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Ab Initio Calculations of the Quantum Mechanical Hydrogen Exchange Coupling in the $[(C_5H_5)Ir(PH_3)H_3]^+$ Complex

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The proton NMR spectra of several transition-metal trihydride complexes L_nMH_3 have recently attracted considerable interest.[1-3] The three hydride protons exhibit the expected AB_2 pattern, but the apparent J_{AB} values show large temperature dependence and striking isotope effects. The large J_{AB} values ranging from 61 to 1565 Hz in a series of $[(C_5H_5)IrLH_3]^+$ complexes (L = various phosphine and phosphite ligands) are well outside the normal range of H–H coupling constants.[1b] The physical phenomenon has been identified as due to quantum mechanical exchange of a pair of hydrides[4] giving rise to an exchange coupling constant $-2J$ which is added to the magnetic coupling constant J_m leading to the total observed coupling $J_T = J_m - 2J$. The exchange coupling $-2J$ is the difference in energy between the higher energy antisymmetric and the lower energy symmetric eigenfunctions of a coupled double well. Heinekey *et al.*[4b,c] have estimated the value of that coupling constant in the above mentioned series of iridium complexes by using a set of parameters suitable for a pair of protons in Landesman's model.[5] This model is a crude approximation based on a hard spheres potential. Barthelat *et al.*[6] have used the same formula taking the parameters from *ab initio* calculations of $[Cp_2MH_3]^+$ complexes with M = niobium and tantalum to show that the Nb complex presents high couplings whereas they are absent in the isostructural tantalum complex.

In this communication we present, for the first time, a theoretical study of these couplings which combines the construction of an *ab initio* potential energy surface with a realistic tunneling model using the basis set method.[7] We have focused our interest on the $[(C_5H_5)Ir(PH_3)H_3]^+$ complex. As mentioned above, Heinekey *et al.*[1b,4c] have performed an extensive study for systems of the same kind, all of them showing unexpectedly large exchange couplings. Besides, the geometry of the $[(C_5H_5)Ir(PMe_3)H_3]^+$ complex is known from neutron diffraction methods showing a trihydride structure.[1b]

Ab initio calculations have been performed[8] with the GAUSSIAN 90 series of programs.[10] The minimum energy structure of the complex was found by full geometry optimization[11] at the RHF level. Correlation was introduced in the energy calculations by means of the Møller–Plesset perturbative theory up to second order (MP2)[12] which recently has been shown to correctly reproduce the relative stability of classical structures having terminal hydride ligands and nonclassical polyhydride complexes containing η^2-H_2 ligands.[13]

Table I. Relevant Geometrical Parameters[a] for the $[(C_5H_5)Ir(L)H_3]^+$ Complexes

	calcd[b]	exptl[c]		calcd[b]	exptl[c]
Ir–H_1	1.581	1.591	$\angle H_1IrH_2$	59.6	64.7
Ir–H_2	1.585	1.583	$\angle H_1IrH_3$	59.6	63.6
Ir–H_3	1.585	1.588	$\angle H_2IrH_3$	110.4	114.4
Ir–P	2.422	2.273	$\angle H_1IrP$	103.4	98.3
Ir–C[d]	2.373	2.238	$\angle H_2IrP$	81.9	74.7
C–C[d]	1.431	1.412	$\angle H_3IrP$	81.9	75.8

[a] Distances in angstroms and angles in degrees. [b] *Ab initio* optimized values for the $[(C_5H_5)Ir(PH_3)H_3]^+$ complex. [c] Neutron diffraction experimental values for the $[(C_5H_5)Ir(PMe_3)H_3]^+$ complex.[1b] [d] Mean values for the C_5H_5 fragment.

The more relevant geometrical parameters of the minimum structure are given in Table I. It is clearly seen that it presents a four-legged piano stool geometry and corresponds to a trihydride structure. The obtained parameters are in good agreement with the neutron diffraction experimental results also shown in Table I.

Given that it has been proposed that the anomalous J_{AB} values come from the exchange of a pair of hydrides, we have built a tridimensional potential energy surface by taking as grid parameters the distance between the two hydrogens that are interchanged, H_1 and H_2 (R_{HH}), the distance between the Ir and the midpoint (X) of the H_1–H_2 segment (R_{MX}), and the rotational angle θ of the H_1–H_2 bond in the plane orthogonal to the MX direction (see Figure 1). The remaining geometrical parameters were fixed at the fully optimized values. Using such a geometrical definition the minimum energy structure corresponds to R_{HH} = 1.57 Å, R_{MX} = 1.37 Å, and $\theta = 0°$. About 400 SCF energy calculations were performed in order to build up this tridimensional surface. The energies of more than 50 points belonging to the most significant regions of the potential energy surface were recalculated in order to introduce correlation energy so that all the energies reported here correspond to the MP2 level.

From the analysis of the surface, two different reaction paths are seen as feasible to exchange the two hydrogens. These two mechanisms have very recently been proposed by Limbach *et al.*[14] and are schematically depicted in Figure 2. Mechanism I simply consists of dihydride rotation in such a way that only the above mentioned rotation angle θ varies, the R_{MX} and R_{HH} distances being fixed at the values corresponding to the minimum energy structure. When $\theta = 90°$, an energy maximum appears which is 20.7 kcal/mol above the minimum.

