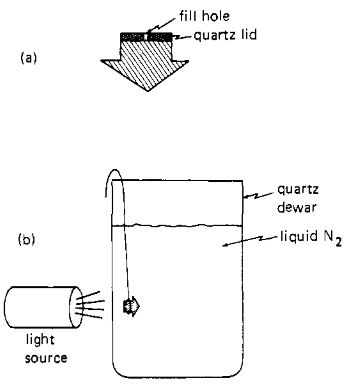


Figure 1. (a) MAS rotor fitted with a quartz lid and fill hole; (b) apparatus for photolyzing precursor in an organic glass in the rotor shown in Figure 1a.

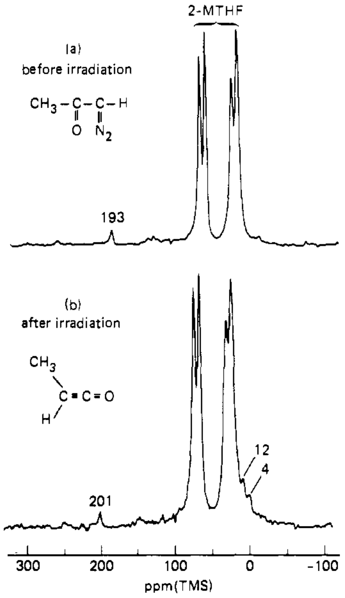
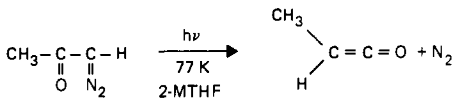


Figure 2. (a) Proton-decoupled ^{13}C CPMAS spectrum at 80 K of the 1-diazo-2-propanone (**1**) in 2-MTHF before photolysis; (b) proton-decoupled ^{13}C CPMAS spectrum of the material in the rotor after photolyzing for 24 h at 77 K, showing conversion to methyl ketene (**2**).

To illustrate the method, we have chosen a particularly simple photochemical reaction, the conversion of 1-diazo-2-propanone (**1**) to methyl ketene (**2**).[3]



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{N_2}{\|}}{C}-H \xrightarrow[77\,K,\ 2\text{-MTHF}]{h\nu} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=C=O + N_2$$

1 2

A 10 mol % solution of **1** in 2-methyltetrahydrofuran (2-MTHF) was loaded into a rotor fitted with a quartz lid, shown in Figure 1a. The solution was quenched slowly in liquid nitrogen and transferred into the MAS apparatus at temperatures well below the "softening" temperature of the glass (about 100 K for pure 2-MTHF).[4] The proton-decoupled ^{13}C CPMAS spectrum of this sample obtained at 80 K is shown in Figure 2a. The four intense high-field peaks are from the carbons of the solvent, while the single downfield peak at 193 ppm is due to the carbonyl carbon of the diazo ketone precursor (**1**).[5] The resonance of the methyl

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(1) B. Meyer, "Low Temperature Spectroscopy"; Elsevier: New York, 1971.

(2) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201.

(3) Meier, H.; Zeller, K. P. *Agnew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(4) Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918. Despite the high concentration of precursor, the solid solution was clear before photolysis, but fracturing did occur during the course of irradiation.

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and diazo carbons at 54 and 26 ppm (Me_4Si reference) are masked by the solvent peaks. The sample was removed from the spectrometer (again without melting) and immersed in a quartz Dewar containing liquid nitrogen, shown in Figure 1b. The rotor was suspended so that the quartz lid faced the radiation from a 150-W xenon high-pressure lamp (ILC Model VIX-150) fitted with a Pyrex filter. The sample was then photolyzed for 24 h at 77 K. The rotor was removed and again transferred without melting to the MAS apparatus.[6,7] The ^{13}C spectrum of the photolyzed material was obtained at 80 K and is shown in Figure 2b. The same four solvent peaks are observed; however, the downfield peak has shifted further downfield by 8 ppm, while two new peaks appear on the upfield edge of the MTHF resonances. These three peaks, at 201, 12, and 4 ppm, are within 1 ppm of the carbonyl, terminal, and methyl carbon peaks reported in the ^{13}C solution spectrum of **2**.[8] The spectra show that the precursor (**1**) has been quantitatively converted to the ketene (**2**).

Although the techniques described here appear to be promising as a general method for the study of photolytically generated species by NMR spectroscopy, refinements may lead to even wider applicability. For example, if the photoproduct absorbs the light, it may not be possible to build up a concentration of product that is sufficiently high for detection by NMR. Therefore, the use of a much more dilute solution of the precursor is desirable to reduce optical density. In turn, this would also decrease the strength of the ^{13}C signals, so that enrichment of the precursor in ^{13}C may be necessary. The spectra obtained in this study suggest that it should be possible to use 0.1 mol % solutions of enriched precursor, which would decrease such internal filtering effects considerably. Another problem could arise (and is seen in the spectra in Figure 2) if the strong solvent peaks interfere with the spectrum of the precursor or photoproduct.[5] This challenge could be met by using deuterated solvents, which should reduce solvent peaks and concomitant spectral interference considerably. The reason for this is that the strength of the ^{13}C signals in a CP experiment is roughly proportional to the inverse third power of the distance between carbon and proton(s), so that deuterated solvent molecules would not gain carbon polarization nearly so efficiently as the protonated precursor or photoproduct.

