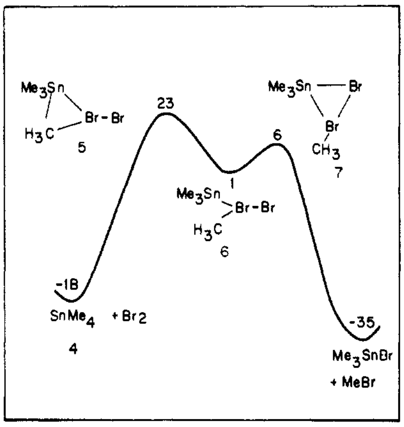

Figure 1. MNDO calculated reaction path for the electrophilic attack of Br_2 on tetramethylstannane.

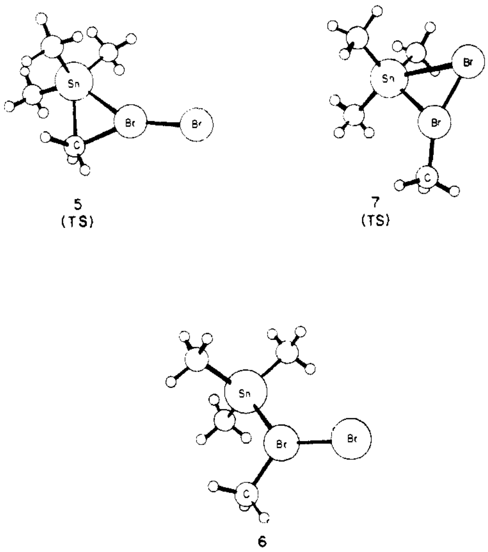

Figure 2. Stationary points on the reaction path between $(CH_3)_4Sn$ + Br_2 and $(CH_3)_3SnBr$ + CH_3Br.

We have now studied the reactions of tetramethylstannane (**4**) with bromine theoretically, using the MNDO[6] model as implemented in the MOPAC[7] set of computer programs together with the recently developed parameters for tin.[8] All geometries were optimized and those of the TSs and intermediates confirmed by calculation of their force constants.[9] The calculated reaction path for **4** with Br_2 is shown in Figure 1. The geometries of the intermediate and the TSs are shown in Figure 2.

As can be seen from Figure 2, attack by Br_2 has occurred in such a way that the Br-Br and C-Sn bond axes in the first TS (**5**) are nearly perpendicular. **5** leads to the hypervalent intermediate **6**. The geometry predicted for **6** may well be incorrect because MNDO is known[10] to predict analogous Y-type geometries for compounds of this kind (e.g., BrF_3) which are known to be T-shaped. The error may be due either to neglect of d AOs or overestimation of nonbonded repulsions. In the gas phase, **6** decomposes via **7** to the products CH_3Br and $(CH_3)_3SnBr$.

These calculations suggest a mechanism for the bromination of alkyltin compounds which, we believe, is in accord with the stereochemical results in both polar and nonpolar solvents. In nonpolar solvents, alkyltins have been found to react with retention of stereochemical configuration at carbon if radicals are rigorously excluded.[1a-c] In this case, we propose that the reaction simply corresponds to the gas-phase pathway (Figure 1) which leads exclusively to retention. In more polar solvents, inversion has been observed[1,2] and the ratio of inversion to retention increases with the size of the nonreacting alkyl groups at tin.[1a-c] These results are easily rationalized by postulating heterolytic cleavage of the weak Br-Br bond in **6**, resulting in an ion pair:

$$\mathbf{6} \rightarrow \underset{\mathbf{8}}{[(CH_3)_3SnBrCH_3]^+} + Br^- \qquad (1)$$

Nucleophilic attack by Br^- on the carbon atom in **8** will lead to inversion, while attack at tin will leave the configuration of the carbon atom unchanged. Since anionic substitution at tin is expected to be a solvactivated[11] process, like analogous reactions on silicon,[12] attack by Br^- on **8** should normally take place more easily at tin than at carbon. The relative reactivity at tin should, however, be reduced by bulky substituents or by increasing the polarity of the solvent.

The available experimental data concerning the stereochemistry of electrophilic substitution of alkyltins by bromine can thus be explained in terms of a single unified mechanism, involving no unreasonable or ad hoc assumptions and based on theoretical calculations using a well-tested procedure.

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Registry No. 4, 594-27-4; Br_2, 7726-95-6.

