as well as ligand substitution and decomposition mechanisms for $NaHFe_2(CO)_8$ will be reported subsequently.

Note Added in Proof. We have found that at higher HOAc concentrations, protonolysis of **III** becomes kinetically important.

Acknowledgment. This work was supported by NSF Grant MPS75-17018.

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(6) Two recent studies have shown that odd d^n binuclear carbonyl clusters may act, via homolysis, as sources of reactive paramagnetic monomers. J. P. Fawcett, R. A. Jackson, and A. Poë, *J. Chem. Soc., Chem. Commun.*, 733 (1975); E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975).

(7) In this case the nature of the active species has not been defined. T. Kitamura, N. Sakamoto, and T. Joh, *Chem. Lett.*, 379 (1973).

(8) Commercially available from Ventron Corporation, Alfa Products.

(9) GLC and ^1H NMR analysis shows X to be between 3 and 4. Removal of THF under vacuum affords $Na_2Fe_2(CO)_8$ as a yellow powder.

(10) The sodium acetate by-product is easily removed by centrifugation, although its presence does not hinder synthetic reductions.

(11) (a) $NaHFe_2(CO)_8$ was prepared by adding dry HOAc to isolated $Na_2Fe_2(CO)_8$, centrifuging, and using the homogeneous supernatant. Strict anerobic conditions were maintained at all times. THF was distilled under nitrogen from sodium and benzophenone. (b) The reaction was monitored by quenching aliquots with excess HOAc and dimethyl maleate and analyzing for both reactants (e.g., ethyl crotonate) and products (e.g., ethyl butyrate) by flame ionization GC using the internal standard technique. Following the appearance of reduced product directly by ^1H NMR in THF, d_8 gave the same rate constant within experimental error as the GLC kinetics.

(12) H. B. Chin, Ph.D. Thesis, University of Southern California, Los Angeles, Calif., 1975.

(13) Organic products and $Fe(CO)_5$ were measured by GLC. Iron hydride concentrations were determined by ^1H NMR.

(14) $Na^+(CH_3CH_2CH(Fe(CO)_4)C(=O)OEt)^-$ prepared independently from $NaHFe(CO)_4$ and *trans*-ethyl crotonate had ^{13}C and 100-MHz ^1H NMR spectra identical with that of our observed product.

(15) H. Simon and O. Berngruber, *Tetrahedron*, **26**, 1401 (1970); C. D. Ritchie, "Physical Organic Chemistry, the Fundamental Concepts", Marcel Dekker, New York, N.Y., 1975, pp 217, 237.

(16) The inverse isotope effect requires that $k_{-2} > k_3$ and that the concentration of III be small. The isotope effect arises from zero point energy differences between C–H and Fe–H vs. C–D and Fe–D vibrations. Using $Ru_4H_4(CO)_{12}$ as a model (S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975)), two bands are observed at 1585 and 1290 cm^{-1} which shift to 1153 and 909 cm^{-1} in the deuteride. For the alkyl intermediate, chloroform was used as a model. The chloroform C–H bond shows a stretching vibration at 3019 cm^{-1} and a twofold degenerate bending vibration at 1259 cm^{-1}. These values are shifted to 2256 and 908 cm^{-1}, respectively, in $CDCl_3$ (see R. W. Alder, R. Baker, and J. M. Brown, "Mechanisms in Organic Chemistry", Wiley-Interscience, London, 1971, p 15). These values give $K_D/K_H = 3.3$. While these calculations are not intended to be definitive, they do show that a preequilibrium of the type II $\rightleftharpoons$ III will account for the observed isotope effect.

(17) It has been shown in our laboratory that $NaHFe(CO)_4$ regiospecifically and irreversibly adds iron to the α-position. J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).

(18) (a) We have shown Noyori's preparation ($Fe(CO)_5 + NaOH + CH_3OH$) affords a light pink solution of slightly impure $NaHFe(CO)_4$. R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1542 (1972). (b) T. Mitsudo, Y. Watanabe, M. Yamashite, and Y. Takegami, *Chem. Lett.*, 11, 1385 (1974). We and Takegami have shown that addition to α,β-unsaturated carbonyl compounds are greatly inhibited by CO. The slow step in these reactions is presumably CO dissociation, $NaHFe(CO)_4 \rightleftharpoons CO + NaHFe(CO)_3$. We have demonstrated rapid ^{13}CO exchange with $NaHFe(CO)_4$.

