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6

Multiple Spin-State Scenarios in Organometallic Reactivity

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6.1 Introduction

The influence of spin-state changes on reaction mechanisms involving transition metals is a topic that has received increasing interest over the past 20 years. The rapid development of computational methods uncovered new mechanisms which proceed through multiple spin states and helped in understanding why some multi-state reactions proceed slowly while others are fast. It also explained some rate anomalies in reactions of transition metal complexes (or ions) for which the substrates and the products have the same spin state but proceed via a spin-crossing reaction pathway leading to an unexpected product distribution. Understanding multi-state reactivity of organometallic compounds is of particular importance for the development of new base-metal catalysts. Whereas the noble second and third row transition metal complexes (e.g., Ru, Rh, Pd) are mainly low spin due to the large energy splitting of their d-orbitals, first row transition metal complexes (e.g., Fe, Co, Ni) often exist in multiple spin states with similar energies. Since the stability of their high-, intermediate- and low-spin configurations depends on both the coordination number and the donor strength of the ligands, it is not uncommon that elementary steps such as migratory insertion, oxidative addition or reductive elimination lead to a change in the spin state of the metal along a catalytic reaction pathway. This can (but does not necessarily have to) lead to “spin blocking” of the reaction of a coordination compound if the barrier for spin-crossing between the different spin states is high, in which the reaction proceeds slowly or not at all. Spin transitions can also lead to unexpectedly fast reactions (spin acceleration) when a facile spin-crossing opens a lower energy pathway.

In this chapter, we give an overview of the different spin-state crossing scenarios affecting the reactivity of organometallic compounds. For clarity, we excluded any open-shell reactivity introduced by single-electron oxidation or reduction of organometallic complexes producing metallo- or ligand-centered radicals. Such scenarios are covered extensively in a number of other recent reviews and book chapters (an example would be Chapter 11 of this book) [1, 2]. Here we focus on the effects of crossing spin states in a number of elementary reactions typically observed for organometallic compounds, such as ligand exchange, oxidative addition, reductive elimination, migration/insertion, β -hydride elimination, C–H bond activation and intramolecular electron transfer between a transition metal and a coordinated redox active ligand. These processes are highly relevant for catalysis, which is the final topic covered in this chapter. We did not attempt to write a full comprehensive review, including all reactions reported to involve spin-crossing processes. Instead, we aimed to exemplify the important principles and effects of spin-crossing in reactions on the basis of illustrative examples, covering the most important reaction types in organometallic chemistry. In Section 6.2, we start by giving a brief overview of the existing theories of reactions involving spin-state changes, which we explain in a manner accessible to a broad readership.

6.2 “Spin-Forbidden” Reactions and Two-State Reactivity

The majority of chemical reactions proceed (or are thought to proceed) on single potential energy surfaces (PES) with uniform spin multiplicity: all the intermediates and transition states (TS) have the same spin state as the reactants and the products. The reaction rate depends on the energy of the (highest) transition state, which is a saddle point (SP) on the PES. The reactions in which the total electronic spin state changes are named “spin-forbidden.” However, as pointed out by Poli and Harvey, a more appropriate statement would be that such changes are associated with a certain extent of spin-forbiddenness depending on the magnitude of the spin-orbit coupling (SOC) [3]. As a result, for light atoms the change in the spin state is accompanied by a large barrier (more spin forbidden; an example being the slow reaction of organic molecules with triplet oxygen, as compared with the fast spin-allowed reaction with singlet oxygen) [4], while for transition metals such spin changes are generally quite facile (i.e., less spin forbidden; examples being spin-crossover compounds). Therefore, one should always consider the possible influence of the change of the spin state when considering organometallic chemistry reactivity patterns.

To address the influence of the spin-crossing on the reaction rate, Schröder et al. introduced the two-state reactivity (TSR) concept [5], which applies if the overall kinetics for product formation results from an interplay between the barriers for the spin-inversion and the barriers on the high- and low-spin surfaces (see Figure 6.1). In principle, TSR pathways provide short-cut routes for processes which are otherwise difficult when proceeding at a single-spin surface (single-state reactivity (SSR)) [5, 6]. In general, TSR is only relevant if it has an influence on the kinetics of the reaction (i.e., if it *lowers* the barrier). For a spin-state change to occur, the two spin-state surfaces with different spin-multiplicity have to be separated by a sufficiently small energy gap. This is often the case in coordinatively unsaturated (bare) organometallic and inorganic compounds, in particular for first row transition metals. In addition, the probability of TSR participating in chemical reactions depends on the magnitude of the SOC constant [7].

The smaller the energy gap between two spin states and the larger the SOC contributions, the greater the probability of a spin-crossing process [5, 7, 8]. Different spin states of a molecule are orthogonal. Hence, in zero-order approximation, a transition from one spin surface to another is “forbidden.” To enable spin-crossing, a (spin) state mixing mechanism is required, such as (vibronically induced) SOC. If SOC is small (i.e., for molecules built from light atoms), the transition from one spin surface to another can only occur if the spin surfaces are close in energy. This means, the point close to the exact crossing point of spin surfaces is defined as the minimum energy crossing point (MECP, see Figure 6.2) [3]. At this point, level mixing of

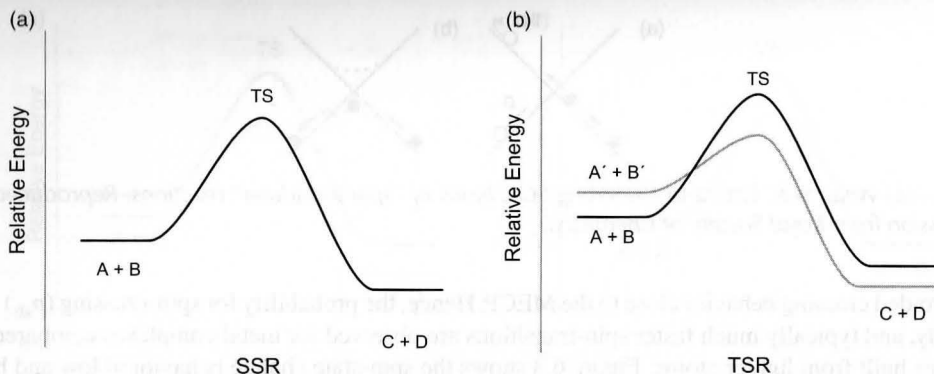


Figure 6.1 Reaction energy profiles of (a) single-state reactivity (SSR) and (b) two-state reactivity (TSR) processes. At the crossing point between the two energy surfaces, spin inversion occurs, providing a short-cut lower energy pathway. Reproduced from [5] with permission from American Chemical Society.

the spin surfaces through SOC leads to a low (but non-zero!) probability for spin-crossing. In the weak SOC limit, low spin-crossing probabilities can have a substantial influence on the spin-crossing rates.

The rate of “spin-forbidden reactions” can be described with the Eyring rate equation modified with a surface-hopping probability factor (p_{sh}). The latter is in fact a measure for the magnitude of SOC. See equation (6.1) [7],

$$k(T) = \frac{k_B T}{h} \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \times p_{sh} \times \exp\left(\frac{-\Delta S^\ddagger}{R}\right). \quad (6.1)$$

Since SOC is a relativistic effect, heavier atoms typically have larger SOC constants (l). As a result, SOC in metal complexes (especially for the heavier metals) is much larger than in organic molecules, thus leading to

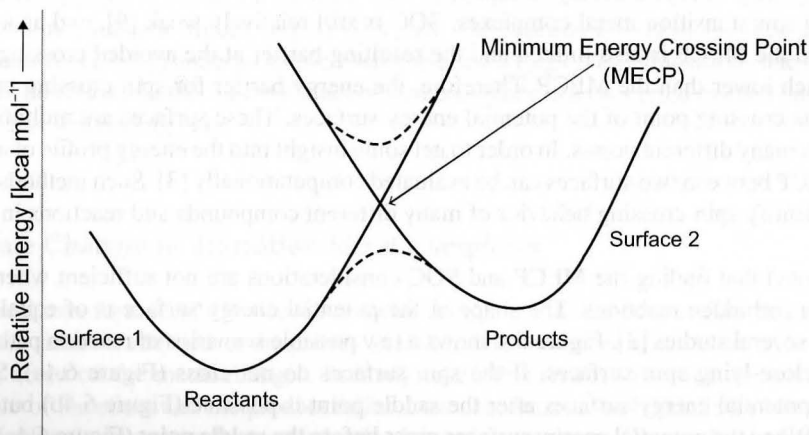


Figure 6.2 Potential energy surfaces (PES) in spin-forbidden reactions. Reactants cross from spin surface 1 to spin surface 2. The probability for crossing from one spin surface to another is highest when the energy gap between the surfaces is small (MECP). The spin-crossing probability increases with the magnitude of SOC. Reproduced from [8] with permission from Royal Society of Chemistry.

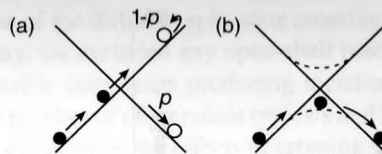


Figure 6.3 (a) Weak SOC limit and (b) strong SOC limits of “spin-forbidden” reactions. Reproduced from [3] with permission from Royal Society of Chemistry.

stronger avoided crossing behavior close to the MECP. Hence, the probability for spin-crossing (p_{sh}) increases substantially, and typically much faster spin-transitions are observed for metal complexes compared to those in molecules built from lighter atoms. Figure 6.3 shows the spin-state change behavior at low and high SOC limits. At the weak SOC limit, near-crossing of the spin surfaces (induced by motion of the atoms) is possible, and only around the MECP, vibronically induced SOC enables surface hopping with a certain (nonzero, but limited) probability (Figure 6.3a). In the strong SOC limit, as is the case for many transition metals, the system reveals strong avoided crossing behavior around the MECP. This lowers the barrier, and in addition in this region of the PES the probability for spin-transition is high, thus allowing a smooth transition from one spin surface to another (Figure 6.3b). The heavier the atoms, the larger the SOC, and hence the smoother the spin-crossing proceeds. Therefore, the degree of “spin-forbiddenness” gradually decreases going down the periodic table [3], and for many transition metals the barriers for spin-transitions are similar or lower than those observed for spin-conserving reactions. For the heavy third row transition metals, spin transitions become particularly facile. In that sense, geometric distortions required to bring the spin surfaces closer in energy are often the most important contributions to the spin transition barriers of transition metal complexes (i.e., similar to the electron transfer Marcus theory). In addition to geometrical distortions associated with a spin transition, an intrinsic low spin-crossing probability, p_{sh} , factor (i.e., crossing of the spin surfaces occurs without a spin transition, despite having an optimal geometry for a spin-crossing) might further contribute to lowering the spin-crossing rates. How relevant low probability, p_{sh} , factors really are for transition metal complexes is not so clear, as evaluating SOC effects typically requires expensive relativistic calculations. Hence, such reports are not (yet) widely available.

For many first row transition metal complexes, SOC is still relatively weak [9], and as a result the level of mixing around the MECP is also limited and the resulting barrier at the avoided crossing region is energetically not much lower than the MECP. Therefore, the energy barrier for spin-crossing can be estimated by calculating the crossing point of the potential energy surfaces. These surfaces are multidimensional, and therefore cross in many different points. In order to get some insight into the energy profile of a spin-forbidden reaction, the MECP between two surfaces can be evaluated computationally [3]. Such methods have been used extensively to identify spin-crossing behavior of many different compounds and reactions in organometallic chemistry.