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Rapid Olefin Hydrogenation Catalyzed by Anion-Promoted Ruthenium Clusters

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Recent studies[3-6] of the interaction of anions with $Ru_3(CO)_{12}$ have established that the carbonyl ligands are labilized from the $[Ru_3(CO)_x\text{–anion}]^{1-}$ (where x = 10 or 11) complex. These studies have made use of this anion effect to catalyze phosphine and ^{13}CO substitution and in one case H_2 activation[4] at room temperature with rates that are orders of magnitude faster than the reaction without the anion. The basic requirement for facile substitution in most homogeneous catalytic reactions of olefins[7] led us to question whether olefin hydrogenation would be catalyzed by anion-promoted ruthenium clusters. In this paper, we report that olefins can be rapidly hydrogenated under mild conditions using anion (especially isocyanate)-promoted ruthenium clusters.

A tetrahydrofuran (THF) solution of $[Ru_3(\mu_2\text{-}NCO)(CO)_{10}]$,[1-6] (**1**) can be prepared directly from $Ru_3(CO)_{12}$ and $(PPN)(N_3)$ or

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(2) Fellow of the Alfred P. Sloan Foundation, 1983-1985.

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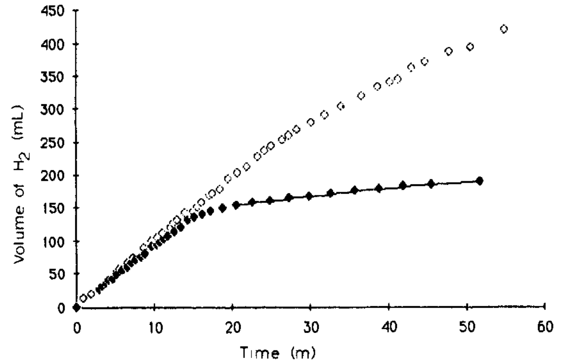

Figure 1. (Open diamonds) Plot of volume of hydrogen consumed vs. time under typical reaction conditions ($[Ru_3(NCO)(CO)_{10}]^{1-}$ = 1.4 mM; [olefin] = 0.38 M; P_{H_2} = 0.74 atm; THF at 25.0 °C). Rate = 5.2 turnovers/min. (Shaded diamonds) Plot of change in amount of hydrogen consumed as a result of added CO ($[Ru_3(NCO)(CO)_{10}]^{1-}$ = 1.4 mM; [olefin] = 0.38 M; P_{H_2} = 0.75 atm). Rate = 4.9 turnovers/min. After addition of 0.88 mmol of CO, rate = 0.6 turnovers/m.

(PPN)(NCO) (PPN = bis(triphenylphosphine)iminium cation). The atmosphere was switched from N_2 to H_2 by three brief evacuations, followed by the admission of H_2. This effectively removed the CO present from the catalyst generation step. Upon saturation of this solution with hydrogen for 5 min followed by addition of the olefin (3,3-dimethylbutene), immediate absorption of H_2 begins. In the absence of H_2, no reaction occurs between the cluster and the olefin. Two important observations are illustrated by the typical plot of the raw data shown in Figure 1. First, there is no induction period upon addition of the olefin, and, second, the rate of H_2 uptake (measured at constant pressure using an automatic H_2 titrator) is linear for several hundred turnovers. The solution remains clear throughout the reaction. An infrared spectroscopic study of a working catalyst solution revealed that only one species, **1**, could be correlated to the catalytic activity. The other species that eventually form as the activity decreases are $[HRu_3(CO)_{11}]$,[1-8] $[H_3Ru_4(CO)_{12}]$,[1-9] and $[H_2Ru_4(NCO)(CO)_{12}]$.[1-6] The identity of these clusters was confirmed by ^1H NMR spectroscopy. This same mixture of hydrido clusters also forms within minutes when **1** is allowed to react with H_2 in the absence of olefins. None of these clusters individually or in concert show any catalytic activity under these mild conditions. Conditions such as high concentrations of **1** or H_2 increase the rate of disappearance of **1**, independent of the presence of olefin. Additional results on the reaction kinetics are discussed below.

The catalyst selectively reduces terminal, unactivated olefins. Acrylonitrile, methylacrylate, and cyclopentene are not hydrogenated. Isomerization of 1-pentene to both isomers of 2-pentene is observed during its hydrogenation to pentane. We have also found that Br^- and Cl^-, but neither I^- nor NCS^-, can be used in place of the NCO^- for promoting the catalysis.

All of the kinetics have been studied in THF at 25.0 °C with use of 3,3-dimethylbutene. The rate of reaction was determined from the slopes of plots similar to Figure 1 for the first 90–100 catalytic turnovers. At 1.4 mM **1**, 0.38 M olefin, and a partial pressure of H_2 of 0.74 atm, the rate was 5.9 turnovers/min. In the range 0.28–0.99 atm, the rate exhibited a first-order dependence on H_2. From 0.1 to 1.0 M olefin no significant effect on the rate was observed. The dependence of the rate on the concentration of **1** (Figure 2) indicates the reaction is one-half order in **1**. The experimentally derived rate law for the catalysis is $-d[H_2]/dt = k_{obsd}[\mathbf{1}]^{1/2}[H_2]$. The simplest interpretation of this kinetic behavior involves a preequilibrium in which the cleavage of one particle of **1** into two particles occurs rapidly. These two particles need not be identical, and simple CO dissociation as well as the cleavage of two M–M bonds could equally well fit the data.