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[8] The basis set used was of valence triple-ζ quality for the iridium atom,[9a] valence double-ζ for phosphorus,[9b] carbons,[9c] and hydrogens[9c] of the C_5H_5 and PH_3 groups, and double-ζ plus polarization functions for the three hydrides.[9c,d] An effective core potential operator has been used for the core electrons of iridium[9a] and phosphorus atoms.[9b]

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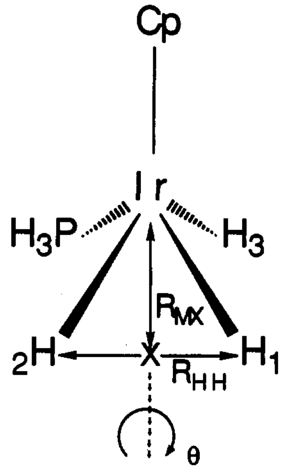

Figure 1. Geometrical parameters used to build up the reduced potential energy surface for the two-hydrogen exchange reaction.

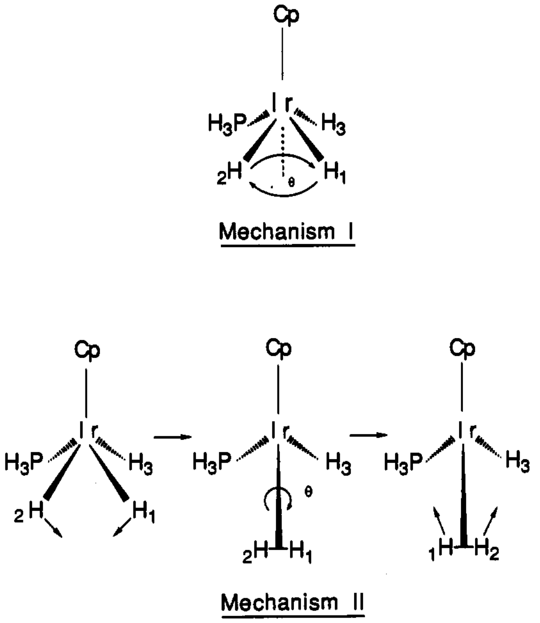

Figure 2. Mechanisms analyzed for the two-hydrogen exchange.

On the other hand, mechanism II goes through a η^2-H_2 structure, an H_2 entity (R_{HH} = 0.88 Å) being in this case the rotating group. This structure is reached by means of two concerted motions, the shortening of the H–H distance and the lengthening of the Ir–X distance. Such a structure, corresponding to R_{HH} = 0.88 Å, R_{MX} = 1.67 Å, and $\theta = 0°$, is 8.7 kcal/mol above the minimum. This value is similar to the one recently reported by Hall *et al.*[15] for the same system. The η^2-H_2 geometrical configuration is not a true minimum in our MP2 potential energy surface but only a thermally accessible configuration. As a matter of fact, only this condition is required in order to facilitate the proton exchange process. The energy maximum along the H_2 rotation appears at R_{HH} = 0.88 Å, R_{MX} = 1.72 Å, and $\theta = 90°$, implying an energy barrier of 14.4 kcal/mol relative to the trihydride minimum. After rotation, with both hydrogens already exchanged, the lengthening and shortening of the H–H and Ir–X distances, respectively, lead again to the trihydride complex.

Once mechanisms I and II have been analyzed on the reduced potential surface, the quantum process will be treated in terms of a one-dimensional tunneling model.[7c] Symmetric profiles have been built by using cubic spline functions fitted in such a way that the energy barrier and the path length coincide with the estimated values obtained by analysis of the tridimensional surface. For this purpose we have taken a basis set of 95 localized Gaussian functions equally spaced along the coordinate space. A variational calculation provides the lowest eigenvalues of the one-dimensional vibrational system which are seen to occur in a nearly degenerate pair of a symmetric state and a higher energy antisymmetric state. An explicit calculation of the exchange coupling $-2J$ proceeds by evaluation of the difference in energy between those two states: $-2J = E_A - E_S$. By doing this we have obtained for the potential reproducing mechanism I an exchange coupling of 1.1 Hz whereas mechanism II has a value of 59.1 Hz. So it is clear that only through mechanism II can the anomalous high values of $-2J$ be explained. The different values of the coupling of the two mechanisms can be understood by considering the quite lower energy barrier of mechanism II that cannot be fully compensated by the shorter path length of mechanism I. It has to be noted that the experimental value of the $[(C_5H_5)Ir(PMe_3)H_3]^+$ complex, which is quite similar to the one studied here, is 96 Hz at 176 K. Given the extreme sensitivity[1c] of the J values to the parameters of the potential surface, the obtained value of 59.1 Hz can only be taken as an approximation.

The calculations reported here provide theoretical evidence that the exchange coupling $-2J$ in transition-metal trihydride complexes has an order of magnitude such that it can be added to the magnetic coupling leading to a total value that can be measured experimentally in the NMR spectra. It also has been clearly seen that the presence of a low-energy η^2-H_2 geometrical configuration makes possible the hydrogen exchange through mechanism II recently proposed by Limbach *et al.*[14] Finally it is notable that whereas experimentally the variation of the coupling with temperature is very important, the value of the coupling obtained here does correspond to the ground state vibrational splitting. Theoretical work devoted to studying the temperature dependence of the splitting is now in progress in our laboratory.

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