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The Cyclooligomerisation of Acetylene at Metal Centres

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Density-functional theory (DFT) and QCISD(T) calculations have been used to investigate the mechanism of cyclodimerisation and cyclotrimerisation of acetylene at a cyclopentadienyl-Co^I centre. In contrast to earlier investigations, we find that the most favourable mechanism for the formation of benzene involves the insertion of an acetylene molecule into a Co–C bond of the well known cobaltacyclopentadienyl intermediate. The product of this reaction then undergoes very facile ring-closure to benzene. This mechanism is found to be more favourable than the concerted Diels–Alder path, which is the highest in energy of the three mechanisms considered. The remaining reaction path involves initial addition of an acetylene molecule to the cyclopentadienyl ligand followed by rearrangement to give a 1,3,5-hexatrien-1-ylcyclopentane ligand system, which cleaves to give benzene and cyclopentadienyl ligands. Spin crossovers between the singlet and triplet states are found for the ring-closure of the cobaltacyclopentadienyl intermediate to give a cyclobutadiene complex and for the concerted Diels–Alder process. These spin crossovers and the reaction mechanisms in general are rationalised in terms of the concept of electron-transfer catalysis.

Introduction

The dimerisation, trimerisation and tetramerisation of acetylene to cyclobutadiene complexes,[1] benzene[2] or cyclooctatetraene[3] provide a prototypical example of the activation of small molecules by complexation to transition-metal centres. However, the closely related [2s+2s] dimerisation of ethylene to cyclobutane also serves as a prototype for the important class of "hole-catalysed" reactions,[4] in which the rate of the reaction in the one-electron oxidised system (usually the radical cation) is many orders of magnitude higher than that in the parent system. We[5–8] have introduced the concept of "electron-transfer catalysis", which provides a link between reactions of organic moieties in the coordination spheres of metals with hole-catalysed reactions and their equivalents that are accelerated by one-electron reduction of the parent system. The principle involved, which is explained in a review[8] and will therefore only be touched on here, is that an electron is transferred between the metal centre and the (usually organic) ligand somewhere along the reaction path near the transition state. This results in a lower activation barrier because the reaction actually takes place for the one-electron oxidised or reduced species. After passing the transition state, the electron is transferred back to give the original oxidation states for the constituents of the complex. We have developed a stepwise calculational protocol to investigate such reactions. First, the one-electron oxidised and reduced reactions are calculated without a metal atom. This provides us with the basic characteristics of the radical ion reactions. Secondly, the reaction is calculated as a complex with the abstracted model redox-active metal centre Be^I. This model allows us to assess the electrostatic effects of the metal centre without covalent overlap effects (for instance with valence d-orbitals) or ligand–ligand interactions. Finally, a representative experimental system is calculated and compared with the abstracted models. We now report a study that uses this protocol to investigate the dimerisation and trimerisation of acetylene to give cyclobutadiene and benzene, respectively.

These reactions have been investigated extensively, both experimentally[1–3,9] (including a pyridine synthesis[10]) and theoretically,[11–18] so that our primary aim in this work was not originally to determine the mechanism, but rather to introduce and investigate new concepts related to the activation of small molecules in the coordination sphere of redox-active metal centres. These concepts involve charge-transfer within the complex and small singlet-triplet energy gaps,[18,19] neither of which may be treated adequately by the density-functional theory (DFT) techniques used in most theoretical studies so far, so we have used DFT geometries for higher level ab initio calculations in order to be more confident of our results. Also, a previously unconsidered reaction pathway emerged in the course of our calculations. It is not the most favourable pathway, but deviates quite strongly from those reported in the most complete study so far[18] and may have consequences in similar reactions in other systems as it involves reaction of the cyclo-

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pentadienyl ligand directly. Our discussion starts with the underlying radical ion reactions and proceeds over a simple model system to the full experimentally observed catalysed reaction and attempts to relate these different levels of abstraction.

Results and Discussion

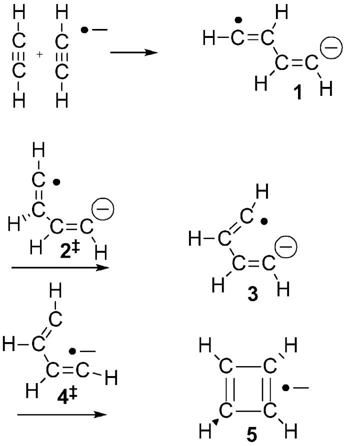
Acetylene + Acetylene$^{+\cdot}$

The reaction of a neutral acetylene molecule with the acetylene radical cation (i.e. the hole-catalysed dimerisation of acetylene, which is formally analogous to the well known[4] hole-catalysed [2s+2s]-cycloaddition of two olefins) has been treated in detail by Hrouda, Roeselová and Bally.[20] They find that a T-shaped complex initially formed collapses smoothly to a cyclobutadiene radical cation via a linear complex, or possibly a cyclopropylmethylene radical cation. The activation barriers between the minima along the reaction path are all found to be very small, so that the dimerisation can be regarded as a true hole-catalysed reaction.

