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MECHANISMS OF DIHYDROGEN ACTIVATION BY ZIRCONOCENE ALKYL AND HYDRIDE DERIVATIVES

A MOLECULAR ORBITAL ANALYSIS OF A 'DIRECT HYDROGEN TRANSFER' REACTION MODE

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Summary

The formation of an adduct between a dihydrogen and a d^0 species of the general type $(C_5R_5)_2Zr(R')_2$ (R,R' = H or CH_3) is suggested to involve a process analogous to that in CO adduct formation, and is studied by an extended Hückel molecular orbital analysis. Back donation into σ^* H_2 orbitals arises from high-lying M—R' bonding orbitals and determines the stability of alternative adduct geometries. Two isomeric H_2 adducts can interconvert by an intramolecular hydrogen shift. With D_2, this reaction sequence leads to hydrogen isotope exchange. The transition state of this reaction mode contains a three-centre $(H\cdots H\cdots H)^-$ ligand configuration with bonding properties similar to those of an allyl ligand; it does not involve an oxidative change in the charge on the metal nor generation of a positively charged, protonic hydrogen species by heterolytic H_2 cleavage. The term 'direct hydrogen transfer' is proposed for this type of elementary reaction. For H_2-induced alkane elimination from group IV metallocene alkyl derivatives, an analogous reaction mechanism, involving formation of a H_2 adduct and a subsequent intramolecular hydrogen shift toward the alkyl ligand, is predicted to proceed with moderate activation energies.

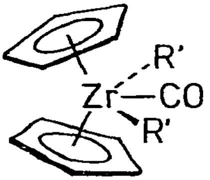
Introduction

Transfer of hydrogen from molecular dihydrogen to a metal-bonded substrate is a common feature of homogeneous catalysts. Two distinct elementary mechanisms are frequently considered to exist in the conversion of dihydrogen into a reactive metal hydride species, from which the required hydrogen transfer to a metal-bonded substrate, e.g. to an olefin or to an alkyl group, might then proceed, viz., (a) oxidative addition of the dihydrogen molecule to a low-valent metal centre, resulting in a metal dihydride intermediate, and (b) heterolytic cleavage of H_2 by an electrophilic metal centre, which after transfer of a proton onto a basic solvent or ligand molecule leaves a metal-bonded monohydride species.

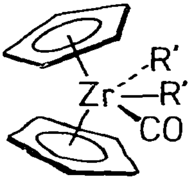
Recently, Gell and Schwartz [1] and McAlister, Erwin and Bercaw [2] described in detail some reactions of zirconocene alkyl hydride derivatives with dihydrogen, which are difficult to reconcile with either of these mechanisms.

The reactant species, of general type $(C_5R_5)_2ZrHR'$, contains a zirconium centre of formal oxidation state +IV. With such a zirconium(IV) centre, an oxidative addition of H_2 does not appear feasible. To explain their observations, McAlister, Erwin and Bercaw [2] proposed a fast pre-equilibrium involving an intramolecular rearrangement to the formal zirconium(II) species $(C_5R_5)(C_5R_5H)ZrR'$, which might then take up H_2 in an oxidative addition reaction. In view of the overriding tendency of zirconium(II) to be transformed into a zirconium(IV) species, if necessary even by oxidative addition of a hydrocarbon C—H bond, a spontaneous rearrangement of zirconium(IV) to zirconium(II) does not appear plausible, however. Neither would a heterolytic separation of a coordinated H_2 molecule into a hydride and a proton moiety, which was proposed by Gell and Schwartz [1] to account for the H_2-dependent alkane elimination, appear to be a likely reaction mode in the non-polar reaction media employed. [*] In order to provide a satisfactory description of H_2 activation by these and some related catalytic reaction systems, I present below the results of a molecular orbital analysis of a possible reaction mode which is based on the idea that H_2 might form a transient adduct at any coordination site at which CO can form a stable adduct.