It has to be noted that finding the MECP and SOC considerations are not sufficient when looking at the reactivity of spin-forbidden reactions. The shape of the potential energy surface is of equal importance, as demonstrated in several studies [3]. Figure 6.4 shows a few possible scenarios of reaction pathways involving species having close-lying spin surfaces. If the spin surfaces do not cross (Figure 6.4a), SSR dominates. Crossing of the potential energy surfaces after the saddle point is possible (Figure 6.4b) but does not affect the overall rate. When the potential energy surfaces cross before the saddle point (Figure 6.4c), or both before and after the saddle point (Figure 6.4d), TSR can truly affect the overall rate (provided SOC, and therewith p_{sh} , is large enough) [5].

As pointed out by Poli and Harvey, some reactions which seemingly appear to proceed at a single spin surface can be accelerated by following a TSR pathway. This is the concept of spin acceleration [3]. Spin

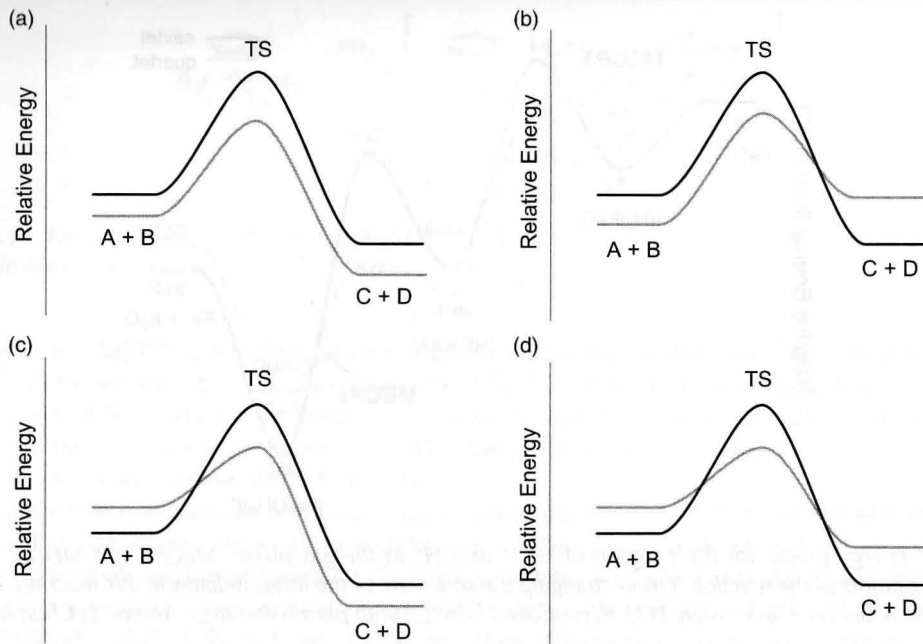


Figure 6.4 Spin-state scenarios in chemical reactions. Reproduced from [5] with permission from American Chemical Society.

acceleration can only occur with a large p_{sh} transmission factor and if the MECP occurs at a lower energy than the saddle point of the SSR transition state. In this manner a spin-state change gives access to a lower energy pathway (Figure 6.4d).

A representative example of a reaction showing TSR involves the reaction of FeO^+ with H_2 , which has been recognized in two independent studies (Figure 6.5) [10]. The reaction is overall spin-conserving. However, the sextet reactants (FeO^+ , H_2) undergo spin-crossing to a low-lying quartet transition state ($[\text{HFeOH}]^+$) (see also Chapter 8 in this book). In this case the reaction can take place in a concerted manner and bond activation is energetically less demanding [11].

6.3 Spin-State Changes in Transition Metal Complexes

During a chemical transformation of a transition metal complex (e.g., ligand association/dissociation, reductive elimination/oxidative addition or migratory insertion/elimination reaction), the coordination number and/or electron count on the metal changes. In many cases, this results in a situation where the electronic spin ground state of the educt and the product differ. Low coordinate metal complexes often have high spin, while higher coordination numbers frequently lead to low-spin complexes. Obviously, the ligand field strength as well as the steric requirements of the ligands will also have an influence on the relative stability of the high- and low-spin configurations. Therefore, one can expect that ligand association and oxidative addition reactions should proceed smoother on the low-spin surface, while ligand dissociation and reductive elimination reactions should be more facile on the high-spin surface.

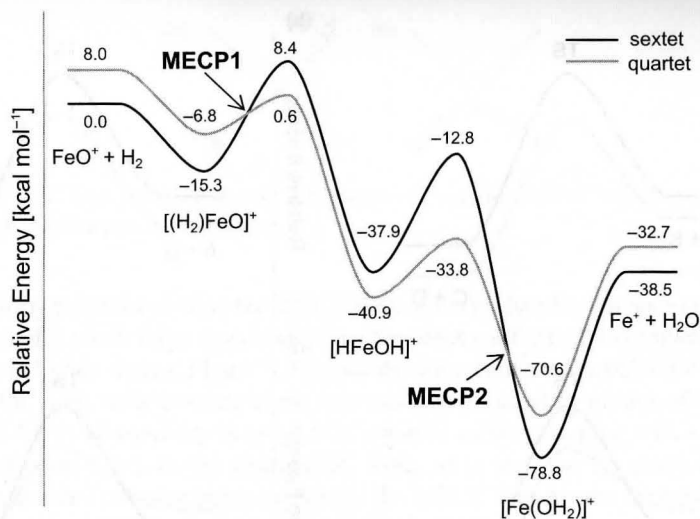
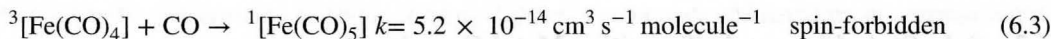
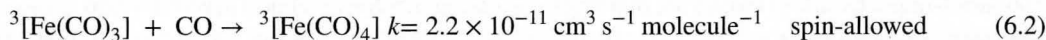


Figure 6.5 Energy profile for the reaction of FeO^+ and H_2 in the gas phase. MECPI and MECPI2 reflect the spin-crossing points of the reaction. Upon changing the spin-state of the intermediates in this reaction, a low-lying energy pathway becomes accessible [11]. Reproduced from [5] with permission from American Chemical Society.

6.3.1 Influence of the Spin State on the Kinetics of Ligand Exchange

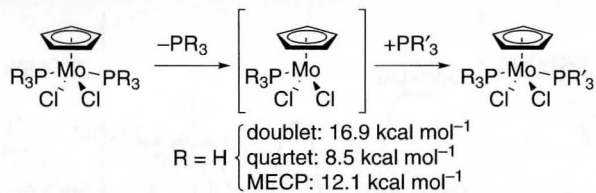
The simplest cases in which the spin state of the metal influences the reactivity are ligand exchange reactions. Addition or removal of a ligand leads to a change of the geometry around the metal and of the electron count on the metal. In general, low coordinate complexes have a higher tendency to form high-spin complexes, while coordinatively saturated species are more often low spin. Therefore, the reactants, intermediates and products formed in a ligand exchange reaction can have ground states with a different spin state. In such cases the spin-crossing that needs to occur along the reaction pathway might influence the overall kinetics of the ligand exchange, in extreme case leading to the so-called “spin blocking” effect, which occurs if the probability of surface hopping is close to zero (equation 6.1).

An illustrative example of this phenomenon is the large difference in the reaction rate constants of the addition of CO to (photo-generated) $[\text{Fe}(\text{CO})_3]$ and $[\text{Fe}(\text{CO})_4]$ in the gas phase (equations 6.2 and 6.3) [12]:



The first CO addition is spin-allowed and proceeds on the triplet surface, while the latter reaction yields a singlet product and is hence “spin-forbidden.” The rate constant of the spin-forbidden reaction was measured to be over 400 times smaller than that of the spin-allowed reaction. This reaction has been investigated computationally, and the MECPI could be located, giving a relatively good agreement with the experimental rate [13].

The change of the spin state along the reaction pathway can also have an influence on the relative rates of addition of various ligands to the transition metal center. This is illustrated by the N_2 and CO additions to $[\text{Cp}^*\text{Mo}(\text{Cl})(\text{PMe}_3)_2]$, which in both cases proceeds via a triplet-to-singlet spin-state change. CO addition to this complex is faster by three orders of magnitude than N_2 addition, while the rates of addition of these ligands to related 16 valence electron (VE) species with a singlet ground state are within the same order of magnitude [14]. According to DFT studies, the difference in relative rates are the result of a different location of the



Scheme 6.1 Fast phosphine exchange for $[\text{CpMo}(\text{Cl})_2(\text{PR}_3)_n]$ complexes ($n = 1, 2$) occurs via a doublet-to-quartet spin-state change.

spin change event (MECP) along the reaction coordinate. Due to the repulsive Mo–N₂ interaction in a triplet state, the high-barrier spin change has to occur before the Mo–N bond can be formed. In comparison with N₂, CO has more diffuse orbitals and interacts more strongly with the metal already at large Mo–C distances, resulting in the stabilization of the singlet state. This leads to an easier high-spin to low-spin transition, and as a result a lower activation barrier for CO binding [14].

The change of the spin state can lead to spin acceleration as in the case of 17 electron $[\text{CpMo}(\text{Cl})_2(\text{PR}_3)_2]$ (R=Me, Et, Ph) complexes which have a doublet ground state. These complexes show unexpectedly fast dissociative phosphine exchange kinetics [15]. DFT calculations revealed that the ligand dissociation is accelerated by a spin-state change [16]. According to this study, the ground state of the model intermediate $[\text{CpMo}(\text{Cl})_2(\text{PH}_3)]$ formed after initial phosphine dissociation has a quartet ground state which lies 8.5 kcal mol⁻¹ higher in energy than the starting complex $[\text{CpMo}(\text{Cl})_2(\text{PH}_3)_2]$ but 8.4 kcal mol⁻¹ lower than the asymptote of the doublet dissociation product. The MECP between the doublet and quartet state was located 4.8 kcal mol⁻¹ lower than the doublet dissociation asymptote, which is in accord with the observed ligand exchange rate. The SOC constant (250 cm⁻¹) was shown to be high enough to enable surface hopping close to the MECP (see Scheme 6.1). Overall, the spin-state change facilitated the ligand dissociation process by lowering the activation enthalpy compared to the spin-allowed pathway.

The occurrence of multiple spin states can be used to explain the different reactivity patterns of transition metals from the same group. Already in 1975, Brintzinger and coworkers proposed that the low stability of the CO adduct to chromocene was a result of a high spin-pairing energy for Cr upon formation of singlet $[\text{Cp}_2\text{Cr}(\text{CO})]$ [17] from triplet $[\text{Cp}_2\text{Cr}]$ [18]. The heavier analogues $[\text{Cp}_2\text{Mo}]$ and $[\text{Cp}_2\text{W}]$, which have a singlet ground state, thus form much stronger CO adducts. Analogously, the high stability of the triplet configuration of photo-generated $[\text{CpCo}(\text{CO})]$ prevents the formation of its adducts with alkanes, and hence also oxidative addition reactions of C–H bonds to the metal, while such reactivity is facile for $[\text{CpRh}(\text{CO})]$ and $[\text{CpIr}(\text{CO})]$ [19]. However, in analogy to $[\text{Cp}^*\text{Mo}(\text{Cl})(\text{PMe}_3)_2]$ [14], the more strongly binding ligand CO can trigger the spin-orbit-induced spin-crossing to the singlet state, and as a result the binding of CO to $[\text{CpCo}(\text{CO})]$ is fast. A reverse reaction – fast CO dissociation from singlet $[(\text{Tp}^{i\text{-Pr,Me}})\text{Co}(\text{CO})_2]$ to form a triplet $[(\text{Tp}^{i\text{-Pr,Me}})\text{Co}(\text{CO})]$ complex has also been reported [20]. The equilibrium reaction involves a triplet-to-singlet spin-state change, fast enough to rule out any “intrinsic” activation barrier for spin-state change. This observation showed that the reactions involving different spin multiplicities of educts and products do not always lead to “spin blocking.”

