Group 9 open-shell organometallics: reactivity at the ligand

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Chapter 7

Hydrogen Atom Transfer in Reactions of Organic Radicals with (por)Co$^{II}•$ and in Subsequent Addition of (por)Co–H to Olefins*

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Chapter 7

7.1 Introduction

From the previous chapter it becomes evident that cobalt porphyrin systems can be successfully used to promote catalytic radical-type reactions of the non-innocent carbene ligand with olefins. One of the elementary steps in this reaction is the homolytic cleavage of the cobalt-carbon bond resulting in the formation of a cyclopropane. The ease of homolytic cleavage of the weak Co–C bond, resulting in reversible formation of alkyl radicals, is also the \textit{modus operandi} of the cobalamin based enzymes and this feature has been also successfully employed in polymer chemistry, opening new avenues in radical polymerizations.

Reactions of metal-centered radicals (M•) and organo-metal complexes (M–R) with oligomer radicals (•C(CH3)(X)CH2P) are implicated in several forms of controlled radical polymerization of olefins (Scheme 1).1-4

\[ \begin{align*}
(A) & \quad M^\bullet + \cdot C(CH_3)(X)R & \xrightarrow{(1) k_{comb}} & M-C(CH_2)(X)R \\
& \xrightarrow{(2) k_{p-H}} & M-H + CH_2=C(X)R \\
(B) & \quad M-C(CH_3)(X)R + \cdot C(CH_3)(X')R' & \xrightarrow{k_{ex}} & M-C(CH_3)(X)R' + \cdot C(CH_3)(X)R
\end{align*} \]

\textbf{Scheme 1.} Reactions of metal-centered radicals and organo-metal complexes with organic radicals.
(A) Reactions of organic radicals with metal-centered radicals relevant to control of radical polymerization.
(B) Exchange of organic radicals with the organic units in organo-metal complexes.

Reactions of organic radicals (•C(CH3)(X)R) with metal-centered radicals (M•) either produce an organometallic complex (M–C(CH3)(X)R) or a metal hydride (M–H) and an olefin (CH2=C(X)R) by the metallo-radical M• abstracting a \( \beta \)-hydrogen atom from the organic radical •C(CH3)(X)R (Scheme 1A).5

An additional process that may occur in this type of systems is the exchange of radicals in solution (•C(CH3)(X')R') with the organic group (•C(CH3)(X)R) in the organo-metal complex (M–C(CH3)(X)R) (Scheme 1B).6

Occurrence of these organo-radical reactions with metal complexes during the radical polymerization of a monomer such as vinyl acetate (CH2=CH(OAc); –OAc = –OC(O)Me) provides several mechanisms to attain control over the radical polymerization process. A wide range of metal-centered radicals and organo-metal complexes manifest at least a portion of the reactions shown in Scheme 1. An expanding range of transition metal species including complexes of Cr1,7 MoIII8 FeI9 V010 TiIII11 and Co II 1-4,12 have found applications in controlling radical polymerization of olefins. The best chain transfer catalysts reported so far are low spin cobalt(II) complexes4 and organo-cobalt(III) species, which function as latent storage sites for organo-radicals required to obtain living radical polymerization.1 Cobalt porphyrins reveal each of the processes shown in Scheme 1, and they are functional models to illustrate experimentally how these processes provide control over radical polymerization through both living radical polymerization and chain transfer catalysis.

Reaction of the cyanoisopropyl radical •C(CH3)2CN from AIBN (2,2’-azobisisobutyronitrile) with cobalt tetramesityl-porphyrin ((TMP)Co II•) in the presence of vinyl acetate (CH2=CH(OAc)) results in formation of transient (TMP)Co–C(CH3)2CN,13,14 and (TMP)Co–H complexes which proceed to form
Hydrogen Atom Transfer in Reactions of Organic Radicals with (por)Co

(TMP)Co−CH(OAc)CH3 as the thermodynamically favored organometallic product (equations 1-5).

\[
\text{AIBN} \rightarrow 2 \cdot \text{C(Me)}_2\text{CN} + \text{N}_2 \quad (1)
\]

\[
(\text{TMP})\text{Co}^{\text{II}}\cdot + \cdot\text{C(Me)}_2\text{CN} \rightleftharpoons (\text{TMP})\text{Co}−\text{C(Me)}_2\text{CN} \quad (2)
\]

\[
(\text{TMP})\text{Co}^{\text{II}}\cdot + \cdot\text{C(Me)}_2\text{CN} \rightleftharpoons (\text{TMP})\text{Co}−\text{H} + \text{CH}_2=\text{C(Me)}\text{CN} \quad (3)
\]

\[
(\text{TMP})\text{Co}−\text{H} + \text{CH}_2=\text{CH(OAc)} \rightleftharpoons (\text{TMP})\text{Co}−\text{CH(OAc)CH}_3 \quad (4)
\]

\[
(\text{TMP})\text{Co}−\text{P} + \cdot\text{P}^* \xrightleftharpoons[k_{\text{ex}}]{k_p} \text{m} (\text{TMP})\text{Co}−\text{P}^* + \cdot\text{P} \xrightleftharpoons[k_p]{k_{\text{ex}}} \text{m} \quad (5)
\]

