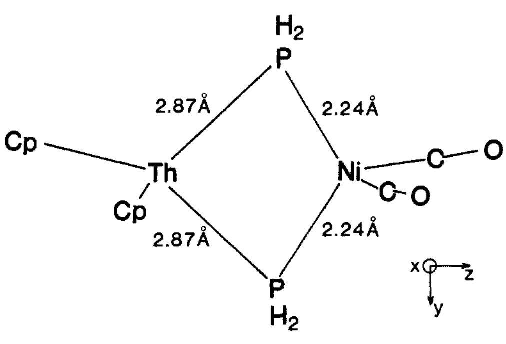

Figure 1. ThP_2Ni quadrilateral with assumed M–P distances and surrounding ligands.

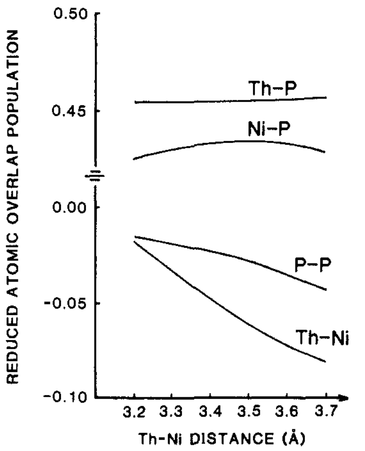

Figure 2. Reduced atomic overlap populations as a function of Th–Ni distance.

fragment and the symmetrized combinations of $3a_1$ and $1b_1$ PH_2 orbitals. The latter are delocalized to some extent onto the Th in a bonding relationship. Therefore, this first interaction is net antibonding between Th and Ni, as well as antibonding between Ni and P. (The overall Ni–P bonding relationship is sustained by acceptance of P lone pair density by empty spd Ni orbitals.) As the geometry is varied, these relationships are conserved.

This brings us to the second source of Th–Ni interaction, between the filled d levels of $Ni(CO)_2$ and the many empty levels of $Cp_2Th(PH_2)_2$ that are centered on Th. Counting the ligands of the latter fragment as anions gives Th^{4+} with a d^0f^0 electron count. Seven empty f orbitals in this C_{2v} fragment give rise to two levels each of b_1, b_2, and a_1 symmetry, plus one a_2 level. Less than 0.4 eV separates the highest (−5.6 eV) from the lowest (−6.0 eV) f-like orbital of $Cp_2Th(PH_2)_2$. About 1 eV higher in energy are four metal-centered spd hybrids of b_2, a_1, a_2, and b_1 symmetry. The largest interaction involves the $Ni(CO)_2$ HOMO, a hybrid of xz and x that points toward the Th in the plane of the Ni fragment's atoms. A similar hybrid ($3b_2$) of xz,x and xz^2 on the Th fragment has an overlap population with the $Ni(CO)_2$ HOMO of 0.054.[5] The $1b_2$ orbital of this fragment is not as diffuse. This mostly xz^2 orbital gives an overlap population of 0.009 with the $Ni(CO)_2$ HOMO; the radial extent of the d Th orbitals is superior for bonding at the distances under consideration here. (The $2b_2$ fragment MO has little bonding influence.) $Ni(CO)_2$'s second HOMO, a mixture of Ni $x^2 - y^2$, z^2, s, and z, has a_1 symmetry. Just above the $3b_2$ orbital of $Cp_2Th(PH_2)_2$ in energy is a z^2,s,z hybrid, $3a_1$, which has an overlap population with $Ni(CO)_2$'s second HOMO of 0.027. As with the previously mentioned b_2 pair of interactions, there is also a stabilization effected by a member of the f orbital set; this time it is the $2a_1$ (z^3) orbital that stabilizes the Ni fragment MO to give an overlap population of 0.005. All of the overlap populations given above obtain for the shortest Th–Ni distance and are reduced by 40–60% when the Th–Ni distance is increased to 3.70 Å. This explains why the Th–Ni curve in Figure 2 ascends with decreasing Th–Ni separation. Letting the z axis define pseudosymmetry implies that the a_1 mixings are σ bonding and that the b_2 mixings are π bonding.

There is a weak donor–acceptor relationship between Ni and Th. This is made possible by the flexibility of the P bridges with respect to bending about the Th as is illustrated by the flatness of the Th–P curve in Figure 2. In an ordinary phosphido-bridged system with no metal–metal bonding, the crucial reduced metal–metal overlap population is negative. The Th center has many unfilled levels which can diminish this antibonding relationship if the Th–Ni distance is reduced.

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(5) The overlap populations cited from here onward are in terms of the basis of fragment MO's of $Cp_2Th(PH_2)_2$ and $Ni(CO)_2$, not in terms of the atomic orbital basis.

