

State Correlation Diagrams for the Photochemical Reactions of Organometallics

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State correlation diagrams are proposed for a number of photochemical reactions of organometallics. Spin-orbit coupling is found important to understand the reactivity of these organometallics.

Key words: State correlation diagram – Photochemistry of organometallics – Spin-orbit coupling.

We have previously used state correlation diagrams, based on the symmetry and spin conservation rules, to identify the photoactive excited state in a number of photochemical reactions of organometallics [1]. In this note:

- (i) we extend this treatment to new photochemical reactions which have been reported recently [2, 3];
- (ii) we refine our previous treatment through the inclusion of spin-orbit coupling and the explicit consideration of the relative energetics of the reactant and the products;
- (iii) we show that a number of apparent counter-examples may be explained within the framework of this theory.

1. We consider first the following photochemical reactions:

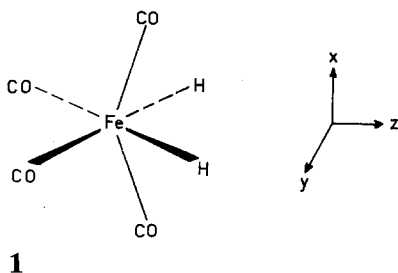
- (i) the photoinduced elimination of molecular hydrogen from tetracarbonyldihydridoiron [2]



- (ii) the photochemical homolysis of the Re–H bond in $[(\eta\text{-C}_5\text{H}_5)_2\text{ReH}]$ [3]



1.1. $\text{Fe}(\text{CO})_4\text{H}_2$ has the structure shown in **1** [4].



We assume that the reaction is concerted and that the hydrogen atoms remain in the equatorial plane during the course of the reaction so that C_{2v} symmetry is retained along the reaction path. On the basis of the energy levels given for $\text{Fe}(\text{CO})_4\text{H}_2$ by an *ab initio* SCF calculation [5], we expect for this molecule a 1A_1 ground state (with an electronic configuration d^6 for the metal) and a low excited state 3B_2 of the ligand-field type (there are two other 3B_2 excited states of the charge-transfer ligand-to-metal type but probably at higher energies). The ground state of $\text{Fe}(\text{CO})_4$ has been shown experimentally [6] and theoretically [7] to be 3B_2 (with an electronic configuration d^8 for the metal). A state correlation diagram is shown in Fig. 1. The excited state 3B_2 of $\text{Fe}(\text{CO})_4\text{H}_2$ correlates with the ground-state of $\text{Fe}(\text{CO})_4 + \text{H}_2$ as a consequence of an avoided crossing (this avoided crossing results from the fact that the Fe atom has different oxidation numbers in the reactant and the product, see for instance Ref. [8] for the definition of a natural correlation diagram). We conclude that:

- (i) this reaction is thermally forbidden;
 - (ii) the photoactive excited state should be 3B_2 (probably a ligand-field state).
- The construction of the *ab initio* potential energy surfaces at the CI level is now under way for this reaction.

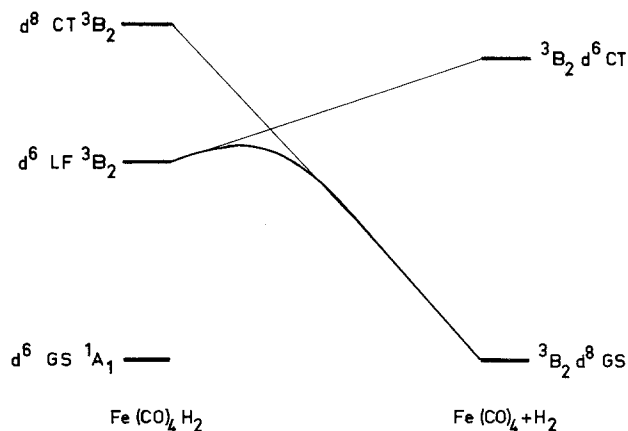
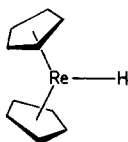


Fig. 1. State correlation diagram for the photochemical dissociation of H_2 from $\text{Fe}(\text{CO})_4\text{H}_2$

1.2. The most probable structure for ReCp_2H is **2** with C_{2v} symmetry and we assume that the H atom leaves along the C_2 axis, so that this symmetry is retained along the reaction path.