Acetylene + Acetylene$^{-\cdot}$

Ab initio or DFT calculations on anions in the gas phase (in vacuo) require diffuse[21] or even Rydberg[21] functions for a proper description of their often very diffuse electron density. However, states with very diffuse electron density are quenched in condensed phases[22] so that the anions may behave very differently to the gas phase.[23] We[24] pointed out that the effect of condensed phases could be mimicked by limiting the extent of the most diffuse orbitals in the basis set, a technique that was adopted by Guerra and called the "boxing" procedure.[25] We have therefore investigated the reaction of acetylene with its radical anion (the electron-catalysed dimerisation of acetylene) using basis sets with and without diffuse function in order to simulate the effect not only of condensed phases, but also of a neighbouring positive charge. The electrostriction caused by complexing a radical anionic system to a positively charged metal centre should be equivalent to constricting the orbital extent in the radical anion, so that it is probably appropriate to compare the results for reactions in metal complexation spheres with those calculated for the radical anion without diffuse functions.

The initial addition of an acetylene radical anion to acetylene is extremely exothermic and occurs without activation energy to give the *trans* adduct **1**. The adduct **1** subsequently isomerizes via the transition state **2**‡ to the *cis* adduct **3**, which can ring close via the transition state **4**‡ to give the cyclobutadiene radical anion **5**.



The calculated energies for this reaction sequence are shown in Table 1. In contrast to the radical cation reaction, the ring-closure to the cyclobutadiene radical anion **5** from the initial *trans* adduct **1** is only slightly exothermic. As might be expected from such a result, the activation energies for the intermediate steps are therefore also higher than those found for the analogous radical-cation reaction. The rotation around the C–C bond to give the *cis* adduct **3** via transition state **2**‡ is calculated to have an activation barrier of 9 kcal mol^{-1}, both with the 6-31G(d) basis set (no diffuse functions) and with 6-31+G(d). The ring-closure reaction to give **5** proceeds via the transition state **4**‡ with an activation energy of 13.7 kcal mol^{-1} with 6-31G(d) and 14.5 kcal mol^{-1} with 6-31+G(d). Note that we find a C_{2h} structure for the cyclobutadiene radical anion with both basis sets, whereas earlier density functional calculations[26] found a planar structure. We have investigated planar cyclobutadiene$^{-\cdot}$ and find the resulting structure to be 2.5 kcal mol^{-1} less stable than **5** at QCISD/6-31+G(d) and to have 3 imaginary frequencies. The geometries of structures **1**–**5** are shown in Table S1 of the Supporting Information.

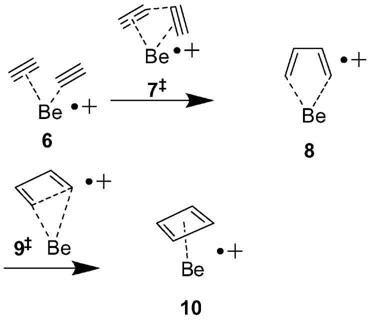
Table 1. Calculated total (a.u.), zero-point (ZPE, kcal mol^{-1}) and relative energies (rel., kcal mol^{-1}, including zero-point correction) for **1**–**5**. All minima have no imaginary normal vibrations and all transition states one. The planar cyclobutadiene radical anion has three.

	QCISD/6-31G(d) Total energy	ZPE	Rel.	QCISD/6-31+G(d) Total energy	ZPE	Rel.
C_2H_2 + $C_2H_2^{-\cdot}$	–154.06560	30.7	23.9	–154.11576	31.0	19.2
1	–154.11161	35.7	0.0	–154.15377	35.7	0.0
2‡	–154.09543	34.8	9.3	–154.13954	35.0	9.6
3	–154.10107	35.3	6.2	–154.14218	35.3	6.9
4‡	–154.07864	34.9	19.9	–154.11841	34.9	21.4
5	–154.12813	36.0	–10.1	–154.16745	35.3	–9.0
Planar cyclobutadiene radical anion				–154.16349	33.9	–7.9

The Model $Be^{+\cdot}$-Catalysed Reaction

We have previously used Be^{I} as a model for reductive redox-active transition-metal centres.[5–8] As shown below, this simple model system also shows a remarkable similarity to the experimental system in the case considered here.

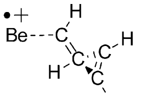
The starting point for the dimerisation reaction in the coordination sphere of a beryllium cation is the bis-acetylene complex **6**. This complex is formed in two very exothermic steps in which two acetylene molecules are coordinated successively to the metal center. The alternative process in which the second acetylene reacts directly to form a new C–C bond with one already coordinated to the metal was also investigated. The complex **11** thus obtained was found to be about 35 kcal mol^{-1} less stable than **6** and was not considered further.



The calculated energies for this reaction are shown in Table 2.

Table 2. Calculated total (a.u.), zero-point (ZPE, kcal mol^{-1}) and relative energies (rel., kcal mol^{-1}, including B3LYP zero-point correction) for **6**–**11**. All minima have no imaginary normal vibrations and all transition states one in this and the following tables.

