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LIMITS ON THE TRANSITION STATE GEOMETRY FOR METAL INSERTION INTO A CARBON-HYDROGEN BOND

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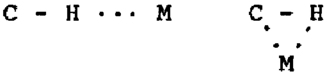
SUMMARY: Using chelating ligands to fix the position of the metal and C-H bond, evidence is found which favors a triangular geometry for metal insertion.

The interaction of a transition metal complex with a C-H bond in solution has been the subject of increasing interest.[1] Understanding this interaction may lead to new procedures for hydrocarbon functionalization and also provide model systems for the carbon-hydrogen and carbon-carbon bond breaking steps which occur over heterogenous catalysts. Two limiting geometries, a linear and a triangular, have been proposed as the transition state for metal insertion into a carbon-hydrogen bond.[2]



Linear Triangular

The linear transition state is similar to that proposed for the insertion of a singlet carbene into a carbon-hydrogen bond. Both extended Hückel[3] and MINDO/2 calculations[4] predict carbene insertion begins with CH_2 attacking along a carbon-hydrogen bond axis, leading to hydrogen atom abstraction followed by recombination of the radical pair. Shilov has proposed, similarly, that alkane activation by square planar Pt(II) complexes occurs via a linear interaction in which the alkane approaches along the Pt p_z orbital, followed by hydrogen atom abstraction to give a Pt(III)hydride-alkyl radical pair which collapses to form the intermediate alkyl Pt(IV) hydride.[5] The other limiting geometry, the triangular transition state, is that expected for a three center two-electron interaction. This has been mentioned by Parshall as a possible transition state in the cyclometalation of coordinated ligands.[1a]

A continuum of possibilities has been recognized to exist between these two extreme geometries. Neutron and X-ray diffraction studies have uncovered several examples of metal-hydrogen interactions and the observed geometries, which cover a wide range of metal-hydrogen-carbon angles, are summarized in Table 1.

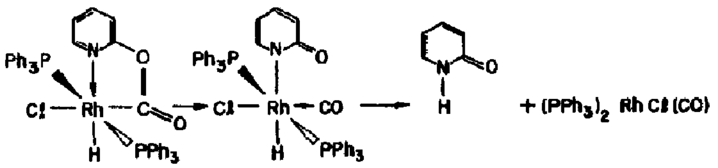
TABLE 1. Geometries of M ··· H-C Interactions in the Solid State

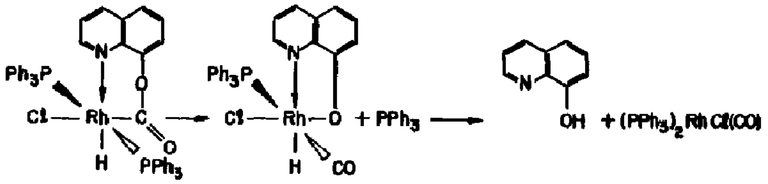
M =	> CH ··· M	M ··· H(Å)	M ··· C(Å)
Mo[2]	132°	2.15	3.05
Fe[6]	101°	1.88	2.35
Rh[7]	81°	2.56	2.62
Rh[8]	118°	2.79	3.43
Cu[9]	144°	2.01	2.78

For the molybdenum complex, dynamic NMR measurements have indicated the strength of the interaction to be a robust 17-20 kcal mole^{-1}.[10] While these structural studies show the hydrogen of a carbon-hydrogen bond can occupy a coordination site on a metal, it is not established that these observed interactions are on the path leading to bond breaking. None of the complexes in Table 1, upon heating, form new carbon-metal bonds.

We sought to investigate intramolecular metal insertion, as has been done to study the transition state geometry for carbene insertion into a C-H bond.[11] In this approach a ligand is used which undergoes intramolecular metalation. The metal's position is fixed by its attachment to the ligand atom and its approach to the particular C-H bond to be broken depends upon the ligand's geometry and flexibility. Two coordinating ligands which allow different M ··· H-geometries are 2-pyridyl formate **1** and 8-quinolinyl formate **2**.[12] In both compounds $RhCl(PPh_3)_3$ is expected to undergo rapid insertion into the formate C-H bond.[13] Inspection of molecular models (Dreiding) shows that upon coordination of rhodium to the pyridyl nitrogen in **1**, a range of M ··· H-C angles, from 60° - 140° are possible at a metal-hydrogen distance of 2.4Å. The formate **2** is much less flexible and at a distance of 2.4Å, only M ··· H-C angles of 50-90° are attainable. Thus, while both **1** and **2** can accommodate a triangular M ··· H-C interaction, only **1** can attain a nearly linear M ··· H-C geometry. If a strong preference exists for linear or nearly linear attack of Rh(I) on the formate C-H bond, **1** should metalate faster than **2**.