6.3.2 Stoichiometric Bond Making and Breaking Reactions

6.3.2.1 Reactivity in the Gas Phase

The first investigations leading to the development of the TSR concept were based on gas phase reactivity studies of transition metal ions with alkanes [5]. The mechanistic insight gained from these studies helped

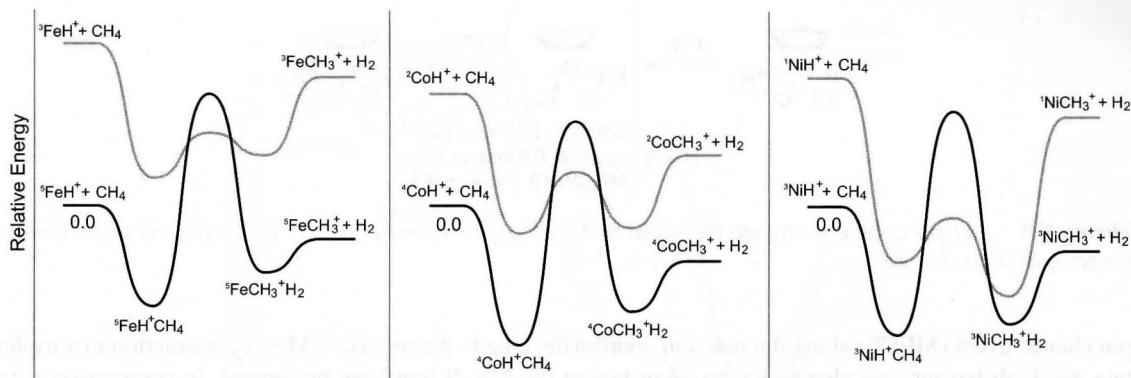
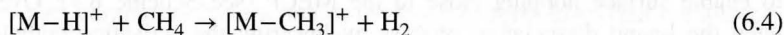


Figure 6.6 Influence of the high-spin–low-spin separation of the metal center on the rate of methane activation.

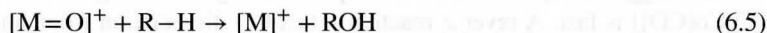
in understanding the reactivity of condensed phase systems involving a spin-state change. The gas-phase reactivity of transition metal ions toward alkanes has been extensively reviewed (see also Chapter 8 of this book), and in many of these examples two- or multi-state reactivity has been proposed [21]. Here we describe some of the representative examples.

During C–H bond oxidative addition to a transition metal, both the coordination number and the oxidation state of the metal increase. Hence, for many first row (3d) transition metal complexes, this transformation will be accompanied by a high-spin to low-spin transition, in which case the reaction follows a two-state (or multistate) pathway. In some cases, spin acceleration is observed as well. A representative example is the activation of methane by FeH^+ , CoH^+ and NiH^+ (equation 6.4):



While NiH^+ activates methane at room temperature in the gas phase, FeH^+ and CoH^+ do not [22]. DFT calculations revealed that the enthalpic barriers along the high-spin potential energy surface are prohibitively high for all three metal hydrides, but spin-crossing substantially reduces the activation barrier. As a result, these reactions are spin-accelerated. The reactivity order $\text{NiH}^+ > \text{CoH}^+ > \text{FeH}^+$ is a result of differences in the energy separation between the high- and low-spin configurations of these metals. In the case of NiH^+ , both the MECPs and the transition state of oxidative addition of methane on the low-spin PES lie below the energy of the reactants, which allows this reaction to proceed without any external activation (Figure 6.6).

The concept of multi-state reactivity also helped in the understanding of the reaction of metal oxides with alkanes, which is a model reaction, e.g. for methanol synthesis from natural gas (equation 6.5):



Two mechanistic pathways were considered: (i) hydrogen atom transfer from the alkane substrate to the oxo-ligand to form a hydroxide complex and an alkyl radical, which attacks the hydroxide ligand in a radical rebound mechanism to form the alcohol product, and (ii) insertion of the metal oxo into the R–H bond to form $[\text{R}-\text{M}-\text{OH}]$ followed by reductive elimination of the alcohol. In the first mechanism, the overall spin is conserved, while the situation in the second mechanism is more complex. Bare late transition metal ions and many of their oxides typically have a high-spin ground state, and the insertion product $[\text{R}-\text{M}-\text{OH}]$ is often low spin. Therefore, two spin-state changes can be expected along the reaction pathway associated with the alkane insertion and reductive elimination steps to form the high-spin bare metal ion and the alcohol product [5].

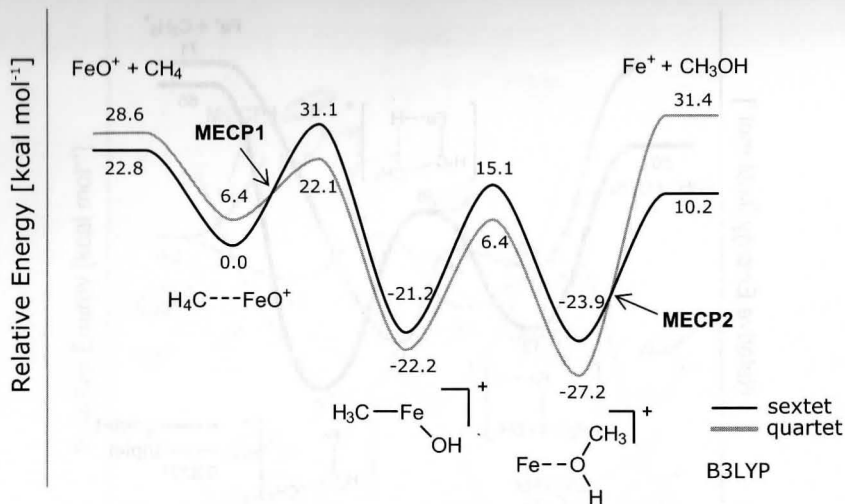


Figure 6.7 Energy profile for methane activation by FeO^+ [23].

A nice illustration of a pathway involving such TSR is the reaction of the FeO^+ cation with methane [23]. According to DFT, two spin inversions between the sextet and quartet states occur in the course of the reaction. The first change (from sextet to quartet) is prior to the four-centered transition state in which the C–H bond of methane is being broken. This significantly decreases the barrier height from 31.1 to 22.1 kcal mol^{-1} (at the B3LYP level). The final release of methanol again invokes a spin-state change, back from the quartet to the sextet surface, which decreases the energy for methanol dissociation from 57.2 to 37.4 kcal mol^{-1} (Figure 6.7). Other late transition metal oxide cations, for example CoO^+ and NiO^+ , show reactivity patterns similar to that reported for FeO^+ . Early transition metal oxides such as ScO^+ , TiO^+ , VO^+ , CrO^+ and MnO^+ have, however, low-spin ground states and as a consequence only one spin-state change takes place after reductive elimination of the alcohol.

Another gas phase reaction that helped in the understanding of how spin-state changes can lead to acceleration of a reaction is the reversible β -hydrogen transfer of the iron alkyl species $[\text{Fe}(\text{C}_2\text{H}_5)]^+$ to form the ethane hydride species $[\text{HFe}(\text{C}_2\text{H}_4)]^+$ [24]. Both compounds exist in the quintet state, while the transition state with the lowest barrier between them lies on the triplet surface (according to DFT). This transition state has an agostic interaction of the C–H bond, which requires an empty metal orbital. As such, according to DFT (B3LYP), the intermediacy of this (intermediate-spin) triplet transition structure lowered the activation energy of the β -hydride elimination by 8 kcal mol^{-1} compared to the reaction that would proceed solely on the quintet surface (Figure 6.8).

6.3.2.2 Reactivity in the Condensed Phase

The gas phase reactions described above greatly added to our understanding of “spin-forbidden” reactions in general, also to those proceeding in the condensed phase, for which substrates and products are isolable compounds. Insight into such elementary reactions is important, as they often determine the rate of a catalytic process. Spin-state changes can further be of influence on the selectivity of a reaction. For reactions proceeding on a single potential energy surface, the selectivity is typically determined by the relative heights of the transition state energy barriers leading to any accessible product (reactions involving bifurcated transition

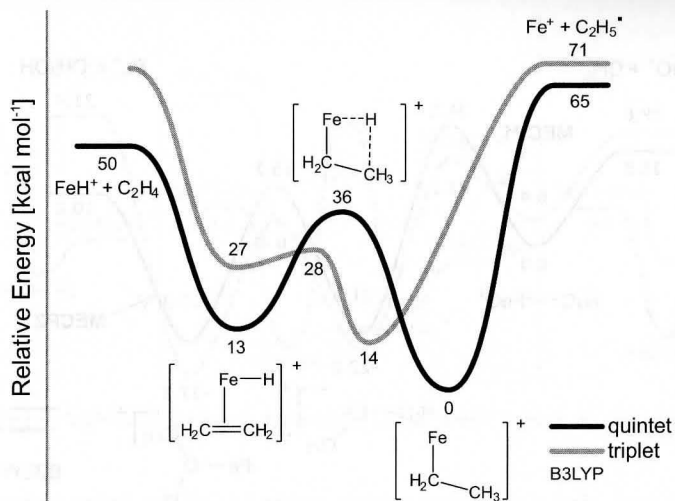


Figure 6.8 Reversible β -hydrogen transfer between $\text{Fe}(\text{C}_2\text{H}_5)^+$ and $\text{HFe}(\text{C}_2\text{H}_4)^+$.

states being exceptions [25]). However, this picture becomes more complicated when multi-state reactivity is at play, in which case not only the relative transition state barriers but also MECPs can be of influence. In the next section, some examples of synthetically relevant elementary reactions proceeding at different spin surfaces and involving spin-transitions are presented.

