J. Am. Chem. Soc. **1983**, *105*, 1393–1394

Formation and Identification of Methylene on Ru(001)

Patricia M. George,[1] N. R. Avery,[2] W. H. Weinberg,* and
F. N. Tebbe[3]

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Received November 8, 1982

Although methylene has been postulated as an important intermediate in the Fischer–Tropsch synthesis of hydrocarbons,[4] it has been difficult to isolate and identify unambiguously such a species on transition-metal surfaces. In an attempt to mimic the Fischer–Tropsch synthesis, Brady and Pettit[5] inferred from observed reaction product distributions that methylene was formed when diazomethane was passed over transition-metal surfaces. Following the synthesis of the first homogeneous complex containing a bridging methylene group,[6] the synthesis of a large number of such homogeneous complexes has been reported.[7] Recently, Herrmann et al.[8] demonstrated that diazomethane could react with coordinately unsaturated $(RhC_5Me_5)_2(CO)_2$ in solution to form a bridging methylene complex, while Clauss et al.[9] showed that a similar reaction occurs with $Os_3(CO)_9(C_2Ph_2)$. High-resolution electron energy loss spectroscopic (EELS) results are reported here that demonstrate for the first time the formation of bridging methylene adspecies from the decomposition of both ethylene and diazomethane on the Ru(001) surface.

While the adsorption and decomposition of ethylene has been examined on several transition-metal surfaces,[10-15] the adsorption of diazomethane under ultrahigh vacuum conditions has received little attention. In all cases, ethylene has been found to adsorb associatively at temperatures near 100 K, rehybridizing to form a di-σ-like bond to the surface. As it warms to room temperature, either ethylidyne ($CH_3C\equiv$) is observed (on Pt, Pd, and Rh)[10-12] or decomposition to acetylene and hydrogen occurs (on Ni, Fe, and W).[13-15] In contrast to these results, low coverages of both ethylene and diazomethane adsorb dissociatively on Ru(001) at 80 K, giving identical electron energy loss spectra that are quite different from those observed previously.[10-15] At higher coverages, each adsorbate forms a molecular multilayer that can be removed by annealing to 120 K. The dissociatively adsorbed species is stable to approximately 180 K, at which temperature self-hydrogenation occurs.

The experiments were performed in two ultrahigh vacuum, stainless steel systems that have been described previously.[16,17] High-resolution EELS and thermal desorption mass spectrometry were used to characterize reactions occurring on the Ru(001) surface between 80 and 700 K. All gases were introduced via a leak valve after condensible impurities were removed. Pure diazomethane was prepared each day by the reaction of sodium hydroxide with MNNG.[18] The gas lines and vacuum chamber were conditioned with diazomethane for several days until background mass spectra indicated that reactions at the walls were negligible.

