Electronic Supporting Information
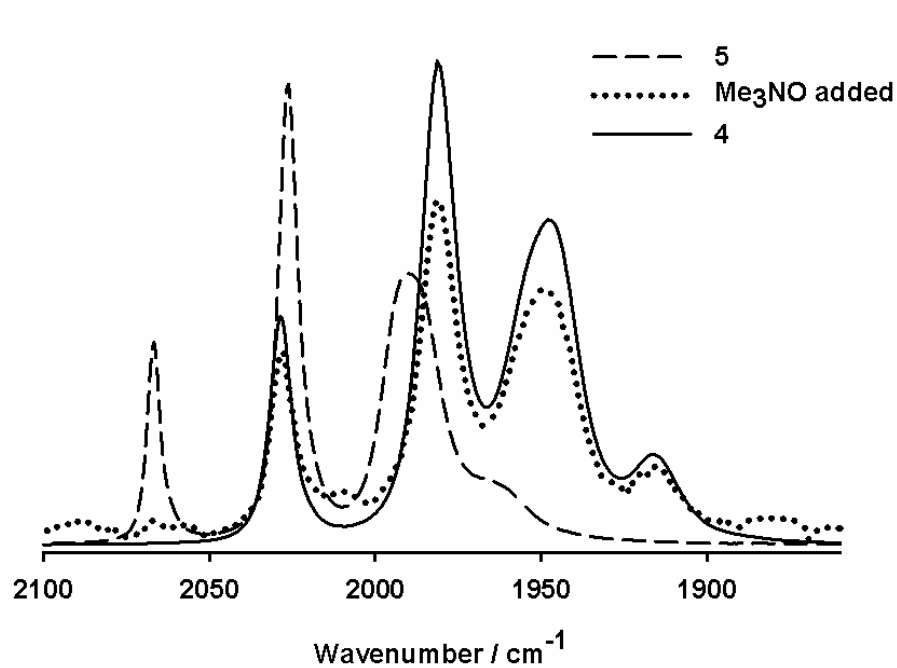

Figure S1 Infrared spectra of the complex **5** in dichloromethane without (dash line)

and with (dot line) the presence of Me$_3$NO and the spectrum of complex **4** isolated
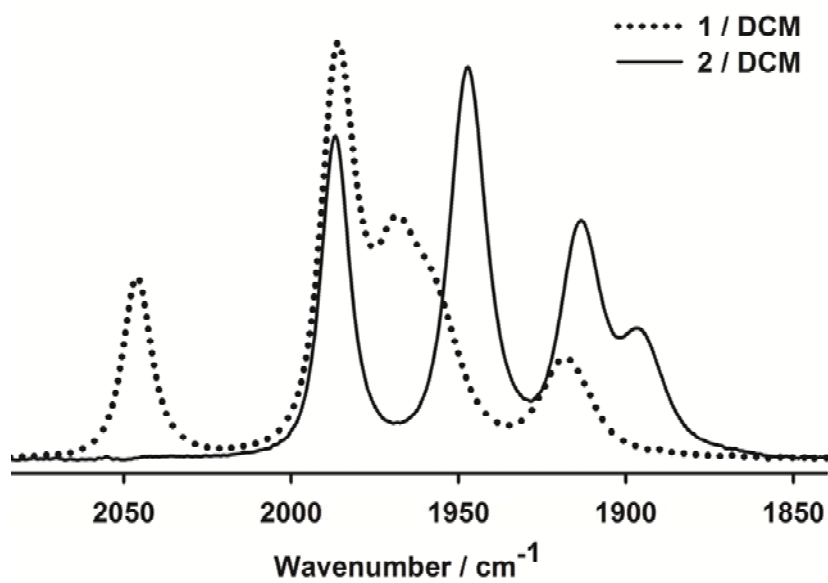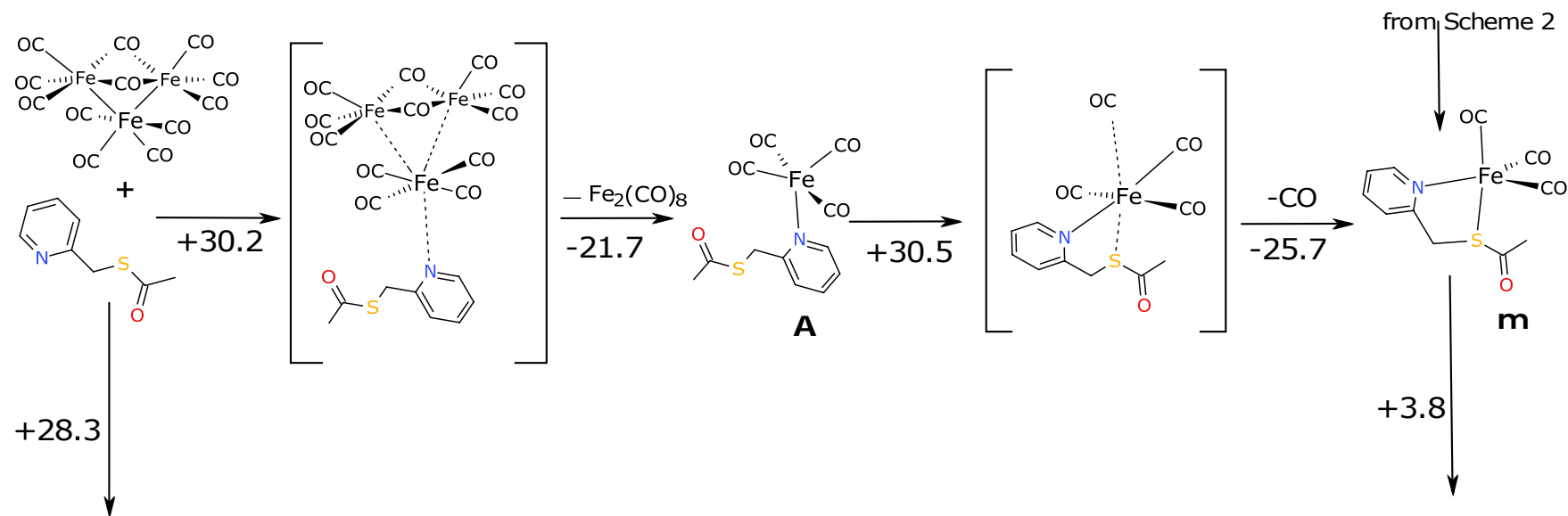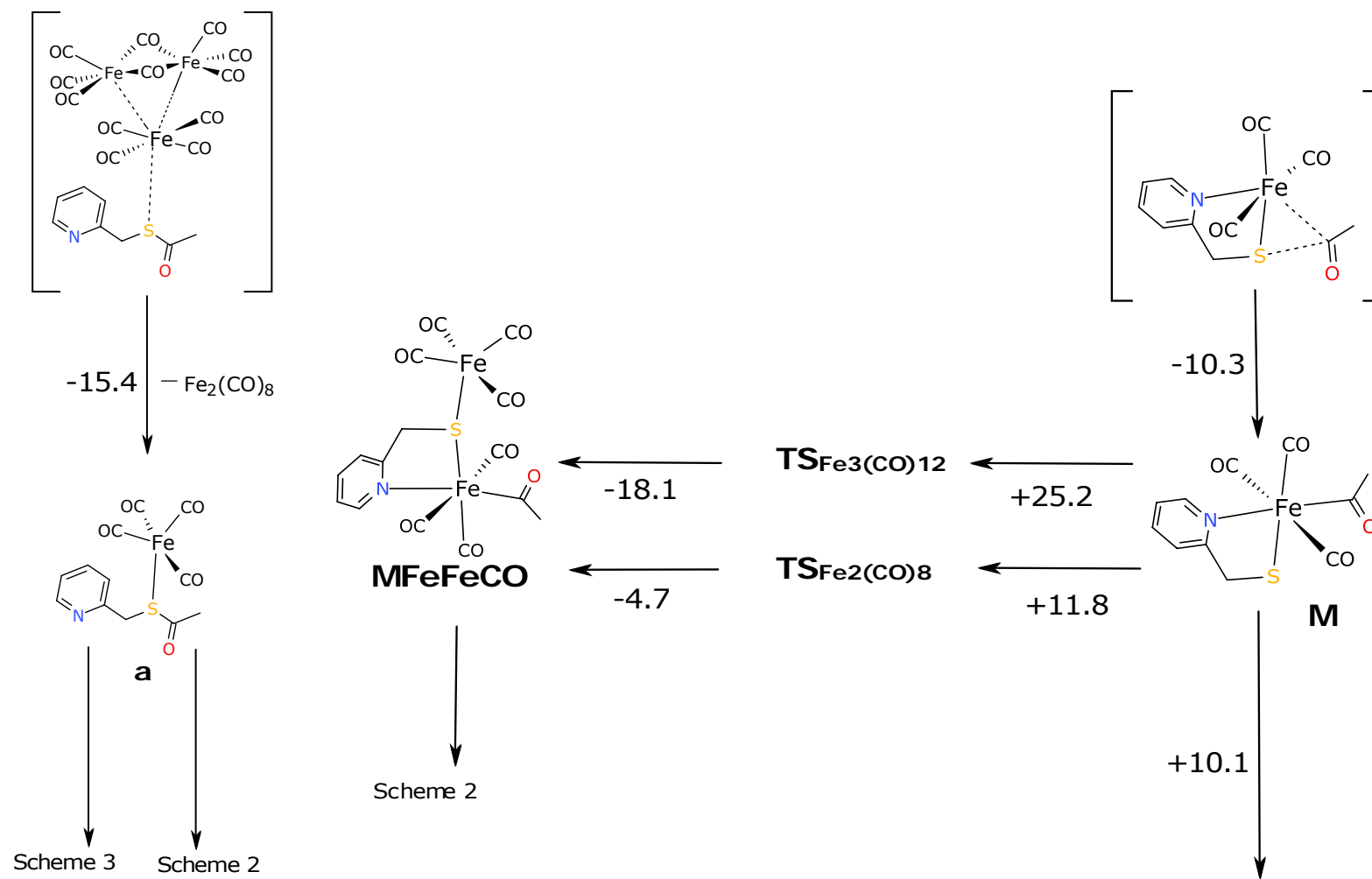
from the reaction.

Figure S2 Infrared spectra of complexes **1** and **2** in dichloromethane.