Species	B3LYP/6-311+G(d) Total energy	ZPE	Rel.	QCISD(T)/6-311+G(d) Total energy	Rel.
C_2H_2 + C_2H_2:$Be^{+\cdot}$	–169.10399	34.1	64.4	–168.53084	90.1
6	–169.20938	35.8	0.0	–168.67711	0.0
7‡	–169.18159	36.4	18.0	–168.65703	13.2
8	–169.23804	40.7	–13.1	–168.71102	–16.4
9‡	–169.18584	38.9	17.9	–168.65879	15.6
10	–169.20226	40.0	8.7	–168.68143	1.5
11	–169.14320	38.0	43.7	–168.62401	35.5



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The two acetylene ligands in **6** can form a new C–C bond via the transition state **7**‡ to give the berylliacyclopentadiene radical cation **8**. This step is exothermic by 16 kcal mol^{-1} with a calculated activation barrier of 13 kcal mol^{-1}. The cation **8** proves to be the most stable structure found for $(C_2H_2)_2$:$Be^{+\cdot}$ The ring-closure reaction to give the cyclobutadiene complex **10** proceeds via the transition state **9**‡, in which the forming C–C bond is only moderately shortened relative to **8** (2.30 compared with 2.73 Å) but in which the beryllium is bent out of the plane of the hydrocarbon ligand (Be–C–C–C dihedral angle: 40°). The geometries of structures **6**–**10** are shown in Table S2 of the Supporting Information.

Figure 1 shows a comparison of the calculated reaction profiles for the radical anion dimerisation and that catalysed by Be^{I}. The two reactions are moderately similar, the most noticeable effect of the metal being the strong stabilisation of the berylliacyclopentadiene radical anion intermediate **8**. This stabilisation is not surprising as **8** contains two essentially normal covalent Be–C bonds that serve to stabilise it strongly. We were not able to find an alternative tetrahapto-bound structure for the $(CH)_4Be^{+\cdot}$ complex.

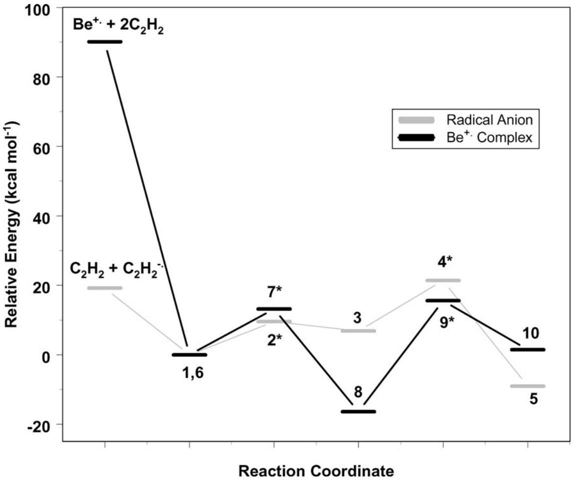
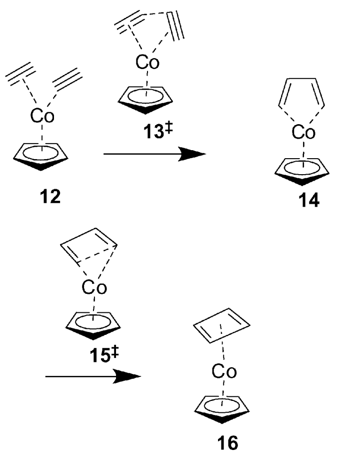


Figure 1. Comparison of the calculated reaction profiles for the acetylene dimerisation reaction for the radical anion [gray, QCISD/6-31+G(d)] and the $Be^{+\cdot}$ complex [black, QCSD(T)/6-311+G(d)//B3LYP/6-311+G(d)].

Cobalt-Catalysed Dimerisation

The path of the acetylene dimerisation in the coordination sphere of (cyclopentadienyl)cobalt, one of the experimentally known catalysts,[1] is remarkably similar to that found for the simple model Be^{I}.

Starting point for our calculations is the diacetylene complex **12**, which rearranges via the transition state **13**‡ to give the metallacyclopentadiene complex **14**. The calculated



energies for this reaction are shown for both the singlet and triplet states in Table 3. The geometries of structures **12**–**16** are shown in Table S3 of the Supporting Information.

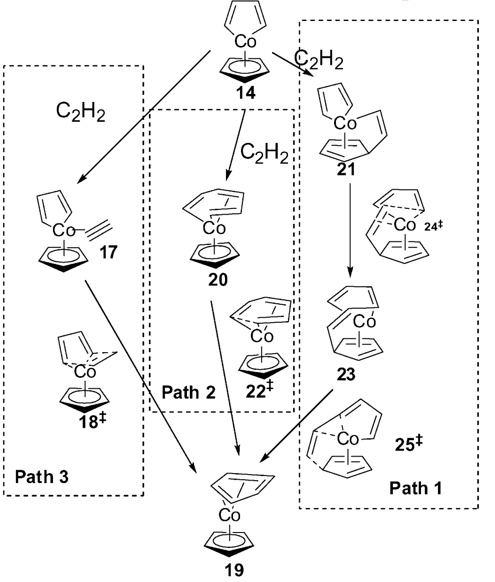
Table 3. Calculated total (a.u.), zero-point (ZPE, kcal mol^{-1}) and relative energies (rel., kcal mol^{-1}, including B3LYP zero-point correction) for **12**–**16**. The headings S and T represent singlet and triplet multiplicities, respectively.

