Table I. 6-31G* MP2 Energies (hartrees) Calculated at RHF and UHF Optimized Geometries

molecule	geometry	MP2 energy
$CF_2{=}CF_2$	equilibrium (D_{2h})	–474.3367
	twisted, pyramidal (C_2)	–474.2576[a]
	twisted, one C planar (C_s)	–474.2453[a]
	twisted, both Cs planar (D_{2d})	–474.2369[a]
$HCF_2{-}CF_2^{\bullet}$	equilibrium (C_s)	–474.9150
	carbon planar (C_s)	–474.9004
$HCF_2{-}CHF_2$	equilibrium (C_{2h})	–475.5749

[a] Triplet energy at UHF triplet geometry.

kcal/mol,[10] which is in good agreement with the experimental estimates.[3,6]

Our calculations were performed with GAUSSIAN 86,[11] with use of the 6-31G* basis set.[12] Geometries were optimizied with SCF or UHF wave functions;[13] and electron correlation was included in energy calculations at these geometries through the use of second-order Moller–Plesset (MP2) perturbation theory.[14] The calculated energies are given in Table I and lead to a π bond energy of 51.2 kcal/mol for tetrafluoroethylene, which is in excellent agreement with the experimental value of Wu and Rodgers.[15]

Another definition of π bond energy is the energy required to break a π bond by rotation to the diradical transition state for cis–trans isomerization. Dobbs and Hehre have found very close agreement between the π bond energies computed in this way (e.g., 66.5 kcal/mol for ethylene) and those calculated by using Benson's definition.[10,16] From the difference in the computed energies in Table I between planar (D_{2h}) tetrafluoroethylene and the twisted (C_2) triplet diradical,[18] a value of 49.6 kcal/mol is obtained for the π bond energy.

Unlike the case in twisted ethylene, the presence of two electronegative fluorine substituents at each carbon causes the carbons to be highly pyramidalized in the twisted tetrafluoroethylene diradical.[19] The pyramidalization angle between each CF_2 plane and the extension of the C–C bond is 43° in the C_2 diradical. As shown in Table I, going from the C_2 twisted diradical, where both carbons are pyramidalized, to the D_{2d} twisted diradical, where both carbons are planar, raises the energy by 13.0 kcal/mol. Consequently, recomputing the π bond energy of tetrafluoroethylene with the carbons in the diradical constrained to be planar gives a value of 62.6 kcal/mol, which is only slightly less than the 66.5 kcal/mol calculated for ethylene.[10,23] Thus, our calculations indicate that the energetic cost of planarizing both carbons in tetrafluoroethylene is the major factor responsible for making the π bond strength in this molecule significantly less than that in ethylene.

Another estimate of the reduction in the π bond energy of tetrafluoroethylene, due to the energetic cost of planarizing the two carbons, is provided by twice the energy of 9.2 kcal/mol that is computed to be required to planarize the radical center in $HF_2C{-}CF_2^{\bullet}$. Because of the differences in stereoelectronics between this monoradical and the twisted diradical, twice the energy necessary to planarize the CF_2 group in the monoradical is not the same as that required to planarize both CF_2 groups in the diradical. However, the energetic cost of 7.7 kcal/mol for planarizing just one carbon in the twisted diradical ($C_2 \rightarrow C_s$) is much more nearly comparable to that required for the equivalent conformational change in the monoradical.

In summary, the results of our calculations indicate that the lower π bond energy of tetrafluoroethylene, compared to ethylene, is largely attributable to the cost of planarizing the two CF_2 groups.[24] In this sense Bernett's assertion[21] that the difference between tetrafluoroethylene and ethylene is that the former is more strained in a planar geometry than the latter seems to have been correct.

Acknowledgment. We thank the National Science Foundation for support of this research and for partial funding of the purchase of the Convex C-2 computer on which some of these calculations were performed. We also thank the San Diego Supercomputer Center for a generous allocation of computer time.

Supplementary Material Available: SCF and UHF optimized geometries and energies for the molecules in Table I (10 pages). Ordering information is given on any current masthead page.

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(13) Optimized geometries and SCF and UHF energies are available as Supplementary Material. Ordering information is given on any masthead page.