MNDO Study of the Reaction of Tetramethylstannane with Bromine

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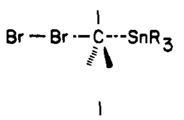
The mechanism of the brominolysis of alkyl tin compounds has been of considerable interest to organometallic chemists primarily due to the observation of stereochemical inversion, as well as retention, at carbon under certain conditions.[1,2] A wide range of mechanistic pathways have been proposed for this reaction, which has been found, in general, to be first order in both Br_2 and the alkyltin.[1,3] These proposed mechanisms included both concerted,[1-3] stepwise,[3] and charge-transfer[4] processes. To rationalize the observed stereochemistry at carbon, three transition states (TS) have been proposed, **1**, below, leading to inversion and **2** and **3** leading to retention. Note however, that reaction via **3** would be a forbidden process.[5]



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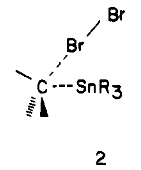

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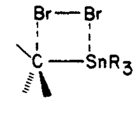

3

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(1) (a) Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177. (b) McGahey, L. F.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 4397. (c) Rham, A.; Peryre, M. *Ibid.* **1977**, *99*, 1673. (d) Jensen, F. R.; Davis, D. D. *Ibid.* **1971**, *93*, 4048. (e) Chambers, R. L.; Jensen, F. R. "Aspects of Mechanism and Organometallic Chemistry"; Brewster, J. H., Ed.; Plenum Press: New York, 1978.

(2) Olszow, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1676.

(3) (a) Gielen, M.; Frosty, R. *J. Chem. Res., Synop.* **1977**, 214. (b) Gielen, M.; Frosty, R. *J. Chem. Res., Miniprint* **1977**, 2379. (c) Gielen, M. *Acc. Chem. Res.* **1973**, *6*, 198.

(4) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141.

(5) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.

0002-7863/86/1508-0551$01.50/0

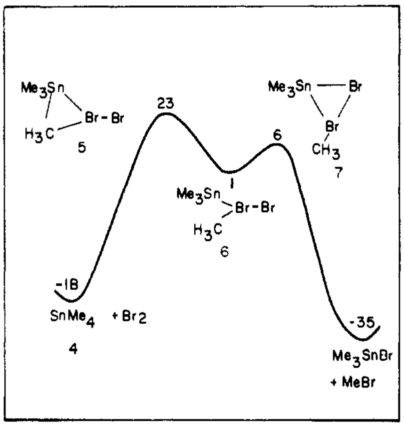
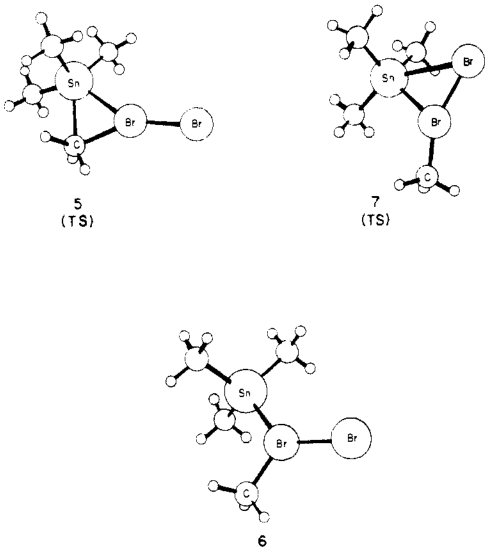


Figure 1. MNDO calculated reaction path for the electrophilic attack of Br_2 on tetramethylstannane.



5 (TS)

7 (TS)

6

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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(6) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(7) QCPE Publication 455, Dept. of Chem. Indiana University, Bloomington, IN 47405.

(8) Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771.

(9) (a) McIver, J. W., Jr.; Komornicki, J. *J. Am. Chem. Soc.* **1972**, *94*, 2625. (b) McIver, J. W., Jr.; Komornicki, J. *Chem. Phys. Lett.* **1971**, *10*, 303.

(10) Dewar, M. J. S.; Healy, Eamonn F. *J. Comput. Chem.* **1983**, *4*, 542.

(11) Dewar, M. J. S.; Storch, Donn M. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 2225.

(12) Dewar, M. J. S.; Healy, Eamonn F. *Organometallics* **1982**, *1*, 1705.

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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(1) National Science Foundation predoctoral fellow, 1982–1985.

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

(3) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647–4648.

(4) Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696–3697.

(5) Darensbourg, D. J.; Gray, R. L.; Pala, M. *Organometallics* **1984**, *3*, 1928–1930.

(6) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774–1780.

(7) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319.

0002-7863/86/1508-0552$01.50/0