Species	Total energy Singlet	Triplet	ZPE S	T	Rel. S	T
	B3LYP/SHAsv+pol					
12	–1730.58109	–1730.56905	89.0	87.3	0.0	5.9
13‡	–1730.56407	–1730.54293	89.2	87.6	10.9	22.5
14	–1730.61613	–1730.64176	91.8	91.5	–19.1	–33.9
15‡	–1730.57578	–1730.58071	90.6	89.7	5.0	1.0
16	–1730.67781	–1730.62860	93.5	91.3	–56.1	–27.5
	QCISD(T)/SHAsv+pol//B3LYP/SHAsv+pol					
12	–1728.28599	–1728.26796			0.0	9.6
13‡	–1728.27543	–1728.23314			6.9	31.8
14	–1728.31232	–1728.33002			–13.7	–25.1
15‡	–1728.26427	–1728.29018			15.3	–1.8
16	–1728.38278	–1728.32545			–56.2	–22.5

Cobalt-Catalysed Trimerisation

As suggested by previous theoretical investigations,[13,17,18] the addition of a third acetylene molecule to give a benzene complex is mechanistically far more complex than the dimerisation. Here, we have not considered a possible concerted [2s+2s+2s] cyclotrimerisation. Addition of a third acetylene to the cobaltacyclopentadiene **14** can give the acetylene complex **17**, which then undergoes the theoretically characterised[13,18] metal-assisted Diels–Alder reaction via the transition state **18**‡ to the product **19**. This reaction path (path 3) has been reported in previous theoretical studies for singlet[13,17,18] and triplet[17,18] multiplicities. However, an additional path (path 2) that proceeds via the addition product **20**, which can also be formed without activation barrier from acetylene and **14** and rearranges to **19** via the transition state **22**‡, was also reported recently for the Ru-catalysed reaction.[15] An important point is that the van der Waals complex **17** could not be found in any of the previous computational studies. Finding such a flat minimum is not trivial and depends heavily on several parameters. We consider the intramolecular Diels–Alder path found here to be equivalent to the intermolecular one found previously.

We have found a third path (path 1) in which the intermediate **21** is first formed without barrier from acetylene and **14**. The intermediate **21** can rearrange to the unusual intermediate **23**, in which the added acetylene is now bonded to both the cyclopentadienyl ligand and an α-carbon of the cobaltacyclopentadiene system of **14**, via the transition state **24**‡. The intermediate **23** undergoes a concerted sigmatropic rearrangement and ring-closure to give the final product **19** via the transition state **25**‡.



The lowest energy path (path 2) found for the addition of acetylene to **14** to give the benzene complex **19** is the addition of acetylene to an α-carbon of the cobaltacyclopentadienyl complex **14** to give the cyclohexatriene-1,6-diyl complex **20**, which then undergoes a facile ring-closure (the activation energy is slightly negative at B3LYP after ZPE correction) to give the product **19**. This is the most favourable path reported in ref.[15]

Note, however, that none of the three pathways involves an intermediate or transition state higher in energy than the starting point. We therefore cannot assign a "correct" path on the basis of the energies of intermediates and transition states as the shape of the energy hypersurface will determine which path is followed most often. We are, however, more concerned with defining possible paths for such reactions and the electronic principles involved than determining which of the pathways found is operative, or indeed if all three play a role. Table 4 shows the calculated energies for singlet and triplet states for the addition of an acetylene molecule to **14** to give **19** and Table S4 of the Supporting Information gives their geometries. These data do not allow us to determine the fate of **14** definitively, but rather point out the complexity of the energy hypersurface and outline several possible modes that the reaction may follow.

We investigated the individual reaction paths in great detail. In order to confirm that **17**, **20** and **21** are all formed without activation barriers and that we have identified the transition states correctly. We used both the IRC technique[26] implemented in Gaussian03 and the LST/QST transition-state searching facility in DMol3[27] as implemented in MS Modeling 3.2[28] using the PW91 functional[29] and the DND basis set.[27] The LST/QST procedure indicated that neither the formation of **20** nor that of **21** from acetylene and **14** entail an energy barrier. In order to characterise the reaction path more thoroughly, we confirmed these results using the nudged-elastic-band (NEB) technique, which also indicated that there are no overall activation barriers or intermediates. We also used

Table 4. Calculated total (a.u.), zero-point (ZPE, kcal mol^{-1}) and energies relative to **12** + C_2H_2 (rel., kcal mol^{-1}, including B3LYP zero-point correction) for **17**–**25**. The headings S and T represent singlet and triplet multiplicities, respectively.

