Acknowledgment. This research was supported through a grant from the National Institutes of Health (AM-13339) and through funds for the purchase of a gas chromatograph from the National Science Foundation (CHE82-17950).

Reductive Coupling of H–H, H–C, and C–C Bonds from Pd Complexes

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Received June 18, 1984

Reductive coupling to form H–H, C–H, and C–C bonds from transition-metal complexes is of fundamental importance in many catalytic processes. However, despite numerous experimental[1] and theoretical[2] studies, there remain a number of puzzles concerning these processes. For example, reductive elimination of methane from $Pt(H)(CH_3)(PPh_3)_2$ is quite facile at −25 °C,[1d] while $Pt(CH_3)_2(PPh_3)_2$ is quite stable (it decomposes at 237 °C!).[1t] This puzzle is exacerbated by the theoretical results of Siegbahn and co-workers[2e,f] whose calculations lead to essentially the same barriers for C–H and C–C reductive elimination.

In this work we show that the activation barrier for reductive elimination is sensitive to the nature of the bond being formed. Hydrogen has a spherically symmetric 1s valence orbital allowing it to simultaneously form H–H bonds while breaking M–H bonds, leading to small (1.55 kcal) intrinsic barriers. The directionality of the methyl sp^3 hybrid orbital makes it more difficult to convert from M–C to form C–C or C–H bonds during reductive elimination. Thus the CH_3 group needs to have a different orientation for the M–C and C–C bonds, and in the transition state a compromise must be reached that is not optimal for either bond. The result is an intrinsic barrier of 10.4 kcal for C–H coupling and 22.0 kcal for C–C coupling.

Studies on a prototypical oxidative addition/reductive elimination process[3]

$$Pt(PH_3)_2 + H_2 \leftrightarrow Pt(H)_2(PH_3)_2 \quad (1)$$

showed that oxidative involves promotion of the d^{10} configuration

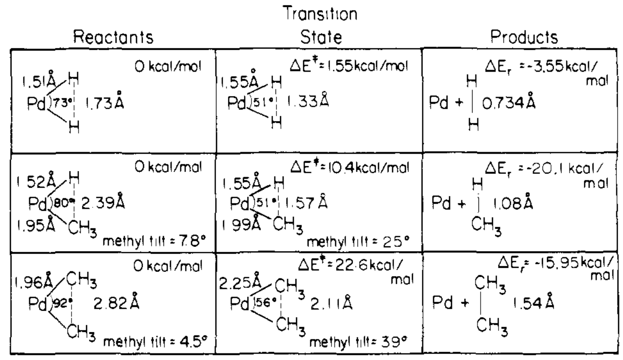

Figure 1. Geometries and energetics for the reactions $PdH_2 \rightarrow Pd + H_2$, $PdH(CH_3) \rightarrow Pd + CH_4$, and $Pd(CH_3)_2 \rightarrow Pd + C_2H_6$. The angle between the Pd–C bond and the vector from the C atom to the center of mass of the methyl hydrogen atoms is defined to be the methyl tilt.