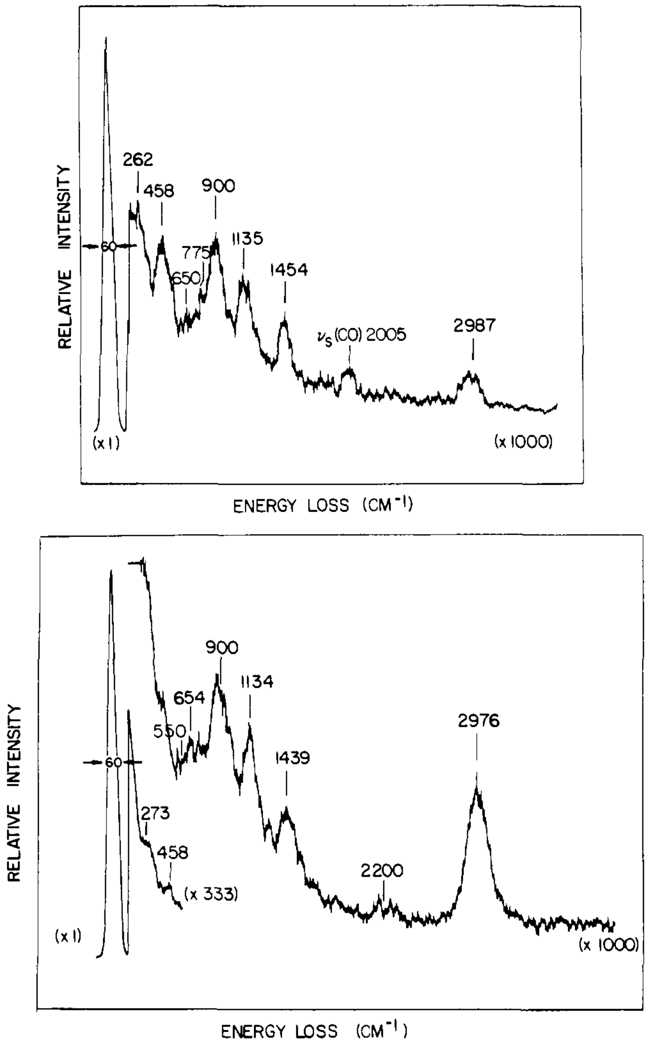


Figure 1. Electron energy loss spectra of (a) 0.8 L of $CH_2{=}CH_2$ and (b) 0.1 L of CH_2N_2 at 80 K. Spectra a and b are representative of a bridging methylene species.

Table I. Mode Assignments for IR and Electron Energy Loss Spectra for Gas-Phase Ethylene (Diazomethane) and Molecular Multilayers of Ethylene (Diazomethane) on Ru(001)

$CH_2{=}CH_2$			CH_2N_2		
mode	gas phase[19]	on Ru(001)	mode	on Ru(001)	gas phase[20]
$\nu_a(CH_2)$	3106	3096	$\nu_a(CH_2)$	3161	3185
$\nu_s(CH_2)$	2989	2998	$\nu_s(CH_2)$	3074	3076
$\nu(C{=}C)$	1623	1657	$\nu(NN)$	2104	2102
CH_2 scissors	1444	1460	CH_2 scissors	1422	1414
CH_2 wag	949	970	CH_2 rock	1135	1111
			CH_2 wag	970	920
			$\nu(CN)$	830	852
			CNN skeletal bend	469	422 408

---

[1] Present address: Aerojet Electrosystems Co., Azusa, CA 91702.

[2] Present address: Division of Materials Science, CSIRO, University of Melbourne, Parkville 3052, Victoria, Australia.

[3] Present address: Central Research, E. I. du Pont de Nemours, Wilmington, DE 19898.

(4) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, 97–116. For recent reviews see, for example: Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447–474. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103.

(5) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

(6) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245–251.

(7) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 192–263.

(8) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 193–196.

(9) Clauss, A. D.; Shapley, J. R.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387–7388.

(10) Steininger, H.; Ibach, H.; Lehwald, H. *Surf. Sci.* **1982**, *117*, 685–698 and references therein.

(11) Kesmodel, L. L.; Gates, J. A. *Surf. Sci.* **1981**, *111*, L747–L754.

(12) Dubois, L. H.; Castner, D. G. Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234–5240.

(13) Erley, W.; Baro, A. M.; McBreen, P.; Ibach, H. *Surf. Sci.* **1982**, *120*, 273–290.

(14) Bertolini, J. C.; Rousseau, J. *Surf. Sci.* **1979**, *83*, 531–544.

(15) Hamilton, J. C.; Swanson, N.; Waclawski, B. J.; Celotta, R. J. *J. Chem. Phys.* **1981**, *74*, 4156–4163.

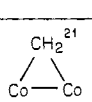
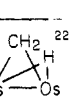
(16) Williams, E. D.; Weinberg, W. H.; Sobrero, A. C. *J. Chem. Phys.* **1982**, *76*, 1150–1160.

(17) Thomas, G. E.; Weinberg, W. H. *Rev. Sci. Instrum.* **1979**, *50*, 497–501.

(18) The synthesis is adapted from a procedure described by the Aldrich Chemical Co., Inc. for use with their reagent *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (MNNG) and will be discussed in detail in a full account of this work.