Species	Total energy		ZPE		Rel.	
	Singlet	Triplet	S	T	S	T
	B3LYP/SHAsv+pol					
12 + C_2H_2	–1807.84564	–1807.83360	105.9	104.2	0.0	5.9
14 + C_2H_2	–1807.88068	–1807.90631	108.7	108.4	–19.2	–33.9
17	–1807.88590	–1807.90987	109.3	109.0	–21.9	–37.2
18‡	–1807.86625	–1807.88957	109.3	109.3	–9.5	–24.2
19	–1808.06231	–1808.09202	115.7	115.0	–126	–146
20	–1807.95283	–1807.93323	112.7	113.5	–60.4	–46.7
21	–1807.90930	–1807.90855	111.9	111.6	–33.9	–33.7
22‡	–1807.95249	–1807.91718	112.3	110.4	–60.6	–40.3
23	–1807.95952	–1807.96788	114.1	113.7	–63.2	–68.9
24‡	–1807.89995	–1807.89152	112.1	111.0	–27.8	–23.6
25‡	–1807.91891	–1807.94641	112.4	112.8	–39.5	–56.3
	QCISD(T)/SHAsv+pol//B3LYP/SHAsv+pol					
12 + C_2H_2	–1805.31335	–1805.29532			0.0	9.6
14 + C_2H_2	–1805.33968	–1805.35738			–13.7	–25.1
17	–1805.35033	–1805.37036			–19.9	–32.7
18‡	–1805.33886	–1805.34851			–12.7	–18.7
19	–1805.52852	–1805.55009			–125	–140
20	–1805.43823	–1805.38445			–71.6	–37.0
21	–1805.37834	–1805.35053			–35.0	–17.6
22‡	–1805.43268	–1805.36936			–68.5	–30.7
23	–1805.43499	–1805.41265			–68.1	–54.5
24‡	–1805.35800	–1805.35316			–21.8	–13.9
25‡	–1805.39017	–1805.39513			–41.7	–44.4

IRC calculations to confirm that the transition states **18**‡, **22**‡, **24**‡ and **25**‡ connect the appropriate minima, as shown above. The details of this mechanism and the intermediates will be discussed below.

Discussion

The above results reveal a new path for the oligomerisation of acetylene using a CoCp catalyst that has not been considered in previous theoretical investigations, although analogous mechanisms have been discussed in the context of experimental studies.[30,31] This new path proceeds via the structure **20** and represents an alternative mechanism for the formation of benzene that proceeds without a net activation barrier relative to **19** + acetylene, like the more stable path reported previously.[18] Another striking feature of these reaction paths is the energetic adjacency of the triplet energy hypersurface to the singlet one. This aspect was discussed extensively in a recent theoretical study,[18] but we will show that it is a consequence of the underlying electron-transfer catalysis. Because these two aspects of our results are largely unrelated, we discuss them separately.

Mechanistic Details

Singlet Reaction Paths

At first it seems remarkable that we should be able to find a new reaction path not found in earlier studies. We emphasise, however, that any progress that we have been able to make is primarily due to hard- and software advances since 1999, when the first study of this reaction was published[13] and to serendipity. More recent work[18] found path 2 (**14** + $C_2H_2 \rightarrow$ **20** $\rightarrow$ **19**), and also considered the triplet state. Nevertheless, the third reaction path revealed in this work is both new and fascinating.

This reaction path (path 1, **14** + $C_2H_2 \rightarrow$ **21** $\rightarrow$ **23** $\rightarrow$ **19**) involves the addition of acetylene to the cyclopentadienyl ring to give the [(hexatrien-6-yl)cyclopentadiene]cobalt complex **23**. This path is found to occur without net activation energy at both the B3LYP and QCISD(T) levels but lies significantly higher in energy than the more stable path.

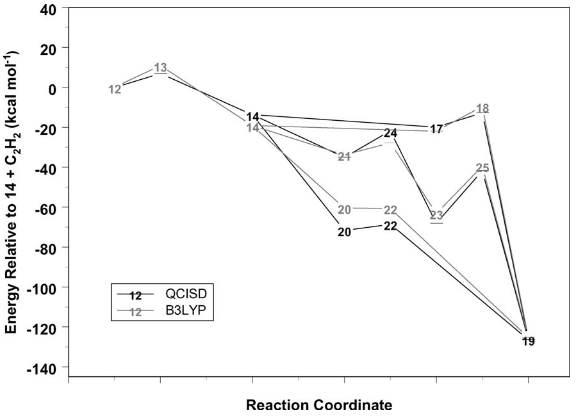


Figure 2. Comparison of the B3LYP (gray) and QCISD(T) (black) calculated energy profiles for the trimerization of acetylene starting from **14**.

The third alternative is that originally proposed,[13] the concerted Diels–Alder like addition via complex **17** that leads directly to **19**. This path crosses a barrier 6.4 kcal mol^{-1} higher in the energy than the starting point (**14** + C_2H_2) and is thus the only one of the three alternative paths with an overall activation barrier relative to **14** + C_2H_2.