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(15) Obtained by using eq 1 and measured heats of formation for X = F.[2]

(16) Dobbs and Hehre[10] performed singlet UHF calculations to locate the transition states. Singlet UHF wave functions are actually mixtures of singlet and triplet spin states, but the geometries and energies of the singlet transition states and the triplet minima are quite similar for twisted π bonds.[17]

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(18) In addition to locating the triplet UHF minimum, we also found the transition state for a pure single state,[16] by using a two-configuration (TC) SCF wave function.[13] At the latter geometry the triplet UHF energy of –473.3759 hartrees is 0.3 kcal/mol higher than at the triplet UHF minimum. The TCSCF barrier height is 50.3 kcal/mol, which again is significantly lower than the TCSCF barrier of 65.6 kcal/mol for cis–trans isomerization in ethylene.

(19) The pyramidal geometries of fluorinated carbon radical centers[20] have been rationalized on the basis of hybridization arguments[21] and also within the context of MO theory.[22]

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(23) If the triplet MP2 energy of the twisted diradical is used, 67.7 kcal/mol is calculated for the π bond energy of ethylene.

(24) The low barriers to stereomutation in 1,1,3,3-tetrafluoroallyl radicals[25] probably have a similar origin.[26]

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Reductive Cleavage of Carbon Monoxide by Tetranuclear Tungsten Alkoxide Clusters

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We describe evidence for a general reaction leading to the cleavage of carbon monoxide and the formation of $W_4(\mu_4\text{-}C)$ clusters supported by alkoxide ligands.

When CO (1 equiv) is allowed to react in hydrocarbon solvents with $W_2(OR)_6$ (2 equiv), there is evidence for the formation of $W_4(\mu_4\text{-}C)$ containing compounds when R = *i*-Pr and CH_2-*t*-Bu.[1] When CO is allowed to react with $W_4(OR)_{12}$ compounds (R = CH_2-c-Bu, CH_2-c-Pen, CH_2-c-Hex, and CH_2-*i*-Pr),[2] there is

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*Author to whom correspondence should be addressed.

(1) Note the use of dry and oxygen-free atmospheres (N_2) and solvents. The synthetic strategy implied in this sequence involves the preparation of a $W_2(\mu\text{-}CO)$ compound that then reacts further with the W≡W bond of $W_2(OR)_6$ as an inorganic analogue of a ketone. See: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Organometallics* **1985**, *4*, 986. Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.

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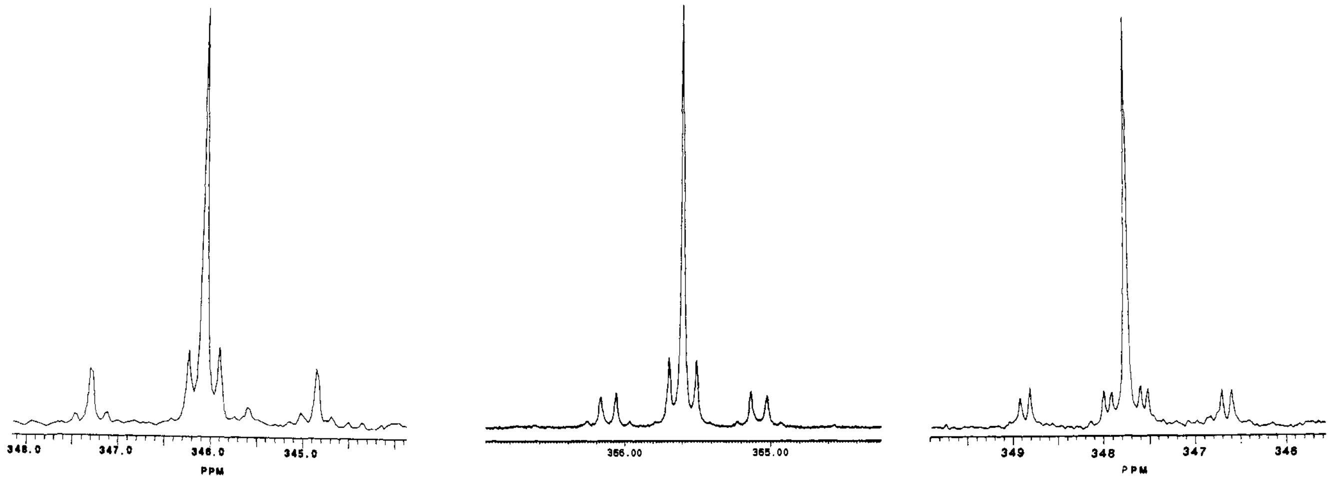