(19) For a CO dissociative pathway with most of the iron present as $NaHFe_2(CO)_8$, one expects a rate law $\propto [NaHFe_2(CO)_8]^{1/2}$ [olefin] or $[NaHFe_2(CO)_8]$ $[olefin]^0$ while a second-order rate law was observed under all conditions. The lack of ^{13}CO exchange with $NaHFe_2(CO)_8$ on the time scale of reduction of faster substrates (e.g., dimethyl maleate) and the CO independence of the reductions are also inconsistent with a CO dissociative pathway.

(20) The empty, low-energy, antibonding, intermetallic orbital in binuclear cluster compounds may be important in this association. R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975), and references contained therein.

(21) If protonation occurred prior to k_3, the rate would depend on the [HOAc], but the overall rate is independent of [HOAc].

(22) We have studied kinetically using NMR the rapid reaction of $[(Ph_3P)_2N]^+[CH_3CH(Fe(CO)_4)CO_2Et]^-$ and HOAc in THF Dimerization of $Fe(CO)_4$ (derived from photolysis of $Fe(CO)_5$ in a nitrogen matrix) has been reported. (M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).) If $NaHFe_2(CO)_8$ is treated with strong acid, H_2, $NaHFe_3(CO)_{11}$, and $Fe(CO)_5$ are observed, suggesting the following reactions have occurred:

$$NaHFe_2(CO)_8 + HX \rightarrow Fe_2(CO)_8 + H_2 + NaX$$

$$Fe_2(CO)_8 + NaHFe_2(CO)_8 \rightarrow NaHFe_3(CO)_{11} + Fe(CO)_5$$

(23) During the submission of this communication, Shapley,[24] in a study of the reactions of $H_2Os_3(CO)_{10}$, has independently obtained evidence which supports some steps of this mechanism. Specifically, he found the addition of $H_2Os_3(CO)_{10}$ to ethyl acrylate is regiospecific, yielding the hydrido alkyl intermediate $HOs_3(CO)_{10}(CH(CH_3)CO_2Et)$. His data also indicate reversibility in the migratory insertion step, and suggest the reverse of the insertion step competes favorably with intramolecular reductive-elimination from the hydridoalkyl intermediate yielding alkane (e.g., $CH_3CH_2CO_2Et$) and the highly unsaturated $Os_3(CO)_{10}$.

(24) J. B. Keister and J. R. Shapely, *J. Am. Chem. Soc.*, **98**, 1056 (1976).

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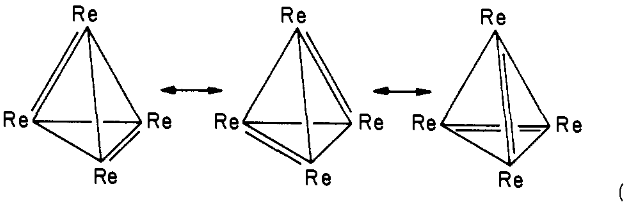
The Molecular Structure of $H_4Re_4(CO)_{12}$. Evidence for Face-Bridging Hydrogen Atoms

Sir:

$H_4Re_4(CO)_{12}$[1] is unusual among metal cluster compounds in that it is one of the few non-EAN, or "unsaturated",[2] carbonyl clusters known to exist. To account for the unsaturation and for the high symmetry[3] of the compound, resonating multiple-bonded structures (I) were proposed.[1] The high symmetry of the molecule also suggested triply bridging (face-bridging) positions for the hydrogen atoms.



(I)

In earlier papers we and others have shown how bridging hydrogen positions can be inferred from distortions in metal–metal distances.[4-6] In this communication we show that in certain instances the orientation of carbonyl groups can constitute a powerful indication of hydrogen positions in a metal cluster. We also introduce in this work a Fourier-averaging method that can be used to derive average hydrogen positions in molecules of high symmetry.

