regular octahedron where the averave C(ax)–Cr–C(eq) angle is 90.7°. The Cr–SC(O)H bond distance is 2.447 (1) Å and the Cr–C(ax) bond length is 0.057 Å shorter than the average Cr–C(eq) distance.[9] The thioformate ligand resides in a position above the C(3)–Cr–C(4) quadrant and is contained in a plane which is almost perpendicular to and bisects the C(3)–Cr–C(4) angular arrangement.

The carbon monoxide ligands are quite labile in both $Cr(CO)_5O_2CH^-$ and $Cr(CO)_5SC(O)H^-$, where 63 and 75% CO exchange with ^{13}CO in solution (40 kPa) is observed after only 10 min at ambient temperature. Nevertheless, although CO loss constitutes a necessary step in the extrusion of CO_2 from $M(CO)_5O_2CH^-$ with concomitant $M(CO)_5H^-$ formation or the reverse process of carboxylation,[10] because of the added strength of the M–S bond the $M(CO)_5SC(O)H^-$ derivatives showed no tendency toward COS expulsion.[11] Consistent with this observation $Cr(CO)_5SC(O)H^-$ did not undergo exchange reactions with CO_2 or CS_2 to afford the formato or dithioformato complexes, e.g., reaction 2 was irreversible.

In a manner dissimilar to its hydrido analogue, $W(CO)_5CH_3^-$ exhibits no propensity for dissociative CO loss at ambient temperature; nonetheless, the insertion reaction depicted in reaction 4 occurs under mild conditions in THF solution pressurized with

$$CH_3W(CO)_5^- + CO_2 \rightarrow CH_3CO_2W(CO)_5^- \qquad (4)$$

CO_2 (100–300 kPa). Reaction conditions and yields are summarized in Table I.[12,13] Runs 1–3 afforded a product with $\nu(CO)$ infrared (THF solution: 2059 w, 1955 w, 1907 s, and 1842 m) and ^{13}C NMR (CD_3CN solution: 205.0 (axial CO), 200.3 (equatorial CO), 175.7 (carboxylic carbon), and 22.1 ppm (methyl carbon); the corresponding values in $CDCl_3$ are 206.4, 200.5, 177.4, and 23.7 ppm) spectral properties identical with that observed for the (acetato)pentacarbonyltungsten species obtained from reaction 5.[9,14]

$$[PNP][ClW(CO)_5] + AgO_2CCH_3 \xrightarrow[CH_2Cl_2]{25\ ^\circ C} [CH_3CO_2W(CO)_5][PNP] + AgCl \qquad (5)$$

The presence of lithium salts was found to accelerate the rate of CO_2 insertion into the methyl–tungsten bond (see runs 4 and 5 in Table I). Although there were no apparent changes in the solution $\nu(CO)$ infrared spectrum of the $CH_3W(CO)_5^-$ anion upon addition of LiCl, the once formed acetate derivative in the presence of lithium salts exhibited slightly shifted $\nu(CO)$ and ^{13}C NMR spectral characteristics from that of pure $[PNP][CH_3CO_2W(CO)_5]$. The $\nu(CO)$ infrared bands in THF were found at 2060 w, 1955 w, 1910 s, and 1846 m, and ^{13}C NMR resonances in $CDCl_3$ were observed at 202.9, 198.8, 173.8, and 25.8 ppm. Although these spectral shifts are small, they were reproducible and are indeed significant. Hence, the electron-donating ability of the acetato ligand in the presence of the lithium cation is decreased, as indicated by the direction of the shift of both the $\nu(CO)$ and ^{13}C NMR spectral parameters. This most likely is indicative of complexation of the lithium cation at the nonbonding oxygen atom of the acetate group.[15] Presumably an ion-pairing interaction of this type in the transition state lowers the barrier of CO_2 insertion into the alkyl–tungsten bond.[16] Independent experiments employing ^{13}CO demonstrated that lithium salts neither accelerate the reactivity of $CH_3W(CO)_5^-$ toward methyl migration nor labilize the complex anion toward CO dissociation. The sodium cation has an even more dramatic effect on the nature of the CO_2 reaction (see run 6 in Table I). In addition to enhancing the reactivity of the $CH_3W(CO)_5^-$ anion toward CO_2, the thus formed $CH_3CO_2W(CO)_5^-$ readily decomposes in the presence of sodium ion to afford $W(CO)_6$.