These reactions precede the onset of a living radical polymerization of vinyl acetate mediated by organo-Co(TMP) complexes.\(^6\) Detailed kinetic-mechanistic studies of this reaction system provided an unusual opportunity to observe and determine rate constants for the exchange of radicals in solution with the organic groups in organometallic species like that depicted in Scheme 1B (equation 6).\(^6\)

\[
(\text{TMP})\text{Co}−\text{R} + \cdot\text{R}^* \rightleftharpoons (\text{TMP})\text{Co}−\text{R}^* + \text{R}• \quad (6)
\]

Recently, combined experimental studies and DFT calculations examining the pathway and kinetics for the exchange of radicals from solution with the organo-groups in organo-cobalt tetramesitylporphyrin ((TMP)Co−R) complexes (Scheme 1B) were reported. Rapid radical exchange is an important pathway to obtain a narrow polymer molecular weight distribution in a living radical polymerization by a degenerative transfer mechanism\(^1\) that is observed for this system.\(^9\)

In this Chapter we examine the formation of cobalt hydride, organo-cobalt complexes and mechanistic features of the hydrogen transfer processes shown in Scheme 1A and equations 2-4 using DFT to obtain more insights to controlled radical polymerization of olefins, and in particular catalytic chain transfer mediated by cobalt complexes. The relevance of these processes exceeds the chemistry of metal mediated radical polymerizations, as hydrogen atom transfer pathway can be an alternative for olefin insertion into an M–H bond, especially when no cis-vacant sites are available in the coordination sphere of the metal.

7.2 Results and discussion

7.2.1 DFT computational methods

Extensive DFT computational studies of cobalamin derivatives have illustrated that the observed Co–C bond dissociation enthalpies (BDE) and internuclear distances are better reproduced by the nonhybrid BP86 functional than by the widely used B3LYP functional.\(^{15,16}\) The hybrid B3LYP functional and related hybrid HF/DFT functionals tend to overestimate the correlation terms that stabilize open-shell species, while nonhybrid functionals like BP86 are thought to underestimate the open-shell stabilization terms. The empirical observation for the case of alkyl cobalamins\(^{15,16}\) and related cobalt porphyrins\(^6\) is that the nonhybrid BP86 functional gives the best representation of the Co–C (BDE) and that the B3LYP functional substantially underestimates Co–C BDE values because of overestimating radical stabilities.\(^{15,17}\) For these reasons we used the non-hybrid BP86 functional with the TZVP basis set on all atoms. The calculated internal energies are adjusted for zero-point energy, entropy, and
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approximately for solvent effects (see Experimental Section). The non-functionalized porphyrinato ligand (por\(^2\)-) was used as a smaller model of the experimentally used tetramesitylporphyrinato (TMP\(^2\)-) and tetraphenylporphyrinato (TPP\(^2\)-) ligands.

7.2.2 Closed-shell descriptions of radical pairs

From a strictly theoretical point of view the DFT method may not give the most precise description of radical coupling and atom abstraction reactions. *Ab initio* ROHF and MCSCF/CASSCF treatments produce results that are more easily and straightforwardly interpretable as biradical properties. In contrast, DFT describes the properties of species in terms of "equivalent non-interacting electrons", thereby excluding easy interpretation of two-electron properties such as biradical character. However, at present it is the only practical approach to study realistic models of complicated transition metal species. The broken-symmetry formalism, commonly used to describe radical reactions and properties of biradical species, generally produces very reasonable energies despite the fact that it does not correspond to pure spin states. In fact, even for cases where DFT produces a "closed-shell configuration", the actual system may still have considerable "biradical character". Therefore, we use the standard broken-symmetry approach here to calculate energy profiles, but refrain from attaching much significance to the point at which DFT switches between "closed-shell" and "broken-symmetry" solutions.