$H_4Re_4(CO)_{12}$ was prepared by pyrolyzing $H_3Re_3(CO)_{12}$ in refluxing *n*-octane for 2 h.[1] Recrystallization from CH_2Cl_2 afforded small dark red crystals having the following unit cell parameters: space group $P2_1/c$ (monoclinic); $a = 14.449$ (3), $b = 10.103$ (2), $c = 13.860$ (3) Å; $\beta = 110.66$ (1)°; $V = 1893.1$ Å^3; $Z = 4$. One quadrant of data was collected on an automated Nonius CAD-3 diffractometer with Mo Kα radiation up to a 2θ maximum of 45°.[7] The structure was solved by heavy atom methods. All non-hydrogen atoms were located and re-

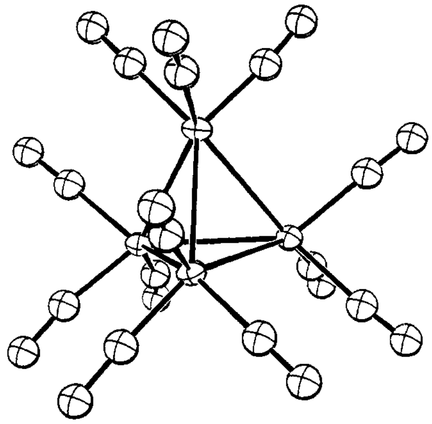
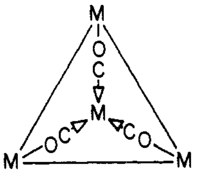


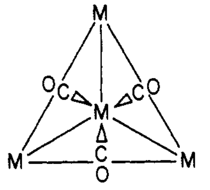
Figure 1. A molecular plot of $H_4Re_4(CO)_{12}$, showing non-hydrogen atoms.

fined to give a final R factor of 7.2% for 1539 nonzero reflections.[8]

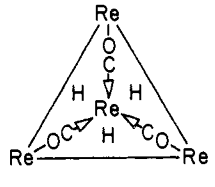
The molecular geometry of $H_4Re_4(CO)_{12}$, which is essentially tetrahedral, is shown in Figure 1. The individual Re-Re distances are 2.945 (3), 2.930 (3), 2.904 (3), 2.901 (3), 2.900 (3), and 2.896 (3) Å,[9] and other distances and angles (averaged) in the molecule are: Re-C = 1.90 (2) Å, C-O = 1.16 (2) Å, Re-C-O = 174.2 (7)°, C-Re-C = 86.0 (4)°, Re-Re-C = 92.9 (6)° and 136.9 (5)°. The most interesting feature of the molecule is the fact that the carbonyl groups are eclipsed with respect to the M-M edges (II), in contrast to those of $Ir_4(CO)_{12}$[13] and $[H_6Re_4(CO)_{12}]^{2-}$,[5] which are in a staggered conformation (III). The disposition of the carbonyl groups in II is strongly indicative of the presence of face-bridging hydrogen atoms (IV). Since the "saturated" complex $[H_6Re_4(CO)_{12}]^{2-}$ is believed to have edge-bridging hydrides (V), it is apparent that the 60° rotational difference of the $Re(CO)_3$ moiety in the two compounds is necessitated by the approximately octahedral $H_3Re(CO)_3$ coordination about each rhenium atom. Other tetrahedral metal clusters with face-bridging ligands such as $Os_4O_4(CO)_{12}$,[11] $Re_4(CO)_{12}(SCH_3)_4$,[14] and $H_4W_4(CO)_{12}(OH)_4$[15] also have carbonyl groups disposed as in II.