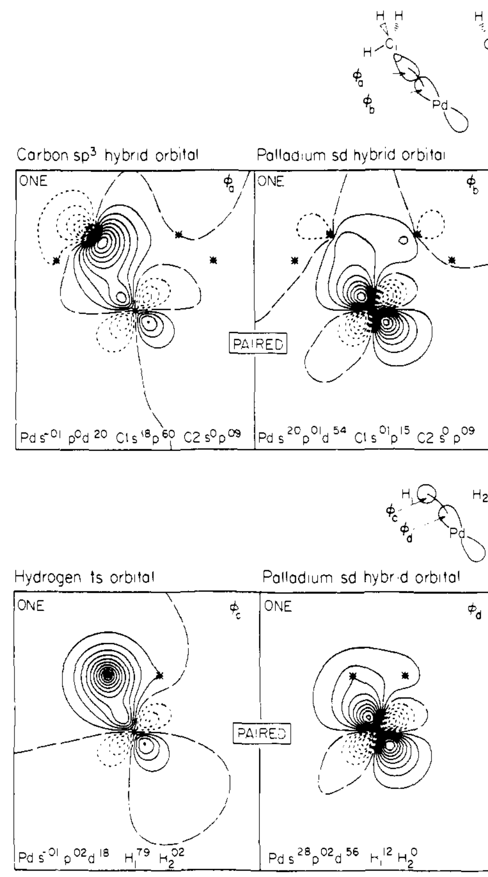

Figure 2. GVB orbitals for the Pd–C bonds at the transition state for the reaction $Pd(CH_3)_2 \rightarrow Pd + C_2H_6$ and the GVB orbitals for the Pd–H bonds for the reaction $PdH_2 \rightarrow Pd + H_2$. The Mulliken populations are listed with each orbital to show the hybridization of each orbital.

for $Pt(PH_3)_2$ to an s^1d^9 configuration involving two *covalent* bonds to the hydrogens. In order to clarify the nature of H–H, H–C, and C–C processes without the complication of steric interactions with phosphorus or other metal ligands, we have examined

$$Pd(H)_2 \leftrightarrow Pd + H_2 \quad (2)$$

$$Pd(H)(CH_3) \leftrightarrow Pd + CH_4 \quad (3)$$

$$Pd(CH_3)_2 \leftrightarrow Pd + C_2H_6 \quad (4)$$

Since the Pd atom has a low-spin d^{10} ground-state configuration and an s^1d^9 configuration when it forms two convalent bonds, it can serve as a model for reductive elimination from Pt(II), Pd(II), Ni(II), and Au(III) complexes.

The calculated energetics for reductive elimination from PdH_2, $PdH(CH_3)$, and $Pd(CH_3)_2$ are shown in Figure 1. The overall bonding energies correspond to an average Pd–H bond energy (D_e)

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of 53 kcal and a Pd–CH_3 bond energy of 40 kcal. The critical geometries are shown in Figure 1, where we see that each methyl group leads to a substantial increase (8 to 12 kcal) in the barrier for reductive coupling. As indicated above, the origin of this increase is the directionality of the orbital for the alkyl groups that prevents the carbon atom from simultaneously forming strong C–H and C–C bonds while retaining a strong Pd–C bond in the transition state. This idea is supported by the orbital plots shown in Figure 2. Further support for this idea is that the Pd–H bond stretches only by 2% (1.51 to 1.55 Å) in going to the transition state for reductive elimination of H_2 from PdH_2, while the Pd–CH_3 bond stretches by 10% (1.96 to 2.20 Å) for reductive elimination of C_2H_6 from $Pd(CH_3)_2$. The calculated barriers for reductive elimination suggest an activation energy of ~10 kcal/mol for each Pd–C bond and ~1 kcal/mol for each Pd–H bond. Therefore the barrier for a concerted reductive coupling of C–C bonds should be twice as high as the barrier for coupling C–H bonds.

For Pd + H_2, we also find a 4.4-kcal well for an H_2 adduct in which the H–H bond is not activated (R_{HH} = 0.81 Å, ∠HPdH = 26°, R_{PdH} = 1.83 Å). This represents an η^2-H_2 Lewis base–Lewis acid complex to the Pd. This minimum at long Pd–H distances has previously been observed theoretically[2f,4] and may be compared with the $M(CO)_3(PR_3)_2H_2$ (M = Mo, W; R = Cy, *i*-Pr) complex studied experimentally by Kubas et al.[5a] and theoretically by Hay.[5b]

Previous theoretical studies[2f,4] of $Pd(H)_2$ did not find the local minimum corresponding to a Pd dihydride complex. These calculations did *not* include relativistic effects and consequently the d^9s^1 (^{3}D) state [important in the $Pd(H)_2$ complex] is 15 kcal/mol too high relative to the d^{10} state.[6] Since our calculated barrier is only 1.5 kcal/mol, it is not surprising that in the nonrelativistic calculations this minimum does not exist.