7.2.3 (por)Co–R Bond Dissociation Enthalpies (BDE) (R = H, C(CH\(_3\))\(_2\)CN, CH(OAc)CH\(_3\))

Calculated thermodynamic parameters for the homolytic dissociation of the (por)Co–R bond (equation 7) in (por)Co–H, (por)Co–C(CH\(_3\))\(_2\)CN, and (por)Co–CH(OAc)CH\(_3\) are listed in Table 1.

\[(\text{por})\text{Co} \rightleftharpoons \text{(por)Co}^{\text{II}} + \text{R} \quad (7)\]

<table>
<thead>
<tr>
<th></th>
<th>(\Delta G^\circ) (kcal mol(^{-1}))</th>
<th>(\Delta H^\circ) (kcal mol(^{-1}))</th>
<th>(\Delta S^\circ) (cal mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(por)Co–H</td>
<td>+47.2</td>
<td>+50.6</td>
<td>+11.4</td>
</tr>
<tr>
<td>(por)Co–C(CH(_3))(_2)CN</td>
<td>+4.5</td>
<td>+14.6</td>
<td>+33.6</td>
</tr>
<tr>
<td>(por)Co–CH(OAc)CH(_3)</td>
<td>+19.1</td>
<td>+27.4</td>
<td>+28.0</td>
</tr>
</tbody>
</table>

The ability to obtain reliable computed thermodynamic bond dissociation parameters for (por)Co–R species requires accurate representations for both the closed-shell (por)Co–R complexes and the open-shell (por)Co\(^{\text{II}}\) and R\(^\cdot\) species. The calculated properties are evaluated in the following sections and compared with the available experimental data.

7.2.3.1 (por)Co\(^{\text{II}}\)

Unrestricted DFT calculations at the BP86 level using the TZVP basis set for all atoms correctly describes (por)Co\(^{\text{II}}\) as a low spin (\(S = \frac{1}{2}\)) complex with an \(^2\)A\(_{1g}\) ground state arising from a \((d\_xy)^2(d\_x^2)^1(d\_xy\_z)^3\) electron configuration. The \(^2\)A\(_{1g}\) ground state is experimentally observed by EPR studies\(^{21}\) and the computed electronic structure is closely related to that obtained by using the ADF program.\(^{22}\)
An interesting feature of the U-DFT computed electronic structure is that the half filled \( d_{z^2} \) orbital is lower in energy than the filled \( d_{xz,yz} \) orbitals. Larger unfavourable inter-electronic repulsions for electrons in \( d_{z^2} \) orbital compared to the \( d_{xz,yz} \) orbitals (which are expanded by mixing with the por \( \pi^* \) orbitals) appears to be the dominant contribution in producing the unusual result.\(^{23}\)

The effectiveness in using DFT to estimate bond dissociation energy parameters is dependent on the accuracy of the calculated energy value for (por)Co\( \text{II}^\bullet \), which is assessed by comparison with results from experimental studies.

### 7.2.3.2 (por)Co–H

The DFT estimate of 50.6 kcal mol\(^{-1}\) for the Co–H bond dissociation enthalpy (BDE) of (por)Co–H (equation 8) (Table 1) represents one of the lower BDE values known for transition metal-hydrogen bonds.\(^{24}\)

\[
{\text{Co}} - {\text{H}} \rightleftharpoons \text{(por)Co}^\text{II}^\bullet + \cdot \text{H} \tag{8}
\]

The computed Co–H BDE is consistent with the inability to obtain NMR observable concentrations of (por)Co–H complexes from the reaction of (por)Co\( \text{II}^\bullet \) with \( \text{H}_2 \) (\( P_{\text{H}_2} < 4 \text{ atm}, T = 298\text{K} \)) which places an upper limit of \( \sim 53 \text{ kcal mol}^{-1} \) (i.e. half the BDE of \( \text{H}_2 + 1 \text{ kcal mol}^{-1} \)) on the (por)Co–H BDE. Rapid hydrogen atom abstraction by (por)Co\( \text{II}^\bullet \) complexes from \( \cdot \text{C(CH}_3^\text{2})_2\text{CN} \) which has a C–H BDE \( \sim 50 \text{ kcal mol}^{-1} \) (equation 9),\(^{14}\) indicates that the Co–H BDE can not be much smaller than 47 kcal mol\(^{-1}\) (below which value the thermodynamic contribution to the overall kinetic barrier would become \( > 3 \text{ kcal mol}^{-1} \)).

\[
\cdot \text{C(CH}_3^\text{2})_2\text{CN} \rightleftharpoons \text{CH}_2=\text{C(CH}_3^\text{2})\text{CN} + \cdot \text{H} \tag{9}
\]

The computed (por)Co–H BDE of \( \sim 51 \text{ kcal mol}^{-1} \) thus falls within the experimental limits (47 < Co–H\( \text{BDE} < 53 \)), and is an indication of the reliability of the BP86 functional for DFT calculations applied to this class of complexes.