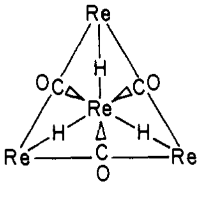
(II)



(III)



(IV)



(V)

The positions of the hydrogen atoms were confirmed by a subsequent search in difference Fourier maps. Anticipating that the successful location of individual hydrogen atoms simultaneously bonded to three rhenium atoms would prove extremely difficult, we decided to synthesize composite difference maps, superimposing the electron density functions calculated for the six mirror planes of the tetrahedron. The idea, of course, was that with this "image-enhancing" approach random noise would be hopefully canceled out while true peaks would be enhanced. The result (Figure 2) nicely shows a well-resolved hydrogen atom at the expected position with a measured H-Re distance of 1.75-1.79 Å, in reasonably good agreement with known M-H(br) bond lengths.[16] No attempt was made to refine this idealized H position.

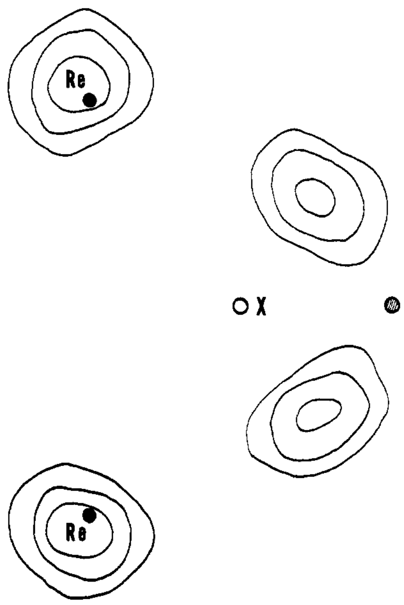
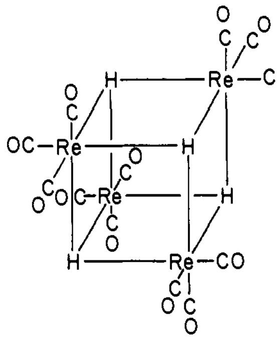


Figure 2. A composite difference Fourier map synthesized by superimposing and averaging the individual maps calculated for the six mirror planes of the $H_4Re_4(CO)_{12}$ tetrahedron. X represents the centroid of the Re_4 tetrahedron and Y represents the midpoint of a Re-Re edge. This map was calculated using data having a (sin θ/λ) maximum of 0.45 $Å^{-1}$. Contours are drawn at 0.4, 0.6, 0.8, and 1.0 $eÅ^{-3}$. The measured H position corresponds to a H-Re distance of 1.75-1.79 Å, and is about 0.3 Å out of plane of a tetrahedral face. Note how the H peaks are collinear with the Re-X vectors, as is to be expected. Also note the complete absence of a peak at the edge-bridging position (slightly to the left of the midpoint of the vertical Re-Re bond). This map demonstrates the usefulness of "image enhancing" techniques in molecules of high symmetry in cases where conditions for locating individual H atoms are unfavorable.

The average Re-Re distance in $H_4Re_4(CO)_{12}$ (2.913 (8) Å) is significantly shorter[17] than the single-bonded Re-Re distance in $Re_2(CO)_{10}$ (3.02 Å)[18] and is in fact very close to that found in the "double bonded" complex $H_2Re_2(CO)_8$ (2.896 (3) Å).[19] One can rationalize this in terms of the unsaturated nature of the cluster as dipicted in I, or by geometric considerations: the shortness of the Re-Re distance in $H_4Re_4(CO)_{12}$ may simply be a reflection of the fact that the rhenium atoms have to approach each other closely to form four HRe_3 4-center bonds. The exact nature of the multiple bonding between hydrogen-bridged metal atoms is somewhat ambiguous, as has been pointed out by Bennett and Graham[19] and by Churchill[20] in discussing the structures of $H_2Re_2(CO)_8$ and $[H_2W_2(CO)_8]^{2-}$. In our recent neutron-diffraction analysis of the W-H-W bridge bond in $HW_2(CO)_9(NO)$[21] we presented evidence that there is substantial M-M bonding character in a M-H-M bridge bond, and that the original picture of such a bond as a "protonated M-M bond" may not be too far from the truth. An alternative way of looking at the multiple bonding in $H_4Re_4(CO)_{12}$, then, is to imagine the M-M overlap as being part of the HRe_3 four-center bonds themselves. Conceptually this corresponds to a distorted cubic model in which direct metal-metal bonding is replaced by the framework of HRe_3 four-center overlaps (VI).[22]