2

An energy level scheme has been reported for Cp_2ReH [9]. The ground state should be ${}^1A_1(1a_1)^2(2a_1)^2(1b_2)^2$ with one low-lying empty orbital $3a_1$ ($2a_1$, $3a_1$ and $1b_2$ being metal d orbitals while $1a_1$ is mostly a hydrogen orbital). We consider the excitations $1b_2 \rightarrow 3a_1$ giving rise to the ligand-field states ${}^{1,3}B_2$ and $1a_1 \rightarrow 3a_1$ giving rise to the states ${}^{1,3}A_1$ (CT $L \rightarrow M$). Most probably the ground state of ReCp_2 will be ${}^2E_{2g}$ (corresponding to the electronic configuration $(a_{1g})^2(e_{2g})^3$) in D_{5d} symmetry and ${}^2B_2 \oplus {}^2A_1$ in C_{2v} symmetry so that the ground state of the products will be ${}^{1,3}B_2 \oplus {}^{1,3}A_1$. From the state correlation diagram of Fig. 2, one finds that:

- (i) there will be a barrier for the thermal reaction;
- (ii) the states 3A_1 and ${}^{1,3}B_2$ of ReCp_2H go directly to the products in their ground state (without barrier for 3A_1 and with a small barrier for ${}^{1,3}B_2$);
- (iii) the reaction may also occur through internal conversion of the 1A_1 excited state as a consequence of an avoided crossing;
- (iv) we have assumed in this diagram that the photoactive excited states ${}^{1,3}A_1$ correspond to the charge transfer excitation $1a_1 \rightarrow 3a_1$ but we cannot rule out ligand-field states corresponding to the excitation $2a_1 \rightarrow 3a_1$. This would not greatly alter the diagram of Fig. 2.

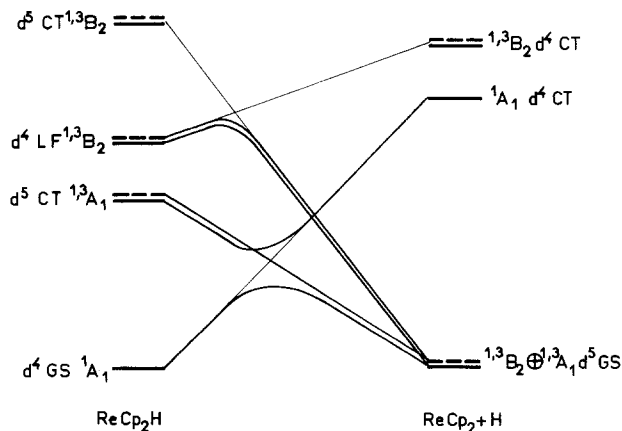


Fig. 2. State correlation diagram for the dissociation of the hydrogen atom from ReCp_2H

2. Before we refine the theoretical model, let us comment briefly on some original predictions made in Ref. [1]:

2.1. We considered the photodissociation of $\text{Fe}(\text{CO})_5$



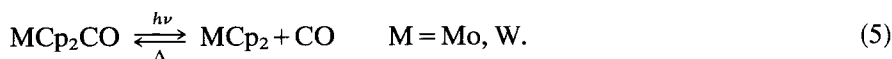
and concluded that the photodissociation should occur through the ligand-field state ${}^3E'$. *ab initio* CI calculations show indeed that a single potential energy surface connects the excited state ${}^3E'$ of $\text{Fe}(\text{CO})_5$ with the ground state 3B_2 of $\text{Fe}(\text{CO})_4 + \text{CO}$ without any barrier [7].