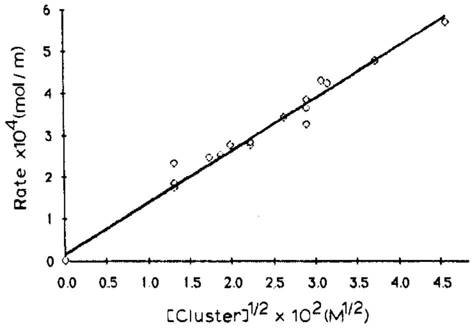

Figure 2. Plot of rate vs. $([Ru_3(NCO)(CO)_{10}]^{1-})^{1/2}$.

Some of the candidates for this preequilibrium are shown in eq 1–3. In any reactions involving cleavage of two M–M bonds at

$$[Ru_3(NCO)(CO)_{10}]^{1-} \rightleftharpoons CO + [Ru_3(NCO)(CO)_9]^{1-} \quad (1)$$

$$[Ru_3(NCO)(CO)_{10}]^{1-} \rightleftharpoons Ru_2(CO)_8 + \text{“}[Ru(NCO)(CO)_2]^{1-}\text{”} \quad (2)$$

$$[Ru_3(NCO)(CO)_{10}]^{1-} \rightleftharpoons [Ru_2(CO)_8]^{2-} + \text{“}[Ru(NCO)(CO)_2]^{1+}\text{”} \quad (3)$$

least one of the fragments will contain multiple sites of unsaturation which would undoubtedly require stabilization by solvent molecules. Two means for differentiating the possible reactions involve (1) the study of the CO dependence on the reaction and (2) evaluating the solvent effect. Increasing the solvent polarity from THF to acetone causes the rate to *decrease* by a factor of 3. Since eq 3 involves an increase in charge separation, more polar solvents would be expected to have the opposite effect. Complicating this interpretation, however, is the fact that acetone, a better ligand than THF, might be affecting the rate of one of the other reaction steps. Figure 1 also shows the inhibiting effect of adding a very small amount of CO to the H_2 during the reaction. No changes were observed in the infrared spectrum after addition of the CO, suggesting that with such small amounts of CO little of **1** is converted back to $[Ru_3(NCO)(CO)_{11}]^{1-}$. This CO inhibition is strong evidence in favor of eq 1 being the first step in the catalytic reaction.

A reaction sequence consistant with these data is shown in eq 4–6.[10] The observed deuterium isotope effect of k_H/k_D = 1.7

$$[Ru_3(NCO)(CO)_{10}]^{1-} \overset{K_1}{\rightleftharpoons} CO + [Ru_3(NCO)(CO)_9]^{1-} \quad (4)$$

$$[Ru_3(NCO)(CO)_9]^{1-} + H_2 \xrightarrow{k_2} [H_2Ru_3(NCO)(CO)_9]^{1-} \quad (5)$$

$$[H_2Ru_3(NCO)(CO)_9]^{1-} + \text{olefin} + CO \xrightarrow{\text{fast}} \text{alkane} + [Ru_3(NCO)(CO)_{10}]^{1-} \quad (6)$$

is consistant with a rate-determining oxidative addition of dihydrogen.

Other examples of catalysis by carbonyl clusters (or monomers) typically require more vigourous temperature and often pressure conditions.[11-13] The importance of this work is that it establishes that halides and pseudohalides can be used to promote olefin-based catalytic reactions under conditions that are mild enough that the cluster *may* remain intact. The nature of this activating influence as well as additional details of this catalysis is under study.

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(10) Since CO is generated and consumed along with $[Ru_3(NCO)(CO)_9]^{1-}$, the following equality will be true: $[CO] = \chi_{CO}[Ru_3(NCO)(CO)_9]^{1-}$, where χ_{CO} is the mole fraction of CO in solution. The equilibrium (4) can now be expressed as $K_1 = \chi_{CO}([Ru_3(NCO)(CO)_9)^2/[\mathbf{1}]$. Solving for $[Ru_3(NCO)(CO)_9]^{1-}$ and substituting into the rate expression gives $-d[H_2]/dt = k_2K_1^{1/2}\chi_{CO}^{1/2}[\mathbf{1}]^{1/2}[H_2]$.

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