The dihydride derivative $(C_5R_5)_2ZrH_2$ ($R = CH_3$) has been reported by Bercaw et al. [4] to form a CO adduct which is stable in toluene solution at —78°C. For such a tricoordinate metallocene derivative two structures, I and II, are to be



I



II

considered. From an ^1H NMR spectrum with only one signal for both hydride ligands, Bercaw et al. assigned the symmetrical structure I, with a centrally coordinated CO ligand, to this zirconocene dihydride carbonyl adduct. The dimethyl derivative $(C_5R_5)_2Zr(CH_3)_2$ ($R = H$), on the other hand, does not form a stable adduct; instead, η^2-acyl derivatives have been observed by Fachinetti et al. [5] to be formed in a facile, reversible methyl migration reaction. The reversibility of the CO uptake reaction requires that a primary transient CO adduct is formed in an essentially thermoneutral reaction. With regard to the structure of such a primary CO adduct, a preference for the unsymmetrical isomer II with a laterally coordinated CO ligand is indicated by a recent study by Erker and Rosenfeld

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[*] Homolytic H_2 activation analogous to that operative in certain Ag^+ reactions [3] is not consistent with the general reactivity patterns of the zirconium(IV) derivatives considered here.

[6]. The first stable product of CO uptake by a zirconocene diphenyl derivative is reported to be a η^2-benzoyl species which has its carbonyl oxygen atom bound in a lateral position.

In a previous theoretical study on the coordinating capabilities of transition metal dicyclopentadienyl derivatives, Lauher and Hoffmann [7] pointed out that a 16-electron species of the type $(C_5R_5)_2M(R')_2$ (M = Ti, Zr) should add another ligand preferentially at a lateral coordination site, since a laterally extending orbital of the $(C_5R_5)_2MX_2$ fragment represents the lowest-lying acceptor orbital for the σ electron pair of an incoming ligand. Such a preference appears to be counterbalanced, however, particularly in case of the dihydride derivatives [4], by some factor which favours the central coordination site: We have to consider the possibility that π-type back donation is a major contributor to the stability of CO adducts even for these formal d^0 species.

The most likely source of such a back donation of electron density to the CO ligand are the two metal—hydrogen bonding pairs, which are accommodated in rather high-lying molecular orbitals. The preference of CO for coordination at the central ligand site of a $(C_5R_5)_2ZrH_2$ molecule could result from this π-type interaction, since the π^* orbital of a centrally coordinated CO ligand can overlap with both of the electron-rich M—H bonds. Similar π-type interactions will have to be considered for the interaction of zirconocene hydride and alkyl derivatives with a dihydrogen molecule.

Results and discussion

Hydrogen isotope exchange

In order to define the essential features of a comparatively simple model reaction, an initial molecular orbital analysis was conducted on the possible modes of interaction of $(C_5R_5)_2ZrH_2$ with a H_2 or D_2 molecule.

Placement of an intact H_2 molecule with unchanged bond length of 74 pm in bonding contact with the metal centre of a $(C_5R_5)_2ZrH_2$ species (i.e., at a metal—hydrogen distance of 160 pm) results in a modest repulsive energy rise. Relative energy minima are obtained at angular parameters which correspond to a position of the H_2 molecule either at the central coordination site or at one of the lateral coordination sites of the $(C_5R_5)_2ZrH_2$ molecule (Fig. 1). The energy change associated with the formation of these H_2 adducts increases from practically zero for low-lying d orbital energies of —9.0 eV to about 0.7 eV for higher d orbital energies of —7.0 eV; the two isomeric adduct structures are found at virtually identical energies, however, irrespective of the metal d orbital energies considered.

Inspection of charges and overlap populations indicates that both donation from the H_2 σ orbital to the metal and π back donation of M—H electron density into the σ^* orbital of the H_2 molecule contribute to the metal—H_2 interaction. This electron redistribution results in a slight negative charge of about 0.1 units on the H_2 ligand molecule. A concomitant decrease of negative charge on both hydride ligands is in accord with the notion that π back donation originates from metal hydride electron density.