0002-7863/83/1505-1393$01.50/0

Table II. Mode Assignments for Methylene on Ru(001) (with Isotopic Shift Ratios) Compared to Those of CH_2I_2 and Relevant Organometallic Complexes

mode	$>CH_2$ on Ru(001)[a]	$\nu(CH_2/CD_2)$	CH_2I_2[23]	 [21]	 [22]
ν_s(MCM)	460 (m)	1.0		467	
δ(MCM)	550 (w)	*b*		566	
ν_a(MCM)	650 (w)	1.04	484	635	660
CH_2 rock	775 (sh)	*b*	716	774	811
CH_2 twist	900 (s)	1.33	1031	906	869
CH_2 wag	1135 (s)	1.35	1105	1127	961
CH_2 scissors	1450 (s)	1.20	1350	1360	1428
$\nu_s(CH_2)$	2940 (s)	1.33	2967	2918	2935
$\nu_a(CH_2)$	3050 (m)	1.33	3047	2981	2984

[a] $>CH_2$ from both C_2H_4 and CH_2N_2. [b] Not resolved.

An energy loss spectrum for a coverage of approximately 10^{15} methylenes/cm^2, corresponding to an exposure of 0.8 L (1 L $\equiv$ 10^{-6} torr s), on Ru(001) at 80 K is shown in Figure 1a. For comparison, a similar spectrum corresponding to an exposure of 0.1 L of diazomethane on Ru(001) is shown in Figure 1b. All pressures reported are uncorrected ionization gauge readings. The electron energy loss measurements of Figure 1 were made in the specular direction with an incident energy of approximately 4 eV and a resolution of approximately 60 cm^{-1} (fwhm of the elastically scattered beam).

At surface coverages below one monolayer (cf. Figure 1, a and b), the ethylene and diazomethane spectra are identical. Adsorbing successively increasing coverages of both ethylene and diazomethane results in multilayer formation as judged by the fact that the electron energy loss spectra agree well with IR spectra of the molecular species (cf. Table I).[19,20] In addition, complementary thermal desorption mass spectra show that molecular ethylene desorbs only below 115 K from a condensed multilayer. Spectra similar to Figure 1, a and b, are obtained on annealing these multilayers between 120 and 180 K. The first layer, which adsorbs dissociatively to $>CH_2$ at 80 K, decomposes to yield surface carbon and hydrogen. This hydrogen desorbs at 345 K, independent of coverage. No hydrogen associated with the ruthenium substrate is observed unless H_2 is either preadsorbed or postadsorbed with the ethylene. When approximately $^1/_4$ monolayer of H_2 is adsorbed prior to an exposure of 1 L of C_2D_4, complete isotopic mixing occurs, and two thermal desorption peaks are observed, one reaction-limited, at 345 K, the other desorption-limited, at 400 K.

Interpretation of the electron energy loss spectra of the dissociated fragments was facilitated by a comparison with high-resolution FT IR spectra of $(\mu\text{-}CH_2)[CpCo(CO)]_2$ and $(\mu\text{-}CD_2)[CpCo(CO)]_2$ in KBr,[21] kindly provided by Theopold and Bergman, and recent vibrational spectra of metal cluster complexes published by Oxton et al.[22] The assignment of bridging methylene on Ru(001) was made by comparing the energy loss spectra with these IR data together with those of CH_2I_2,[23] as summarized in Table II.[24] The presence of terminal methylenes was ruled out on the basis of observed ν_s(RuCRu) and ν_a(RuCRu) modes. Formation of ethylene from possible surface diffusion of $>CH_2$ on Ru after dissociation is both not expected at 80 K and not observed in the spectra at this temperature.

On warming the surface to 180 K, the $>CH_2$ scissors mode decreases in intensity, and a peak at 1373 cm^{-1} emerges. This can be attributed to the formation of CH_3 groups.[25] By 280 K, the energy loss spectra indicate a combination of CH_2, CH, CH_3, and C species of which the hydrocarbon fragments decompose below 500 K. At 700 K, only carbon remains on the Ru, as evidenced by peaks at 820 and 600 cm^{-1}. On the basis of reactions with O_2 and CO, we tentatively assign the 820-cm^{-1} peak to a C–C stretch while assigning the 600-cm^{-1} peak to a C–Ru stretch.

Further experiments are currently underway to examine the reactions of this bridging methylene with reagents of catalytic interest.

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE82-06487. We thank Dr. T. P. Garrett, Jr., for useful information concerning the IR spectrum of diazomethane and the safe handling of this compound, and we are grateful to Dr. T. H. Theopold and Professor R. G. Bergman for supplying the IR spectra of $(\mu\text{-}CH_2)[CpCo(CO)]_2$ and $(\mu\text{-}CD_2)[CpCo(CO)]_2$ prior to publication. Finally, we appreciate very helpful discussions with E. Carter, Dr. J. Mayer, and Dr. P. Watson.