2.2. We considered the photochemical homolysis of the Co–H bond in $\text{HCo}(\text{CO})_4$ [10]



and predicted that the photoactive excited states would be the CT $L \rightarrow M$ ${}^{1,3}A_1$ states. Sweany has assigned the photochemical reaction to a $L \rightarrow M$ CT band found at 227 nm and arising from a $\sigma \rightarrow \sigma^*$ excitation, with the electron density of the σ orbital residing mostly on the hydrogen [12].

3. In the original treatment [1] we had assumed that the spin is conserved during the photochemical reaction and the effect of spin–orbit coupling was therefore not considered. We had mentioned that, in a case like the one of Fig. 3 with spin–orbit coupling mixing a singlet and a triplet potential energy surfaces, the photochemical reaction which was possible by going along a single potential energy surface would probably remain operative. Also, for the sake of simplicity, the state correlation diagrams were drawn with the assumption that the stabilities of the reactants and the products are the same. Clearly this is not true for reaction (3) ($\Delta H_{\text{exp}} = 55$ kcal/mole [13]) nor for reaction (4) ($\Delta H_{\text{exp}} = 58$ kcal/mole [14]). We have found that introduction of the spin–orbit coupling and a proper consideration of the energetics of the reaction are needed in order to account for instance for the following reaction:



The experimental evidence is that (i) the dissociation occurs by photolysis; (ii) the barrier to the thermal loss of CO is large; (iii) the barrier to the thermal

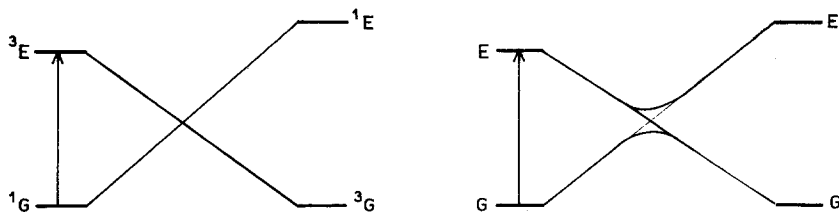


Fig. 3. The crossing between a singlet and a triplet potential energy surface, without spin–orbit coupling (left) and with spin–orbit coupling (right). The capital letters G and E refer to the ground and excited states, respectively

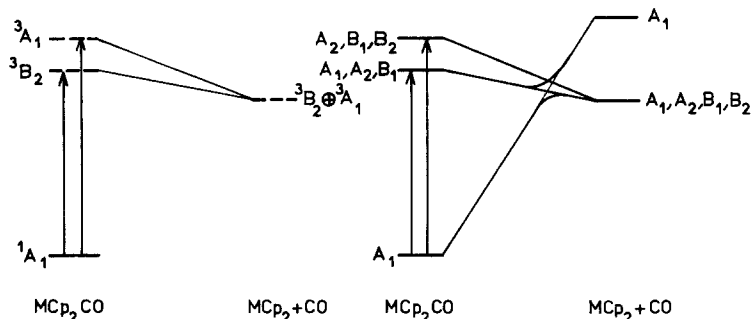
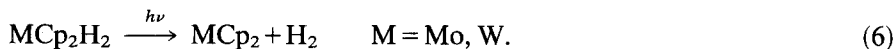


Fig. 4a, b. State correlation diagram for the photodissociation of the carbonyl from MCP_2CO without (a) and with (b) spin-orbit coupling

recombination is extremely low [15, 16]. Fig. 4 is a qualitative correlation diagram based on Fig. 5 of Ref. [1], assuming that the products are thermodynamically less stable than the reactant (Fig. 4a) and including spin-orbit coupling (Fig. 4b) [17]. The diagram of Fig. 4b accounts (i) for the photochemical reaction through the excited states (either along a single potential energy surface or through internal conversion); (ii) for the high barrier to the thermal loss of CO; (iii) for the low barrier to the thermal recombination.

