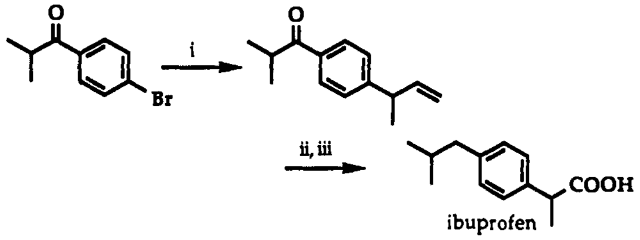
Scheme II[a]



[a] (i) (*E*)-Crotyltrifluorosilane, $Pd(PPh_3)_4$ (5 mol %), TBAF (1.0 equiv), THF, 100 °C, 90 h, 95%; (ii) $KMnO_4$, $NaIO_4$, K_2CO_3, *t*-BuOH, H_2O, 0 °C, 2 h, 70%; (iii) $HSiEt_3$, CF_3COOH, room temperature, 24 h, 78%.

fluorosilane afforded isomerically pure γ-coupled products.[8,9,10] Similar conditions were successfully applied to the allylation of both aryl triflates and an allyl acetate, achieving the cross couplings at the γ-carbon of crotyltrifluorosilane exclusively (entries 4 and 5). The use of the $Pd(OAc)_2$ (5 mol %)/1,4-bis(diphenylphosphino)butane (dppb) (10 mol %) system[11] coupled with tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF)[12] (1.0 equiv) as a F^- source was found particularly effective for γ-selective cross couplings with enol triflates (entries 6 and 7).

Under typical conditions, (3-methyl-2-butenyl)trifluorosilane also smoothly coupled with aryl halides or enol triflates at the sterically crowded γ-carbon to afford 3-substituted 3-methyl-1-butenes in good yields (entries 8-10). These results sharply contrast with the fact that coupling reactions of higher order 3-methyl-2-butenylcuprate with enol triflate take place with complete α-attack.[1a]

High chemoselectivity also deserves special comment. Ester and ketone carbonyls and even an amino group were tolerated. The C-I bond reacted in preference to the C-Br bond of 2-bromo-1-iodobenzene as seen in the example of entry 3.

The synthetic utility of this process was well demonstrated by the synthesis of ibuprofen (Scheme II).[13] Oxidative cleavage of the C=C bond of isomerically pure γ-coupled product has provided a facile route to this potent antiinflammatory agent with good overall yield.

In conclusion, γ-selective allylation of organic halides, triflates, and acetate has been realized using allyltrifluorosilanes together with a Pd catalyst and fluoride ion. The reaction reported here should give a unique solution to the long-standing problem of regiochemical control in allylic coupling. The high γ-selectivity of allyltrifluorosilanes as compared with other allylic organometallic compounds may be explained in terms of the enhanced nucleophilicity of the γ-carbon of the intermediate pentacoordinate allylic silicates[14] formed from nucleophilic attack of fluoride ion on allyltrifluorosilanes.

Supplementary Material Available: Spectral and analytical data of new compounds and literature references or registry numbers of known compounds (3 pages). Ordering information is given on any current masthead page.

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(8) The reaction of (*E*)-crotyltrifluorosilane with 4-bromoacetophenone mediated by $Pd(PPh_3)_4$/TBAF under the same conditions gave a small amount of α-coupled product with a 1:6.2 ratio of α:γ products.

(9) The kinds of silyl groups in the allylsilanes strongly influenced both the regioselectivity and the yields of the coupled products. Thus, the reaction of (*E*)-crotyltriethoxysilane or (*E*)-crotyltrimethylsilane with 4-iodoacetophenone gave a mixture of α- and γ-coupled products. Although 3-(trimethylsilyl)-1-propene effectively coupled with cinnamyl bromide under the influence of Pd catalyst and fluoride ion, this reaction could not be applied to vinylic and aromatic substrates: Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

(10) The reaction of crotyltrifluorosilane with (*E*)-1-iodo-1-octene under the influence of $Pd(PPh_3)_4$/TBAF afforded ca. 20–30% yields of γ-coupled product with the recovery of a considerable amount of the starting material.