Figure 1. ^{13}C signals or the carbido carbon atoms in $W_4(\mu_4\text{-}C)$ alkoxide-supported clusters where OR (from left to right) is OCH_2-*t*-Bu, OCH_2-*i*-Pr, and O-*i*-Pr. Spectra were recorded at 125.76 MHz, 22 °C from toluene-d_8 solutions.

competitive formation of $W_4(OR)_{12}(CO)_3$ (preferred with excess CO) and a $W_2(\mu_4\text{-}C)$ cluster (preferred with ca. 1 equiv CO at 0 °C). The latter compounds have been isolated as dark green crystals, soluble in hydrocarbon solvents but essentially insoluble in acetonitrile and only sparingly soluble in pyridine, in ca. 50% yield based on tungsten.

The $W_4(\mu_4\text{-}C)$ alkoxide supported clusters show ^{13}C signals at ca. 360 ppm assignable to the carbido carbon atom. The satellite spectra arising from coupling to ^{183}W, $I = 1/2$, 14.5% natural abundance reveal the formation of three different types of $W_4(\mu_4\text{-}C)$ clusters as a function of the attendant alkoxide ligands (see Figure 1). In one (R = *i*-Pr) there is no element of symmetry leading to four distinct $^{183}W-^{13}C$ couplings. In another (R = CH_2-*t*-Bu) there is evidently C_{2v} symmetry, while in the third type there is a single mirror plane (R = CH_2-c-Bu, CH_2-c-Pen, CH_2-c-Hex, and CH_2-*i*-Pr). The coupling constants fall into two distinct ranges ca. 25 and ca. 140 Hz assignable to backbone and wingtip W atoms of a $W_4(\mu_4\text{-}C)$ butterfly of the type seen in $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$.[3]

Regrettably no crystal suitable for a molecular structure determination by X-ray diffraction has yet been obtained, and the detailed nature of the $W_4(\mu_4\text{-}C)$ compounds is not known. Specifically we cannot tell whether or not the carbonyl oxygen atoms is retained in the cluster. The number of alkoxide ligands, based on elemental analyses and NMR studies, appears to be 12 for R = *i*-Pr and CH_2-*t*-Bu and 14 for R = CH_2-c-Bu, CH_2-c-Pen, CH_2-c-Hex, and CH_2-*i*-Pr. In the latter case it is possible to say that two of the 14 alkoxides are in reality coordinated alcohol molecules. However, it seems likely that all these compounds are related to the structurally characterized $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ molecule in that they share a central butterfly $W_4(\mu_4\text{-}C)$ unit.

The strongest evidence for carbonyl C–O bond cleavage comes from studies of reactions and products obtained by use of a 60:40 mixture of $^{13}CO:^{13}C^{18}O$. The ^{13}C signal of the carbido carbon is insensitive to this labeling, whereas the ^{13}C signals associated with carbonyl carbon atoms where the C–O bond is present reveal a small but detectable isotope shift[4] (see Figure 2).

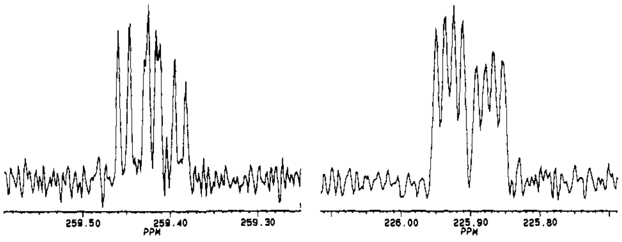

Figure 2. The central ^{13}C signals (satellites due to coupling to ^{183}W are not shown) of a terminal CO (right) and the μ-CO (left) of $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ prepared from the reaction between $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$ and a 60:40 mixture of $^{13}CO:^{13}C^{18}O$. In both cases the ^{13}C signals are a doublet of doublets due to $^{13}C-^{13}C$ coupling to neighboring carbonyls. The isotope shift is sufficiently large for the terminal CO ligand that two well-separated doublets of doublets are observed, whereas for the μ-CO ligand the doublet of doublets overlap.