In contrast to reaction 4 the analogous process involving COS as a substrate to yield the sulfur-bonded (thioacetato)pentacarbonyltungsten derivative takes place much more readily (reaction 6). That is, reaction 6 is completed in less than 3 h at

$$CH_3W(CO)_5^- + COS \rightarrow CH_3C(O)SW(CO)_5^- \qquad (6)$$

room temperature at COS pressures between 100–200 kPa. This observation is probably indicative of metal–sulfur bond formation, a process more favorable than metal–oxygen bond formation, concurrent with or prior to carbon–carbon bond formation. Studies into the scope and intimate mechanism of CO_2 and COS insertions into group 6B metal alkyl bonds, along with subsequent CO_2 reduction processes, are currently under way. For example, the acetato derivatives are smoothly and quantitatively alkylated by alkyl halides to provide alkyl acetates and the precursors to metal–alkyl complexes, metal pentacarbonylhalide anions.[17]

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 80-09233) is greatly appreciated.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (6 pages). Ordering information is given on any current masthead page.

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[9] A similar observation was noted in the (acetato)pentacarbonylmetalates. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

[10] The rate of decarboxylation of the $M(CO)_5O_2CH^-$ (M = Cr and W) derivatives is greatly retarded when carried out under an atmosphere of carbon monoxide. Darensbourg, D. J.; Rokicki, A., unpublished results.

[11] For example, the $Cr(CO)_5SC(O)H^-$ anion did not expel COS at temperatures ranging from ambient to 83 °C. The reaction of $Cr(CO)_5O_2CH^-$ was incorrectly reported in ref 1 to reversibly add CS_2 with concomitant formation of $Cr(CO)_5S_2CH^-$. The reaction is *not* reversible under the conditions studied. This oversight will be corrected in a full paper in preparation describing these insertion processes.

[12] $[PNP][W(CO)_5CH_3]$ was prepared according to the published procedure.[13]

[13] Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

[14] Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.*, in press.

[15] The interaction of alkali cations with carboxyl oxygens of metal carbonyl *acyl* anions is well-known: Darensbourg, M. Y.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970. Collman, J. P.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 5905.

[16] This cation effect is not a reflection of reaction 4 involving an equilibrium process, since control experiments starting with $CH_3CO_2W(CO)_5^-$ revealed no $CH_3W(CO)_5^-$ and CO_2 formation.

[17] Darensbourg, D. J.; Kudaroski, R., unpublished results.

Structure and Dynamics of the Trimethylcyclopropenyl Radical As Determined by Electron and Nuclear Magnetic Resonance[1]

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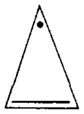
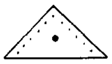
Received August 14, 1981

The structure of the simplest cyclic conjugated radical, cyclopropenyl radical, is of considerable theoretical interest. Theory predicts that the molecule will deviate from D_{3h} symmetry because of the Jahn–Teller effect. The simplest distortion compatible with the Jahn–Teller theorem yields a molecule with C_{2v} symmetry as represented by either **1a** or **1b**, with **1a** being the more likely structure. However, it is likely that the molecule has only C_s symmetry because the substituent at the smallest angle of the isosceles triangle **1a** may be located substantially away from the ring plane. In addition to the structural problem, there exists the interesting problem regarding the barrier height in the threefold


1a


1b

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[1] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