The significant transfer of electron density into the H_2 σ^* orbital suggests that the force constant resisting opening of the H—H bond is substantially reduced in

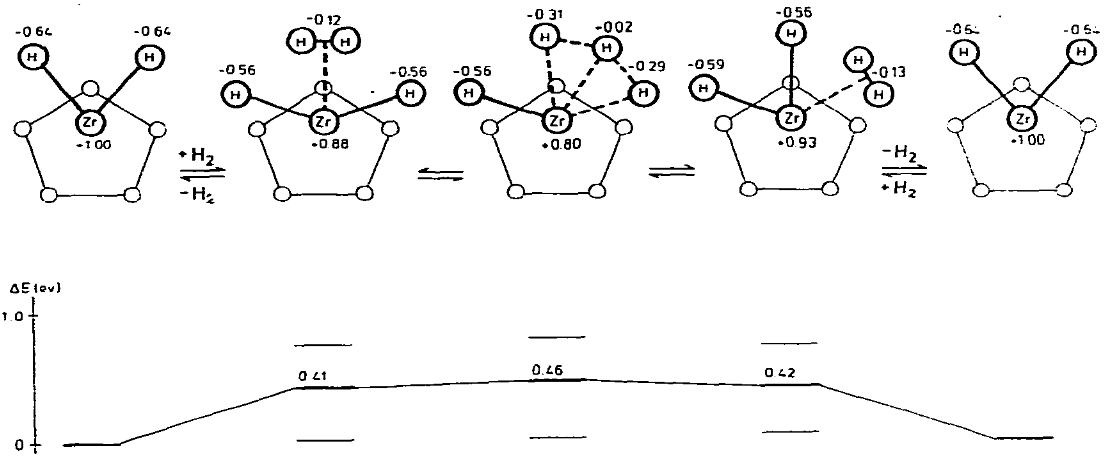

Fig. 1. Reaction path for hydrogen isotope exchange between $(C_5R_5)_2ZrH_2$ and D_2: Rearrangement of hydrogen ligands in the symmetry plane of the molecule. (Projections of both five-ring ligand functions into this plane coincide.) Charges indicated are calculated for H_{ii} (d) = —8.0 eV (see Table 1). Energy profile for this reaction calculated for H_{ii} (d) = —8.0 eV. Levels above and below this graph represent energies calculated for H_{ii} (d) = —7.0 eV and —9.0 eV, respectively.

these adducts, and that the two isomeric H_2 adducts might interconvert by an intramolecular transfer of one of the hydrogen atoms of a coordinated H_2 molecule to an adjacent hydride ligand. The energy profile calculated for this reaction (Fig. 1) is indeed void of any significant energy barrier. Interconversion of the two isomeric H_2 adducts by an intramolecular hydrogen transfer is thus portrayed as a facile reaction mode. If D_2 instead of H_2 enters into such a transfer reaction, a hydrogen isotope exchange results, which would lead primarily to HD and $(C_5R_5)_2ZrHD$. Such a reaction was found by Bercaw et al. to occur rapidly even at —78°C [8].

The transition state of this hydrogen transfer reaction contains four hydrogen atoms in bonding contact to the metal, of which three are separated by distances of just over 100 pm, while the fourth, which is not involved in the exchange process and remains essentially stationary, is separated by about 170 pm from its nearest hydrogen neighbour. Even this reaction intermediate with its four 'separate' hydrogen ligand atoms does not involve an 'oxidative addition' of H_2 to the metal centre. The metal retains its charge practically unchanged throughout the exchange process; the three exchanging hydrogen ligand atoms, on the other hand, retain their total negative charge at a similarly constant value. The transition state of the exchange reaction is best described as containing a $(H\cdots H\cdots H)^-$ ligand configuration, in which each of the terminal hydrogen atoms carries a charge of about —0.3 units, while that of the migrating middle hydrogen is found at about —0.02 units. This $(H\cdots H\cdots H)^-$ ligand configuration appears to be rather similar to an allyl ligand group in its charge distribution and in its bonding properties.