Fig. 5 is a similar diagram, based on Fig. 2 of Ref. [1], for the reaction [15]



The destabilization of the products relatively to the reactant is probably smaller for this reaction than for the decarbonylation reaction (5) [19]. The diagram accounts for the photochemical reaction and for the large barrier to the thermal loss of H_2 .

4. We now examine a number of apparent counter-examples.

4.1. While the barrier to loss of H_2 from MCP_2H_2 ($\text{M} = \text{Mo, W}$) is large, the barrier to loss of CH_4 from $\text{WCp}_2(\text{CH}_3)\text{H}$ must be much smaller since this

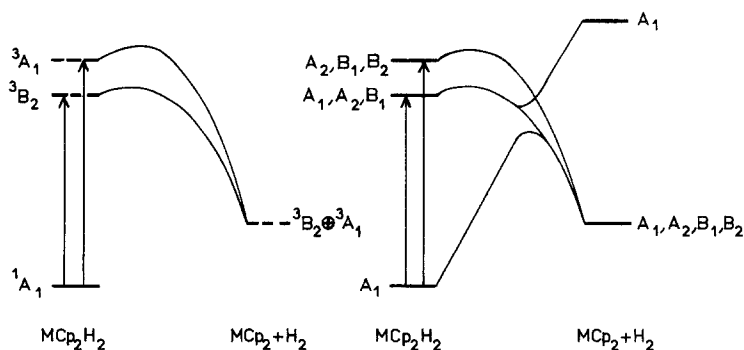


Fig. 5a, b. State correlation diagram for the dissociation of H_2 from MCP_2H_2 without (a) and with (b) spin-orbit coupling

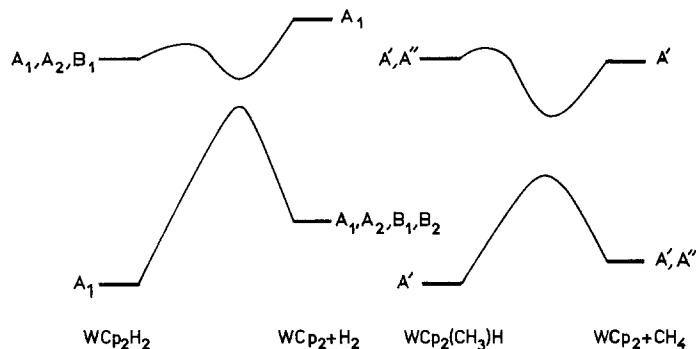


Fig. 6. State correlation diagrams (including spin-orbit coupling) for the dissociation of H_2 and CH_4 from WCp_2H_2 and $WCp_2(CH_3)H$, respectively

compound decomposes at $50^\circ C$ with evolution of methane [20]. This looks contradictory to the high barrier to the thermal reaction of Fig. 5b. The reduction in the symmetry point group, from C_{2v} to C_s , cannot account for this reduction of the barrier. There are two possible explanations for this difference.

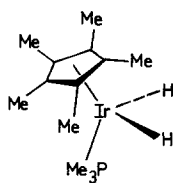
(i) The first one is that the CH_4 elimination does not occur by a simple intramolecular reductive elimination. A similar hypothesis has been explicitly considered for other transition metal alkyl hydrides [21].

(ii) The other explanation is that the methyl hydride complex is comparatively less stable than the dihydride. A number of arguments support this hypothesis [21]. It means that the energy gap between the reactant and the products will be smaller for the reaction



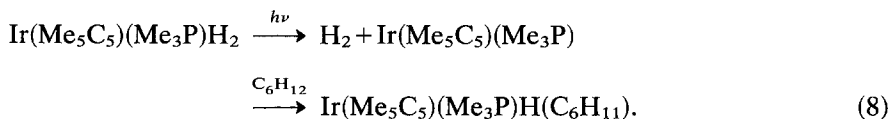
than for the elimination reaction (6) from the dihydride. From the diagrams of Fig. 6 one may see that the same should be true for the barrier to the reaction.