### 7.2.3.3 (por)Co–C(CH\(_3\)\(_2\))CN and (por)Co–CH(OAc)CH\(_3\) Bond Homolysis

The thermodynamics (\( \Delta H^\circ = 17.8 \text{ kcal mol}^{-1} \), \( \Delta S^\circ = 23 \text{ cal K}^{-1} \text{ mol}^{-1} \))\(^{14}\) and activation parameters (\( \Delta H^\ddagger = 19.5 \text{ kcal mol}^{-1} \), \( \Delta S^\ddagger = 12 \text{ cal K}^{-1} \text{ mol}^{-1} \))\(^{25}\) for (TPP)Co–C(CH\(_3\)\(_2\))CN bond homolysis have been experimentally evaluated by equilibrium and dynamic measurements. The Co–C bond dissociation enthalpy for (por)Co–CH(OAc)CH\(_3\) complexes is too large for determination by the equilibrium method used for (TPP)Co–C(CH\(_3\)\(_2\))CN. However, differences in the Co–R BDE values are dominated by the relative stability of the radicals (R\( ^\bullet \)), which are reflected by changes in the C–H BDE values of the organic radicals. The calculated difference in the C–H BDE values for H–CH(OAc)CH\(_3\) and H–C(CH\(_3\)\(_2\))CN of 8 kcal mol\(^{-1}\) thus places the (por)Co–CH(OAc)CH\(_3\) BDE at \( \sim 26 \text{ kcal mol}^{-1} \). The computed (por)Co–C(CH\(_3\)\(_2\))CN BDE of 14.6 kcal mol\(^{-1}\) is somewhat smaller than the measured BDE of 17.8 kcal mol\(^{-1}\) and the computed (por)Co–CH(OAc)CH\(_3\) BDE may be slightly overestimated at 27.4 kcal mol\(^{-1}\). Nonetheless, the computed Co–R BDE values are remarkably close to the
experimental values, which provides confidence in the reliability of the computational method for this class of cobalt porphyrin complexes.

Constraint geometry optimizations of the (por)Co−R species with elongated Co−C bonds only leads to regular energy increase until complete bond dissociation to (por)CoII and R•. Formation of (por)Co−R from (por)CoII and R• is thus clearly barrierless on the electronic energy surface, and thus the most important factor contributing to the barrier for the radical capture must be the entropy required to bring together the organic radical and the cobalt complex. In order to find the transition states for radical capture, the free energy landscape would need to be computationally searched, which is not possible with the applied static DFT methods.26

7.2.3.4 (por)Co−R Bond Distances

The calculated Co−R bond distances for (por)Co−H, (por)Co−C(CH3)2CN, and (por)Co−CH(OAc)CH3 are in accord with expectations and fit well with the experimental data currently available (Figure 1). The calculated Co−H internuclear distance of 1.444 Å is in the range for first row transition metal M−H bond distances and close to the sum of the atomic radii. The calculated Co−C bond of 1.982 Å in (por)Co−CH(OAc)CH3 is in the range for relatively strong Co−C bonds and matches well with the mean Co−C distance of 1.98 Å reported by Stolzenberg for organo-Co(por) complexes.27 The longer Co−C distance of 2.060 Å calculated for (por)Co−C(CH3)2CN is consistent with the much smaller observed Co−C BDE.

Figure 1. Co−R bond lengths of (por)Co−H, (por)Co−CH(OAc)Me and (por)Co−C(Me)2CN.

7.2.4 Hydrogen Atom Transfer

Results of DFT (BP86) computations probing the pathway by which the separated metal-centred and organic radicals ((por)CoII•, R•) interact and ultimately react by β-hydrogen atom transfer to form (por)Co−H and the respective olefins, and the microscopic reverse through addition of (por)Co−H to the olefins to form eventually (por)Co−R species are given in Tables 2 and 3 and Figures 3 and 4.

7.2.4.1 H-atom Transfer between •C(CH3)2CN and (por)CoII•

Approach of the metal-centered radical (por)CoII• to a methyl group of •C(CH3)2CN reveals a local internal energy minimum for a close contact radical pair (Figure 3, species C). The transition state (TS1) for H-atom transfer from the cyano-isopropyl radical (CN)(CH3)2C• to (por)CoII• yielding (por)CoIII−H was readily found by first exploring energy profiles through constrained geometry optimizations with fixed Co−H and H−CH2C(CH3)2CN bond distances. Starting from the close-contact radical pair C (broken-symmetry solution, <S2> = 0.817), shortening the Co−H bond resulted in a switch to a closed-shell solution (<S2> = 0) at Co−H distance less than 1.50 Å (Figure 2).
Constrained elongation of the C–H bond followed by an unconstrained transition-state search revealed the transition state TS1 shown in Figure 3 and Figure 5.

The computed Co–H (1.48 Å) and C–C (1.37 Å) bond distances of the transition state (TS1) are only slightly elongated compared to the separated (por)Co–H (1.44 Å) and CH2=C(CH3)CN (1.36 Å) species. The transition state appears like a weakly interacting adduct of (por)Co–H with the olefin.