(11) Phosphine ligands affect the regioselectivity of the reactions. $Pd(PPh_3)_4$/TBAF resulted in low regioselectivity for the enol triflates (α:γ = 1:1-3), and a fair amount of reduced substrate was formed. Use of 1,1′-bis(diphenylphosphino)ferrocene or 1,3-bis(diphenylphosphino)propane in place of dppb led to nonregioselective coupling. These observations suggest that a (σ-allyl)palladium species (Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 8253) is a catalytic key intermediate. If the (σ-allyl)palladium species underwent reductive elimination before rearranging to a (π-allyl)palladium species, high γ-selectivity would be achieved. It is well-known that the rate of reductive elimination of an organopalladium species is strongly influenced by the coordinating phosphine ligand: Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

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Reaction of Second-Row Transition-Metal Atoms with Methane

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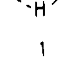
In this communication the first systematic ab initio study is presented, in which all the steps in a chemical reaction have been investigated for a whole row of transition-metal atoms. The reactivities of naked metal atoms are not only of interest as such but are also relevant for a detailed understanding of reaction mechanisms of ligated complexes. Recently, experimental results for the reactions of neutral metal atoms have become available,[1] whereas earlier studies were only concerned with the reactivities of metal cations.[2]

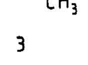
Probably the most important aspect, which has been highlighted by the above-mentioned experimental studies and also several theoretical studies,[3] is the large importance of the atomic spectrum for the reactivity. Exactly how these spectra influence the reactivities is best understood by studying sequences of transition-metal atoms. The most important results from a study of this type, the oxidative addition of methane to the whole sequence of second-row transition-metal atoms, are discussed here. This reaction is of great present interest, mainly as the first step in the catalytic conversion of the abundant and nonreactive alkanes into more useful products. One of the first metals experimentally observed to insert into unactivated C-H bonds was rhodium,[4] and therefore the second row was chosen for this study.

Four regions on the potential energy surface for the reaction of each atom have been studied. The first region is for the reactants. The second region is for the molecular precursor $M-CH_4$ complex **1**. The third region is the transition state **2** for the reaction, and the fourth region is the $MHCH_3$ product region



1

2



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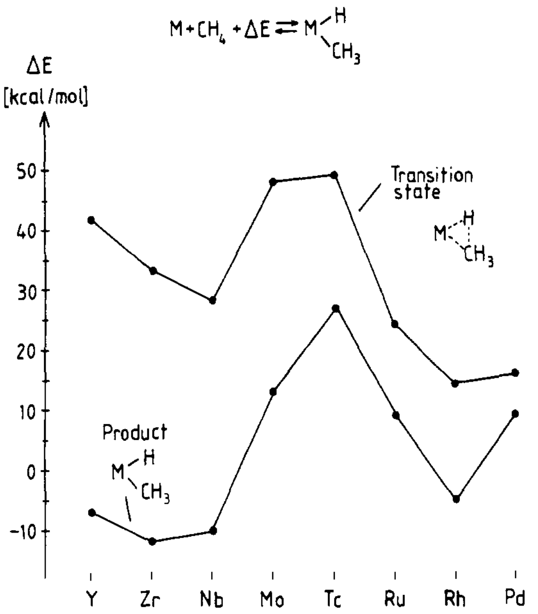

Figure 1. Relative energies for the transition-state structures (upper curve) and the product complexes (lower curve), calculated relative to the ground state of the metal atom and free methane. The upper curve corresponds to the addition barrier and a large positive value for ΔE corresponds to a high activation barrier. The lower curve corresponds to the binding energy of the product complex and a large positive value for ΔE corresponds to a strongly endothermic addition reaction, while a negative value for ΔE corresponds to an exothermic addition reaction.

3. For each metal at least two different spin cases have been considered, the atomic ground-state spin and the product ground-state spin (referred to as the low-spin state). The basis sets and methods used are the same as in ref 5. The basis sets are of double-ζ to triple-ζ quality, including f functions on the metal and d functions on carbon. The correlation energy for all the valence electrons was calculated with use of size consistent methods.

