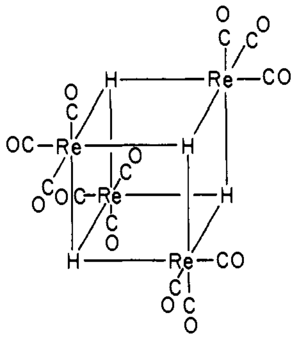

(VI)

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]

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(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]

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(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.

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(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.

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(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.

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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 under these conditions. Especially significant was the observation of variability in activity and the presence of induction periods. These phenomena are attributed to a variable rate of air entry into the reaction mixture during mixing of the reagents and subsequent diffusion through the septa during reaction. Clearly then, WCl_6 is not a catalyst precursor in acyclic olefin metathesis. Activation of the WCl_6 systems may be achieved by oxygen impurities in reagents or solvents or by ingress of air to the reaction flask whereby W-O bonds are formed through hydrolysis of W-Cl bonds or oxidation of W-alkyl bonds (formed rapidly[12] at 25° from the interaction of WCl_6 and the alkylating agent) or M-alkyl bonds.

It is undesirable to rely upon the use of nonrigorous experimental techniques to produce catalytically active mixtures since the variability of such techniques from one trial to another, much less among different researchers, will make quantitative comparisons of metathesis reactions impossible. The addition of oxygen or oxygen containing species can be quantified, however, and there are several examples of such treatment in the literature. For example, pretreatment of WCl_6 with 1 equiv of C_2H_5OH before addition of $C_2H_5AlCl_2$ produces a highly active catalyst.[5b] This pretreatment, which enhances the solubility of the tungsten complex, causes a change in the solution color from dark blue to red and the formation of oxytungsten chlorides.[13,14] In our hands, this system is highly catalytically active though short lived[2] even under conditions of rigorous exclusion of all other oxygen containing species. Similarly, we have established that use of carefully purified[15] $WOCl_4$ directly with $C_2H_5AlCl_2$ as a coreagent[4] produces a catalyst which is highly active with or without rigorous exclusion of oxygen and water and quantitatively (equilibration time of 2-pentane metathesis) equal to or slightly more active than the corresponding ethanol-modified WCl_6 system. Equilibration times of less than 2 min were observed with $C_2H_5AlCl_2$:$WOCl_4$ ratios of ½, 1, 2, and 4 (and olefin:catalyst = 500) with only trace amounts of isomerization or alkylation side reactions in experiments with low Al:W ratios.[16] Under similar conditions, WO_2Cl_2 and WO_3 showed only slight activity over a 24 h period or short-lived activity ($WOCl_4$ "impurity" in the WO_2Cl_2).

Catalyst life of the very active WCl_6-based catalyst recipes is short[2] under "careful" (procedure B) conditions. We found the catalyst life of the $WOCl_4$-$C_2H_5AlCl_2$ system to be long: metathesis rate was undiminished after 9 h under conditions of rigorous oxygen exclusion (procedure A). In contrast, this system underwent substantial loss of activity within 1 h under "careful" conditions (procedure B). Clearly, traces of oxygen or water greatly affect catalyst life. Similar results were obtained with the heterogeneous $WOCl_4$-C_4H_9Li system which has an initial activity never before realized for such a system (equilibration of 2-pentene metathesis in 5 min at BuLi:$WOCl_4$ = 1 and olefin:catalyst = 50).[17] In the C_4H_9Li and $Zn(CH_3)_2$ (vide infra) based $WOCl_4$ recipes, the *optimal* RM/W ratios are one-half those reported[5] for the WCl_6 recipes.

Perhaps the only drawback to these systems is that reaction is so rapid as to preclude accurate monitoring in the early (preequilibrium) stages of the reaction, a desirable feature in some studies.[18] For such studies, a $WOCl_4$-$Zn(CH_3)_2$ catalyst can be used effectively. This inhomogeneous system (at $Zn(CH_3)_2$:$WOCl_4$ = 0.5 and olefin:catalyst = 50) reaches in procedure A or B ca. 80% of the equilibrium values for 2-pentene metathesis in 1 h (roughly the life of the catalyst), permitting convenient sampling after only a few percent reaction.

We have recently found a new catalytic metathesis system that is fully homogeneous and especially suited to mechanistic studies by NMR techniques since both starting materials contain conveniently monitored hydrogen resonances. The essential reagent in this new system is either $W(OCH_3)_6$ or $WO(OCH_3)_4$, compounds that have solubility in aromatic solvents. Reaction of $W(OCH_3)_6$ with $C_2H_5AlCl_2$ in benzene solution yields a colorless to pale yellow solution that catalyzes the metathesis of olefins. Rigorous exclusion of water and oxygen did not detectably impair the catalytic efficiency of this system. However, *chlorine must be present* in the reagent mixture; $W(OCH_3)_6$ or $WO(OCH_3)_4$ in combination with $Al(CH_3)_3$, $Al(C_2H_5)_3$, C_4H_9Li, or $Zn(CH_3)_2$ did not yield a metathesis catalyst. Therefore, both chlorine and oxygen ligand atoms are essential in these W(VI) based catalysts for high metathesis activity for internal olefins at 25°.

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