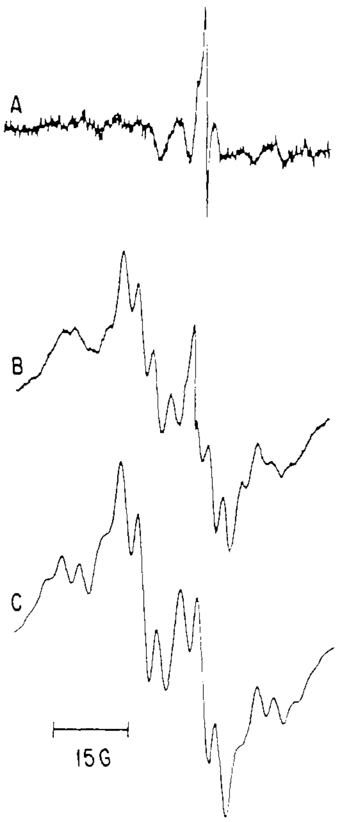
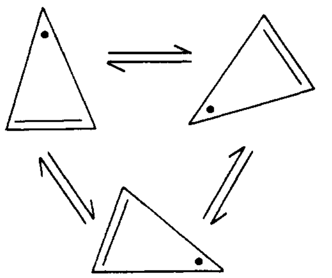


Figure 1. ESR spectra of (A) γ-irradiated aqueous matrix containing 11 M LiCl; (B) same matrix as (A) containing in addition 0.1 M trimethylcyclopropenium fluoroborate, temperature 135 K; (C) simulation of spectrum with hf constants given in the text and line width of 3.5 G.

Scheme I



degenerate potential surface and the associated dynamics of the valence bond tautomerism shown in Scheme I.

These considerations have been borne out by molecular orbital calculations which have predicted a structure as in **1a** with a nonplanar hydrogen and a considerable barrier, with most of the barrier height being generated by the nonplanar hydrogen which has to move near the plane during the valence bond tautomerization.[2] Unfortunately, no experimental verification exists on either the structure or the dynamics of the cyclopropenyl radical because it has never been unambiguously synthesized.[3,4] We wish to report here the results obtained in the closely related trimethylcyclopropenyl radical produced from the corresponding cation by γ-ray or pulse radiolysis and studied by electron and nuclear magnetic resonance.

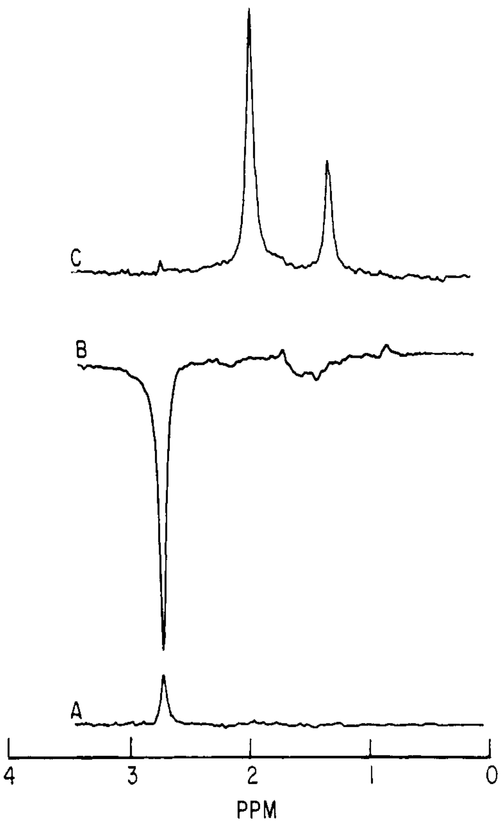


Figure 2. (A) Proton NMR spectrum at 80 MHz of trimethylcyclopropenium fluoroborate in D_2O using a flow system. (B) Same as (A) with electron beams on. The signal is that of the polarized reactant regenerated from the radical by oxidation. (C) Same as (B) but with sodium formate added.

When a glassy matrix containing 10^{-1} M trimethylcyclopropenium fluoroborate[5] in aqueous 11 M lithium chloride is exposed to 10 Mrd γ rays at 77 K, a radical is produced, giving a strong ESR signal at $g = 2.0026$ not present in the LiCl matrix blank. The rather featureless spectrum obtained below 80 K begins to show structure above 120 K, presumably due to the onset of methyl rotation at the higher temperatures, removing some of the dipolar broadening. As shown in Figure 1, the spectrum can be simulated with a set of two hyperfine coupling constants, three hf splittings of 12.5 G and six hf interactions of 3.5 G. To confirm this assignment, an ENDOR experiment was run, yielding a signal of 9.9 MHz (3.5 G) although the higher frequency coupling did not give a signal. An ELDOR spectrum, however, confirmed both coupling constants.[6] This finding clearly speaks in favor of a structure predominantly represented by **1a** because the large coupling constants would be associated with six protons in structure **1b**. When the McConnell relationship[7] is used, it is apparent that **1a** is a good representation for the molecule with more than $^2/_3$ of the spin density at the carbon with the smallest angle and less than $^1/_6$ at each of the other two. The spectrum did not change substantially up to the melting point of the matrix at 135 K, giving an upper limit for the rate of interconversion of the valence bond tautomers as 2.6×10^7.[8] A lower limit for the rate of interconversion at room temperature was obtained from an NMR experiment. When an aqueous solution containing 0.1 M trimethylcyclopropenium fluoroborate and 1 M sodium formate was