6.3.2.2.1 C–H Bond Activation An illustrative example showing how the relative barriers related to transition states and MECPs have an influence on product distribution of a chemical reaction proceeding in solution is the binding of ethylene to the unsaturated complex $[\text{Cp}^*\text{Ir}(\text{PMe}_3)]$. Reacting the *in situ* generated triplet species $[\text{Cp}^*\text{Ir}(\text{PMe}_3)]$ with ethylene yields two singlet products in an approximate 1:2 ratio: the ethylene adduct $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\eta^2\text{-C}_2\text{H}_4)]$ and the vinyl hydride complex $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_3)(\text{H})]$ resulting from the C–H bond activation of ethylene [26]. Thermolysis of the vinyl hydride species leads to the clean formation of the ethylene adduct $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\eta^2\text{-C}_2\text{H}_4)]$, which is the thermodynamic product and thus cannot be an intermediate in the formation of the vinyl hydride species $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_3)(\text{H})]$. Thus, the formation of the kinetic C–H addition product cannot be explained by considering only the singlet potential energy surface (PES). Extensive DFT (B3LYP) calculations on $[\text{CpIr}(\text{PH}_3)]$ model revealed that this intriguing reactivity can only be explained by considering a TSR pathway. The first intermediate, a triplet Van der Waals complex $[\text{CpIr}(\text{PH}_3)(\eta^1\text{-H-C}_2\text{H}_3)]$ can undergo a transformation into a triplet di-radical $[\text{CpIr}(\text{PH}_3)(\text{C}_2\text{H}_4)]$ species through a transition state with a lower barrier than the first MECP (MECP1) to the singlet PES. This di-radical can subsequently transform into the triplet ethylene adduct $[\text{CpIr}(\text{PH}_3)(\eta^2\text{-C}_2\text{H}_4)]$ over a transition state with a slightly higher barrier than the second MECP (MECP2). PES crossing can actually occur before (MECP2) or after (MECP3) this transition state, in both cases leading to the formation of the singlet ethylene adduct $[\text{CpIr}(\text{PH}_3)(\eta^2\text{-C}_2\text{H}_4)]$ via a lower barrier process than its formation from vinyl hydride species $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{C}_2\text{H}_3)(\text{H})]$ on the singlet surface. The kinetic product distribution is therefore determined by the relative barriers of the transition states at the triplet surface, combined with the barriers for PES crossing over the MECPs to the singlet products (Figure 6.9) [27].

Another example of a C–H activation reaction involving multistate reactivity is the activation of arenes by $[\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}]$ [28]. This complex was shown to activate the C–H bonds of benzene, furan, thiophene, thiazole and 2-methylfuran through sigma-bond metathesis. DFT (M06) calculations revealed that

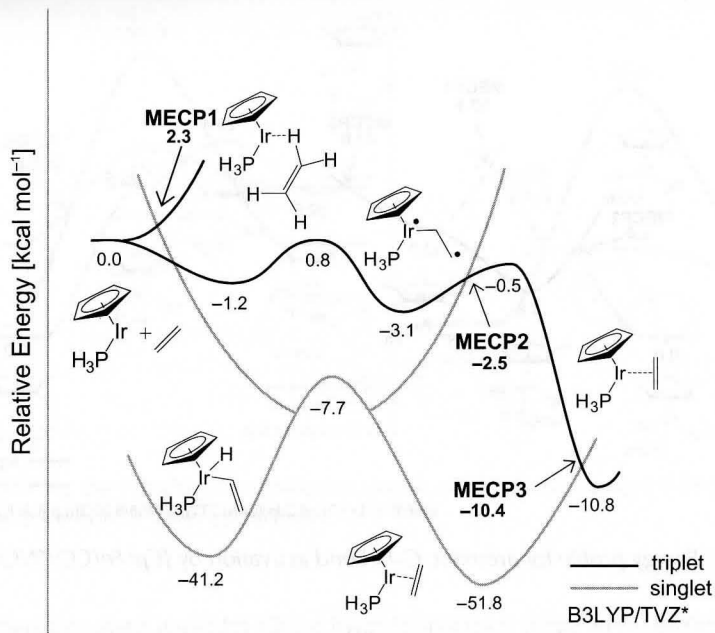


Figure 6.9 The products distribution in the reaction of triplet $[\text{CpIr}(\text{PH}_3)]$ with ethylene is determined by both the transition state barriers at the triplet surface and the MECs connecting the triplet and singlet PES. Reproduced from [27] with permission from John Wiley & Sons.

the initial dissociation of the acetonitrile ligand is spin-forbidden and two pathways leading to the triplet $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$ intermediate were found (Figure 6.10). In the first pathway, the dissociation of MeCN occurs first, which leads to a high energy ($\Delta H = 27.1 \text{ kcal mol}^{-1}$) singlet species $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$, followed by a spin-state change to triplet $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$ over MECP1. In the second pathway, the spin change over MECP2 occurs during partial dissociation of MeCN, with further dissociation leading to the formation of triplet $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$. The second pathway has a calculated barrier of only 9 kcal mol^{-1} , leading to a triplet species with a weakly bound MeCN adduct, which is π -coordinated. Subsequent loss of MeCN is only slightly endergonic, producing the triplet $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$ species. The η^2 -C–H-coordinated benzene complex formed prior to the actual C–H activation event has a singlet state; therefore, another spin-crossing step is required for the reaction to proceed. This can proceed either by the conversion of triplet $[\text{Cp}^*\text{Fe}(\text{CO})\text{Ph}]$ to singlet via MECP1 followed by coordination of the aromatic substrate, or through an intersystem crossing along with benzene coordination through MECP3. The latter route is calculated to be lower in energy and therefore most likely to occur. Finally, the C–H bond cleavage occurs via a four-centered sigma-bond metathesis-type pathway, which leads to the release of benzene. According to the calculations, the rate-limiting step is the sigma-bond metathesis between the phenyl-iron complex and the arene (which is in accord with the observed kinetic isotope effect), therefore the spin-crossing does not seem to have a major influence on the rate (or the kinetic isotope effect) in this case.

6.3.2.2.2 β -hydride Elimination Fast β -hydride elimination reactions typically require the presence of both an empty and a doubly filled d-orbital. Therefore, this process is formally “spin-forbidden” for high-spin alkyl complexes with more than five d-electrons. Hence, high-spin metal-alkyls should be more stabilized compared to their low-spin analogues. This theory allowed the isolation of some remarkably stable high-spin

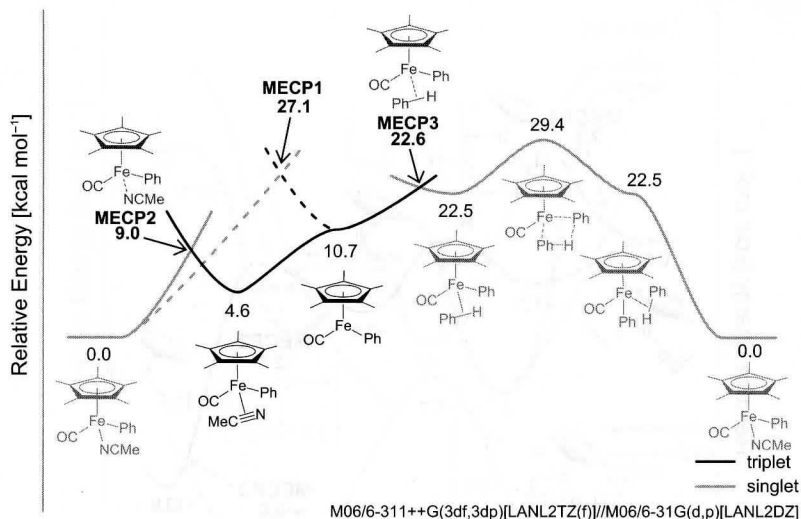
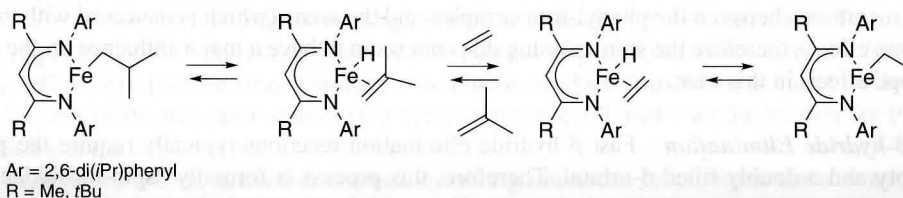


Figure 6.10 Energy profile for aromatic C–H bond activation by $[Cp^*Fe(CO)(NCMe)Ph]$ [28].

manganese(II)-alkyls containing β -hydrogen atoms [29], and proved to have a large impact on catalyst design. The spin-forbiddenness of β -hydride elimination is a likely factor in lowering the chain-transfer rate of olefin polymerization reactions catalyzed by paramagnetic, high-spin iron or cobalt complexes compared to related diamagnetic palladium(II) or nickel(II) catalysts [30], and as a result, higher linearity of polyethylene and longer polymer chains could be obtained. However, this does not always need to be the case, and facile, reversible β -hydride elimination at high-spin iron(II) centers of β -diketiminate complexes has been reported (Scheme 6.2) [31].

In order to get a better understanding on the factors that govern the β -hydride elimination reactions on high-spin metal centers, detailed DFT (B3LYP) calculations were performed on the model iron and cobalt β -diketiminate complexes [32]. In agreement with the experiments, the iron alkyl and the iron alkene hydride species were found to be most stable in the high-spin (quintet) state. For the iron species, both quintet and triplet β -hydrogen elimination transition states that lead to the C–H bond breaking and Fe–H bond formation were found. The triplet transition state was found to be lower than the respective quintet transition state by $10.7 \text{ kcal mol}^{-1}$, which pointed to a mechanism involving the spin-crossing. The first MECP ($16.6 \text{ kcal mol}^{-1}$) lies $2.4 \text{ kcal mol}^{-1}$ lower than the triplet transition state (Figure 6.11). The mechanism involves rotation about the Fe–C bond to form a planar complex featuring an agostic C–H interaction that is favorable on the triplet surface, while on the quintet surface, this interaction is repulsive. The vacant orbital (depopulated during the spin-crossing) accepts the electrons from the β -hydride moiety, leading to the formation of the Fe–H bond.



Scheme 6.2 Alkyl group exchange on β -diketiminate iron(II) complexes.

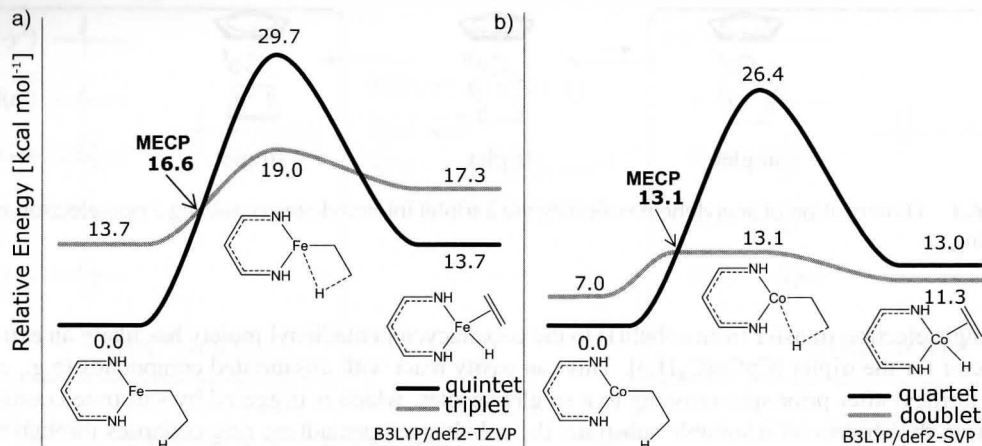


Figure 6.11 (a) MECP for the β -hydrogen elimination step in diketiminate-supported iron–ethyl complexes and (b) diketiminate-supported cobalt–ethyl complexes [32].