The (ZPE corrected) internal energy and enthalpy are lowered by the interaction of (por)CoII and the organic radical to form the radical pair intermediate C and TS1, but the free energy increases ($\Delta G^{\circ}_{298K} = +2.0 \text{ kcal mol}^{-1}$ and $\Delta G^{\ddagger}_{298K} = +3.8 \text{ kcal mol}^{-1}$ for C and TS1, respectively) due to the entropy loss associated with bringing the reactants together.

In qualitative agreement with a fast experimental H-atom abstraction ($k_{\beta-H}(333K) = 5 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$), the calculated free energy change from the separated radicals to the transition state is low ($\Delta G^{\ddagger}_{333K} = +4.4 \text{ kcal mol}^{-1}$; approx. rate constant $9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$), perhaps even too low compared to the experimental value ($\Delta G^{\ddagger}_{333K} = +10.9 \text{ kcal mol}^{-1}$) estimated from the rate constant. This underestimation might be partly explained by steric as the metal centre in the applied (por)Co model in the DFT calculations is not at all hindered contrary to the experimental (TMP)Co system. Moreover standard transition state theory (TST) becomes less reliable with small barriers.

The reverse reaction of (por)Co–H adding with methacrylonitrile to produce separated radicals also has a relatively small activation free energy ($\Delta G^{\ddagger}_{298K} = +8.9 \text{ kcal/mol}$), which complies with the experimentally observed fast insertion reaction.
Figure 3. Energy changes (kcal mol$^{-1}$) for H-transfer from •C(CH$_3$)$_2$CN to (por)Co$^{III}$ along with diagnostic Co–H, Co–C, C–C, and C–H internuclear distances (results taken from Table 2a). (a) Enthalpy change ($\Delta H^\circ$) and internal energy change ($\Delta E_{ZPE}$), (b) Free energy change ($\Delta G^\circ_{298}$).

Figure 4. Energy changes (kcal mol$^{-1}$) for vinyl acetate insertion to (por)Co–H along with diagnostic Co–H, Co–C, C–C, and C–H internuclear distances (results taken from Table 2b). (a) Enthalpy change ($\Delta H^\circ$) and internal energy change ($\Delta E_{ZPE}$), (b) Free energy change ($\Delta G^\circ_{298}$).
Computations of the pathway for addition of (por)Co−H to vinyl acetate (CH$_2$=CH(OAc)) were guided by the results from the methacrylonitrile system, and applying a transition state geometry optimization revealed a single transition state (TS2, Figure 4) for the hydrogen transfer process in the vinyl acetate system. Minimization of the internal energy from TS2 resulted in the close contact radical pair G (analogous to C), for which BP86 still produced a “closed-shell” solution ($<S^2>$ = 0). Since the closed-shell and broken symmetry solutions are very close in energy even for C, this detail is probably not very relevant. Separating the radicals from the radical pair G is very fast and has only a small barrier which was not found computationally. The transition state (TS2) for the hydrogen atom transfer ((por)Co• … H… H$_2$C(OAc)(H)C•) (Figure 4, Table 2) has structural parameters very similar to those of the separated (por)Co−H and CH$_2$=CH(OAc) species and has features like an adduct of the metal hydride and the olefin.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$\Delta E_{ZPE}$</th>
<th>$\Delta G^\circ_{298K}$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B Co−R</td>
<td>−15.1</td>
<td>−14.1</td>
<td>−4.5</td>
<td>−14.6</td>
<td>−32.6</td>
</tr>
<tr>
<td>A separated radicals</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C biradical</td>
<td>−3.4</td>
<td>−4.4</td>
<td>2.0</td>
<td>−4.0</td>
<td>−20.1</td>
</tr>
<tr>
<td>TS1 transition state</td>
<td>1.5</td>
<td>−1.8</td>
<td>3.8</td>
<td>−1.7</td>
<td>−18.4</td>
</tr>
<tr>
<td>D Co−H + olefin</td>
<td>−0.4</td>
<td>−3.2</td>
<td>−5.1</td>
<td>−2.9</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Table 3. Computed thermodynamic values for species relevant to $\beta$-hydrogen atom transfer to (por)Co$^{II}$• and the microscopic reverse addition of (por)Co−H to olefins in reaction between (por)Co$^{II}$• and C(CH$_3$)$_2$CN $^{[a]}$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$\Delta E_{ZPE}$</th>
<th>$\Delta G^\circ_{298K}$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E Co−R</td>
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<td>−27.2</td>
<td>−19.1</td>
<td>−27.4</td>
<td>−28.0</td>
</tr>
<tr>
<td>F separated radicals</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>G biradical</td>
<td>−6.1</td>
<td>−8.4</td>
<td>−2.7</td>
<td>−8.0</td>
<td>−18.1</td>
</tr>
<tr>
<td>TS2 transition state</td>
<td>−5.9</td>
<td>−8.9</td>
<td>−2.2</td>
<td>−9.4</td>
<td>−24.4</td>
</tr>
<tr>
<td>H Co−H + olefin</td>
<td>−8.1</td>
<td>−11</td>
<td>−13.6</td>
<td>−10.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