4.2. The dihydrido-iridium(III) complex **3**, when irradiated in cyclohexane, forms



3

a compound $Ir(Me_5C_5)(Me_3P)H(C_6H_{11})$ presumably through loss of H_2 and oxidative addition of cyclohexane on the intermediate $Ir(Me_5C_5)(Me_3P)$ [22]



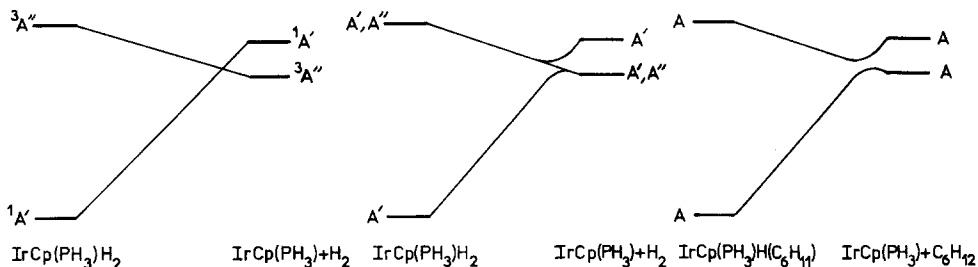
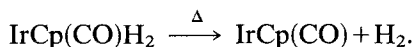


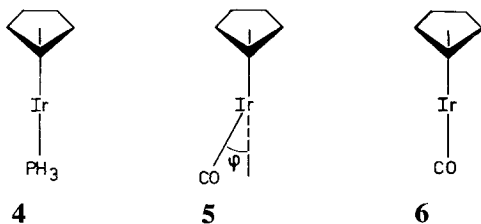
Fig. 7a-c. State correlation diagrams for the dissociation of H₂ (a and b) and C₆H₁₂ (c) from IrCp(PH₃)H₂ and IrCp(PH₃)H(C₆H₁₁), respectively. Spin-orbit coupling was not considered in a but was included in b and c

We consider a model system IrCp(PH₃)H₂ and we assume that one plane of symmetry is retained during the photochemical elimination of H₂ (C_s symmetry). Extended Hückel calculations indicate that the ground state of the reactant is a ¹A' state while the ground state of the intermediate with the assumed structure **4** is ³A₂, corresponding to the configuration (xy)²(x²-y²)²(z²)²(xz)¹(yz)¹, in pseudo C_{5v} symmetry and ³A'' in C_s symmetry. A state correlation diagram is shown in Fig. 7a and 7b for the hydrogen elimination. After introduction of the spin-orbit coupling, this diagram accounts for the photochemical reaction but also for the oxidative addition of cyclohexane (this may be viewed as the reverse reaction of the thermal elimination of dihydrogen) as the result of an avoided crossing. Furthermore, the oxidative addition of cyclohexane is a process devoid of any symmetry element and this results also in an avoided crossing between the two surfaces [23]. Both spin-orbit coupling and symmetry lowering concur to produce a single potential energy surface connecting the ground states of the reactants and product, with a low barrier for the oxidative addition reaction (Fig. 7c).

A related reaction is the thermal elimination of dihydrogen from the compound IrCp(CO)H₂ [24]



The corresponding state correlation diagram must be similar to the one of Fig. 7b, which indicates that the thermal elimination should be symmetry allowed due to spin-orbit coupling. Furthermore symmetry lowering also contributes to make this reaction symmetry allowed. *Ab initio* SCF calculations for the rhodium analog indicate that a structure like **5** should be more stable than **6** (the