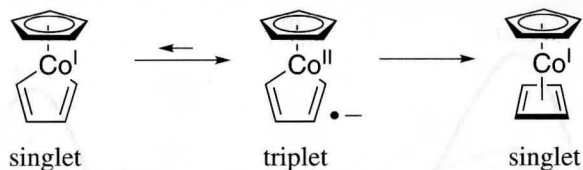
After crossing the transition state, a quartet alkene hydride species is formed (the second MECP has not been calculated), which has a high ($13.7 \text{ kcal mol}^{-1}$) energy compared to the iron alkyl species, which is in accord with the fact that the alkene hydride species has not been experimentally observed. This spin acceleration for β -hydrogen elimination is in agreement with the gas-phase reactivity of $[\text{Fe}(\text{C}_2\text{H}_5)]^+$ reported by Fiedler and coworkers [24]. In addition, the calculations revealed that with increasing steric bulk of the diketiminato ligand, the ability of the complex to form a square-planar intermediate decreases, which results in lower rates for β -hydride elimination. This reaction is a clear example of spin acceleration. Quite similar results were described for some high-spin pyridinediimine-supported Fe complexes [33].

The authors arrived at similar conclusions regarding the spin-state change for the diketiminate-supported cobalt–ethyl complexes (Figure 6.11b). The reaction proceeds via a low-spin (doublet) planar transition state starting from a high-spin (quartet) ground state. The MECP has a similar barrier as the transition state, and according to the calculations, the resulting alkene hydride species remains on the doublet surface.

In addition, DFT calculations on the tris-pyrazolylborate alkyl iron species, $[\text{Tp}^{(\text{iPr}, \text{iPr})}\text{FeEt}]$ and $[\text{Tp}^{(\text{tBu}, \text{Me})}\text{FeEt}]$, which are not prone to β -hydrogen elimination reaction, were performed. The inertness of these complexes was explained by the high steric bulk of the ligand which hampers the formation of the low-spin intermediate with agostic bonding. These observations obviously challenge the true “spin-forbiddenness” of β -hydride elimination reactions for high-spin alkyl complexes with more than five d-electrons.

6.3.3 Spin-State Situations Involving Redox-Active Ligands

All the above examples of spin-crossing occurring during a chemical transformation dealt with changing the spin configuration of the transition metal. However, when the metal- and ligand-based orbital energies are similar, the spin-state change can in principle also be accompanied with electron transfer from the metal to the ligand (or vice versa), giving access to ferro- or antiferromagnetic coupling between the unpaired electrons at the metal and those on the ligand. Such behavior has been recognized by Xu and co-workers for the triplet cyclopentadienyl cobaltacyclopentadiene complex $[\text{CpCo}(\text{C}_4\text{H}_4)]$, which is an active species in acetylene oligomerization (see also Section 6.4) [34].



Scheme 6.3 Dimerization of acetylene proceeding via a triplet intermediate containing a one-electron-reduced carbon ring.

The single electron transfer from cobalt(I) to the cobaltacyclopentadienyl moiety has likely an extra stabilizing factor for the triplet $[\text{CpCo}(\text{C}_4\text{H}_4)]$. This can easily react with unsaturated compounds (e.g., alkynes, alkenes, nitriles) after prior spin-crossing to a singlet species, which is triggered by substrate coordination. However, in the absence of a suitable substrate, the cobaltacyclopentadiene ring collapses through a triplet transition state to form a cyclobutadiene species $[\text{CpCo}(\eta^4\text{-C}_4\text{H}_4)]$, which is the most stable species in its singlet configuration [34]. The involvement of redox non-innocent ligands in altering chemical reaction pathways in organometallic chemistry and catalysis has been recognized in many cases [1, 2], but the behavior of the system displayed in Scheme 6.3 is quite unique in the sense that metal to ligand electron transfer is coupled with spin switching.

There are also situations in which the redox active ligand prevents the occurrence of spin-crossing, leading to kinetic stabilization of a reactive intermediate. In this case, locating an unpaired electron on a light element (e.g., oxygen) which has a low SOC prevents the spin-crossing. An example is the gas-phase reactivity of $[\text{Ni}^{\text{III}}(\text{H})(\text{OH})]^+$. This compound activates methane under thermal conditions to form $[\text{Ni}^{\text{III}}(\text{CH}_3)(\text{OH})]^+$ and H_2 . Notably, the low-energy doublet state (which at the CASSCF level has a 12–17 kcal mol⁻¹ lower energy than the quartet state) [35] is not responsible for this reactivity as it undergoes reductive elimination of water to form $[\text{Ni}^{\text{I}}(\text{OH}_2)]^+$, which is inert toward methane [36]. The calculated activation pathway occurs via the quartet state, which needs to have a sufficiently long lifetime to react. The calculated MECF has a geometry very similar to the one of the quartet state and has an energy which is only 0.3–1.1 kcal mol⁻¹ higher (depending on the method used). This suggests that the kinetic stabilization of the quartet versus doublet state is not energy based. The calculated SOC constants of the quartet and doublet states was found to be 16.8 and 8.0 cm⁻¹ at the CAS(11,11)/6-311+G(d,p) and CAS(13,13)/cc-pVTZ levels respectively. The SOC constant values can range from a few tens to few hundreds of cm⁻¹ for light nonmetals and reach thousands for the late first-row transition metals [9]. Analysis of molecular orbitals revealed that in the quartet state only two unpaired electrons are located on the nickel center, while the third one is located on the oxygen atom of the hydroxyl group (see also Chapter 8 of this book). Thus, the electronic structure of the quartet species is best described as a one-electron-reduced nickel center coordinated to a hydroxyl radical $-^4[\text{Ni}^{\text{II}}(\text{H})(\text{OH}^\bullet)]^+$. As a result, a direct spin-flip to the doublet $^2[\text{Ni}^{\text{III}}(\text{H})(\text{OH})]^+$ configuration is not feasible due to the electronic state mismatch and the low SOC constant of oxygen. An alternative spin-crossing pathway in which the spin-crossing proceeds on the nickel center (forming a doublet excited state $^2[\text{Ni}^{\text{II}}(\text{H})(\text{OH}^\bullet)]^+$, which could relax to the ground state doublet species $^2[\text{Ni}^{\text{III}}(\text{H})(\text{OH})]^+$) proceeds via an MECF that has energy high enough to significantly retard the spin-crossing, despite the much higher SOC constant of the nickel atom (Figure 6.12). This means that the $^4[\text{Ni}^{\text{II}}(\text{H})(\text{OH}^\bullet)]^+$ species cannot easily relax to the doublet ground state via a simple spin-state change, giving it a long enough lifetime to activate small molecules (see also Figures 6.2 and 6.3).

A “non-organometallic” example in which redox active ligands facilitate overcoming a spin-transition is the “spin-forbidden” reaction of PPh_3 with O_2 , catalyzed by a rhenium(V) complex that in the process does not seem to change the oxidation state of the metal. Rhenium complexes are powerful oxo-transfer reagents [37]. However, closed-shell rhenium complexes do not easily react with triplet oxygen, probably due to the

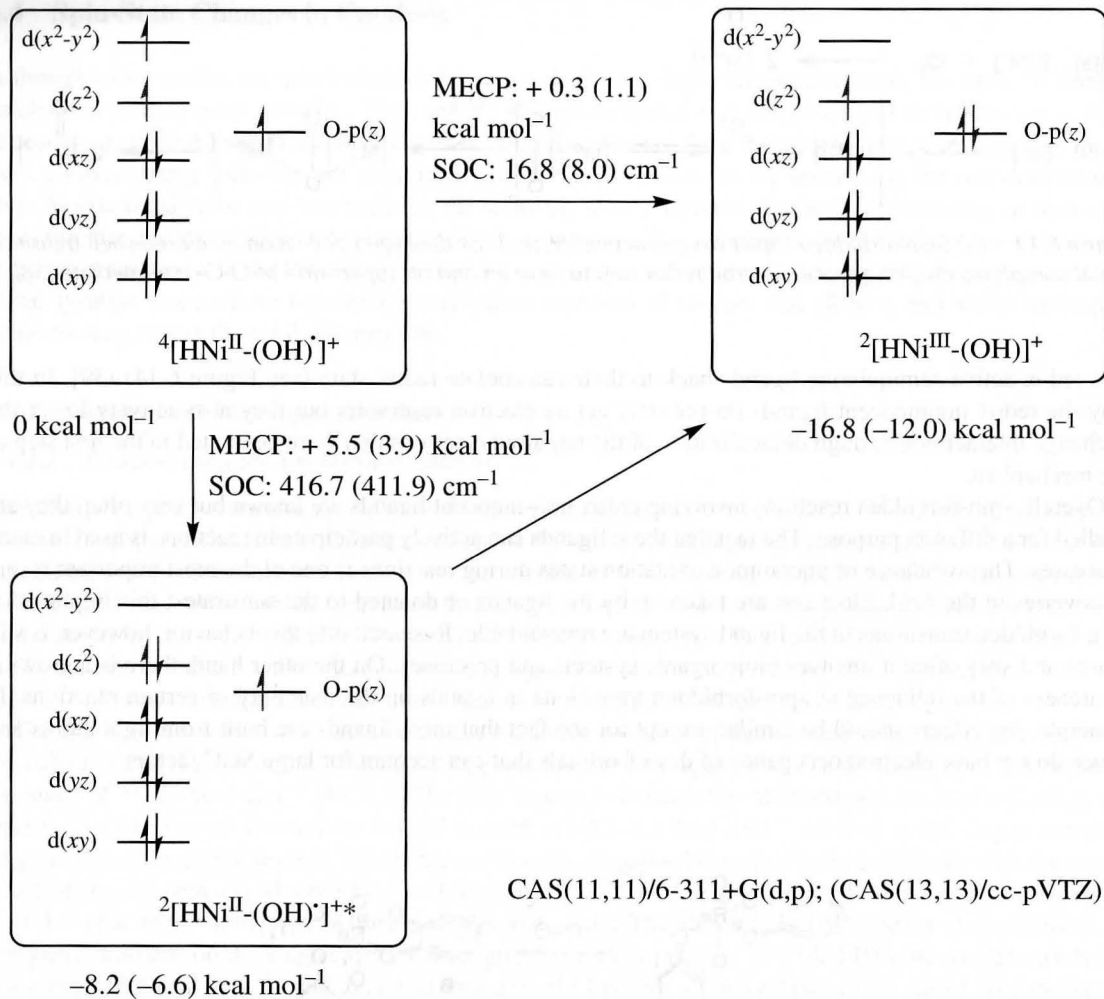


Figure 6.12 Stabilization of the high-spin hydroxyl-radical species $^4[\text{Ni}^{\text{II}}(\text{H})(\text{OH})]^+$ by virtue of the low SOC constant of the oxygen atom [35]. (See colour plate section)

spin-forbidden nature of this reaction (Figure 6.13a), and therefore mostly oxidants other than O_2 are used as the oxygen atom sources. Other closed-shell metal complexes (e.g., Pd, Rh, Ru) have been reported to react with oxygen, circumventing the “spin-forbidden” nature of the reaction by undergoing a one-electron redox step to form an end-on superoxo $\text{M}-\text{O}-\text{O}\cdot$ intermediate [38]. Subsequent homolysis of the $\text{O}-\text{O}$ bond then gives rise to the metal-oxo compound (Figure 6.13b). Closed-shell d^2 $\text{Re}(\text{V})$ complexes have the tendency to react via a two-electron process (rather than one-electron process) and the formation of a superoxide $\text{M}-\text{O}-\text{O}\cdot$ intermediate is deemed unlikely. However, the redox active catechol ligands bound to the Re complex can facilitate the reaction by delivering the required electrons for O_2 reduction in two consecutive one-electron processes oxidizing two catechol ligands to semi-quinone ligands and reducing O_2 to peroxide via a superoxide intermediate while the metal stays in the +5 oxidation state. Only in the subsequent $\text{O}-\text{O}$ breaking step, the redox equivalents of the two metal are used, reducing the peroxide to two oxo fragments and the

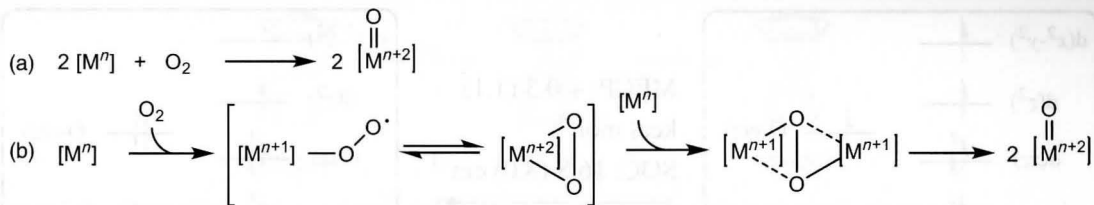


Figure 6.13 (a) Spin-forbidden triplet oxygen activation and (b) di-oxygen activation by closed-shell transition metal complexes involving a one-electron redox step to form an end-on superoxide $M-O-O\cdot$ intermediate [38].

two redox active semiquinone ligands back to their catechol redox state (see Figure 6.14) [39]. In this way the redox noninnocent ligands do not only act as electron reservoirs but they also actively lower the exchange interactions through delocalization of the unpaired electrons that were generated in the first step of the mechanism.