Product studies showed $RhCl(PPh_3)_3$ reacted cleanly with the formate C-H bonds of **1** and **2** slightly above room temperature, although the intermediate acyloxy rhodium hydrides could not be isolated. For 2-pyridyl formate, the intermediate acyloxy rhodium(III) hydride can undergo a 2-hydroxypyridine, 2-pyridone rearrangement and the resulting rhodium-amide hydride can undergo a reductive elimination (probably intermolecular) to give the observed 2-pyridone and $RhClCO(PPh_3)_2$. For 8-quinolinyl formate, the first formed acyloxy rhodium(III) carbonyl hydride can decarbonylate, since the resulting chelate is a relatively strain-free five membered ring. Reductive elimination gives the observed 8-hydroxyquinoline and $RhClCO(PPh_3)_2$.





To determine the effect of possible transition state geometries on the relative rates of insertion of $RhCl(PPh_3)_3$ into the formate C-H bonds of **1** and **2**, it was first necessary to show that coordination precedes insertion. This was shown by the lack of reaction of $RhCl(PPh_3)_3$ with p-tolyl formate in benzene at 50° for eight hours. Both **1** and **2** are decarbonylated rapidly under these conditions. That C-H bond cleavage is the rate-determining step is shown by a deuterium isotope effect of 3.4 for the deuteroquinolinyl formate vs. **2** in its reaction with $RhCl(PPh_3)_3$. The relative rate of insertion of $RhCl(PPh_3)_3$ into the formate C-H bonds of **1** and **2** was found in a competition experiment by rapidly adding ten mole percent of $RhCl(PPh_3)_3$ to a solution of equimolar amounts of **1** and **2** in benzene at 40°. After one hour a quantitative yield of $RhClCO(PPh_3)_2$ was collected and NMR integration of the formate protons showed **1** and **2** to be present in the ratio of 1.06 to 1. This gives a relative rate of reaction of 1.02 to 1 for **2** over **1**.

The virtual equivalence of the rate of metalation of the two formates shows that for insertion of Rh(I) into a formate C-H bond a linear or nearly linear geometry (of the kind calculated for insertion of CH_2 into a C-H bond) is not required. Instead, the reaction most likely proceeds via an initial interaction of the antibonding C-H orbital with the highest occupied molecular orbital on the metal, either a d_{xz} or d_{z^2} orbital, as has been proposed by Vrieze and coworkers.[14] Either interaction is consistent with the triangular transition state suggested by this work. The transition state geometry for metalation with an electrophilic metal center, such as Pd(II) or Pt(II), may be different. However, recent work by Deeming and Rothwell,[15] which shows that metalation of 8-methylquinoline occurs when the methyl group is in the coordination plane of the Pd(II) implies, upon inspection of molecular models, that a linear or nearly linear approach of the electrophilic Pd(II) along the C-H bond axis is likewise not required for facile metal insertion.

References and Notes

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12. Both formates were prepared from the corresponding heterocyclic alcohols, sodium hydride and acetic formic anhydride in THF. 2-Pyridyl formate: ir($CHCl_3$, cm^{-1}) 1730, 1670, 865, 850, 770; nmr (C_6D_6) 8.10 δ (s, 1H), 7.4-7.8 (m, 2H), 6.2-6.7 (m, 2H); mp (hexane) 62-63°. 8-Quinolinyl formate: ir($CHCl_3$, cm^{-1}) 1730, 1605, 750; nmr (C_6D_6) 8.33 (s, 1H) 8.60 (d of d, J=2, 5 HZ, 1H) 6.6-7.6 (m, 5H); mp (hexane) 102-103°.
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