$^{[a]}$ DFT (BP86, TZVP, cosmo $\varepsilon$ = 2.28; benzene). Electronic energies ($\Delta E$), ZPE (zero-point energy) corrected electronic energies ($\Delta E_{ZPE}$), standard free energies ($\Delta G^\circ$), and standard enthalpies ($\Delta H^\circ$) in kcal mol$^{-1}$. Standard entropies ($\Delta S^\circ$) are in cal mol$^{-1}$ K$^{-1}$. Condensed phase (1 L mol$^{-1}$) free energies, entropies, and enthalpies were obtained from gas phase (24.5 L mol$^{-1}$ at 1 bar, 298K) calculations by correction for the condensed phase reference volume.

### 7.2.5 Structural Features of the Intermediates and Transition States in H-transfer Reactions

The bond length changes along the reaction pathways are shown in Figures 3 and 4. The bond lengths change regularly on going from •C(CH$_3$)$_2$CN via TS1 to the alkene CH$_2$=C(CH$_3$)CN, with the expected elongation of the C−H bond, shortening of the C−C bond to form a C=C double bond and shortening of the Co−H bond to form (por)Co$^{III}$−H (Figure 3). The H$_2$C−C and NC−C bonds of C are intermediate between those of CH$_2$=C(CH$_3$)CN and •C(CH$_3$)$_2$CN, as expected for a close-contact radical pair. The structure of TS1 appears roughly as a close contact of (por)Co−H with...
CH₂=C(CH₃)CN, representing a late transition state for H-atom transfer from •C(CH₃)₂CN to (por)CoII• or an early transition state for Co⁻H addition to the olefin. The Co–H bond shortens from 1.926 Å in the contact radical pair (C) to 1.479 Å in the transition state (TS1) and finally to 1.444 Å in (por)CoIII–H. The C–H internuclear distance elongates on going from the radical pair C (1.154 Å) to TS1 (1.788 Å). The C–C bond shortens on going from •C(CH₃)₂CN (1.505 Å) via C (1.480 Å) and TS1 (1.373 Å) to CH₂=C(CH₃)CN (1.356 Å). All these changes, as well as those observed along constrained search pathways, are quite regular and indicate a transition state close to the separated hydride and olefin, without any indications for a sudden switch to a charge-separated intermediate anywhere along the reaction path. The bond lengths also change regularly in the vinyl acetate system in going from CH₂=CH(OAc) via TS2 and radical pair G to the •CH(OAc)CH₃ radical, and reveal the expected shortening of the C–H bond, elongation of the C–C bond in transformation of •CH(OAc)CH₃ into CH₂=CH(OAc), and elongation of the Co–H bond along the pathway (Figure 4). The structure of TS2 is very similar to TS1, and also represents a late transition state for H-atom transfer from the radical •CH(OAc)CH₃ to (por)CoII• or an early transition state for Co–H addition to the olefin.

The close relationship between the two transition states is clearly illustrated by the optimized geometries shown in Figure 5. The primary difference between the methacrylonitrile and vinyl acetate reaction systems is that the •C(CH₃)₂CN radical is stabilized by ~ 11 kcal mol⁻¹ relative to •CH(OAc)CH₃. The (por)CoII• is a highly efficient trap for the •CH(OAc)CH₃ radical because of the strong (por)Co-CH(OAc)CH₃ bond. The reverse dissociation of the organo-cobalt complex into radicals which occurs quickly for (por)Co–C(CH₃)₂CN (k_(333K) ~ 2 · 10⁷ s⁻¹) is very slow for (por)Co–CH(OAc)CH₃ (k_(333K) ~ 1 · 10⁻⁵ s⁻¹).