Overall, spin-forbidden reactions involving redox non-innocent ligands are known but very often they are studied for a different purpose. The fact that these ligands can actively participate in reactions is used in many processes. The avoidance of uncommon oxidation states during reactions is one of the most important recent discoveries in the field. Electrons are taken up by the ligands or donated to the substrates; this implies that spin-forbidden transitions in the ligand system are unavoidable. Research into this behavior, however, is still scarce and very often it involves bioinorganic systems and processes. On the other hand, there is a growing awareness of the influence of spin-forbidden transitions in ligands on the reactivity of certain reactions. In principle, the effects should be similar, except for the fact that most ligands are built from light atoms and hence do not have electron occupancy of d- or f-orbitals that can account for large SOC factors.

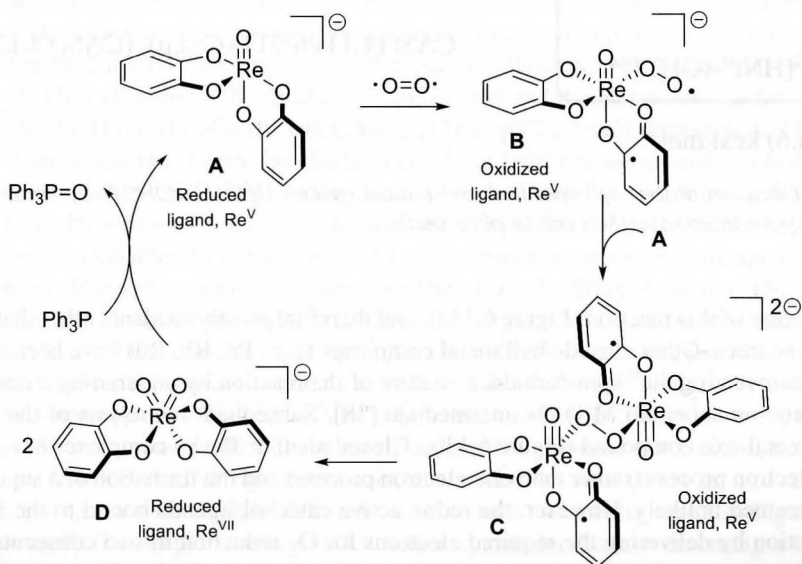


Figure 6.14 Triplet oxygen activation by catechol ligands allowing Re to stay in its stable +5 oxidation state [39]. Reproduced from [1c] with permission from American Chemical Society.

6.4 Spin-State Changes in Catalysis

Although most studies on spin-forbidden reactions deal with single elementary steps, the topic of TSR in catalysis is gaining more attention. The growing field of computational chemistry and methods such as DFT especially provide the right tools to study more complex systems. Spin-forbidden elementary steps can introduce a lower energy pathway and sometimes spin-forbidden processes are involved in the rate-determining step. As discussed in the previous sections, the relatively slow β -hydride elimination proceeding on high-spin transition metal centers rendered paramagnetic first-row transition complexes good catalysts for olefin polymerization reactions. In the following section we will discuss examples of homogeneous first-row transition metal systems that catalyze (cyclo)oligomerization reactions of alkynes and alkenes, and which undergo a spin-crossing during the catalytic turnover.

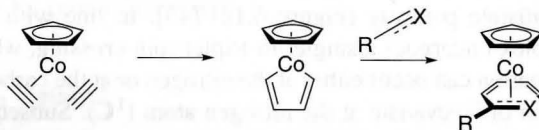
6.4.1 Catalytic (Cyclo)oligomerizations

6.4.1.1 Cobalt-Catalyzed Cyclotrimerizations

The CoCp system is effective in cyclotrimerization of alkynes with unsaturated compounds (e.g., alkynes, alkenes, cyanides; Scheme 6.4). The importance of the spin-state change during these catalytic reactions was first addressed by Dahy and co-workers in the context of trimerization of acetylene [40]. They presented DFT (B3LYP) calculations which revealed that the reaction of a triplet cobaltacyclopentadiene complex with acetylene to form a triplet cobalt η^6 -benzene complex proceeds via a low-lying singlet transition state with easily accessible MECPs. In follow-up studies, Agenet et al. investigated the TSR pathways for both the [2 + 2 + 2] cyclotrimerization of alkynes [41] and the coupling of two alkynes with alkenes [42].

The first spin-crossing event occurs after the oxidative coupling of the two acetylene molecules bound to the cobalt center (Figure 6.15). This coupling proceeds on the singlet surface with energies of activation in the range of 11–13 kcal mol⁻¹ [40, 42]. The thus formed cobaltacyclopentadiene species [CpCo(C₄H₄)] (**B**) relaxes to a triplet state through an MECP located at ~0.1–1.1 kcal mol⁻¹ relative to the singlet complex (depending on the method used). This behavior was also described for substituted acetylenes with the triplet states being energetically favored by 13–16 kcal mol⁻¹ and the MECPs leading to them being in the range of 0–1.3 kcal mol⁻¹ compared with the singlet state [41]. The subsequent Diels–Alder cyclo-addition of acetylene proceeds on the singlet surface through a barrierless process. The MECP to the singlet state has a low energy (6.5 kcal mol⁻¹), and the thus formed singlet benzene adduct relaxes to the triplet state through a very low-energy MECP (Figure 6.15).

The reaction of the [CpCo(C₄H₄)] species with ethene proceeds via a seven-membered metallocyclic intermediate (**D**), which is accessed on the singlet surface (Figure 6.16). The reductive elimination was found to proceed on the triplet surface, leading to the formation of a cyclohexadiene cobalt complex [CpCo(C₆H₈)] (**E**) which relaxes to the singlet state through a low-energy MECP (**MECP5**). The relatively easy crossing from the singlet to the triplet surface (**MECP3**) of the metallocycle **D** prevents the formation of a singlet complex **G** with agostic C–H interaction which could undergo β -hydride elimination, leading to the formation of hexatriene as a side product [42]. This study clearly shows that the spin-crossing pathway allows a



Scheme 6.4 Cyclotrimerization of acetylene and other unsaturated compounds catalyzed by CoCp.

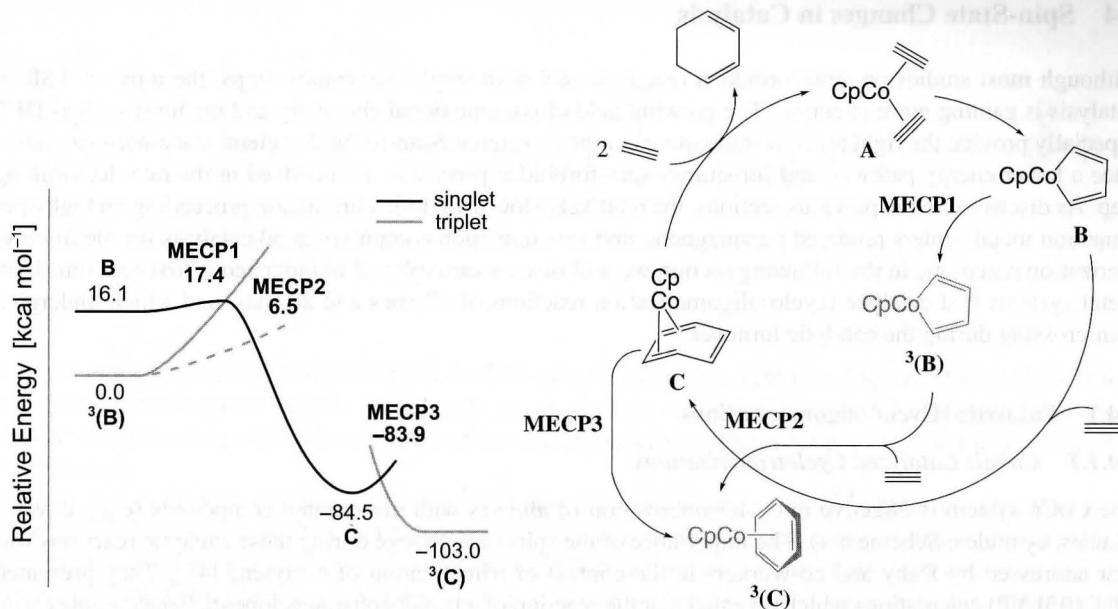


Figure 6.15 Mechanism of cyclopentadiene cobalt-catalyzed trimerization of acetylene.

smooth sequence of elementary steps, in which the species alternates between different spin surfaces. The coordination of alkene requires a low-spin configuration, while the transition to the high-spin configuration favors reductive elimination of the cyclic product over β -hydride elimination (see Section 6.3), which would lead to a linear product (Figure 6.16).

The cyclopentadienyl cobalt system is also a powerful catalyst for the synthesis of substituted heterocycles. Dahy and co-workers studied computationally the reaction of the cobaltacyclopentadiene with nitriles [43, 44] and found that in this case the most favorable mechanism involves multistate reactivity pathways.

Addition of acetonitrile has a mechanism similar to the addition of acetylene, that is, it proceeds via a cyclo-addition mechanism proceeding on a singlet surface (through an easily accessible MECP from triplet surface). In the first step, the acetonitrile molecule coordinates with the singlet metal center. The formation of the η^4 -coordinated 2-methylpyridine complex is followed by another spin-crossing to form the η^6 -coordinated species (Figure 6.17, left).

Electron withdrawing groups (H, CF_3) have a strong influence on the C–C bond-forming step proceeding on the singlet surface. A seven-membered azacobaltacycloheptatriene ring is formed, analogously to the reaction of the cobaltacyclopentadiene with olefins. Reductive elimination of the pyridine can proceed on both low- and high-spin surfaces. The final product is a triplet cyclopentadienyl cobalt pyridine complex (Figure 6.17, right).