Registry No. $(\mu\text{-}CH_2)[CpCo(CO)]_2$, 74656-87-4; $(\mu\text{-}CD_2)[CpCo(CO)]_2$, 84623-10-9; carbon monoxide, 630-08-0; ruthenium, 7440-18-8; diazomethane, 334-88-3; ethylene, 74-85-1; methylene, 2465-56-7; methyl, 2229-07-4; methylidyne, 3315-37-5; diiodomethane, 75-11-6.

---

(19) Shimanouchi, T. *NSRDS-NBS Publication 39*, **1972**, 74 and references therein.

(20) (a) Garrett, T. P. Ph.D. Dissertation, University of Tennessee, 1955. (b) Garrett, T. P.; Fletcher, W. H. *J. Chem. Phys.* **1956**, *25*, 50–55. (c) Crawford, B. L.; Fletcher, W. H.; Ramsay, D. A. *Ibid.* **1951**, *19*, 406–412.

(21) A more detailed analysis can be found in a full account of this work.

(22) (a) Oxton, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1982**, 719–721. (b) Skinner, P.; Howard, M. W.; Oxton, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1203–1215. (c) Howard, M. W.; Kettle, S. F.; Oxton, I. A.; Powell, D. B.; Sheppard, N.; Skinner, P. *Ibid.* **1981**, *77*, 397–404. (d) Oxton, I. A. *Spectrochim. Acta* **1982**, *38A*, 181–184.

(23) Marzocchi, M. P.; Schettino, V.; Califano, S. *J. Chem. Phys.* **1966**, *45*, 1400–1404.

(24) In some cases, peak positions have been identified from spectra with better resolution than those shown in Figure 1.

(25) Cf. IR spectra of CH_3X (X = Cl, Br, I), ref 19, pp 51–53.

ESR Spectrum of Matrix-Isolated CuAgCu[1]

J. A. Howard* and R. Sutcliffe

National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R9

B. Mile

Department of Chemistry and Biochemistry
Liverpool Polytechnic, Liverpool, England L3 3AF

Received November 10, 1982

A small number of triatomic clusters have been identified by electron spin resonance spectroscopy since Lindsay et al.[2] first detected Na_3. K_3 has been observed by Thompson and Lindsay[3] while we have recently prepared Ag_3[4] and Cu_3.[5] ESR spectra indicate that these four trimers are chemically bound, with singly occupied molecular orbitals that have predominantly s character. Na_3, K_3, and Ag_3 have >90% of the s unpaired spin population (ρ) residing on the two terminal atoms with a small amount of negative unpaired spin population on the unique atom. Cu_3 is somewhat different in that 60% of ρ_{4s} resides on the terminal atoms with correspondingly smaller negative ρ_{4s} on the central Cu atom. All four species show a negative *g* shift ranging from −0.0011 for Na_3 to −0.04 for Ag_3. This has been taken as evidence for an "obtuse angled" isosceles triangular geometry with ground-state C_{2v} symmetry in the $^2B_2$ representation.

There are little or no experimental data for mixed metal trimers although the structures of mixed alkali metal trimers have been calculated in the diatomics in molecules (DIM) approximation using empirically evaluated integrals.[6]

---

(1) (a) Issued as NRCC 20948. (b) Cryochemical Studies Part 5.

(2) Lindsay, D. M.; Herschbach, D. R.; Kwiram, A. L. *Mol. Phys.* **1976**, *32*, 1199–1213.

(3) Thompson, G. M.; Lindsay, D. M. *J. Chem. Phys.* **1981**, *74*, 959–968.

(4) Howard, J. A.; Preston, K. F.; Mile, B. *J. Am. Chem. Soc.* **1981**, *103*, 6226.

(5) Howard, J. A.; Preston, K. F.; Sutcliffe, R.; Mile, B. *J. Phys. Chem.*, in press.

(6) Richtsmeier, S. C.; Hendewerk, M. L.; Dixon, D. A.; Gole, J. L. *J. Phys. Chem.* **1982**, *86*, 3932–3937.

0002-7863/83/1505-1394$01.50/0 Published 1983 by the American Chemical Society