S3. DFT Schemes + extended description of the entire reactivity investigated

<u>Scheme 1</u>

-15.4 $-Fe_2(CO)_8$

-10.3

$TS_{Fe3(CO)12}$

-18.1

$+25.2$

MFeFeCO

$TS_{Fe2(CO)8}$

-4.7

$+11.8$

M

a

Scheme 2

$+10.1$

Scheme 3   Scheme 2

3

TS$_{Fe3(CO)12}$

+25.5

-CO

-10.0

M'

+12.4

-15.8

TS$_{Fe2(CO)8}$

-2.7

MFeFe

Scheme 2

Scheme 2

from Scheme 1

from Scheme 3

MFeFeCO

+29.6

-CO
-18.7

+17.0

+17.7

-CO
-19.7

to **1** (see below)

1CO

-45.8 | -CO

from Scheme 1

MFeFe

+32.0

-CO
-52.6

1

-10.6

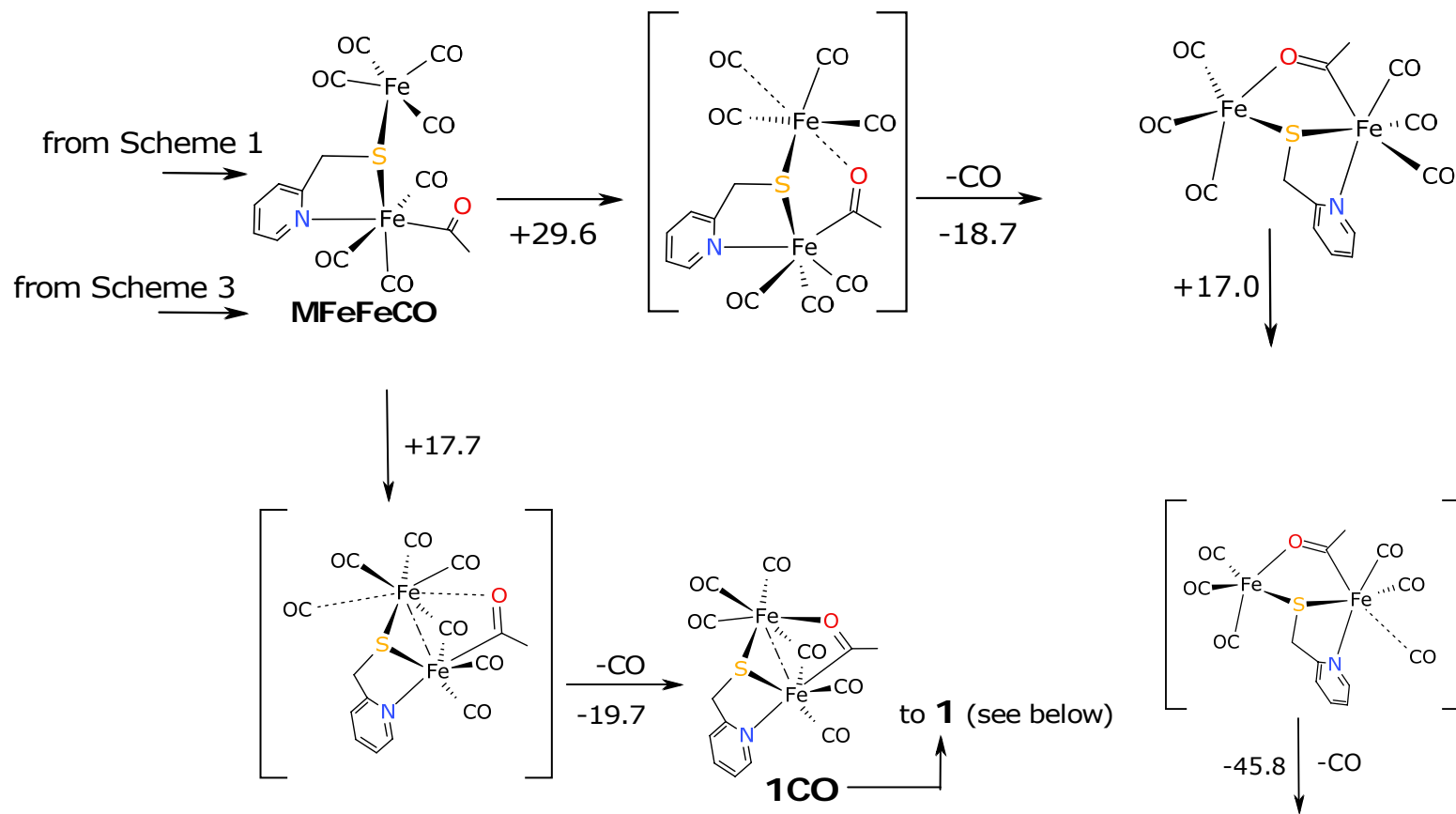**MFeFe'**

+3.3

1CO

+4.4

-CO
-20.3

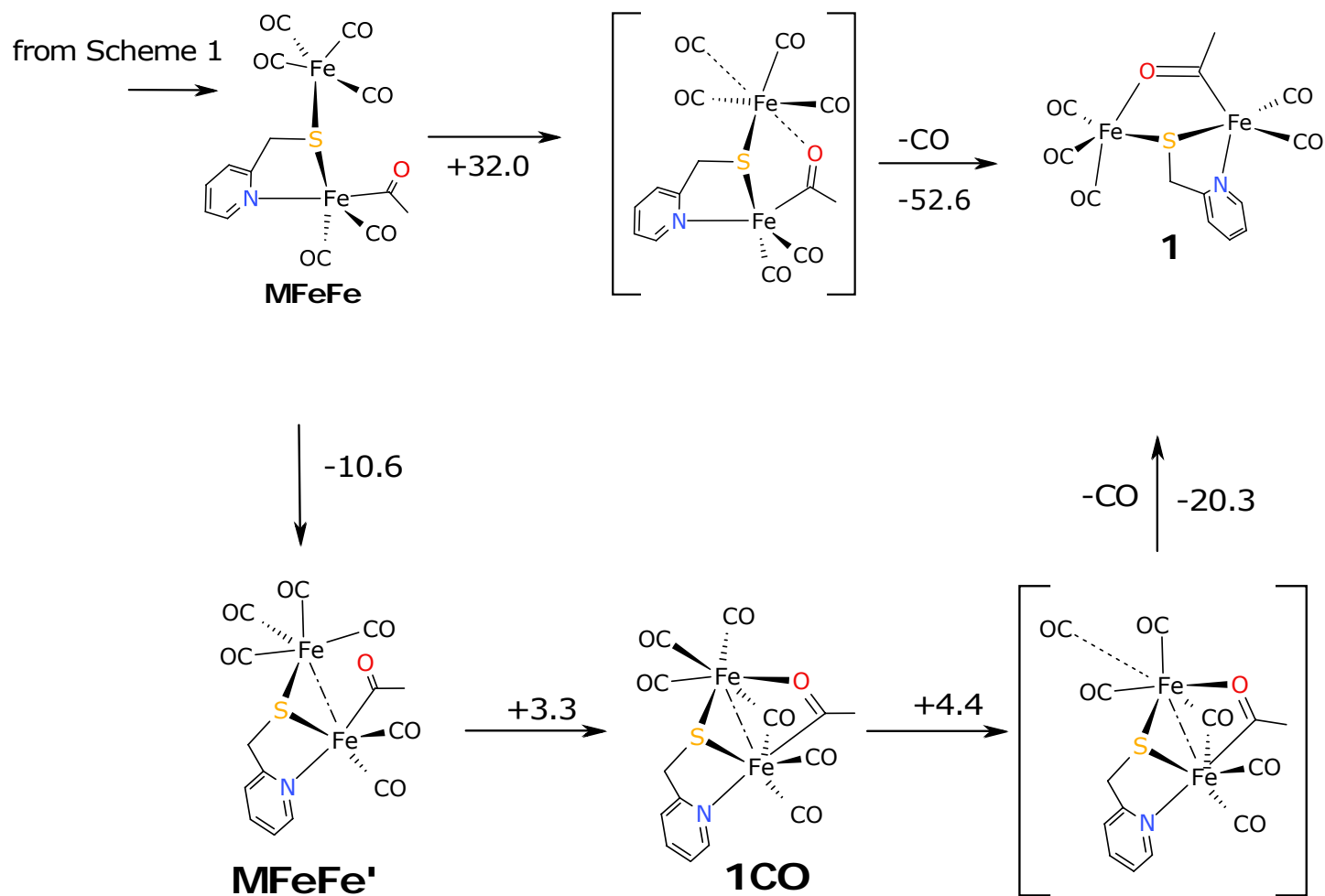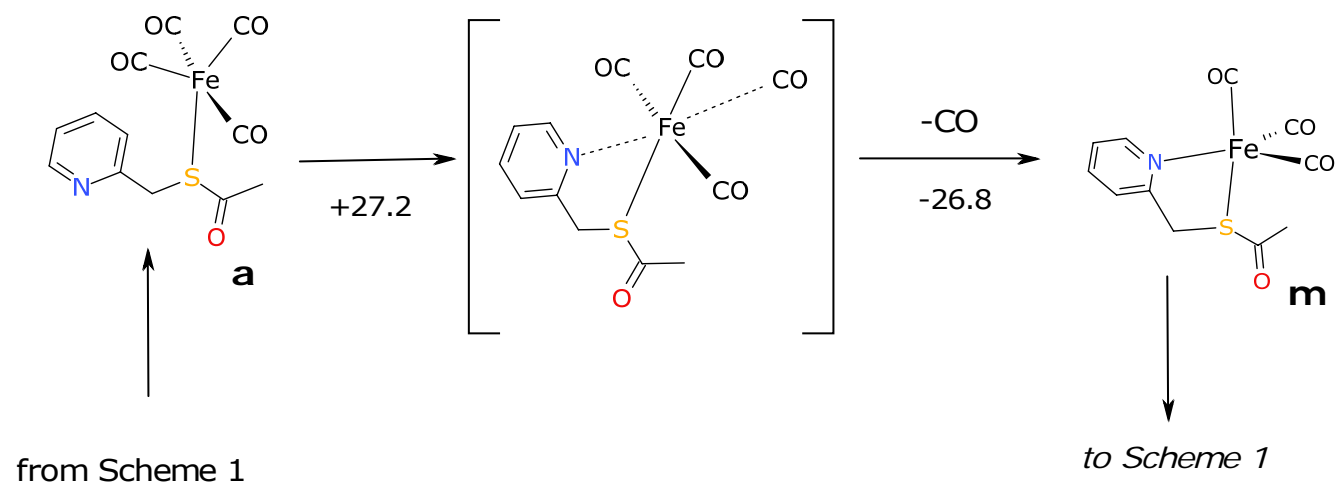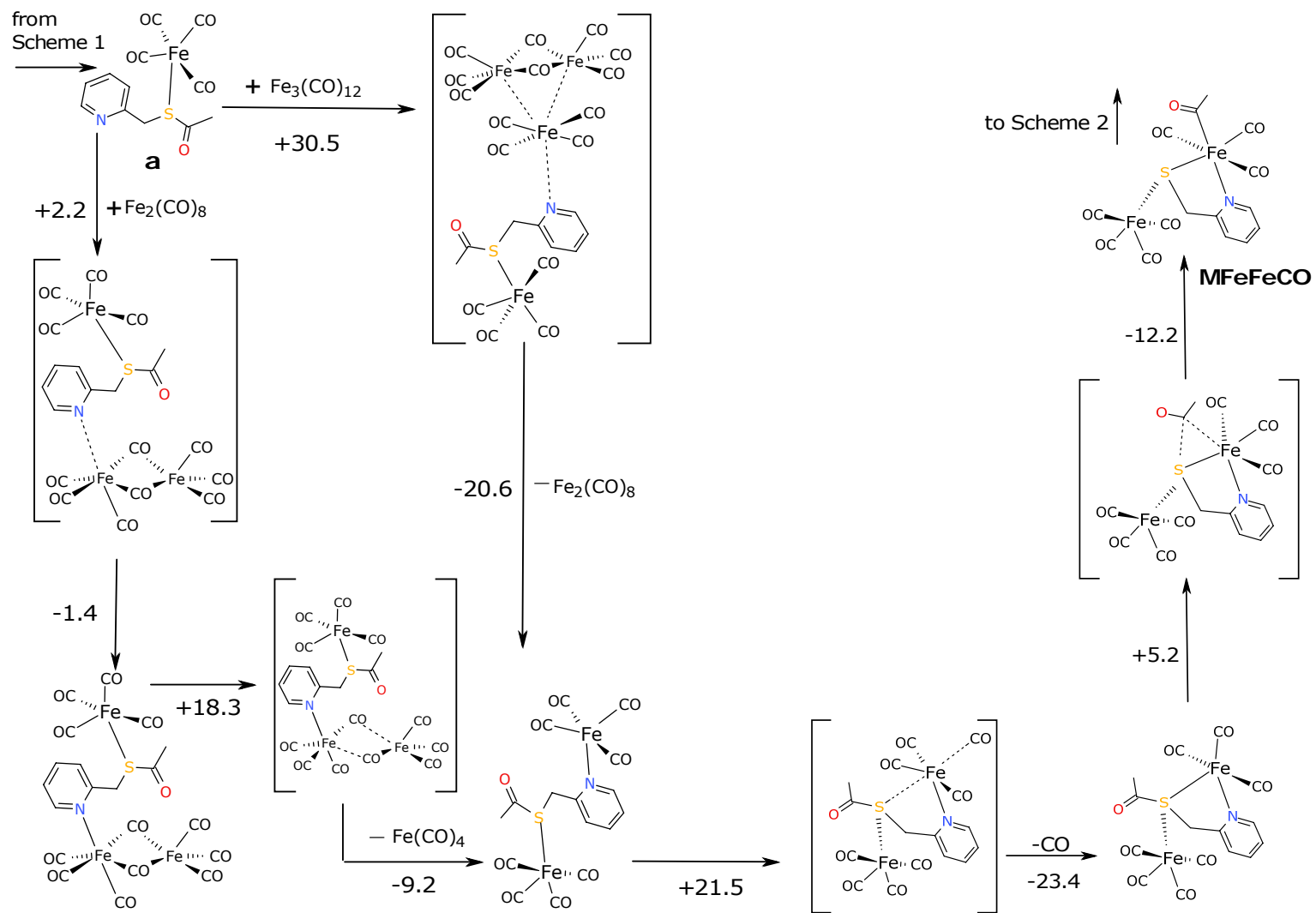from Scheme 1