### 7.2.6 Change of Spin State along the Reaction Coordinate

The hydrogen atom transfer from the methyl group of the radicals (S = ½) (•C(CH₃)₂CN, •CH(OAc)CH₃) to the cobalt(II) metal-centered radical (S = ½) to form the closed-shell diamagnetic (por)Co–H and olefin species obviously involves a spin state change at some stage or trajectory along the reaction coordinate. The transition states (TS1 and TS2, Figure 5) for both reactions are calculated to be closed-shell singlets with internuclear distances similar to the diamagnetic cobalt hydride and olefin products. Although this is suggestive for closed-shell transition states, these BP86 results do not necessarily imply that the actual transition states do not have any biradical character left. As described above, identifying the position on the reaction coordinate...
where the system switches between an open-shell and closed-shell configuration can not be confidently determined from results of DFT calculations. The BP86 computational procedure finds an open-shell singlet solution for the radical pair C between (por)CoII• and •C(CH₃)₂CN at a Co−H distance of 1.93 Å, which has high biradical character ($<S^2>$ = 0.796). As the cobalt approaches closer to the methyl hydrogen the system converts to a closed-shell configuration ($<S^2>$ = 0), which upon optimization converges to the somewhat higher energy ($\Delta E = +2.9$ kcal/mol, TZVP basis set) closed-shell singlet solution C’ with a Co−H distance of about 1.6 Å. Minimization of the close-contact [(por)CoII• •CH(OAc)CH₃] radical pair G at the unrestricted BP86 level produced a closed-shell singlet species, with a Co−H distance of 1.60 Å (Figure 4). It seems reasonable that the more stable radical (•C(CH₃)₂CN) might require a shorter distance and more complete bonding with cobalt prior to converting to the closed-shell singlet, but this (as well as interpreting TS1 and TS2 as 100% closed-shell transition states) is probably an over-interpretation of the results from DFT calculations.

7.2.7 Addition of Metal Hydrides to Olefins by Multi-step Hydrogen Atom Transfer Pathways

The most common pathway for transition metal hydrides to add to olefins is by concerted addition which uses a cis coordination site adjacent to the M−H group to bind the olefin prior to intramolecular hydrogen migration. This process is commonly referred to as “migratory insertion” (Figure 6A/B). Hydrogen atom transfer from the metal hydride is an alternative mechanism that has been observed for metal hydrides with small M−H bond dissociation enthalpies and when the resulting organic radical is particularly stable (Figure 6C).  

![Figure 6](image-url)

**Figure 6.** Mechanisms for olefin insertion into M−H bonds. (A) Concerted migratory 1,2-insertion of a cis-coordinated olefin. (B) Concerted migratory 2,1-insertion of a cis-coordinated olefin. (C) Radical type multistep addition via hydrogen atom transfer to a non-coordinated olefin.
Hydrogenation and hydroformylation of styrene catalyzed by HCo(CO)$_4$ was confirmed to involve a hydrogen atom transfer mechanism by observing CIDNP from radical pairs in these processes.$^{31}$ The (por)Co–H species is a special case, because it does not have an accessible site adjacent to the Co–H, and a multi-step hydrogen atom transfer process is necessary for addition to the olefin at a finite rate. Computed energy changes during the addition of (por)Co–H with CH$_2$=C(CH$_3$)CN and CH$_2$=CH(OAc)CH$_3$ are given in Table 2 and 3, and illustrated in Figures 3 and 4. The multi-step process that involves hydrogen atom transfer from (por)Co–H to the olefin with formation of radicals occurs with relatively low activation free energy for both methacrylonitrile ($\Delta G^\ddagger \sim 8.9$ kcal mol$^{-1}$) which has a highly stabilized radical and vinyl acetate ($\Delta G^\ddagger \sim 11.4$ kcal mol$^{-1}$) with a relatively high energy radical. This result serves as a reminder that addition reactions of metal hydrides with unsaturated substrates could occur by a non-concerted multi-step pathway that involves an effective hydrogen atom transfer. Even when a cis coordination site adjacent to the M–H bond is readily available, a hydrogen atom transfer path should be considered as a potential alternate mechanism for M–H addition reactions.

### 7.3 Conclusions

DFT calculations using the non-hybrid BP86 functional produce a relatively accurate representation of the electronic structures of (por)Co$^{11+}$ (S = ½) and the bond dissociation thermodynamic parameters of (por)Co–H, (por)Co-C(CH$_3$)$_2$CN, and (por)Co–CH(OAc)CH$_3$. DFT calculations and experimental results identify low activation free energy multi-step pathways that involve hydrogen atom transfer in both the formation of (por)Co–H from reactions between (por)Co$^{11+}$ and -C(CH$_3$)$_2$CN and for the net olefin insertion into the Co–H bond of (por)Co–H. The computed transition states for these hydrogen transfer reactions have structures suggestive of an olefin adduct of (por)Co–H. Results from this study suggest that the hydrogen atom transfer pathway could be important in numerous addition reactions of M–H complexes with unsaturated substrates. The low barrier for the multi-step single-site insertion process suggests that even for systems that do have a cis-vacant site, the radical-type insertion might compete with classic migratory insertion. First row transition metal hydrides that have smaller M–H BDE values compared to 2nd and 3rd row transition metal complexes are likely candidates for hydrogen atom transfer, particularly with olefins that form relatively stable radicals.