These results provide an explanation for the trends observed in reductive elimination from Pt(II) complexes. Halpern et al.[1d,e] and Michelin et al.[1f] have observed intramolecular reductive coupling from various hydridoalkylbisphosphineplatinum(II) complexes. However, reductive coupling from Pt(II) dialkyls prefer β-hydride elimination.[7,8] As has been reported elsewhere,[3] calculations on $Pt(H)_2(PH_3)_2$ and $Pt(CH_3)_2(PH_3)_2$ lead to average bond energies of 60 kcal for Pt–H and 36 kcal for Pt–CH_3, so that reductive coupling of H–C and C–C bonds is exothermic for both cases. Thus, the high intrinsic barrier (~22 kcal) for CC coupling vs. C–H coupling (~10 kcal) explains the observations.[7] On the other hand, for H–H coupling the Pd case is downhill 4 kcal, while the $Pt(PH_3)_2$ case is uphill 16 kcal. This is consistent with the fact that reductive elimination to form H–H bonds from $Pt(H)_2L_2$ (L = PMe_3 or PEt_3) has been observed[1q,r] to be very slow under vacuum and that PdL_2 complexes are unreactive with respect to H_2.[1r]

Calculational Details. At each point from reactants to products, we held the R–Pd–R angle fixed and optimized all other internal coordinates[9] (using a Hartree–Fock analytic gradient technique). This generated a potential curve as a function of the R–Pd–R angle. The energetics presented here were obtained from MCSCF calculations [RCI(4/8)*GVBCI(2/6)] on all points along this reaction path. This level of wavefunction was found adequate to describe the correlations between d electrons and the breaking of Pt–H bonds for reaction 1.[3]

The double ζ basis set and relativistic effective potential (including s, p, d, and f projections) used for Pd are those of Hay.[10] The carbon basis set was the Dunning[11] (9s5p/3s2p) valence double ζ contraction. Huzinaga's[11,12] four-Gaussian hydrogen basis scaled by a factor of 1.2 and contracted double ζ was used for the hydrogen atoms bound to the carbon atom throughout the reaction. Huzinaga's[12] six-Gaussian basis unscaled contracted triple ζ was used for hydrogens initially bound to the Pd atom.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (No. CHE80-17774). (J.J.L.) acknowledges support in the form of a fellowship from Exxon.

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Spin Polarization Conservation during the Excitation Energy Transfer in Fluid Solution

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Received August 14, 1984

The possibility of spin polarization conservation in the triplet–triplet energy-transfer process has been demonstrated in single-crystal[1] and glassy matrix.[2] However, there is no experimental study on the spin alignment conservation during energy-transfer process in fluid solution systems, in which the spin–lattice relaxation of excited triplet molecule is usually very fast. Since the generation of a radical from the excited triplet precursor gives all emission or enhanced absorption CIDEP (chemically induced dynamic electron spin polarization) spectrum,[3] similar pattern of the time-resolved ESR should be observed in the system produced by the triplet photosensitization, if the spin polarization is conserved during the excitation energy transfer. In this communication, we present the spin polarization conservation in triplet energy transfer between a pyridinyl radical dimer and aryl ketones with CIDEP observations.

The dimer of the 1,4-dimethylpyridinyl radical was prepared and purified by the method reported previously.[4] The dimer has a photosensitive absorption band at the near-UV region (λ_{max} = 353 nm, ϵ ~5000 in toluene). Time-resolved ESR spectra were obtained with a dc detection (no field modulation) method, using a Varian E-109E EPR spectrometer. ESR signal from the preamplifier was amplified to +40 dB by a handmade wide-band amplifier. The signal was taken into a two-channel boxcar integrator (NF BX-531) at arbitrary times after the laser pulse. Nitrogen laser (5 mJ per pulse, 10-Hz repetition rate) was used as a source of the light pulse. Typical measurements were carried out using degassed toluene solutions containing 50 mM of the pyridinyl radical dimer.

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