This reaction mode bears a certain resemblance to that proposed for heterolytic H_2 activation [9]. H_2 activation in an aqueous solution of copper (II) acetate, for example, has been described by Halpern [9] as involving transformation of a coordinated H_2 molecule into a metal-bound hydride and a ligand-bound proton moiety. In the transition state of such a heterolytic H_2 activation, the reactants would form a four-centre reaction complex involving the metal, a basic ligand, and both hydrogen atoms of the H_2 or D_2 molecule. Formally, the mechanism discussed above might thus be considered as a limiting case of heterolytic H_2 activation. This term would be misleading, however, in that the transition state of the reaction considered here does not involve any positively charged hydrogen moiety; rather, all three hydrogen atoms involved in the hydrogen transfer retain their coordinative interaction with the metal centre as well as their negative charge throughout the exchange process. In order to clarify this distinction from truly heterolytic H_2 reactions, as well as that from mechanisms involving an oxidative addition intermediate, an elementary reaction step of the type described above might be called 'direct hydrogen transfer'.

H_2-induced alkane elimination

As mentioned earlier, a facile elimination of an alkane from species of the type $(C_5R_5)_2ZrHR'$ has recently been shown to depend on the presence of H_2 [1,2]. As a likely mechanism for this reaction, we have to consider a reaction route analogous to that for the hydrogen isotope exchange reaction described above, i.e., formation of a H_2 adduct followed by a direct hydrogen transfer from the coordinated H_2 molecule to the alkyl ligand group. For such a reaction sequence, several possibilities arise. Lateral H_2 coordination *cis* to the alkyl group, or central H_2 coordination between the hydride and the alkyl group, could lead to alkane elimination via intramolecular hydrogen transfer onto the alkyl group. In addition, hydrogen exchange by direct hydrogen transfer onto the hydride ligand could occur from a H_2 molecule coordinated either at the central coordination site or at the lateral one adjacent to the hydride ligand. The analysis of these reaction paths is greatly simplified in that the energy of the adduct in which H_2 is coordinated laterally next to the centrally bonded CH_3 group is calculated to be lower than that of the other two isomers by more than 0.5 eV; apparently a central placement of the CH_3 group dominates the geometrical preferences in this case. This isomer (Fig. 2) can, therefore, be regarded as the only significant point of access for the H_2 molecule. * Alkane elimination and concurrent formation of the dihydride $(C_5R_5)_2ZrH_2$ would then proceed by direct hydrogen transfer from this particular H_2 adduct to the alkyl group. An energetically undemanding path involves a transfer of the migrating hydrogen atom into the metal—carbon bonding region, with simultaneous extension of the metal—carbon distance, so as to give a CH_4 molecule pointing the newly formed C—H bond directly towards the metal atom (Fig. 2). Interestingly, no energy gain is associated with an alignment of the CH_3 axis towards the migrating hydrogen atom in the transition state represented in Fig. 2. Apparently an optimal 3-centre $(H\cdots H\cdots CH_3)^-$ ligand configuration requires maximal overlap of all its parts with the metal centre. For the overall activation energy of the H_2-induced alkane elimination, values of about 0.6 eV are calculated. Even without considering the possibility that a further refinement of the geometry of the transition state would undoubtedly

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* This result indicates that $(C_5R_5)_2ZrD(CH_3)$ is not accessible for hydrogen isotope exchange between D_2 and $(C_5R_5)_2ZrH(CH_3)$. The experimental reports on this aspect are in conflict [1,2].