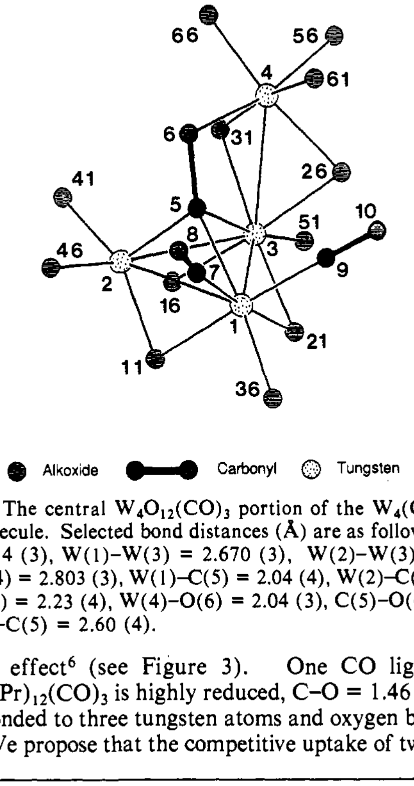

Figure 3. The central $W_4O_{12}(CO)_3$ portion of the $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ molecule. Selected bond distances (Å) are as follows: W(1)–W(2) = 2.814 (3), W(1)–W(3) = 2.670 (3), W(2)–W(3) = 2.734 (3), W(3)–W(4) = 2.803 (3), W(1)–C(5) = 2.04 (4), W(2)–C(5) = 1.99 (4), W(3)–C(5) = 2.23 (4), W(4)–O(6) = 2.04 (3), C(5)–O(6) = 1.46 (5), and W(4)–C(5) = 2.60 (4).

The molecular structure of $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ has been determined[5] and provides possible insight into the mode of cleavage of the C–O ligand by a grouping of four tungsten atoms—the ensemble effect[6] (see Figure 3). One CO ligand in $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ is highly reduced, C–O = 1.46 (5) Å, being carbon bonded to three tungsten atoms and oxygen bonded to the fourth. We propose that the competitive uptake of two additional

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(2) Bu = butyl, Pen = pentyl, Hex = hexyl, Pr = propyl, and *i* and c refer to iso and cyclo isomers, respectively: Chisholm, M. H.; Folting, K.; Hammond, C. E.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3314.

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(5) Crystal data for $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ at −143 °C: $a = 13.361$ (5) Å, $b = 22.703$ (12) Å, $c = 11.627$ (5) Å, $\alpha = 94.46$ (3)°, $\beta = 107.30$ (2), $\gamma = 102.79$ (3)°, $Z = 2$, and space group $P\bar{1}$.

(6) Shriver, D. F.; Sailor, M. J. *Acc. Chem. Res.* **1988**, *110*, 3314. Cleavage of CO has been achieved previously in homogeneous reactions but always with C–C or C–H bond formation. See: LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382.

CO ligands in the formation of $W_4(OCH_2\text{-}i\text{-}Pr)_{12}(CO)_3$ suppresses the C–O bond cleavage in $W_4(OR)_{12}(CO)$. The two additional π-acceptor CO ligands withdraw electron density that otherwise would have been used to form the carbide and oxide ligands. Further studies are in progress.[7]

Supplementary Material Available: Table of fractional coordinates and isotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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(7) We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division for support and the National Science Foundation (CHE-85-13707) and the National Science Foundation (CHE-85-13707) and the National Institutes of Health (PHS-S10-RR-02858-01) for instrumentation grants. We also thank Dr. S. R. Maple and Teresa Wright-Kester for their most valuable technical assistance in obtaining NMR spectra.