+27.2

-CO

-26.8

a

m

to Scheme 1
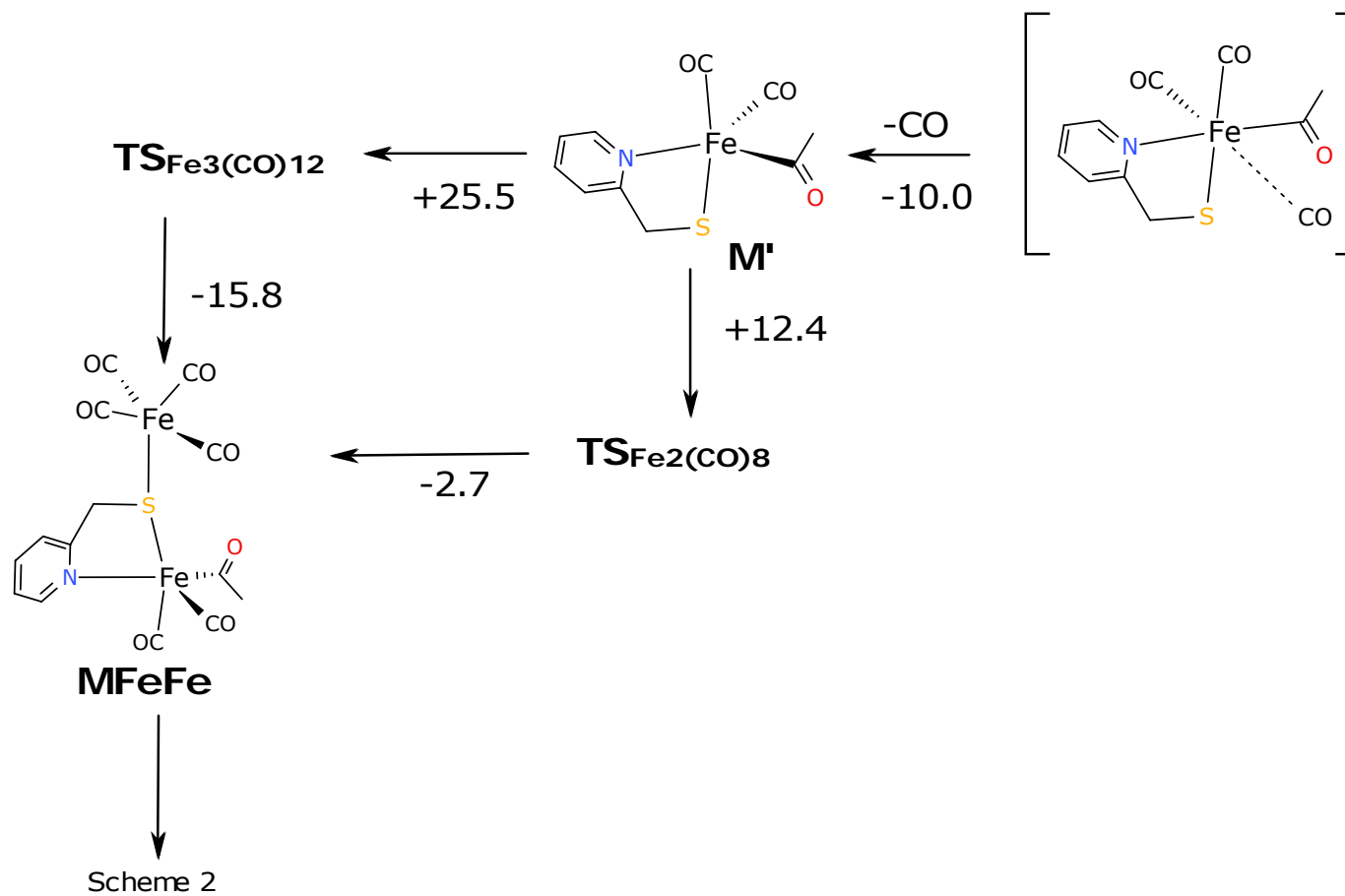
Scheme3

The above schemes report the investigated pathways of **1** formation. Transition state structures are in brackets and dotted lines therein indicate both forming and breaking bonds; energy differences are shown in kcal/mol.

The starting point is the upper left corner of Scheme 1, whereas the ending point is, of course, **1**, which is located only in Scheme 2. Scheme 3 features a possible bypass, which starts at "**a**" (Scheme 1) and ends at "**MFeFeCO**" (Scheme 2). "**a**" in Scheme 1 is a node, which can evolve both to Scheme 2 (bottom) and to Scheme 3, through the bypass represented in Scheme 3. In the former case, the followed route joins again Scheme 1, right at "**m**". The pathway which appears more viable is the one which goes through A and then through **m** (even though **m** can be formed also through a by direct N-chelation and CO expulsion, see the bypass on the bottom of Scheme 2)

After the first $Fe_3(CO)_{12}$ molecule has reacted with L1, and when a second $Fe(CO)_4$ unit must be included, the double possibility has been taken into account that either a second $Fe_3(CO)_{12}$ or a $Fe_2(CO)_8$ molecule (which is always released upon $Fe_3(CO)_{12}$ reaction with L1) can act as a $Fe(CO)_4$ releasing agent. This second case is much more favored and the intimate mechanism for such case is illustrated fully only in Scheme 3, for sake of simplicity. In all other cases in which a double possibility $Fe_3(CO)_{12}$ vs $Fe_2(CO)_8$ occurs, a schematic view has been used. Whilst $Fe_3(CO)_{12}$ reacts via elementary (single step) reaction steps, $Fe_2(CO)_8$ features a two-step/one intermediate reaction mode.

Barriers to overcome are not low, thus indicating a slow global rate of **1** formation. This is in line with experimental indication that it is necessary to warm the system up to 70 °C to observe complex **1** formation. Further, concerning this point, it also possible that the experimental gain in entropy (arising from steps in which events occur such as loss of $Fe_2(CO)_8$ and $Fe(CO)_4$ and especially CO) is higher than the one estimated computationally (which represents an approximation). That would imply some degree of overestimation of the computed activation barriers in steps involving small molecule loss (see for instance, **A→m** and **MFeFeCO→1CO** steps). Also the transient partial

four-coordination occurring at Fe atom is source of these quite high barriers, but, however, only concerted steps concerning CO loss have been located, in these two cases (i.e. no [S,N]-Fe chelated intermediate featuring a hexa-coordination of Fe has been located and, also, no hexa-coordinated Fe has been found to form when the O(=C) closes to chelate the second iron ion. Conversely, the hexa-coordination is present in other species such as M and MeFeFeCO.

The most relevant issue is that the global process turns out to be computationally exergonic ($\Delta G_{[\mathbf{L1}+Fe3(CO)12\rightarrow\mathbf{1}]}$=-4.0 kcal/mol), which fits well with experimental observations. The "oxidative addition step", in which the S-C(=O) bond is cleaved, is extremely fast. As for isomeric species of the presented intermediates, they have not been shown for readability purposes and therefore only productive isomers have been explicitly shown. The intermediate species **A** can evolve similarly to what is shown for its congener **a** (in the bypass shown in Scheme 3), with analogous reactivity, but, in order to prevent the schemes from becoming too complicated, data associated to such route are not shown.

Scheme 4

22.8

+Anion

-21.0

-10.0

J

to Scheme 8

-6.5

10.4

-CO

-27.1

J

J'