The agreement between the DFT results and those obtained at the QCISD(T) level for the singlet trimerisation paths shown above is satisfactory. A comparison of the calculated energy profiles for the singlets is shown in Figure 2.

Electron Transfer and Two-State Reactivity

A further feature of the above mechanisms is the proximity of the triplet hypersurface to the singlet and, in places, the fact that the triplet is the ground state.[17,18] Generally, B3LYP overestimates the stability of the triplet relative to the singlet. This can be corrected by changing the amount of Hartree–Fock exchange in the functional,[32] but we chose in this case to rely on QCISD(T) as we have no calibration data for complexes of this type. Nevertheless, even at the QCISD(T) level, the triplet is found to be the ground state for the product of the trimerisation (**19**) and minimum and transition state immediately preceding it on the "Diels–Alder" pathway (path 3, **17** and **18**‡)[18] as well as for **14** and the transition state (**15**‡) for its ring-closure to the cyclobutadiene complex **16**, which is found to have a singlet ground state. Figure 3 shows comparisons of the singlet and triplet QCISD(T) reaction profiles for the three alternative reaction paths outlined above and for the ring-closure to **16**. The energies of the states of different multiplicity are predicted to cross at least once for each path. The electronic nature of triplet **19** has been discussed previously,[17,18] so that we have concentrated the electronic natures of the triplet intermediates **14** and **15**‡. Their calculated (B3LYP) spin densities are shown in Figure 4.

The spin densities are compatible with our interpretation of the reaction mechanism. Clearly, one electron has been transferred from the metal centre to the reactive ligand system. There is relatively little spin delocalisation onto the cyclopentadienyl ligand.