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(2) E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, **67**, 2191 (1977); P. Poppinger, C. Random, and M. A. Vincent, *Chem. Phys.*, **23**, 437 (1977).

(3) The ESR spectrum observed by Cirelli [G. Cirelli, F. Graf, and H. H. Günthard, *Chem. Phys. Lett.*, **28**, 494 (1974)] and attributed to cyclopropenyl is almost certainly not due to this species because a *g* factor of 2.006 is clearly outside the range of carbon-based radicals.

(4) Schreimer and Berndt [K. Schreimer and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **15**, 698 (1976)] have observed the C-13 ESR spectrum of the tri-*tert*-butylcyclopropenyl radical. The hf constants observed were time averaged and were interpreted to support a structure equivalent to **1a**.

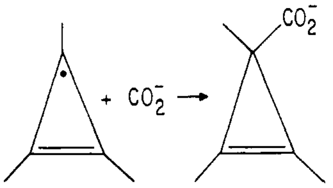
(5) G. L. Closs, W. A. Böll, H. Hyan, and V. Dev, *J. Am. Chem. Soc.*, **90**, 173 (1968).

(6) The ELDOR spectrum was measured on Professor L. Dalton's equipment at the State University of New York, Stony Brook. The frequency differences that gave signals were 9.9 and 35 MHZ.

(7) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956). If the radical deviates from planarity, the relationship is no longer strictly applicable. Therefore, the suggested spin densities are only approximate.

(8) The upper limit for the rate constant is derived from the line width of 3.5 G used for the best simulation of the spectrum.

irradiated with an electron beam from a 3-MeV Van de Graaff accelerator in a magnetic field of 0.5 T with the sample flowing into an NMR spectrometer probe within 1 s, the CIDNP spectra shown in Figure 2 was obtained.[9] The chemistry observed on pulse radiolysis of a formate solution is well established and known to yield CO_2^- by hydrogen abstraction by the OH radical from the formate ion.[10] At the same time, the hydrated electron converts the cyclopropenyl cation to the cyclopropenyl radical. The spectrum shown in Figure 2 is that of trimethylcyclopropenyl carboxylic acid generated by the combination of the CO_2^- with the cyclopropenyl radical.



The important point is that the three methyl groups in the acid are equally polarized,[11] showing that during the lifetime of the correlated pair (10^{-8} s) all three methyl groups are experiencing the same time-averaged hyperfine interaction. This allows us to put a lower limit on the rate constant of the valence bond tautomerization of 10^8 s^{-1} at 292 K.

The limits for the barrier in the potential surface is set between 3.5 and 7 kcal/mol by combining the ESR and NMR data obtained at different temperatures and by estimating the preexponential factor to be 10^{13}. Of course, it is possible that the lower limit is affected by the constraints of the matrix.

Acknowledgment. We are indebted to A. D. Trifunac and L. Dalton for help and advise on the pulse radiolysis-NMR and ELDOR experiments, respectively. G.L.C. acknowledges support by NSF Grant CHE 7821789.

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[9] The apparatus used for this experiment has been described by Trifunac and Evanocho [A. D. Trifunac and W. T. Evanochko, *J. Am. Chem. Soc.*, **102**, 4598 (1980)].

[10] J. Rubani and G. Stein, *Trans. Faraday Soc.*, **58**, 2150 (1962).

[11] The signal intensities of the two types of CH_3 groups are identical after normalizing for the numbers of protons involved.