5CO

5

+11.3

-CO

-10.2
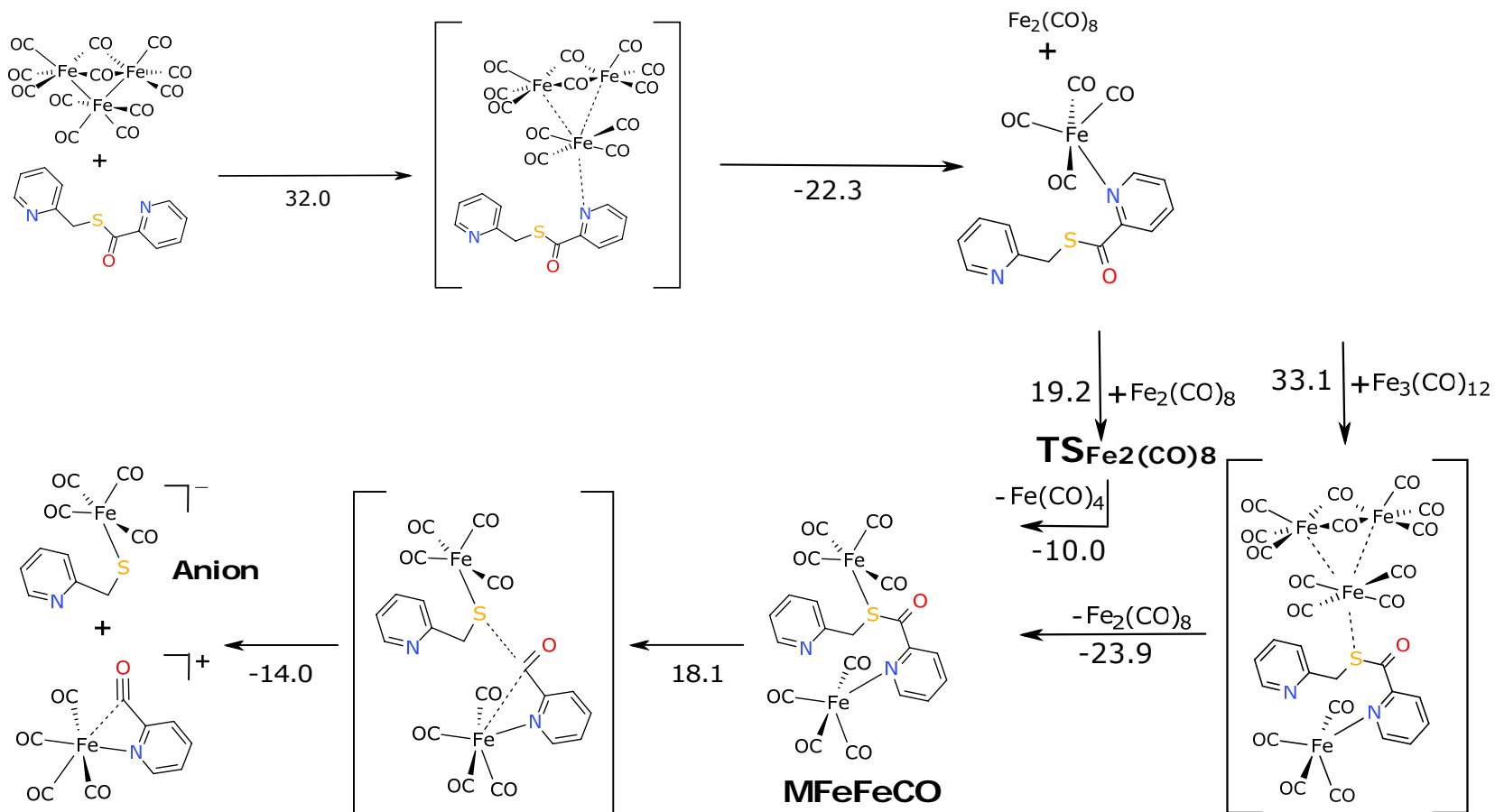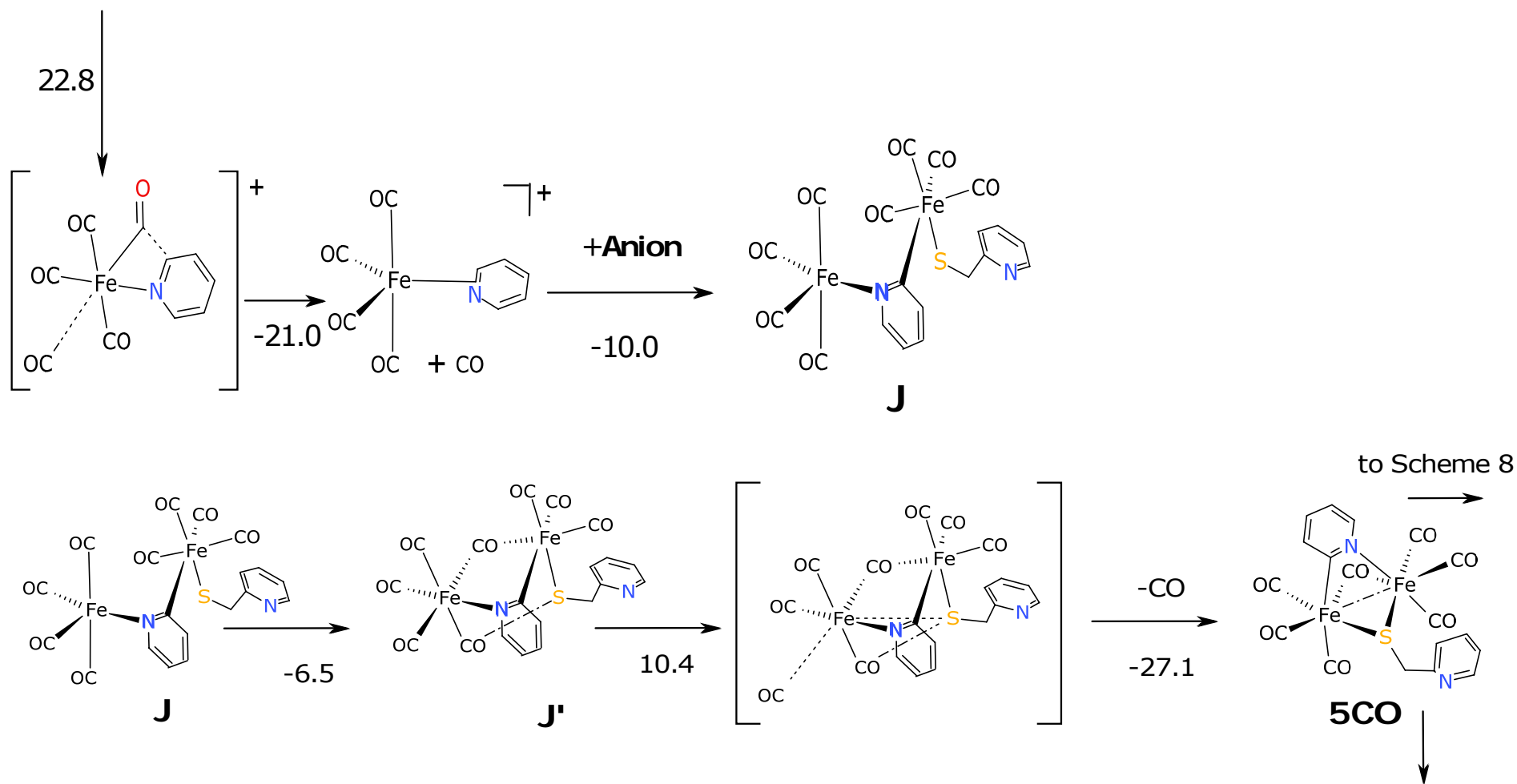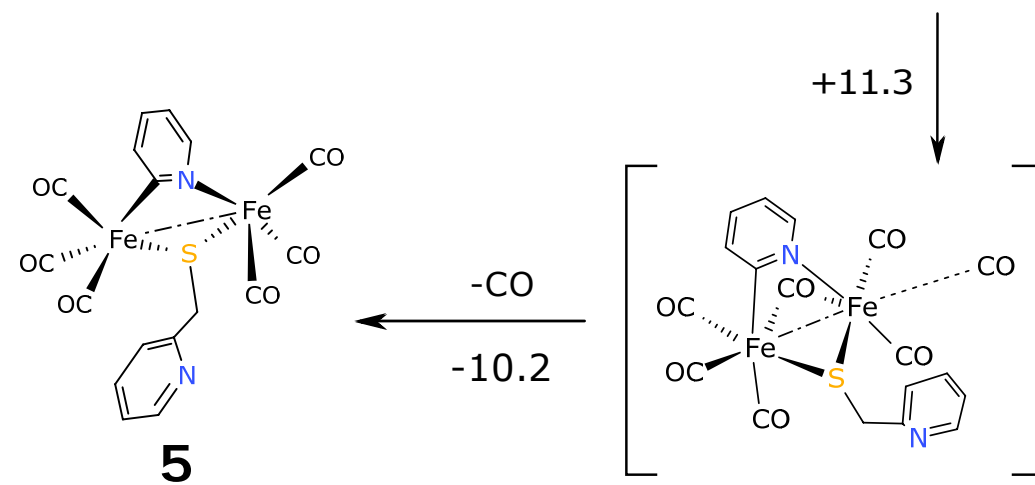
The above reported pathway shows a way of formation of **5** straight from the starting materials L2+Fe$_3$(CO)$_{12}$. The rate determining step is located at very beginning of the path, consisting in the attack of L1 to the first Fe(CO)$_4$ unit, through the N which is closer to CO.

As shown for the L1 multi-step reaction with the trinuclear Fe compound, the Fe$_2$(CO)$_8$ which has been released at the first step might act as a Fe(CO)$_4$ releasing agent of the second iron group. This results a more kinetically favoured process than extracting the same Fe(CO)$_4$ group from a second Fe$_3$(CO)$_{12}$ molecule. Even though it is conceivable that molecules of Fe$_2$(CO)$_8$ rapidly react with CO molecules which form during the whole pathway, nevertheless it may be interesting to analyze the effect of labile species in accelerating some crucial steps which are encountered along the reaction pathway.

The heterolytic S-CO bond cleavage has been found to occur quite easily even without employing implicit solvent corrections (which, at most, can lower further the barrier height). The decarbonylation event, which must occur for the system goes properly to the observed products, has been found to be assisted by the Fe atom of the cationic fragment   which transiently forms after the S-CO bond has been broken. The energy barrier value which is reported and which is associated to the transfer of the pyridine CO to Fe with simultaneous loss of one of the other CO ligands on Fe has been found by employing an ancillary CO acceptor (a Fe$_2$(CO)$_8$, not shown explicitly). The possibility of a radical homolytic cleavage of the S-CO bond has been taken into account, but all barriers associated to the further decarbonylation are extremely high (more than 60 kcal/mol).

The anion previously generated recombines with the decarbonylated Fe complex in a spontaneous way and featuring no barrier to yield **J**, in

which one of the structural features of the final product **5** is formed, namely one of the pyridine rings is bound in a bridging fashion to two Fe atoms through the N atom and its α-carbon. Even more stable is an isomer of **J** (**J'**) in which an extra bridging CO is found, so as a CO-S interaction (see scheme 4). A CO ligand is then lost in trans position to the bridging one, which brings also the two Fe atoms in a closer reciprocal position (about 3 Å), in **5CO**. The last CO is then released (again, in trans position to the bridging CO) to yield the final product **5**. It is noteworthy that all other possible decarbonylation tracks have been investigated, but they lead either to nowhere (no transition structure found)　 or they feature barrier energy which are higher than those presented in scheme 4. That would indicate that the role of the bridging CO, which is absent in the final product **5**, is to trans-direct the CO release. A direct evidence of that is that both in **J'** and in **5CO** the axial CO ligands in trans to the bridging one are more loosely bound to the relative Fe atom than all other congeners.

Scheme 5

Scheme 5'