These ideas have been tested using an 0.1 mol % solution of acetic acid enriched (90%) in the methyl-carbon position in perdeuteriodioxane (98.5 atom % in deuterium). At 100 K, it was possible to observe the methyl carbon in only 2 min with a 2:1 signal-to-noise ratio. No ^{13}C signal was observed for the dioxane, even after several hours. This result suggests that it should be possible to detect concentrations of 0.01 mol % without solvent interference, even at the rather low spectrometer frequency (15 MHz) used in these experiments. Clearly, operation at higher field strengths would permit detection of concentrations at least as low as 10^{-3} mol % (10^{-4} M).

The experimental procedures described in this note, which have resulted in the first detection by NMR of a molecule photochemically generated in the solid state, constitute a prototype experiment for matrix-isolation NMR spectroscopy in organic glasses. Both photochemical production and characterization by NMR were carried out at temperatures very close to 77 K. Thus, the methodology developed here should be applicable to the NMR characterization of species that may not be stable at higher temperatures.

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Registry No. **1**, 2684-62-0; **2**, 6004-44-0.

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[5] The ^{13}C spectrum of **1** shows peak at 192, 54, and 26 ppm for the carbonyl, diazo, and methyl carbons, respectively. The peaks at 54 and 26 ppm are masked by the 2-MTHF solvent peaks in the spectrum shown in Figure 2a.

[6] The geometry of our CPMAS probe would permit in situ photolysis with the light shining on the walls of the rotor.[7] Thus an additional requirement for in situ photolysis is that the rotor material be transparent to the light.

[7] Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208.

[8] Firl, J.; Runge, W. *Z. Naturforsch.* **1974**, *29*, 393.

Coordination and Scission of Alkynes on a Tungsten–Triosmium Framework

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Reports of C≡C bond scission in alkynes to provide bi- or trinuclear dialkylidyne complexes[1] have involved reactions of alkynes with mononuclear complexes, in which cases the nature of the metal unit coordinating the alkyne prior to scission is not clear. We now wish to report the first examples of well-characterized alkyne complexes that undergo clean, unimolecular tranformations into dialkylidyne compounds (eq 1, Cp = η^5-C_5H_5). In addition, both types of compounds display unique structural features.

$$\mathrm{CpWOs_3(CO)_{10}(C_2RR')H} \xrightarrow[-\mathrm{CO}]{\Delta} \mathrm{CpWOs_3(CO)_9(CR)(CR')H} \qquad (1)$$

1, R = R′= Tol(p-C_6H_4Me)
2, R = R′ = Ph
3, R = Tol; R′ = Ph

4, R = R′ = Tol
5, R = R′ = Ph
6, R = Tol; R′ = Ph

The alkyne complexes **1**–**3** have been prepared by treatment of $CpWOs_3(CO)_{12}H$[2] first with Me_3NO and then with the alkyne.[3] Spectroscopic data[4] and an X-ray study of **1** (vide infra) provide characterization. The alkylidyne clusters **4**–**6** are obtained in low yields (10–20%) by direct pyrolysis of the corresponding alkyne complexes either in solution (tolune, 110 °C) or in vacuo (hot tube, 250 °C). However, initial decarbonylation with Me_3NO/MeCN followed by pyrolysis in boiling toluene results in **4**–**6** as major products (ca. 60%).[5] Note that pyrolysis of the unsymmetrical

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[1] (a) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559. (b) Fritch, J. R.; Vollhardt, K. P. C.; Thomson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768. (c) Yamazaki, R.; Wakatsuki, Y.; Aoki, K. *Chem. Lett.* **1979**, 1041. (d) Cash, G. G.; Pettersen, R. C.; King, R. B. *J. Chem. Soc., Chem. Commun.* **1977**, 30. (e) King R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879.

[2] Churchill, M. R.; Hollander, F. J; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534.

[3] A dry CH_2Cl_2 solution of $CpWOs_3(CO)_{12}H$ was treated with a MeCN solution of sublimited Me_3NO (ca. 1.05 equiv) under N_2 and then taken to dryness. The residue was dissolved in dry toluene, excess C_2Tol_2 added, and the resulting solution refluxed under N_2 for 1 h. Purification (TLC, silica, *n*-C_5H_{12}/CH_2Cl_2, 3:2) gave orange **1** in 45% yield. Compounds **2** and **3** were prepared similarly.

[4] Compound **1**: IR(CCl_4) ν(CO) 2080 (vw), 2064 (s), 2019 (vs), 2005 (w), 1988 (m), 1960 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 6.78–6.89 (m, 8 H), 5.50 (s, 5 H), 2.25 (s, 6 H), −21.23 (s, 1 H); MS (field desorption, ^{192}Os, ^{184}W), *m/z* 1312 (M^+). Anal. Calcd for $C_{31}H_{20}O_{10}WOs_3$: C, 28.49; H, 1.54. Found: C, 28.46; H, 1.37. Compounds **2** and **3** had analogous spectroscopic properties and satisfactory elemental analyses.

[5] Compound **1** was treated with sublimed Me_3NO in CH_2Cl_2/MeCN, and then the residue was heated in refluxing toluene for 1 h. Dark red crystalline **4** was isolated in 63% yield. Compound **4**: IR(C_6H_{12}) ν(CO) 2072 (s), 2036 (vs), 2031 (vs), 1999 (w), 1991 (m), 1980 (m) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.03–7.11 (m, 8 H), 5.40 (s, 5 H), 3.75 (m, 1 H, $^1J_{WH}$ = 89 Hz), 2.36 (s, 6 H); MS (70 eV, ^{192}Os, ^{184}W), *m/z* 1284 (M^+). Anal. Calcd for $C_{30}H_{20}O_9WOs_3$: C, 28.18; H, 1.58. Found: C, 28.10; H, 1.56. Compounds **5** and **6** were prepared and characterized analogously.

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