C–H Activation in Completely Saturated Hydrocarbons: Direct Observation of $\mathrm{M + R{-}H \rightarrow M(R)(H)}$

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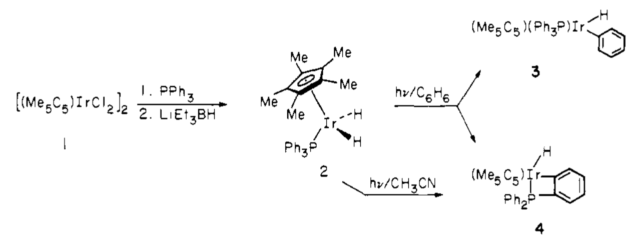
One of the most intriguing goals of homogeneous organotransition-metal chemistry is the possibility of carrying out selective chemical transformations on, or functionalizing, very unreactive materials such as saturated hydrocarbons.[1] The longest known examples of intermolecular C–H activation in saturated hydrocarbons are those involving the use of soluble platinum salts at relatively high temperatures[2] and more recently porphyrin complexes.[3] However, in none of these cases has it been possible to detect intermediate hydridoalkylmetal complexes formed by direct oxidative addition to a C–H bond, and in some there is evidence for free radical mechanisms.[3f,4]

Scheme I



There are a number of cases now known involving *intramolecular* oxidative addition to unactivated C–H bonds.[5] However, most of these systems steadfastly resist reaction with C-H bonds not present in the same molecule as the metal center. In important recent work, it was observed that reactive species generated from certain Ir and Re precursors react with completely saturated hydrocarbons.[6] However, both of these systems involve multiple hydrogen-atom loss in the hydrocarbon and require an added alkene as hydrogen acceptor. Direct, one-stage oxidative addition (reaction 1) has been observed so far only at C–H bonds which

$$\mathrm{M + R{-}H \rightarrow M(R)(H)} \qquad (1)$$

can be considered at least weakly activated,[7] either because they are aryl or vinyl C–H or because they are adjacent to activating groups or atoms (e.g., aryl, carbonyl, cyano, R_3Si, or the metals themselves, as in α or β elimination). We now wish to report the discovery of an organotransition-metal system capable of *intermolecular oxidative addition to single C–H bonds in saturated hydrocarbons*, leading to hydridoalkylmetal complexes in high yield at room temperature in homogeneous solution.

Our investigations began with the preparation of the dihydridoiridium(III) complex **2** shown in Scheme I, which can be obtained in 42% yield by treatment of dimer[8] **1** with triphenylphosphine followed by lithium triethylborohydride. Irradiation

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[2] Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725.

[3] (a) Groves, J. T. *Adv. Inorg. Biochem.* **1979**, *1*, 119. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (c) Groves, J. T.; Van Der Puy, M. *Ibid.* **1976**, *98*, 5290; (d) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413. (e) Groves, J. T.; Kruper, W. J.; Jr. *Ibid.* **1979**, *101*, 7613. (f) Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6374.

[4] We note some examples of C-H activation involving metal atoms in low-temperature matrices and in the gas phase. See, e.g.: (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962. (b) Allison, J.; Freas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332. (c) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *Ibid.* **1981**, *102*, 1574.

[5] For examples, see: (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (b) Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803. (c) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728. (d) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (e) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59 and references cited there; (f) Bennett, C. R.; Bradley, D. C. . *Chem. Soc., Chem. Commun.* **1979**, 29. (g) Andersen, R. A.; Jones, R. A.; Wilkinson, *J. Chem. Soc., Dalton Trans.* **1978**, 446. (h) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (i) Chappell, S. D.; Cole-Hamilton, D. *J. Chem. Soc., Chem. Commun.* **1980**, 238. (j) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (k) Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795. (l) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60.

[6] (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtree, R. H.; Mellea, M. F., Mihelcic, J. M.; Quirk, J. M. *Ibid.*, in press. (c) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, *1243*.

[7] Examples: (a) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton, Trans* **1979**, 1950. (b) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. *Nouv. J. Chim.* **1977**, *1*, 187. (c) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432. (d) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073; **1978**, *100*, 7577. (e) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *Ibid.* **1981**, *103*, 379. (f) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870.

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