### 7.4 Experimental Section

Geometry optimizations were carried out with the Turbomole program package$^{32}$ coupled to the PQS Baker optimizer$^{33}$ at the ri-DFT level using the BP86$^{34}$ functional and the resolution-of-identity (ri) method.$^{35}$ We used the SV(P) basis set$^{36}$ for the geometry optimizations of all stationary points. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerically calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. Improved energies were obtained with single point calculations at DFT/BP86 level using the Turbomole def-TZVP basis set.$^{37}$ Estimated condensed phase (1 L mol$^{-1}$) free energies, entropies and enthalpies were obtained from these data by neglecting the enthalpy RT term and subsequent correction for the condensed phase reference volume $S_{\text{CP}} = S_{\text{GP}} + R\ln(1/24.5)$. Solvent corrections
from single point cosmo calculations ($\varepsilon = 2.28$; benzene) were applied for all species as well. The thus obtained (free) energies (kcal mol$^{-1}$) are reported in Tables 1-3, Figure 3 and Figure 4. The ‘real’ energy $\epsilon_{i}$ of the (multi-determinant) open-shell singlet species C (singlet biradical) was estimated from the energy $\epsilon_{0}$ of the optimized single-determinant broken symmetry unrestricted BP86/TZVP ($<S^2_0> = 0.796$) solution and the energy $\epsilon_{1}$ from a separate unrestricted $m_{s} = 1$ calculation at the same geometry with the same functional and basis set ($<S^2_1> = 2.019$), using the approximate spin correction formula proposed by Yamagushi: \[ E_{s} = \frac{S^2_1 \epsilon_{0} - S^2_0 \epsilon_{1}}{S^2_1 - S^2_0} \]

Single point calculations and optimizations at the b3-lyp, 39 level using the Turbomole def-TZVP basis for the reactions involving spin states changed gave poor results compared to experimentally derived energy values.

7.5 Acknowledgements

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7.6 Notes and References

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23 The electronic configuration of open-shell systems with DFT methods is a bit complicated by the fact that DFT treats the alpha spin (spin up) and the beta spin orbitals (spin down) separately. The energy arrangement of the orbitals which are mainly built from the Co d-orbitals in [(por)CoII] is as follows:

<table>
<thead>
<tr>
<th>alpha</th>
<th>beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>97: -2.080 eV</td>
<td>x²-y²</td>
</tr>
<tr>
<td>94: -5.0134 eV</td>
<td>y²-z²</td>
</tr>
<tr>
<td>93: -5.0147 eV</td>
<td></td>
</tr>
<tr>
<td>92: -4.5921 eV</td>
<td></td>
</tr>
<tr>
<td>91: -4.9679 eV</td>
<td></td>
</tr>
<tr>
<td>90: -5.6038 eV</td>
<td>z²</td>
</tr>
<tr>
<td>88: -6.1780 eV</td>
<td></td>
</tr>
</tbody>
</table>

Often the SOMO is also the HOMO, but not in this case. The alpha orbitals 94 and 93 (mainly dxz and dyz) are nicely oriented along the xz and yz axes defined by the porphyrin, and as expected are higher in energy than the dz² orbital due to unfavourable anti-bonding π-interactions with the porphyrin. Due to the fact that the dxz and dyz orbitals interact with the porphyrin π-orbitals, they are expanded with respect to the dz² orbital, and thus spin-pairing is easier in the dxz and dyz orbitals. In consequence beta orbitals 93 and 92 (mainly dxz and dyz) end up lower in energy than the beta orbital 94 (mainly dz²). The beta orbitals 93 and 92 are spin paired with the alpha orbitals 94 and 93. In this way orbital 90 (mainly dz²) is actually the half-filled orbital. Indeed, a spin density plot reveals a clean dz² orbital. In good agreement with experimental data, we can thus assign the DFT d-electron configuration of (por)CoII as follows: dxy², dz²¹, dxz², dyz², dx²-y²⁰.
26 With the applied static DFT methods, there exist no methods to find transition states which exist only in the free energy landscape, but not in the electronic energy landscape. A way to treat such problems correctly would be Car-Parrinello molecular dynamics, which is beyond the scope of this work.
28 (a) Laidler, K. J; King, M. C. J. Phys. Chem. 1983, 87, 2657-2664. (b) One has to take into account that for very fast reactions solvent and diffusion effects contribute substantially to the condensed phase barriers, and thus the calculated gas phase barriers are then likely to be underestimated.
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33 PQS version 2.4, 2001, Parallel Quantum Solutions, Fayetteville, Arkansas (USA); the Baker optimizer is available separately from PQS upon request; Baker, J. J. Comput. Chem. 1986, 7, 385-395.