The first conclusion about the second-row metals to be drawn from the results in Figure 1 is that the most efficient catalyst for C–H activation should be rhodium, since it has the lowest barrier for the addition reaction and a relatively strongly bound product complex. This conclusion is in agreement with available experimental information for metal complexes.[4] The main reason for the low barrier for rhodium is that both the s^0 ($4d^9$) and s^1 ($4d^85s^1$) states are low in energy. A low-lying s^0 state is also important for the occurrence of the precursor complex **1**. Palladium is the only metal having a bound precursor complex on the atomic ground-state potential surface. Rhodium and ruthenium have bound precursor complexes on the low spin surfaces.

The barrier for the reaction between methane and the transition-metal atoms is a result of a crossing between two surfaces. Before the barrier the C–H bond starts to break and methane prepares for the bonding toward the metal. In this region the interaction between methane and the metal atom is essentially repulsive and the metal adopts the state that is least repulsive. For the atoms to the right with more or equal to five (s + d) electrons the least repulsive state is s^0 whereas for the atoms to the left it is the s^1 state, since for these atoms the lowest s^0 state has the wrong spin. After the barrier the two bonds are formed and for most of the atoms the s^1 state dominates in this region. For the atoms to the left there are significant contributions to the bonding from s^1p^1 states and to the right s^0 states contribute. The barrier height for the addition reaction is thus reduced both by strong bond formation to the s^1 state in the product region and by a low repulsion to the s^0 state in the entrance region. Both these factors influence the position of the crossing point between the two surfaces.

Two effects dominate the variation of the binding energies, the promotion energy to the bonding s^1 state and the loss of exchange energy upon bond formation.[6] If the promotion energy and the loss of exchange energy are subtracted from the ΔE values given in Figure 1, similar values are obtained for all the metals. The lowest elimination barrier is found for palladium, which is a consequence of the unstable product complex in combination with a rather low energy of the transition state.

More details will be published in a separate paper where also the reactions of the second-row transition-metal cations will be discussed.

Registry No. Y, 7440-65-5; Zr, 7440-67-7; Nb, 7440-03-1; Mo, 7439-98-7; Tc, 7440-26-8; Ru, 7440-18-8; Rh, 7440-16-6; Pd, 7440-05-3; CH_4, 74-82-8.

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Reaction of O(^{3}P) with Cyclohexane Clusters. Hint for the Mechanism in the Liquid Phase

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Investigations of gas-phase processes are commonly used to gain microscopic insight on the corresponding liquid-phase reactions.[1] However, there are reactions for which it is known that the products of the gas-phase reaction differ from those in the condensed medium. One such case is the reaction of O(^{3}P) with saturated hydrocarbons. In the gas phase, a rotationally cold OH[2,3] and a free radical are obtained (RH + O(^{3}P) $\rightarrow$ R + OH), indicating a collinear abstraction mechanism.[4] In the condensed phase, alcohols are formed (RH + O(^{3}P) $\rightarrow$ ROH), suggesting biradical recombination in a solvent cage.[5] However, this is not generally compatible with the high retention of configuration observed in chiral carbons.

In the present crossed molecular beam study of the reaction of cyclohexane with O(^{3}P), clusters as small as dimers yield the same product as the liquid, namely cyclohexanol. This suggests that the alcohol is formed through insertion rather than biradical recombination.

An O(^{3}P) atomic beam is produced by microwave discharge in a continuous flow of O_2. It collides with a beam of cyclohexane seeded in various inert gases, which is expanded through a 0.5 mm diameter pulsed nozzle. The molecules cool by the adiabatic expansion and form dimers and larger clusters, depending on the expansion conditions. At the beginning and at the end of the pulse, the molecules expand through an effectively smaller nozzle, and therefore fewer clusters are formed.

The production of OH radicals from monomers and clusters is monitored by laser-induced fluorescence (LIF). The density of the OH (K = 1) is shown in Figure 1 as a function of the time delay between the nozzle and laser pulses, for (A) 100 Torr of cyclohexane seeded in 2.4 atm He and (B) 100 Torr of neat cyclohexane, where cooling is low and clusters are not formed. The dip in the center of Figure 1A indicates that clusters reduce the formation of OH.

The other components of the seeded molecular beam were monitored by a quadrupole mass spectrometer collinear with the

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