The calculated density of $H_4Re_4(CO)_{12}$, 3.806 g cm^{-3}, makes this complex one of the densest metal carbonyl cluster compounds known. The external array of oxygens defines a truncated tetrahedron, as opposed to the oxygen atoms of $Ir_4(CO)_{12}$ and $[H_6Re_4(CO)_{12}]^{2-}$ which are arranged in the form of a cubo-octahedron.[5,13]



(VI)

It is interesting to compare the structures of the "unsaturated" cluster $H_4Re_4(CO)_{12}$ with that of the "saturated" cluster $H_4Ru_4(CO)_{12}$. In $H_4Ru_4(CO)_{12}$, the prediction that the hydrogens are edge-bridging[23] has been confirmed by a single-crystal structure determination on the derivative $H_4Ru_4(CO)_{11}P(OCH_3)_3$, which shows the presence of four long and two short Ru-Ru distances.[24]

Acknowledgment. Financial support from the National Science Foundation (Grant No. GP-42943X) is gratefully acknowledged. Computer time was supplied by the University of Southern California Computing Center.

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(1) R. Saillant, G. Barcelo, and H. D. Kaesz, *J. Am. Chem. Soc.*, **92**, 5739 (1970).

(2) EAN refers to the effective atomic number rule, which when applied to metal clusters predicts "closed shell" configurations of 60 electrons for tetrahedral clusters (see H. D. Kaesz, *Chem. Brit.*, **9**, 344 (1973)). $H_4Os_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ are 60-electron clusters [4(1) + 4(8) + 12(2)] and are considered "saturated", while $H_4Re_4(CO)_{12}$, a 56-electron cluster, is considered "unsaturated".

(3) The infrared spectrum of $H_4Re_4(CO)_{12}$ showed only two bands in the CO-stretching region.[1]

(4) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).

(5) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).

(6) (a) M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971). (b) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 11, 1818 (1972).

(7) The crystal was mounted on a glass fiber. The approximate size of the crystal used in data collection was 0.11 × 0.18 × 0.19 mm. An empirical absorption correction was applied, based on the variation of intensity of an axial reflection ($\chi = 90°$) with ϕ (T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wisc., 1966).

(8) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh and his group at the California Institute of Technology.

(9) The spread in Re-Re distances observed here (0.054 Å) is not too unusual. In other tetrahedral metal clusters such as $H_4Co_4(C_5H_5)_4$, $Os_4O_4(CO)_{12}$, and $Fe_4(CO)_4(C_5H_5)_4$, differences in M-M distances on the order of 0.03-0.06 Å (corresponding to about 10-20 standard deviations) are commonly found.[10-12] In the cases of $H_4Co_4(C_5H_5)_4$ and $Os_4O_4(CO)_{12}$ it was suggested that crystal packing forces may be responsible.

(10) G. Huttner and H. Lorenz, *Chem. Ber.*, **108**, 973 (1975).

(11) D. Bright, *Chem. Commun.*, 1169 (1970).

(12) M. A. Neuman, Trinh-Toan, and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 3383 (1972).

(13) G. R. Wilkes, Ph.D. Dissertation, University of Wisconsin, 1965.

(14) E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *Chem. Commun.*, 1531 (1970).

(15) V. G. Albano, G. Ciani, M. Manassero, and M. Sansoni, *J. Organomet. Chem.*, **34**, 353 (1972).

(16) A recent tabulation of accurate neutron-diffraction measurements of bridging hydrogen-metal bond lengths (see Table VIIIa in R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.*, **98**, 4491 (1976)) shows that these distances remain relatively constant at values of 1.85-1.89 Å for Mo-H-Mo and W-H-W systems. Assuming approximately equal covalent radii for W and Re, and bearing in mind that x-ray measurements of bond lengths involving hydrogen are often a little shorter than their true values, it is seen that the Re-H(br) distance of 1.75-1.79 Å found here is quite reasonable.