The formation of a pyridin-2-one cobalt complex from cobaltacyclopentadiene and isocyanate was also shown to proceed via a multistate pathway (Figure 6.18) [45]. In line with the previously investigated mechanisms, the cobalt complex undergoes a singlet-to-triplet spin-crossing, which allows for coordination of the isocyanate. The coordination can occur either at the nitrogen or at the carbon atom. The most favorable pathway involves coordination of isocyanate at the nitrogen atom (^1C). Subsequently, the coordinated isocyanate inserts into the cyclopentadiene-metallacycle, forming a bicyclic intermediate (^1D), which can rearrange to two different intermediates: a triplet metallacycle (through a rather high-energy MECP), in which

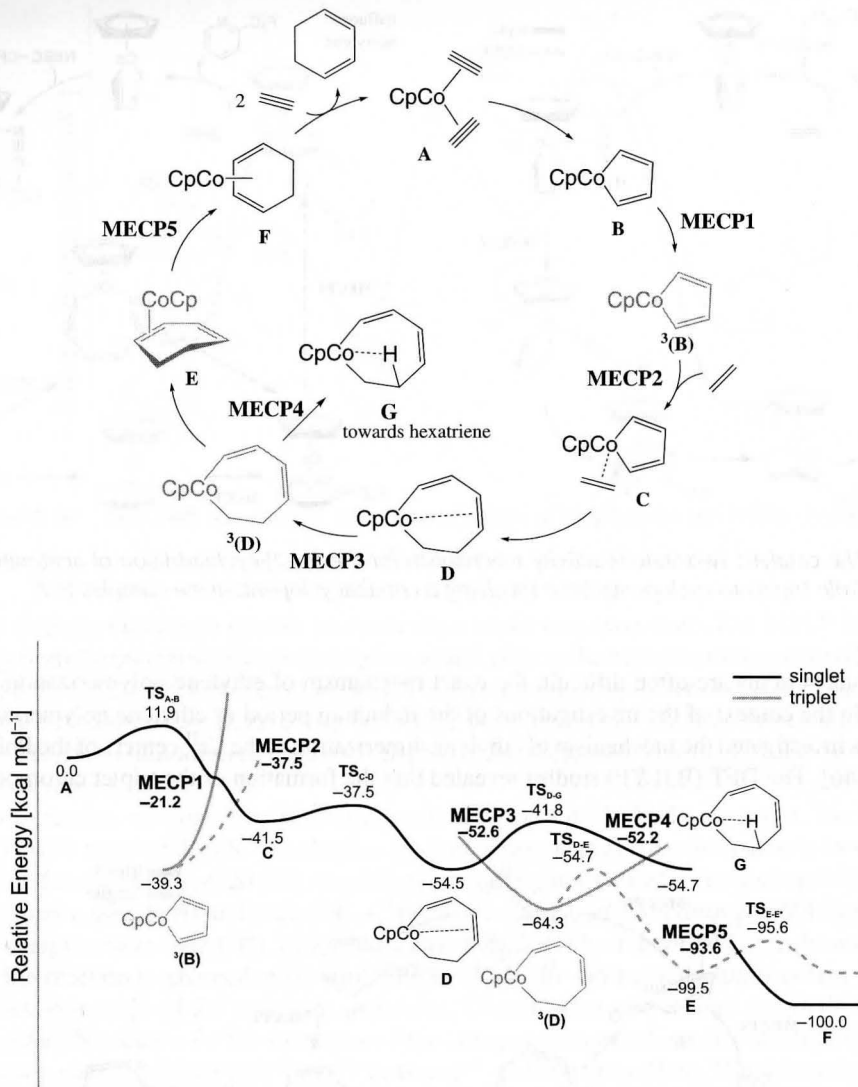


Figure 6.16 Mechanism of cyclopentadiene cobalt-catalyzed co-oligomerization of ethylene with acetylene.

isocyanate is incorporated (^3E), or a singlet η^4 -coordinated pyridin-2-one complex (^1G), which undergoes a spin-crossing to form the triplet η^2 -coordinated species (^3H). The former pathway involves spin-crossing before the intermediate is formed. The latter pathway is the most favorable one and it shows spin-crossing to take place as a driving force for product formation.

6.4.2 Phillips Cr(II)/SiO₂ Catalyst

The Phillips catalyst is one of the most important industrial catalysts for polyethylene production. Several mechanisms of the initiation steps have been proposed for this catalyst, and since the operando investigations

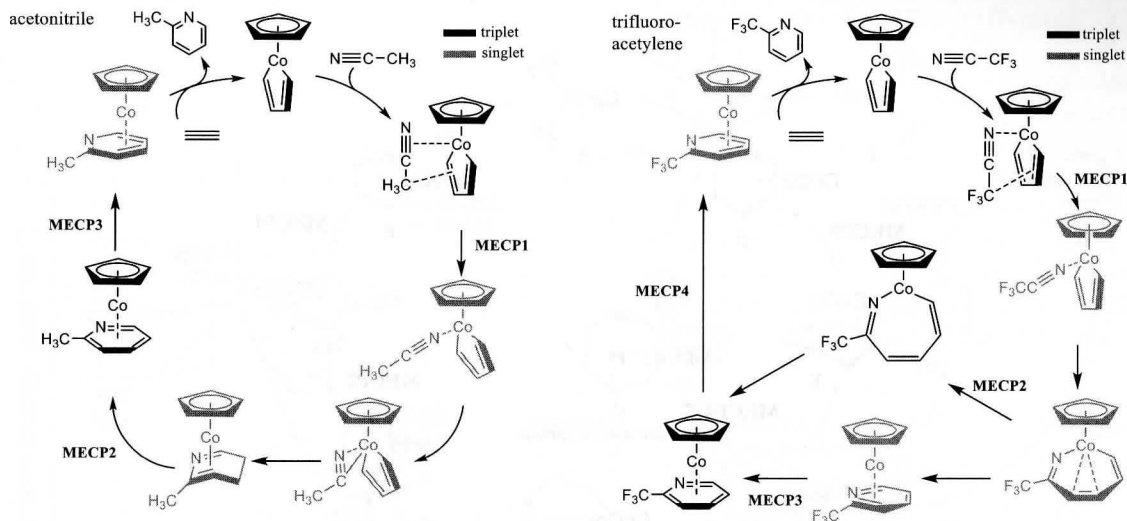


Figure 6.17 The catalytic two-state reactivity mechanism for the [4+2]-cycloaddition of acetonitrile (left) and trifluoroacetonitrile (right) to cyclopentadiene involving a cobaltacyclopentadiene complex [44].

of heterogeneous systems are often difficult, the exact mechanism of ethylene polymerization still remains under debate. In the context of the investigations of the induction period of ethylene polymerization, Zhong and co-workers investigated the mechanism of ethylene dimerization at the Cr^{II} centers of the Phillips catalyst (Figure 6.19) [46]. The DFT (B3LYP) studies revealed that the formation of the triplet chromocyclopentane

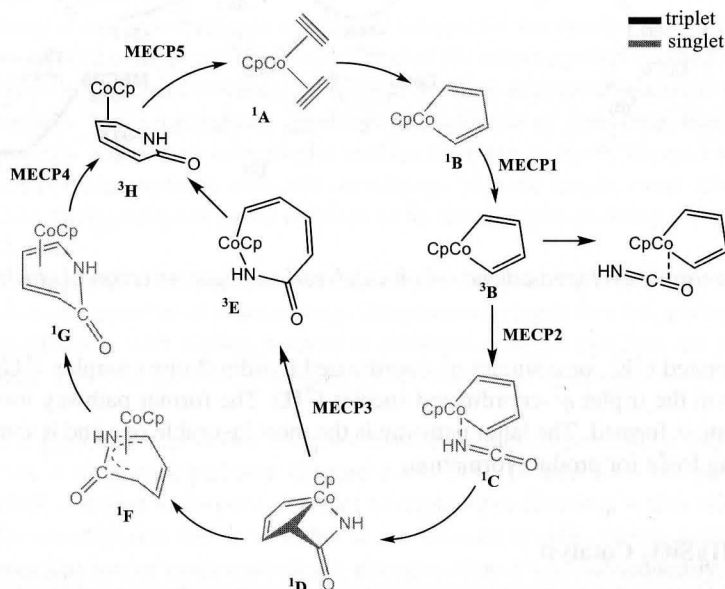


Figure 6.18 Catalytic cycle in the formation of pyridin-2-one by the CpCo catalyst [45].

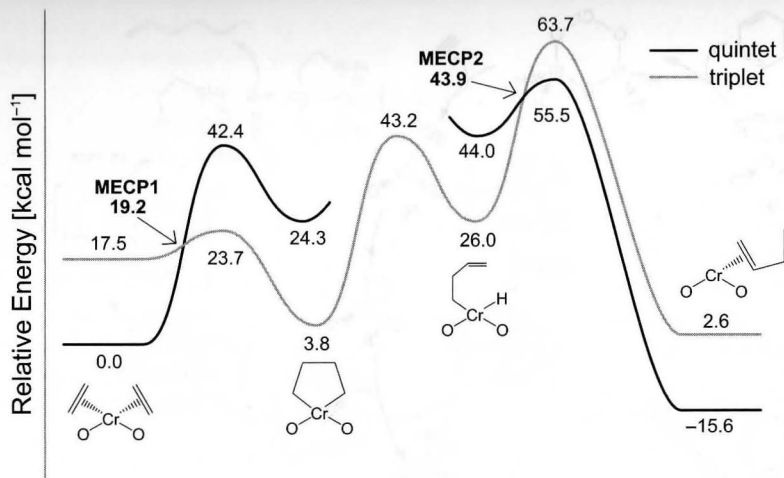


Figure 6.19 Two-state reactivity in the oligomerization of ethylene by the Phillips catalyst [46].

from quintet diethene chromium species proceeds via a triplet transition state. The MECP (23.7 mol^{-1}) for spin-crossing from the quintet surface to the triplet surface, prior to the triplet transition state ($19.2 \text{ kcal mol}^{-1}$) is associated with a relatively low-energy penalty. The rate-limiting step of reductive elimination of 1-butene is also facilitated by a spin-state change with the MECP ($43.9 \text{ kcal mol}^{-1}$) located before the transition state. The calculated barrier is thus lowered from 63.7 (triplet) to $55.5 \text{ kcal mol}^{-1}$ (quintet), but the overall calculated barrier remains very high.

A related mechanism was found for trimerization of acetylene with the Phillips catalyst. The DFT-computed (modified B3PW91 functional with 28% Hartree–Fock exchange energy) reaction pathway involves spin-state changes and is shown in Figure 6.20 [47]. Coordination of acetylene to the Cr^{II} center results in the formation of the adduct with a quintet ground state ($^5\text{A} \rightarrow ^5\text{B}$). A spin-state transition through a $9.4 \text{ kcal mol}^{-1}$ MECP to a (higher energy) triplet state (^3B), which has a structure that is best described as a chromocyclopropene. This allows the reaction to proceed at the triplet PES, which has substantially lower energy barriers for the subsequent insertion steps of the acetylene molecules. Coordination of a second acetylene molecule to the chromium center (^3C) allows for the formation of the chromocyclopentadiene intermediate (^3D) over a low-energy transition state ($12.5 \text{ kcal mol}^{-1}$ vs. 27 kcal mol^{-1} on the quintet PES). The third acetylene binds via hydrogen bond formation with the oxygen atom bound to chromium (^3E) and undergoes a $[4 + 2]$ cycloaddition to metallacycle. The final steps involve spin-crossing back to the quartet PES ($^3\text{F} \rightarrow ^5\text{F}$), followed by elimination of benzene, completing the catalytic cycle.