SFe 26.6 **pre-M** to 8a

−CO −29.5

dead end track

dead end track
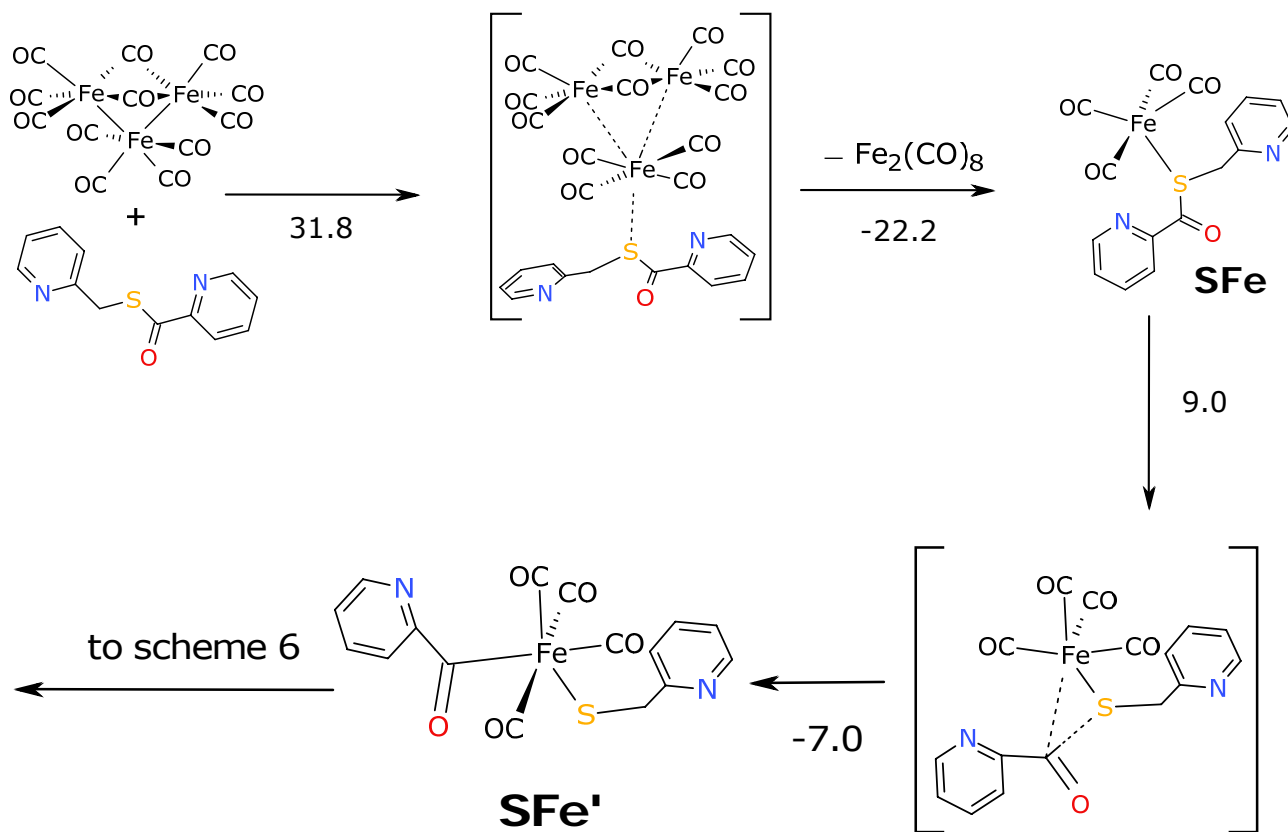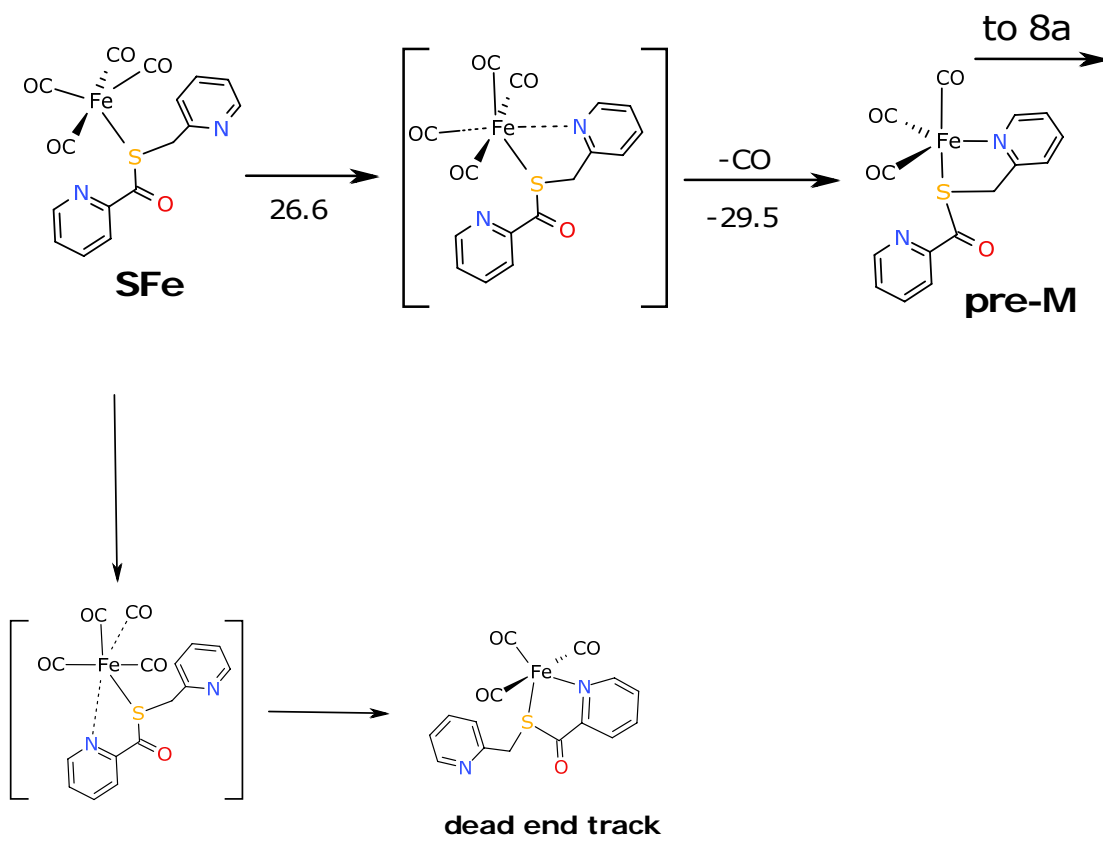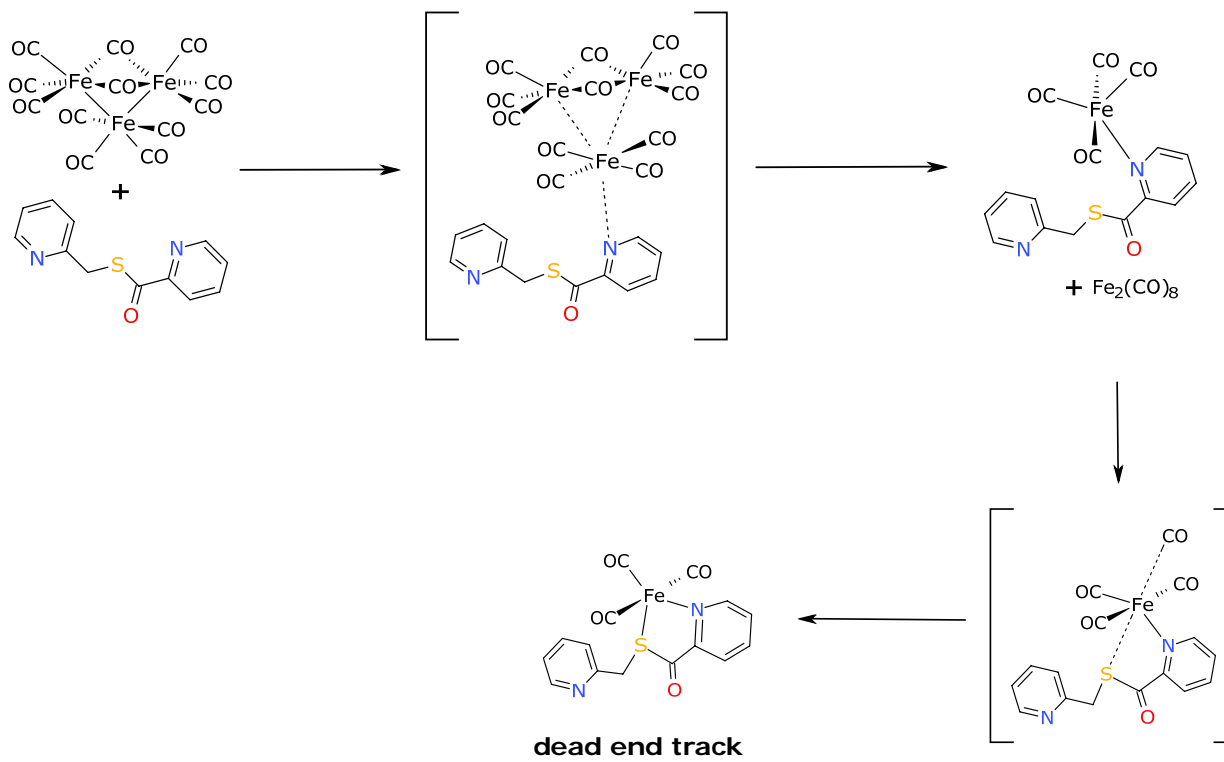
Schemes 5 and 5' above show the beginning of an alternative route for **5** (and **3**+**4** as well) formation which starts with the attack of L2 to Fe$_3$(CO)$_{12}$ through the S atom instead of N. As it can be observed the two types of joint by L2 with the first Fe(CO)$_4$ unit are nearly identical under a kinetic point of view. All those steps leading to "dead end tracks" have not been labelled with energy values for sake of simplicity. Scheme 5'' starts with the same kind of attack which is shown in Scheme 4 (i.e. a one in which L2 attacks through N), but evolves differently, as can be easily viewed. The main reason for which the two species referred to as "dead end tracks" consists in the apparent impossibility to envisage an evolution of the whole pathway toward **5**, **4** or **3** whenever such dead end spots are encountered. Indeed the possibility of transferring to Fe the carbonyl which is in between the S atom and the pyridine fragment has been considered but without useful result. The S-CO cleavage, then followed by CO loss gives rise to very high energy barriers (data not shown), probably due to a transient intramolecular charge separation (with the S portion negatively charged and the Pyr-CO one bearing the positive charge). From **SFe**, a facile oxidative step assists the S-CO cleavage, a key event for product formation. Alternatively, **SFe** might evolve according to an intramolecular SN2-like reaction in which the –CH2-Pyr residues coordinates to Fe with a concomitant CO expulsion (no associative hexa-coordinated [N, S] chelating intermediate species have been located, in this case, which would have implied a "two-step-one-intermediate" mechanism of the N-to-Fe coordination).

Scheme 6

from Scheme 5

SFe'