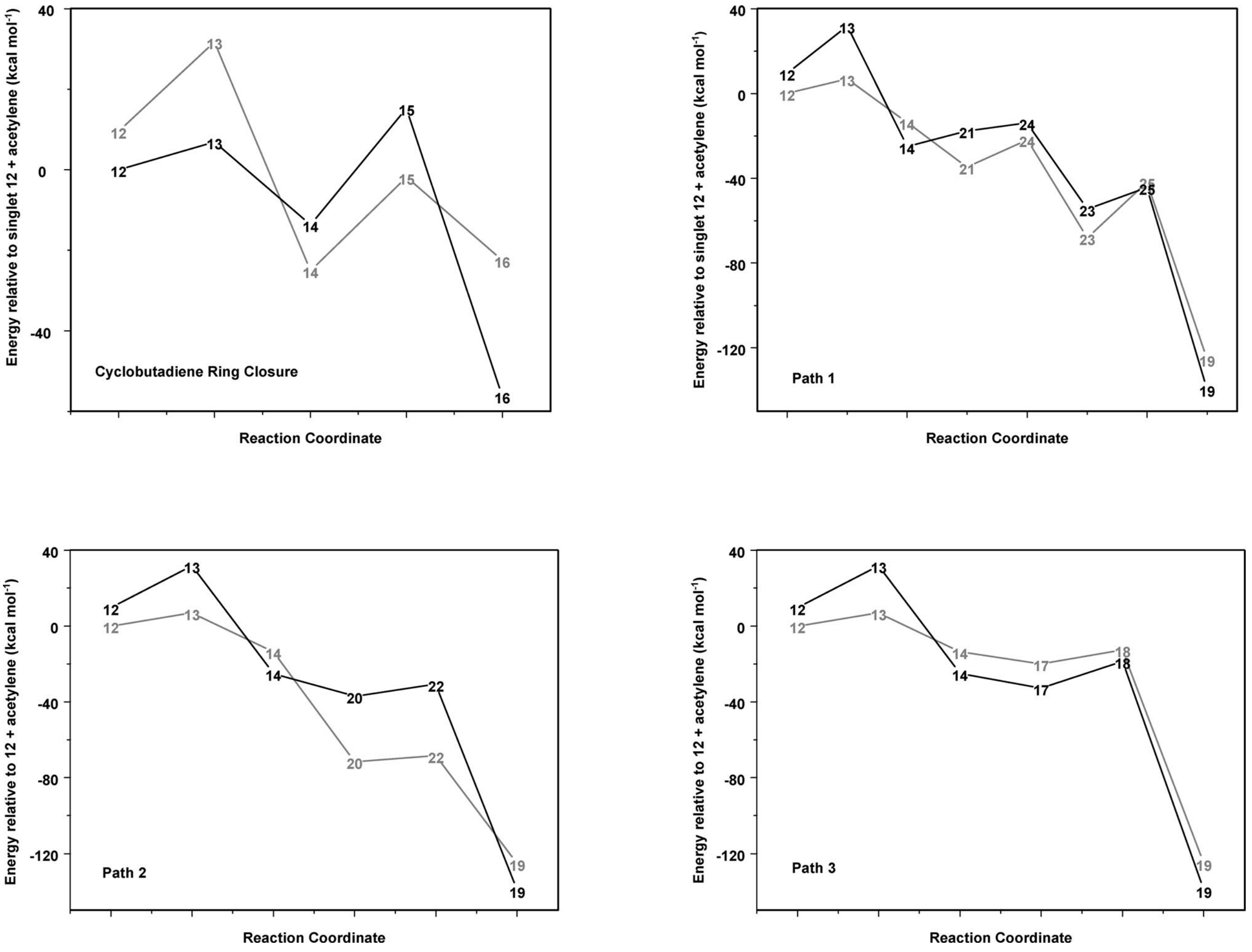


Figure 3. Comparison of the singlet (black) and triplet (gray) QCISD(T) calculated energy profiles for the trimerization of acetylene according to starting from **12** + acetylene. The four different reaction paths shown are; cyclobutadiene ring-closure: **12** → **14** → **16**; path 1: **12** → **14** → **21** → **23** → **19**; path 2: **12** → **14** → **20** → **19**; path 3: **12** → **14** → **17** → **19**.

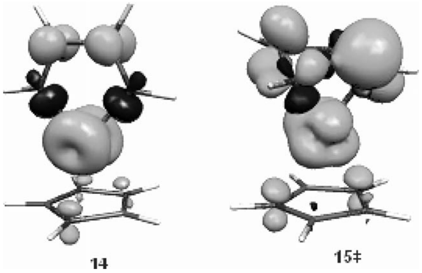
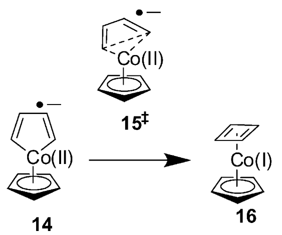


Figure 4. Calculated (B3LYP) spin densities (gray is positive, black negative) for **14** and **15**‡.

The ring-closure of **14** to **16** via **15**‡ can therefore be described as follows:



Note that the radical anion is formed by metal-to-ligand charge-transfer and is therefore purely formally negatively charged. We emphasise that the view of the mechanism shown in the Scheme above is of model character designed to explain the catalysis of the individual reaction steps. It should not be confused with the formation of a real, isolatable radical anion.

Similarly, the "Diels–Alder" pathway involves one-electron reduction of the C_4-unit in **14**, which leads to spin-delocalisation onto the complexed acetylene molecule in the transition state **18**‡, as shown in Figure 5. Note that this spin delocalisation to the C_2H_2 moiety develops during the cycloaddition. There is no significant spin on the acetylene in **17**.

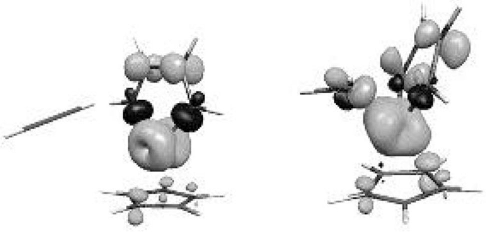


Figure 5. Calculated (B3LYP) spin densities (gray is positive, black negative) for **17** and **18**‡.

We note that the intermediates and transition states for the most favorable pathways (path 2, **20**, and **22**‡ and path 1, **21**, **23**‡, **24** and **25**‡) are all calculated to be low spin, although the starting point **14** and the product **19** are found to be high spin. The cyclobutadiene ring-closure and path 1, however, illustrate the connection between electron-transfer catalysis and changes of spin multiplicity along the reaction path. Specifically, a change from low to high spin for transition states or intermediates is expected to be a common feature of electron-transfer catalysed reactions.

This form of two-state reactivity[33] can be explained using the simple interpretation shown below (Figure 6).

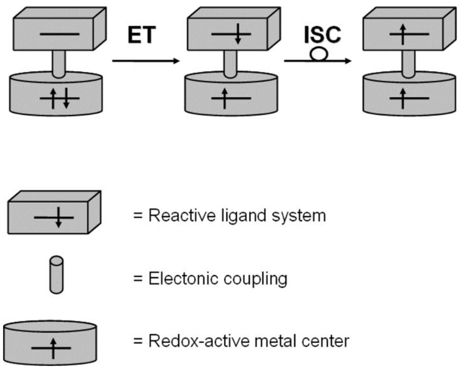


Figure 6. Schematic diagram of how electron transfer (ET) between the metal centre and the ligand can lead to inter-system crossing (ISC) to the triplet state for systems with an even number of electrons.

The reactive ligand system (in this case either C_4H_4 or C_6H_6) can either be reduced or oxidised by the metal centre. The former can lead to hole catalysis and the latter to a facile radical-anion reaction.[5–8] Depending on the magnitude of the electronic coupling between the metal centre and the ligand system, however, the triplet state may be more stable, so that the complex can undergo exothermic inter-system crossing to the triplet. As outlined for electron-transfer catalysis,[8] the electron-transfer may be reversed before the product is reached, resulting in a further inter-system crossing back to the singlet. This is demonstrated by the calculated spin densities shown in Figures 4 and 5. The unpaired electron density in the triplet ground state is clearly divided between the metal centre and the reacting ligand system.