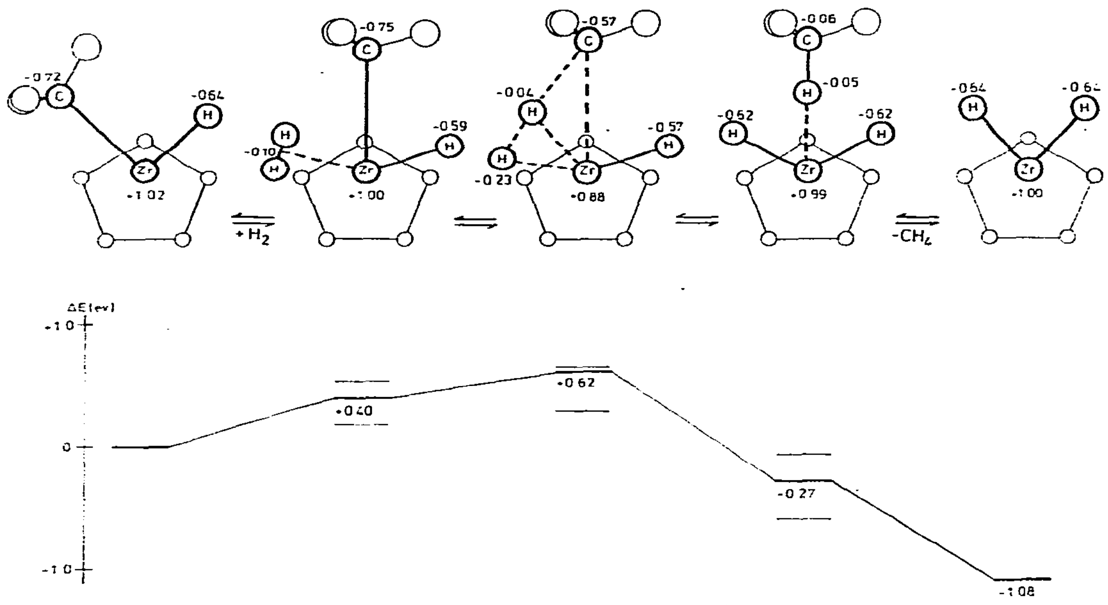

Fig. 2. Reaction path for hydrogenolysis of alkane from $(C_5R_5)_2ZrHCH_3$. For details see Fig. 1.

lead to yet lower activation energy values, we can regard this result as a satisfactory explanation of the facility with which H_2 reacts with $(C_5R_5)_2ZrHR'$ derivatives. Significantly, the transition state of this hydrogen transfer again contains, as in the case discussed above, a migrating hydrogen atom with a negative rather than a positive charge. The elementary reaction step involved in this alkane elimination should thus be classified again as a 'direct hydrogen transfer'.

Conclusions

Activation of dihydrogen by direct hydrogen transfer from a transiently coordinated H_2 molecule has a formal relation not only to heterolytic dihydrogen activation, as discussed above, but also to dihydrogen activation by oxidative addition. Both of these elementary reactions require an electron-rich metal species with an open coordination site in which H_2 can form a transient adduct. * This parallelism points to the possibility that some of the H_2 reactions hitherto described as involving an oxidative formation of a dihydride intermediate may in fact avoid such an intermediate by a direct hydrogen transfer process. For cobalt or rhodium-carbonyl based hydroformylation catalysts, for example, there seems to be no direct evidence for the occurrence of a dihydride intermediate in the final, H_2-induced product elimination step. In recognition of this

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* This requirement would preclude an analogous reaction sequence, for example, in the case of the 18-electron species $(C_5H_5)_2WHCH_3$. With this species, the reductive elimination of CH_4, as reported by Green et al. [11], must be greatly favoured over any H_2-adduct formation; we can estimate an activation energy in excess of 3 eV from our calculations for the formation of a H_2 adduct of $(C_5H_5)_2WHCH_3$ with the geometry represented in Fig. 2.

ambiguity, Orchin and Rupilius [10] have described this hydrogenolysis step as involving an 'incipient dihydro species'. In these and other catalytic reaction systems, in which the oxidation state of the reactive metal centre is sufficiently stabilized, e.g. by its carbonyl ligands, to become resistant to an oxidative addition of H_2, hydrogenolysis is likely to occur via a direct hydrogen transfer reaction process analogous to that described above.

Appendix

In the calculations, an Extended Hückel programme written by Hoffmann and Lipscomb [12] was used to obtain one-electron energies and wave functions. In order to keep the computational complexity at an acceptable level, the following procedures were adopted throughout:

(1) Changes in electron—electron repulsion energies were not taken into consideration. Although we have shown (e.g. for species of formal d^4 configuration) that these terms can occasionally dominate over changes in one-electron energies [13], such effects are not to be expected for the formal d^0 species considered here.