(17) This runs contrary to the observation in $H_2Ru_6(CO)_{18}$[6a] that Ru-Ru distances associated with hydrogen-capped faces are ~0.09 Å longer than nonbridged Ru-Ru distances.

(18) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(19) M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).

(20) M. R. Churchill and S. W. Y. Ni Chang, *Inorg. Chem.*, **13**, 2413 (1974).

(21) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).

(22) The actual configuration of the H_4Re_4 core in $H_4Re_4(CO)_{12}$ is of course significantly distorted from the idealized cubic structure drawn in VI. In reality, the HRe_3 unit is much more coplanar: in other words, the H···H distances are much shorter than the Re···Re distances.

(23) (a) H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.*, 477 (1971); (b) S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, **93**, 4594 (1971).

(24) Preliminary crystallographic results on $H_4Ru_4(CO)_{11}P(OCH_3)_3$ (unit cell $P\bar{1}$ (triclinic); $a = 13.69$, $b = 9.13$, $c = 11.26$ Å; $\alpha = 116.0$, $\beta = 93.2$, $\gamma = 97.1°$; $Z = 2$) show the following values for the Ru-Ru distances: 2.94, 2.94, 2.92, 2.92, 2.76, 2.76 Å. Presumably, the four long distances represent Ru-H-Ru bridge bonds and the two short distances (which are opposite each other) represent unbridged Ru-Ru bonds.

(25) Alfred P. Sloan Fellow, 1974-1976. NIH Career Development Awardee, 1975-80.

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Mechanism of the Olefin Metathesis Reaction. 4.[1] Catalyst Precursors in Tungsten(VI) Based Systems

Sir:

Tungsten hexachloride is the most common transition metal reagent used in catalyst recipes for the olefin metathesis reaction. Using this compound as an invariant reagent in our own mechanistic study of the metathesis reaction, we had encountered difficulties in reproducing the level of catalyst activity.[1-3] In attempts to minimize variability in catalyst activity we sought high purity in solvents and reagents and a reaction atmosphere free of water and oxygen. With such experimental precautions, we discovered that WCl_6, in combination with different alkylmetal compounds, is *inactive* at 25° as a catalyst precursor in the metathesis reaction at least for acyclic internal olefins. Reactions conducted identically except allowing for entry of trace amounts of air were catalytically active. We demonstrate below that $WOCl_4$ is an active catalyst precursor for metathesis of internal olefins under conditions in which oxygen and water are rigorously excluded and that the catalyst ligand requirements in tungsten(VI)-based systems include chlorine and oxygen atoms. Additionally, we have established that the $WOCl_4$-$C_2H_5AlCl_2$ system[4] is an especially distinctive catalyst because of its high activity, long lifetime, and minimal tendency to promote olefin isomerization and solvent alkylation side reactions.

Literature descriptions of metathesis experiments on WCl_6-based systems typically refer to syringe-septum techniques.[5] This procedure would appear to provide good but not total exclusion of atmospheric oxygen and water. To standardize our experimental procedures, we had sought to minimize all potential sources of oxygen. Solvent (benzene) and olefin (*cis*-2-pentene) were dried by reflux over CaH_2 and Na, respectively, distilled under N_2, and stored over activated[6] alumina. Tungsten hexachloride[7] was purified by careful sublimation[8] to remove the ubiquitous $WOCl_4$ and WO_2Cl_2 impurities. Reagents were stored, and reaction solutions were then prepared, in an inert atmosphere chamber maintained at <5 ppm oxygen and water.[9] Reactions were conducted either (A) in the inert atmosphere chamber or (B) in glass vessels, tightly capped with new rubber septa and under positive nitrogen pressure, that were "out" on the laboratory bench. Investigated as the initiating (alkylating) reagents were $C_2H_5AlCl_2$, $Zn(CH_3)_2$, and LiC_4H_9. In procedure A, with rigorous oxygen exclusion, these recipes were inactive as olefin metathesis catalysts (a low level of activity observed for the LiC_4H_9 system is ascribed to the known presence of small quantities of lithium butoxide[11]). In procedure B, the "careful" experimental condition, all metathesis recipes were active and the earlier established activity series of Al > Li > Zn prevailed