10.6

21.3

-13.3 -CO

-28.3 -CO

11.3

-15.6

X

from scheme 8
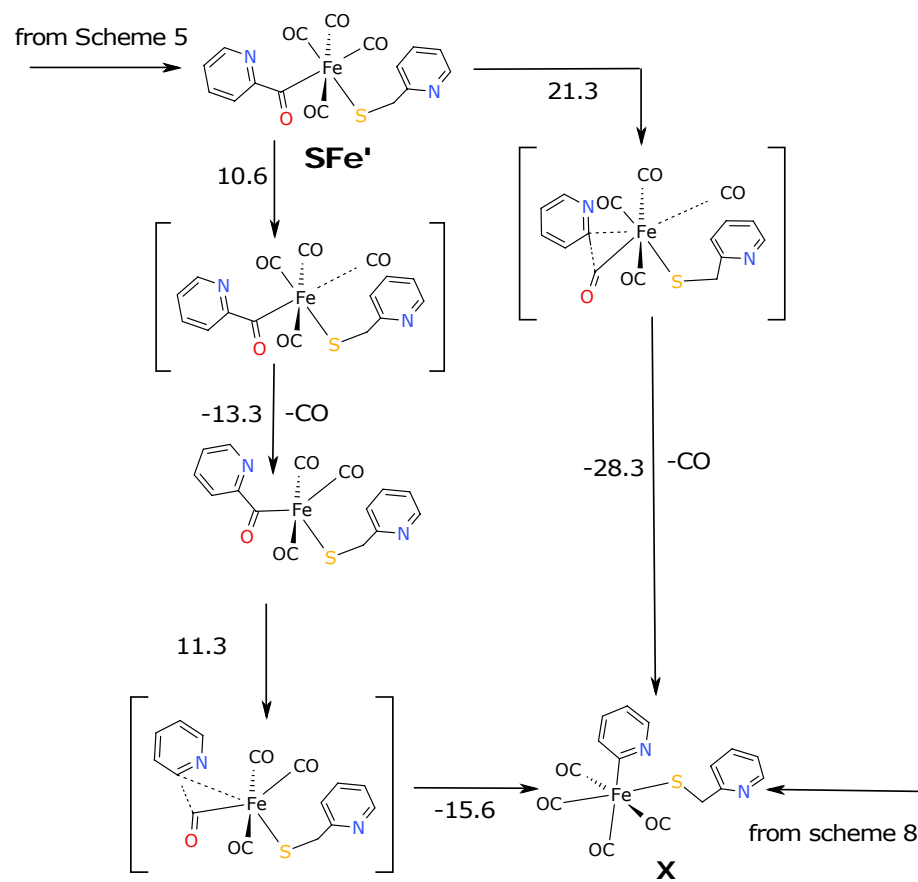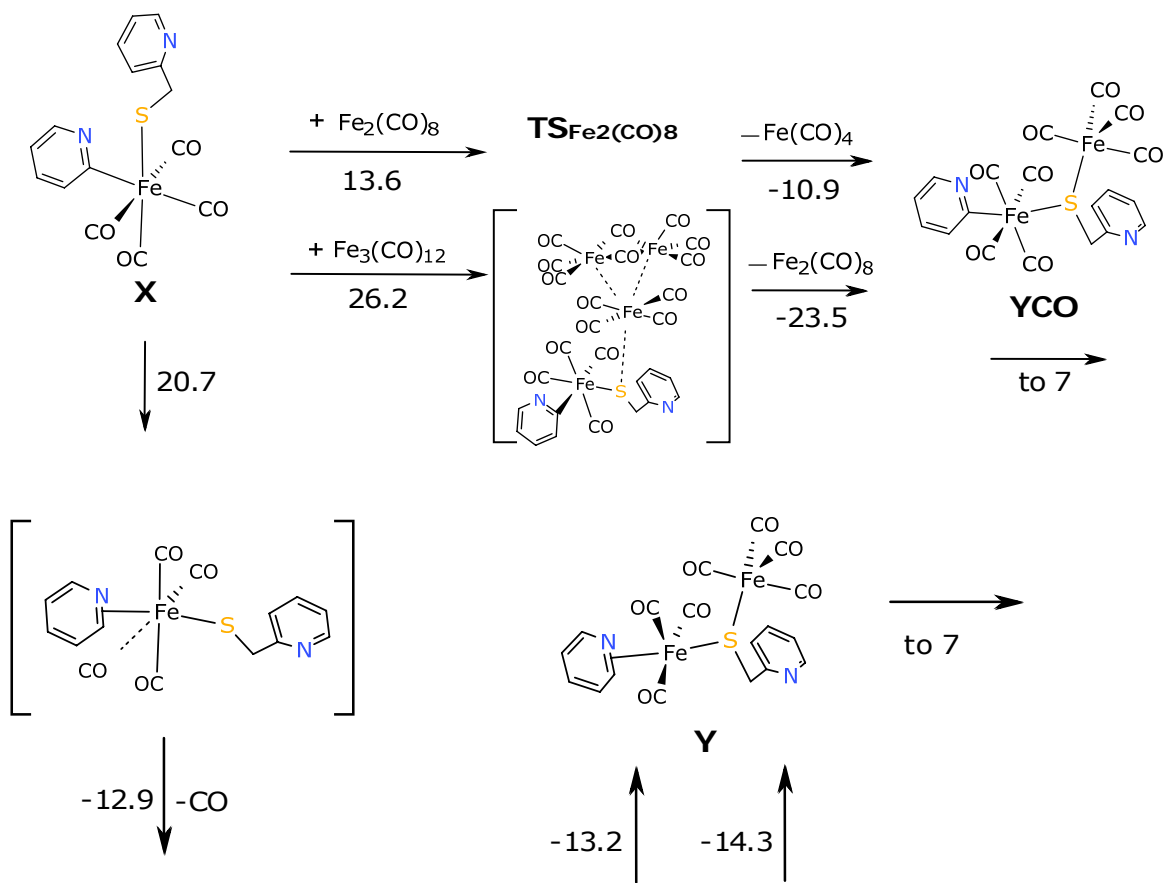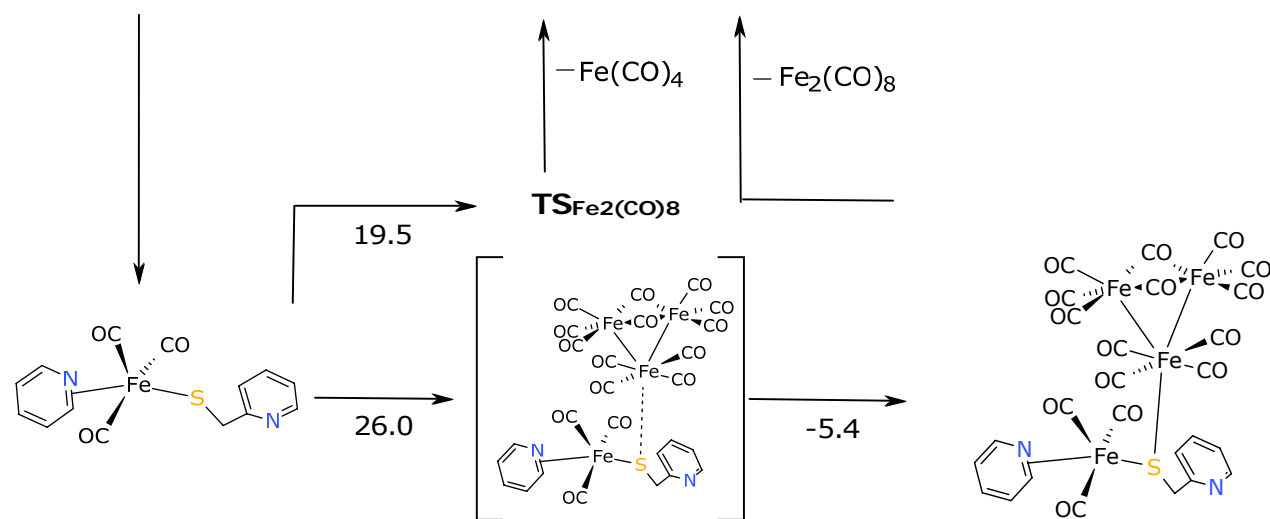
The hexa-coordinated intermediate **X**, which has been generated through **SFe** must then evolve to form the Fe-C(Pyr) bond, which is present in all product **3**, **4** and **5**. This step can occur in a concerted fashion, or, more easily, in two steps: first **X** loses a CO ligand, and, subsequently, the vacant site on Fe is able to host the incoming pyridyl residue, with simultaneous cleavage of the OC-CPyr bond. The so formed **X** intermediate is now able to link the second $Fe(CO)_4$ unit, an event in which we observe the formation of the second Fe-S bond, in **YCO**, which features one Fe in a hexa-coordinated geometry and the other in a five-coordination one. A parallel possibility might consist in **X** to lose a CO ligand, before attacking the $Fe(CO)_4$ releasing agent, thus generating **Y**, in which the two iron ion are both five-coordinated. This second route is, however, slower than the formerly presented.
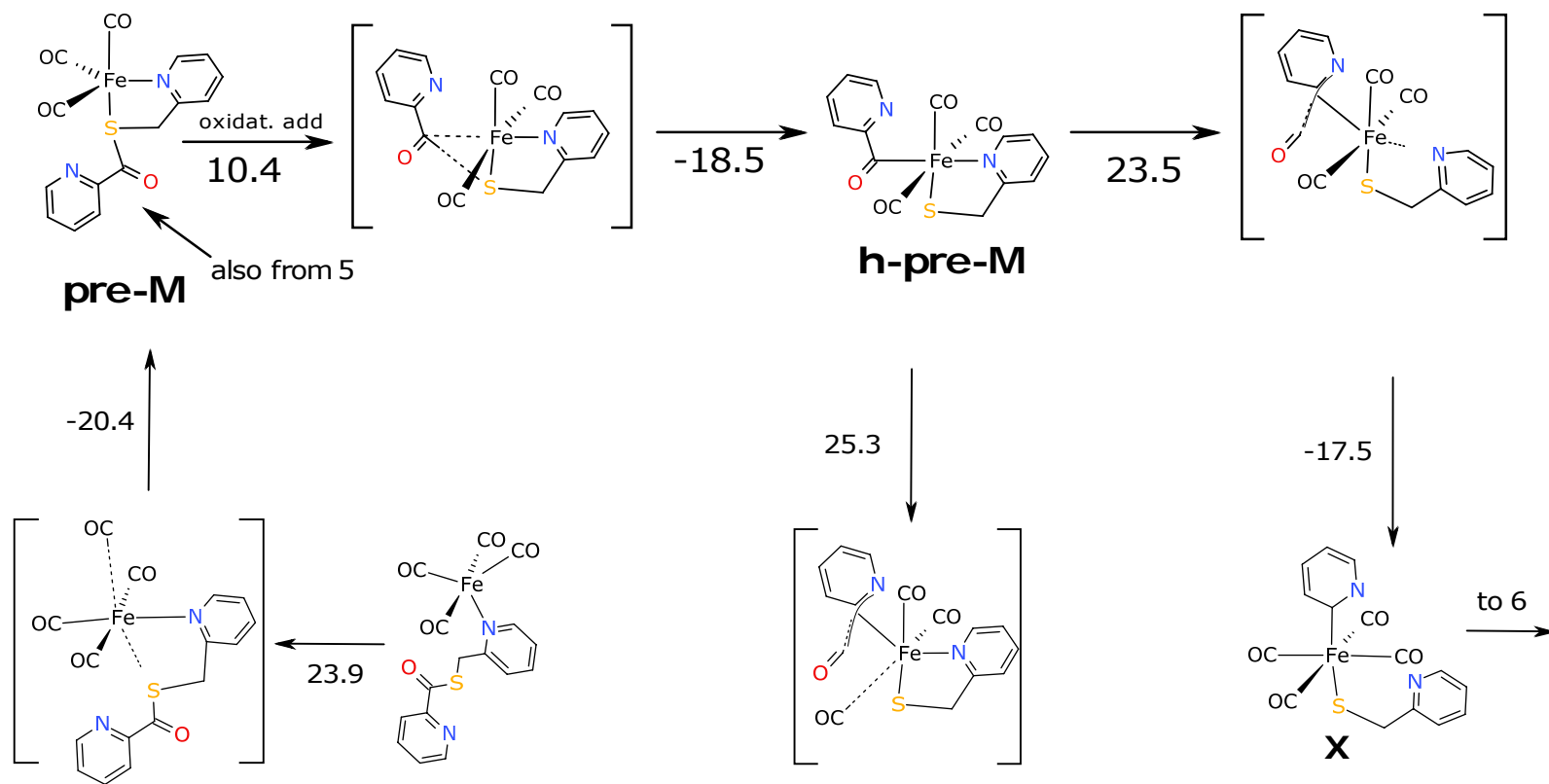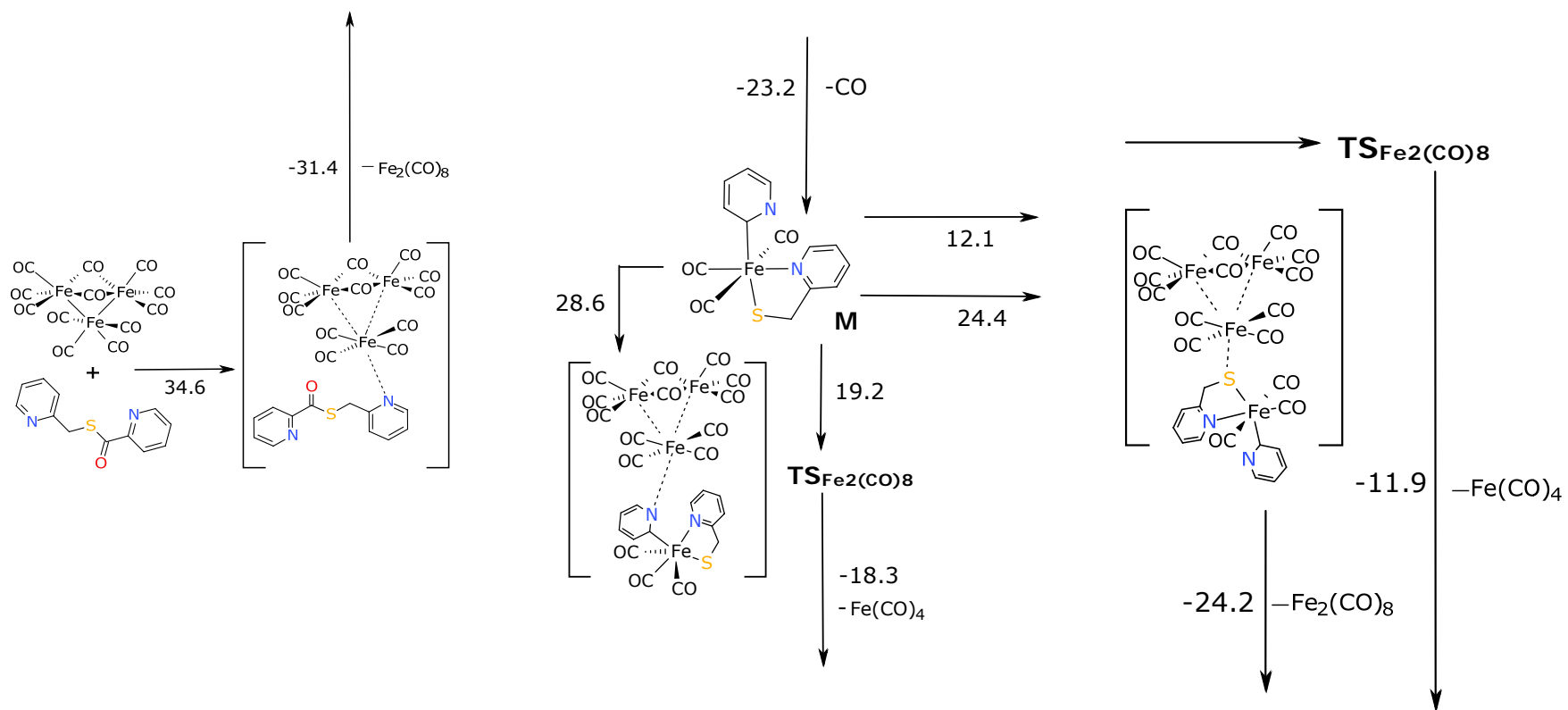
Scheme 7a