Implications of the Mechanisms Found

The reaction pathways and the structures of intermediates and transition states reported here stretch the ability of conventional bonding theory. A referee has, for instance, pointed out that singlet **20** can be regarded as a bicyclic carbene analogous to one reported by Paneque et al.[34] Such structures are well known in Ru-catalysed reactions.[15,35] However, these aspects of possible reaction paths are not our main concern. We wish here to point out the general principles of electron-transfer catalysis in these reactions and not to try to extract mechanistic details that are beyond the accuracy of our calculations. We have therefore, for instance, not attempted to calculate the exact crossing points between singlet and triplet hypersurfaces. Given the uncertainty of the relative energies of the two hypersurfaces and the fact that singlet-triplet energy differences can essentially be adjusted at will in hybrid density functional calculations,[32] calculating exact crossing points would be meaningless. Apart from the electron-transfer catalysis aspect of the results reported above, the presence of several competing activationless reaction paths (Figure 3) underlines the complexity of many reactions of this type and questions the validity of mechanistic interpretations that concentrate on only one path. We do not know which path is followed most, or even of only one path is followed. This is, however, also a consequence of the bonding flexibility conferred by the intramolecular electron transfer process, which opens up the possibility of many radical-like processes.

The thermodynamically most favourable path (path 2) does not lead to any significant new conclusions about the mechanism except for the detail that this path does not represent a classical concerted Diels–Alder process, but rather addition of an acetylene moiety to the terminal carbon atom of the C_4-unit of the cobaltacyclopentadiene **14** followed by a very facile ring-closure to give the product **19** (i.e. a very asynchronous Diels–Alder). The electron-transfer between the cobalt centre and the C_4H_4 moiety is instrumental in favouring this mechanism because the initial barrierless addition **14** can be considered alternatively as a radical addition to acetylene or as an insertion of acetylene into a Co–C bond. We would expect a radical addition to have a low activation barrier and this is clearly lowered even further by the participation of the metal. The very low barrier to aromatisation is expected. Note also that Bischof's arguments[36] regarding the Jahn–Teller nature of the transition states of radical pericyclic reactions suggest that the Diels–Alder like process should proceed via an unsymmetrical transition state. This could conceivably lead to the stepwise reaction found. However, the fact that triplet **18**‡ is slightly unsymmetrical but can still be recognised as a Diels–Alder like transition state (see Table S5 of the Supporting Information) suggests that the Jahn–Teller effect is not enough to induce the stepwise reaction mechanism. It should be mentioned in this context that Jahn–Teller effects in cobalt complexes depend strongly on the basis set used for the calculation,[37,38] although the Jahn–Teller effect discussed here and by Bischof occurs within the radical reaction, not at the metal centre.

The thermodynamically slightly less favourable path 1 is mechanistically important because it involves the intermediate **23**, in which the ligand system is a 1,3,5-hexatrien-1-ylcyclopentadiene. This intermediate provides a clue for reactions such as the formation of ferrocene from five molecules of acetylene and an iron atom[30,31] or the transfer of phosphorus atoms or methane carbons from one ligand to the other in sandwich compounds involving organophosphorus cage ligands that arise from phosphaalkyne oligomerisation.[39] The initial addition to the cyclopentadienyl ligand (**14** + C_2H_2 → **21**) has precedent[40] in the literature but the general nature of reaction path 1 provides important clues as to the mechanism of reactions in which atoms or groups are transferred from one ligand to the other in sandwich-like complexes. We will report computational studies on both the ferrocene and phosphaalkyne mechanisms in due course.

Singlet and Triplet Structures

In general, the Lewis structures of the singlet and triplet states of the species discussed here are very similar. They are compared graphically in Table S5 of the Supporting Information. The largest deviations are found for **12**, in which the cyclopentadienyl ring in the triplet tends towards η^4-coordination, and **19**, for which the η^4-coordination observed for the benzene ring in the singlet becomes essentially symmetrical η^6-coordination in the triplet.[16] There is also presumably a transition state between triplet **14** + C_2H_2 and triplet **21**, although we have not located this structure.

Experimental Section

General: All calculations used Gaussian 03.[41] Geometry optimisations for non-transition-metal systems used the 6-31G(d),[42] 6-31+G(d)[43] and 6-311+G(d)[44] basis sets at both the hybrid density functional (B3LYP[45,46]) and QCISD[47] levels of theory. Cobalt complexes were optimised with B3LYP using the Schaefer–Horn–Ahlrichs split-valence basis set[48] augmented with standard polarisation functions.[49] Optimised geometries were confirmed to be minima or transition states by calculating their normal vibrations within the harmonic approximation at the level of the geometry optimisation. Where noted in the text, reactions paths were followed using the intrinsic reaction coordinate technique[50] in order to confirm the course of the reaction. Single-point calculations at the QCISD(T)[51] level were used to refine the energies using the same basis sets as for the geometry optimisations. Gaussian archive entries for all the species reported are included in the Supporting Information.

Supporting Information (see also the footnote on the first page of this article): Tables S1 to S5 as defined in the text and the Gaussian Archive entries for the calculations reported above.

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