Similar pathways were disclosed for cyclotrimerization of methylacetylene over the same $\text{Cr}(\text{II})$ -catalyst [48], suggesting that spin-crossing mechanisms might be quite general in C–C bond forming reactions with Phillips catalysts.

6.4.3 SNS– CrCl_3 Catalyst

The SNS– CrCl_3 –MAO catalyst system (SNS= $\text{EtS}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{SEt}$, MAO=methylaluminoxane) can trimerize ethylene to 1-hexene with high activity and selectivity. Although the structure of the actual catalyst and the oxidation state of the chromium center are still under debate, a computational study (B3LYP) by

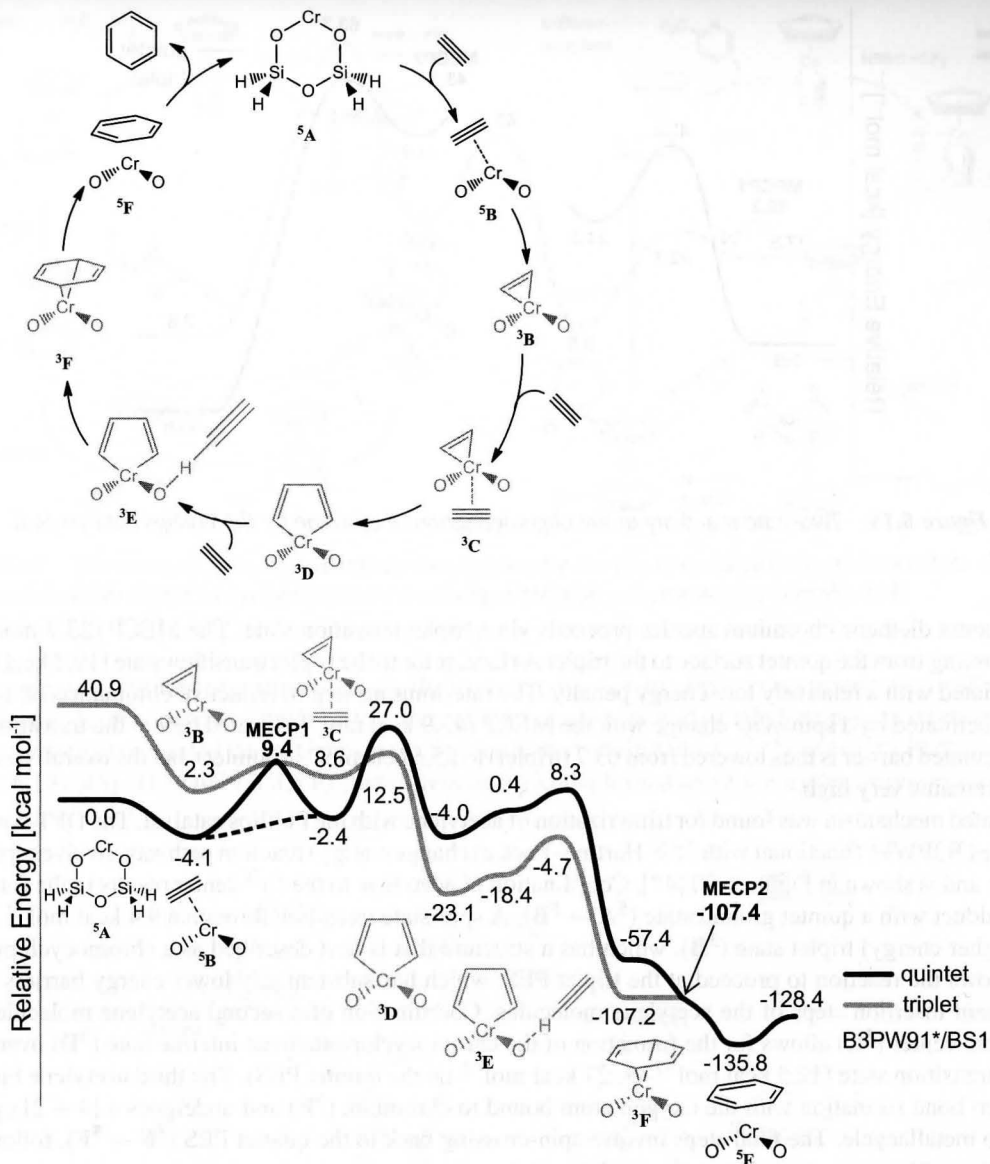


Figure 6.20 The most feasible reaction profile for the cyclotrimerization of acetylene by the Cr(II)/SiO₂ cluster model [47].

Yang and co-workers suggests that this system is another important example of spin acceleration in catalysis [49].

The putative [Cr^I(SNS)(C₂H₄)]⁺ species [under the experimental conditions, containing an excess of MAO, deprotonation of the ligand NH moiety might actually occur, see ref. 50] coordinates another ethylene molecule to form a high-spin (sextet) diethylene complex. The coupling of the two ethane moieties to form the chromocyclopentane intermediate has a prohibitively high barrier on the sextet PES (38.4 kcal mol⁻¹).

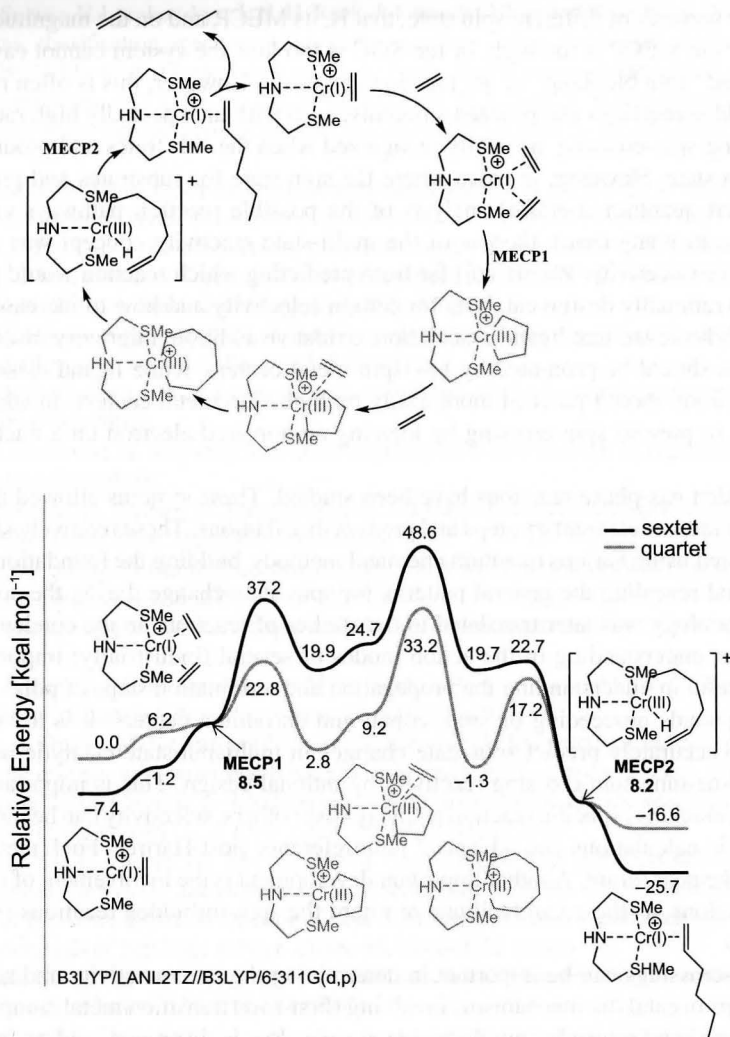


Figure 6.21 The lowest energy pathway for the trimerization of ethylene with the SNS-CrCl₃ catalyst involves spin-state changes between the sextet and quartet surfaces.

However, a low-energy MECP allows for a change to a quartet PES, which lowers the effective barrier to 24.0 kcal mol⁻¹. The subsequent coordination of a second ethylene followed by insertion into one of the Cr-C bonds yields a chromocycloheptane intermediate which transforms through a quartet transition state followed by the MECP to the sextet 1-hexene-coordinated chromium species (Figure 6.21).

6.5 Concluding Remarks

In contrast to “purely” organic transformations, which involve light elements, “spin-forbidden” transitions cannot be disregarded in chemistry proceeding within the coordination sphere of transition metals. Whether the spin state can change on the course of the reaction depends on the energy of the crossing point between

two potential energy surfaces of different spin state, that is, its MECP, and on the magnitude of SOC. In cases where the energy of the MECP is too high, or the SOC is too low, the system cannot easily change its spin state and the so-called "spin blocking" of the reaction can occur. However, this is often not the case and the formally spin-forbidden reactions can proceed smoothly, even with unexpectedly high rates.

Reactions involving spin-crossing are easily recognized when the substrates and products of the reaction have a different spin state. However, in cases where the spin state for substrates and products remains the same, only a detailed quantum chemical analysis of the possible reaction pathways can confirm a spin-crossing mechanism. In many cases, the use of the multi-state reactivity concept was able to explain the unexpected kinetics or selectivity. We are still far from predicting which reaction would proceed via a spin-crossing and how to rationally design catalysts for certain selectivity and how to increase activity. The general expectations are, however, that ligand association, oxidative addition, migratory insertion and β -hydride elimination reactions should be promoted by low-spin metal centers, while ligand dissociation and reductive elimination reactions should proceed more easily on high-spin metal centers. In addition, redox-active ligands can be used to prevent spin-crossing by locating an unpaired electron on a nucleus with low SOC constant.

Many spin-forbidden gas-phase reactions have been studied. These systems allowed the identification of anomalies during the rates of elementary steps and product distributions. These relatively simple systems were thoroughly investigated using various quantum chemical methods, building the foundations for the multistate reactivity concept and revealing the general patterns for spin-state change during the course of a chemical reaction. This methodology was later translated to the studies of reactions in the condensed phase and ultimately led to a better understanding of the action modes of several (industrially) important catalysts. This proved especially useful in understanding the propagation and termination steps of poly- or oligomerization of unsaturated compounds proceeding on iron, cobalt and chromium centers. It is to be expected that we will soon be able to accurately predict spin-state changes in multispin-state catalytic reactions and to use this information to fine-tune spin-crossing reactivity by rational design. This is important, because by spin accelerating (or spin blocking) specific reaction pathways over others, selectivity can be induced. Rapid developments in relativistic calculations and advanced multireference post-Hartree-Fock methods will certainly advance the field in the near future. Another important development is the involvement of redox active ligands in spin-crossing reactions, as these can facilitate or retard the spin-forbidden reactions (which is of interest for catalysis as well).

In summary, spin-crossings can be important in determining the rate, reactivity and selectivity in crucial rate-determining steps in catalytic mechanisms involving (first-row) transition metal complexes. The assumption that reactions involving multiple spin states are always slow is disproven, and an increased awareness of importance of spin-crossing in organometallic chemistry has arisen. However, proving its existence on a mechanistic level is often complicated. DFT calculations have proven to be very efficient in investigations of possible spin-crossing reaction pathways, but more advanced computational methods should be used in the future to properly predict relative spin-state energies for which multireference systems are often required (e.g., in case of open-shell singlet systems). Future research into spin-forbidden reactions will likely be focused on more complex systems, such as full catalytic cycles and systems containing redox-active ligands. Overall, spin-state changes are very important in many commonly known reactions and their influence can, without any doubt, be used in the future to create selective and sustainable catalysts.

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