Use of Methylenecyclopropanone Ketals for Cyclopentane Synthesis. A New Efficient Thermal [3 + 2] Cycloaddition

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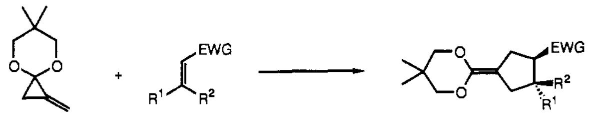
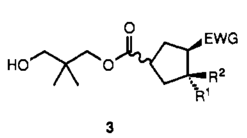
Much interest has recently been focused on reactions that effect direct formation of five-membered carbocycles[1] through [3 + 2] cycloadditions.[2,3] Among these, cycloadditions of trimethylenemethane (TMM)[2] and its organometallic complexes[3] occupy a uniquely important position due to their synthetic as well as theoretical significance. However, except for some intramolecular cases[4] the prototypal thermal reaction of TMM intermediates with olefins have not attained a synthetically useful level of development. We report here that the ketal of methylenecyclopropanone 1 undergoes a highly efficient thermal cycloaddition to electron-deficient olefins which may involve a TMM intermediate (eq 1). An important feature of this reaction is that it is highly regioselective with respect to the three-carbon partner (cf. 4) and stereoselective with respect to the two-carbon acceptor.



(1)



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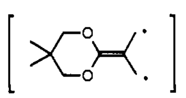

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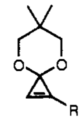

5 a: R = H
b: R = Me

The methylenecyclopropanone ketal 1 has been prepared in two steps from a readily available cyclopropenone ketal 5a.[5a] Thus, methylation of 5a (4.21 g, 30 mmol; BuLi, HMPA/THF at −72 °C; then MeI)[5b] followed by isomerization of the product 5b (*t*-BuOK, 6 mmol, and *t*-BuOH, 9 mmol, in ether at 20 °C)[5c] afforded 1 in 73% overall yield (3.36 g; 70–73 °C/15 mmHg). This compound is a thermally stable, distillable compound, remaining virtually unchanged even after heating for 10 h in CD_3CN (91% recovery). *However, heating 1 with 1 equiv of an electron-deficient olefin leads to a smooth cycloaddition to give a cycloadduct 2 in excellent yield.* Thus, the reaction of 1 (0.77 g, 5.0 mmol) and methyl methacrylate (0.55 g, 5.5 mmol) in 12.5 mL of acetonitrile at 80 °C for 18 h under nitrogen gave the cycloadduct 2 (R^1 = Me, R^2 = H, EWG = COOMe; a single isomer by ^{1}H and ^{13}C NMR) which was hydrolyzed (with 0.5 mL of H_2O and 100 mg of Amberlyst 15 at room temperature) to the diester 3 and isolated in 91% yield (1.25 g). The reaction is subject to only marginal solvent effects, proceeding several times more slowly as the solvent is changed from CD_3CN to THF-d_8 to C_6D_6, producing in each case the same cycloadduct in excellent yield.

A wide range of electron-deficient olefins bearing ester, nitrile, and ketone functionalities[6] take part in the cycloaddition (Table I). The reaction proceeds cleanly not only with acyclic olefins but also with cyclic ones (e.g., entries 5–9), thus providing a powerful new strategy for the construction of cis-fused bicyclo[3.*n*.0] systems. The reaction, tolerating the use of β,β-disubstituted unsaturated carbonyl compounds, allows the preparation of bridgehead substituted products. For instance, a relatively slow reaction of a 3-methyl-2-butenolide with 1 afforded a bridgehead substituted product in 84% yield after heating for 90 h at 80 °C (entry 5). In line with the well-known effects of pressure upon cycloadditions,[7] we observed a significant rate acceleration under high pressure: the cycloaddition to the methylbutenolide under 13 kbar (in CH_2Cl_2) realized 87% yield only after 16 h at 70 °C (entry 6). The stereospecificity of the cycloaddition is noteworthy. The reaction with *E* and *Z* isomers of methyl 2-heptenoate proceeded with 100% and 98% retention of the stereochemistry of the starting materials (entries 3 and 4, respectively). This stereospecificity as well as the fact that thermolysis of simple methylenecyclopropanes has been considered to generate TMMs[2,8]

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