(2) The C_5R_5 π ligands were approximated by pentagonal sets of five 1*s* wave functions placed at a distance of 140 pm from each other and 185 pm from the metal centre. As shown in an earlier paper [13], these pseudo π systems generate a splitting pattern of the metal-centred molecular orbitals at the occupation limit which is closely similar to those resulting from a complete inclusion of all ligand atom orbitals. The geometry of these ligand functions was kept unchanged at an angle of 40° between the two five-ring planes.

(3) Values of *d* orbital exponents are close to those given in ref. 14 for niobium(+I) ion. A change of these exponents to those given in ref. 14 for zirconium(+I) ion or to those given in ref. 15 for titanium(+I) ion did not affect the results to any significant degree.

Effects of changing valence state ionisation energies of the metal centre were investigated by varying these energy values within reasonable limits. In order to avoid an excessive build-up of positive charge on the metal centre for the lower *d* orbital energies studied, the H_{ii} values of the ring—ligand π functions were changed in parallel to those of the metal *d* orbitals (see Table 1).

(4) Normal EHT procedures fail to produce an energy minimum for the H_2 molecule at a H—H bond distance of 74 pm. In order to compensate for this short-coming, a repulsive term was included in our calculations by superimposing each H atom with a doubly occupied, highly contracted pseudo-atom H' (see Table 1). By this means, an energy minimum is generated at the appropriate H—H distance. This procedure necessitates, on the other hand, the use of the altered H_{ii} and orbital exponent values given in Table 1 to arrive at an acceptable value of about —15 eV for the dihydrogen σ orbital energy. For the H—H stretching force constant (a crucial parameter for the present analysis), a value of 4.2 mdyn/Å results from this model, in satisfactory agreement with the value of 4.8 mdyn/Å derived from H_2 Raman spectra.

In order to obtain a reasonably exothermic overall energy change for the reaction $(C_5R_5)_2ZrHCH_3 + H_2 \rightarrow (C_5R_5)_2ZrH_2 + CH_4$, as well as satisfactory equilibrium bond lengths (Zr—H, 160 pm; Zr—CH_3, 230 pm; C—H, 110 pm), Zr and C

TABLE 1

EXTENDED HUCKEL PARAMETERS USED FOR H_2 AND HYDRIDE (HY), METHYL CARBON (CY), RING LIGAND FUNCTION (R) AND ZIRCONIUM CENTRE (ZR)

Repulsive functions H′, C′ and Z′ are superimposed on HY, CY and ZR, respectively. Normal H 1*s* functions with $N = 1$, $EXP = 1.300$ and $H_{ii} = -13.6$ were used for methyl hydrogen atoms. Instead of the ring function and zirconium *d* orbital H_{ii} values listed (*), alternative sets of parameters in which both of these values were raised or lowered by 1.0 eV are also represented in Figs. 1 and 2.

Atom	Number of electrons	*s*-orbitals			*p* orbitals		
		N	*EXP*	H_{ii}(eV)	*N*	*EXP*	H_{ii}(eV)
HY	1	1	1.600	−12.70			
H′	2	1	5.080	−50.00			
CY	4	2	1.625	−21.40	2	1.500	−12.50
C′	8	2	5.400	−50.00	2	5.400	−50.00
R	1	1	1.250	−10.00 *			
Z′	2	4	7.000	−50.00			
ZR	4	5	1.890	−5.00	5	1.850	−4.00
		d-orbitals					
		N	Double ζ exponents				H_{ii}(eV)
ZR		4	4.08 (0.615); 1.90 (0.528)				−8.0 *

atoms were also superimposed with repulsive pseudo atoms Z′ and C′, the parameters of which are included in Table 1. Overlap integrals between each of these repulsive, closed-shell pseudo atoms and the respective Zr, C or H atom, placed at identical position, were set to zero by the programme used.

Energy minima were located by systematic variation of the appropriate bond lengths and bond angles within the symmetry plane of the sandwich molecule.

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