22
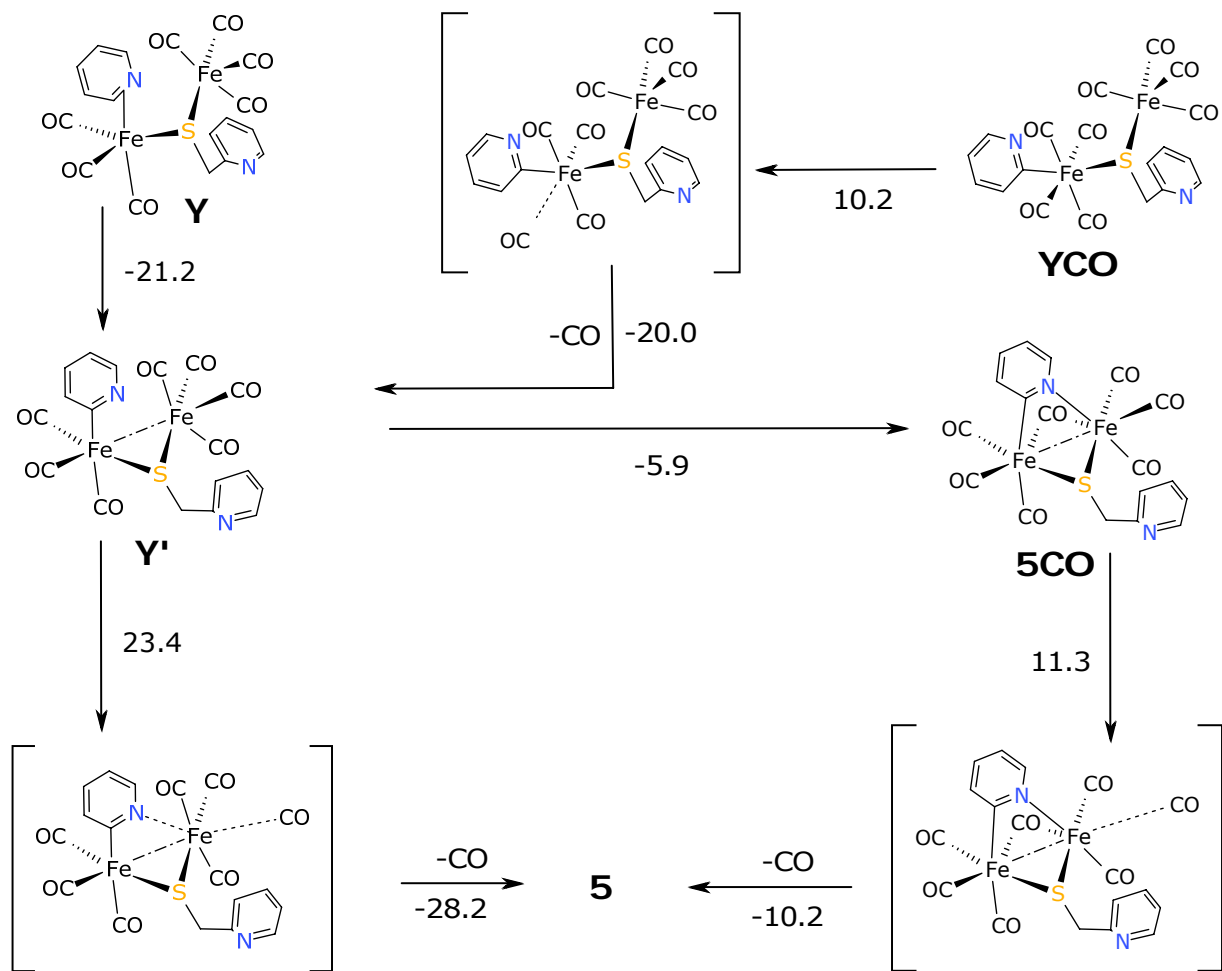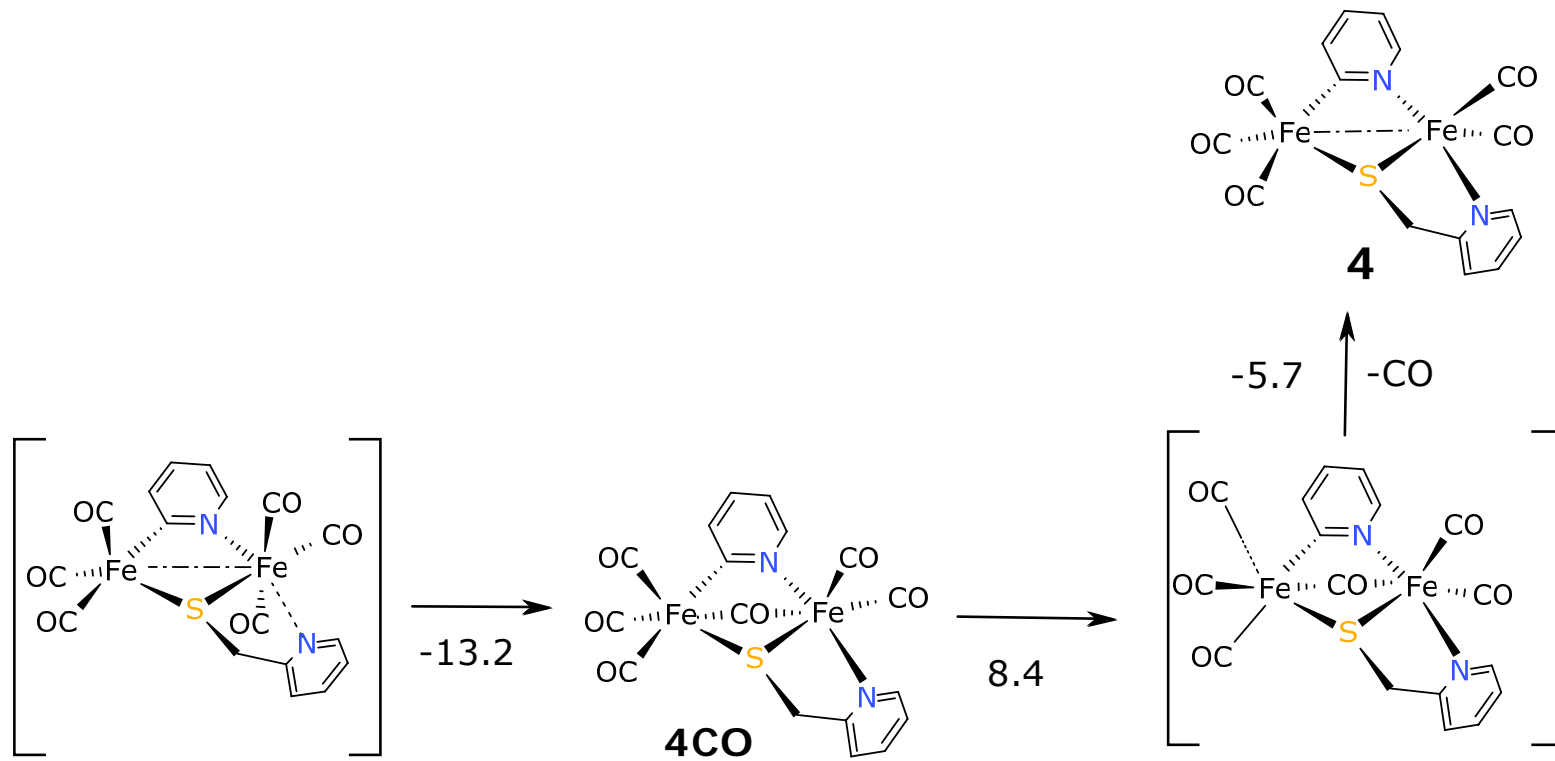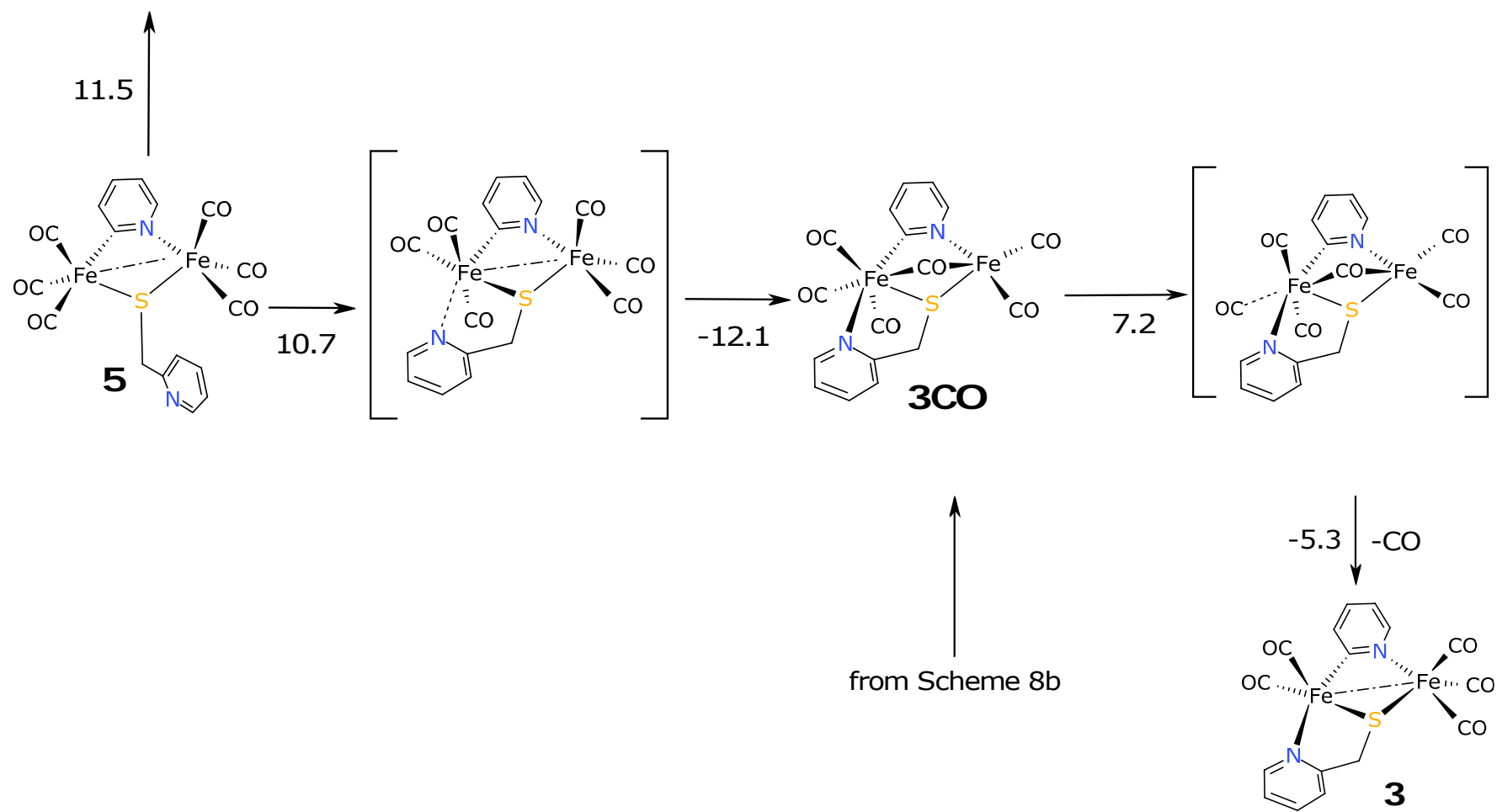
Scheme 7b