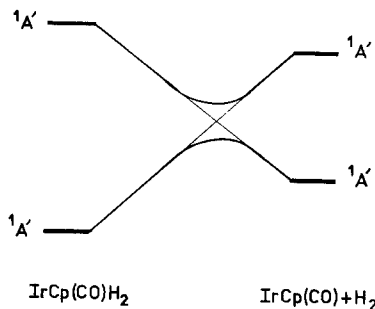


Fig. 8. State correlation diagram for the H_2 dissociation from IrCp(CO)H_2

stabilization for an angle φ optimized to 43° amounts to 43 kcal/mole for the singlet state and to 30 kcal/mole for the triplet state, while the deviation from the five-fold symmetry should be smaller for a phosphine ligand as judged from extended Hückel calculations [25]). From these calculations [27] we infer for IrCp(CO) a ground state $^1A'$ corresponding to an electronic configuration of the closed-shell type $(xy)^2(x^2-y^2)^2(z^2)^2(yz)^2$ (with the CO ligand in the yz plane). Since the ground states are now of the same symmetry and spin for the reactant and the products, they are connected by a single potential energy surface (Fig. 8) prior to the introduction of spin-orbit coupling and the thermal elimination is symmetry allowed.

4.3. In Ref. [1], a state correlation diagram had been proposed for the dissociation of an equatorial ligand of Fe(CO)_5 (reaction (3)). Since the ground state is $^1A'_1$ for Fe(CO)_5 (1A_1 in C_{2v} symmetry) and 3B_2 for the products $\text{Fe(CO)}_4 + \text{CO}$, we concluded that the thermal dissociation is both spin and symmetry forbidden (Fe(CO)_5 has a boiling point of 103°C [28]). The reverse reaction, the recombination of Fe(CO)_4 with CO, would appear to be equally forbidden. However, this reaction takes place at very low temperature [29]! Fig. 9a represents a state correlation diagram for reaction (3), without spin-orbit coupling [1] but now with the proper energetics. From Fig. 9b where it is assumed that the spin-orbit coupling is operative, we see that the reverse reaction is now symmetry allowed with a very low barrier. It may be argued that spin-orbit coupling should be small for iron, but we note that spin-orbit coupling has been recognized as the

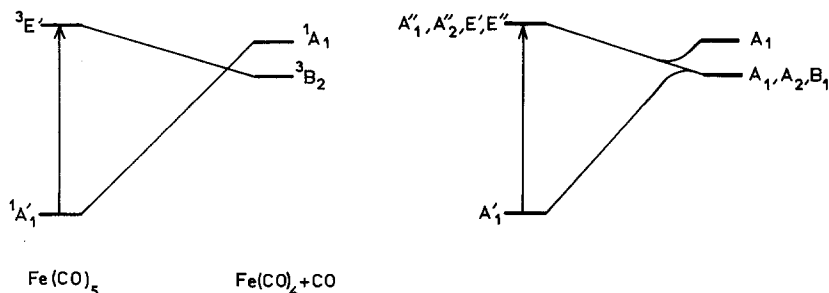


Fig. 9a, b. State correlation diagram for the carbonyl dissociation from Fe(CO)_5 without (a) and with (b) spin-orbit coupling

mechanism for the collisional quenching of $O(^1D)$ with Ar and Kr [30]. Note that lowering the symmetry also contributes to making the reverse reaction symmetry allowed, at least with respect to orbital symmetry. This could be achieved by retaining only one plane of symmetry during the course of the reaction with the incoming ligand CO approaching $Fe(CO)_4$ in a plane which becomes the equatorial plane of $Fe(CO)_5$ [31]. Then the energy surfaces connected with the ground states of the reactants and product belong to the same representation A' of the point group C_5 (corresponding to the orbital symmetry). One will notice from Fig. 9b that the direct reaction remains probably hindered by a large barrier.

To summarize, it appears that consideration of spin-orbit coupling is probably important to understand the reactivity of organometallics [34], even with atoms of the first transition series. On the other hand, one will notice that the introduction of spin-orbit coupling does not require to change our initial hypothesis about spin and symmetry conservation which were used for the identification of the photoactive excited state in Ref. [1].

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