Scheme 7a shows the final part of the pathways started in Scheme 6. Scheme 7b shows how **5** can evolve to yield **3** and **4**.
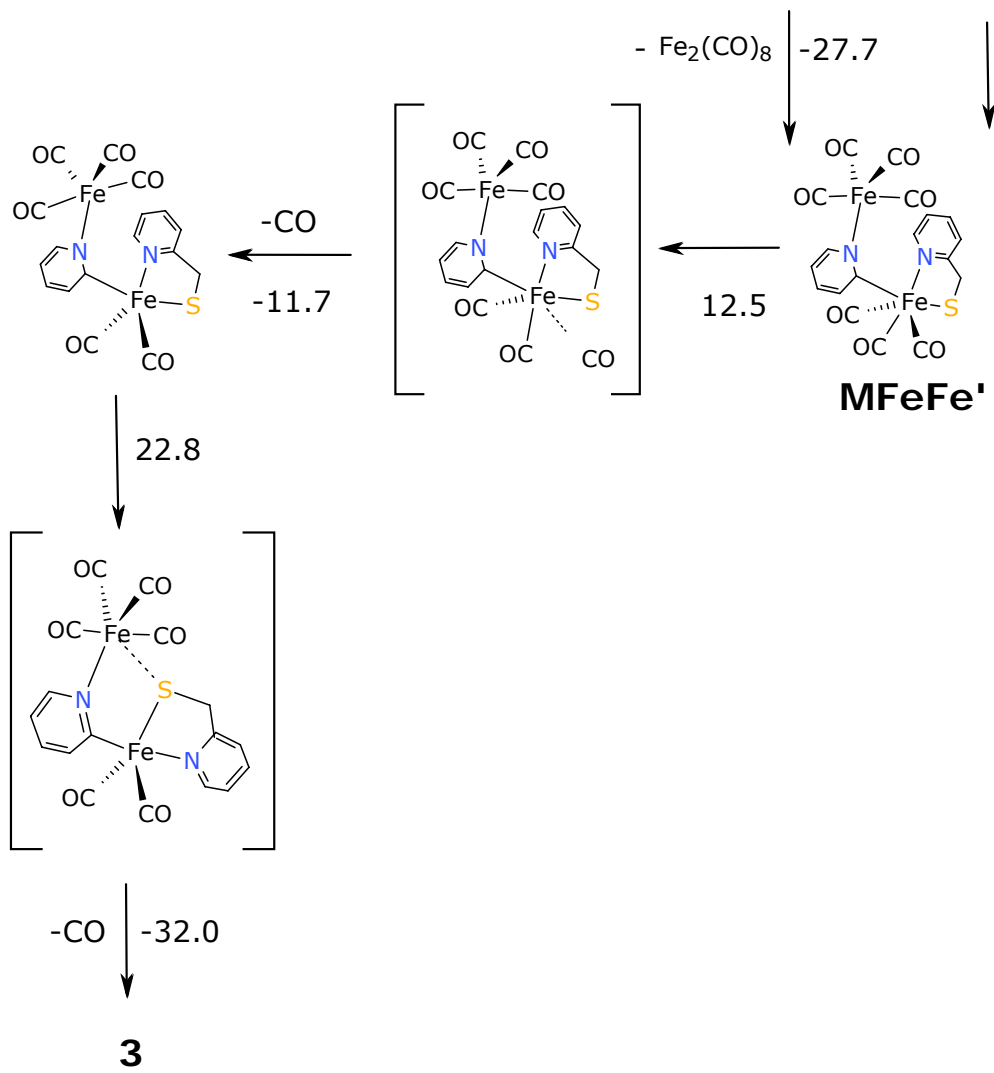
Scheme 7a. **YCO**, which has been formed in Scheme 6, as previously described, can quickly and exergonically lose a CO ligand, thus rejoining in **Y'** the bifurcation line originated at the nodal point X (see Scheme 6). The most important feature of **Y'** is probably the formation of the Fe-Fe bond, which is also present in final products. **Y'** then spontaneously and with no energy barrier forms a µ-CO derivative, in which the pyridine N chelates the second Fe thus generating the final Fe-C(Pyr)N-Fe junction. A final CO loss yields **5**, which, in principle, (but along a disfavoured pathway) might have been formed also through a concerted transition state, in which the N-Fe bond formation is concomitant to CO releasing.

Scheme 7b. In this scheme two parallel routes are shown in which **5** can act as a precursor of either **3** or **4**. The difference in forming either **3** or **4** is basically a regiochemical one: depending on which Fe of **5** undergoes the intramolecular attack by the free pyridine N atom, either **4** or **3** is formed. If N coordinates in trans position to the other N, **4** is obtained (after subsequent CO loss), whereas the attack occurring at other Fe, so that the incoming N has the pyridine C in trans to it, yields **3** (again after CO loss). No evidences have been found of concerted processes in which the N-Fe bond forms simultaneously to the CO loss.

Scheme 8a

pre-M

also from 5

h-pre-M

X

to 6

oxidat. add

10.4

-18.5

23.5

-20.4
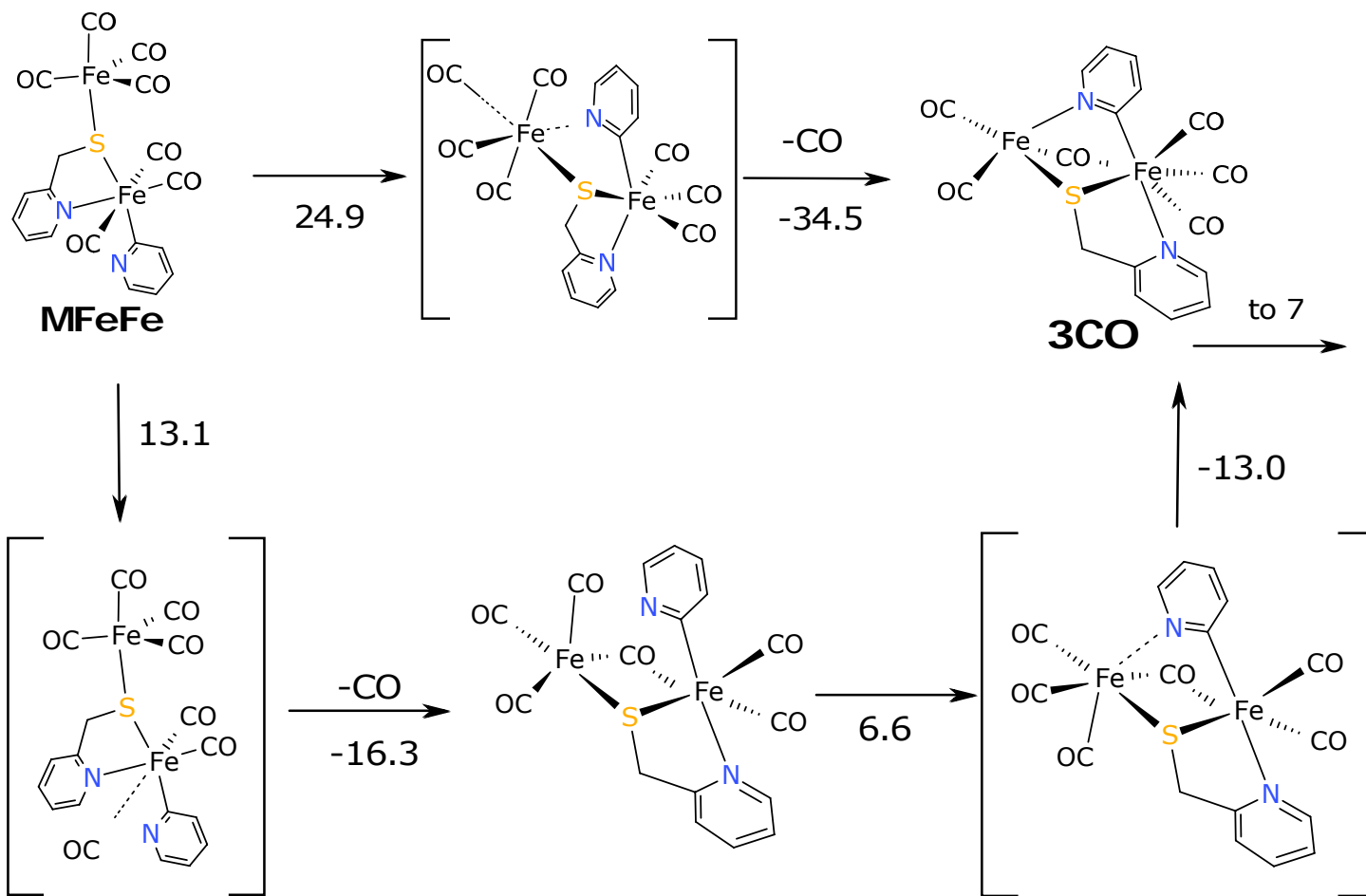
23.9

25.3

-17.5

$- Fe_2(CO)_8$ | -27.7

MFeF e'

$-CO$

-11.7

12.5

22.8

$-CO$ | -32.0

3

MFeFe
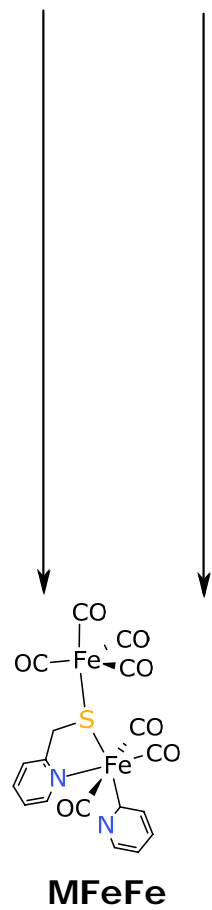
Scheme 8b

Schemes 8a and 8b show the investigated pathways of the L2+Fe$_3$(CO)$_{12}$ reaction which pass through the intermediate, which has been referred to as "**M**". One can envision to reach **M** by arriving from **pre-M** (upper left corner), which, in turn, can be originated by both coming from Scheme and by considering the third possible kind of attack of L2 onto Fe$_3$(CO)$_{12}$, that is through the pyridine N which is farthest from L2 CO. The oxidative addition which **pre-M** can undergo leads to the S-CO cleavage, which is necessary for final products to be formed. The so generated hexa-coordinated intermediate can evolve according to two different intramolecular SN2-like reactions: the O=C-Pyr bond attack (thus being broken) the Fe atom by concomitantly expelling either a CO (which yields **M**) or the bound pyridine ligand so as to generate **X**, already encountered in Scheme 6. As a note, due to the peculiar structure of **M**, in which an alfa-C of one of the two pyridyl rings is bound to Fe, instead of N (which would bear an unstable "free" deprotonated C) only the direct formation (i.e., without passing through **5**) of **3** can be conceived by starting from it and not that of **4** (in which two N atoms, bound to the same Fe are reciprocally in trans). Indeed an unstable isomeric form of **M**, in which two N of the two pyridine residues are "already" mutually in trans position in a "single Fe" unit (such as **M** actually is) would be required if **4** has to be formed without passing through **5**.

In the conditions modelled computationally, such isomer (not shown) does not exist as an energy minimum but evolves in one the unprotonated pyridine C attacks the nearest CO ligand on Fe to form an unusual 4-membered ring Fe-C(=O)-C(=C)-NPyr. It cannot be excluded that using the decarbonylating agent that has been actually employed (Me$_3$NO) in experimental conditions might decarbonylate this species which subsequently might link the second Fe(CO)$_4$ unit through the alfa-C atom, thus generating a precursor of **4**, but, that has not been taken into consideration.

M has two sites which can attack a new Fe(CO)$_4$ unit: the N atom of the pyridine ligand which is alfa-linked to Fe and the S. Whatsoever the

attacking site is, both lead to direct pathways for **3** formation (i.e., without passing through **5**). If the attack is through N, **MFeFe'** forms and, once a CO is lost from the its hexa-coordinated Fe moiety, a SN2-like reaction occurs in which the S atom moves to a bridging position between the two Fe with simultaneously expelling a CO; that finally yields **3**. The attack through S turns out kinetically favoured (and thermodynamically as well, even though very slightly) and forms **MFeFe**. In this case the loss of one CO causes another CO to become Fe-Fe bridged, which triggers the subsequent pyridine chelation through its free N. Thus, **3CO** (already encountered in Scheme 7) is formed and **3** as well from it by following the final part of Scheme 7.

Energetics Summary

L2+Fe$_3$(CO)$_{12}$→**3** ΔG=-6.8 kcal/mol

L2+Fe$_3$(CO)$_{12}$→**5** ΔG=-7.3 kcal/mol

L2+Fe$_3$(CO)$_{12}$→**4** ΔG=-6.3 kcal/mol