

First C–C bond formation in the Pauson–Khand reaction: Influence of carbon–carbon triple bond polarization on regiochemistry A density functional theory study

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Abstract

The influence of carbon–carbon triple bond polarization on the regiochemistry of the Pauson–Khand reaction has been studied with the B3LYP functional. The regiochemistry determining step of this reaction, i.e., olefin insertion leading to cobaltacycle formation, has been examined with ethylene as the olefin and propyne, methyl 2-butynoate, and methyl propiolate as the acetylenes. From this study, it has been concluded that, in absence of overwhelming steric effects of an acetylene substituent, the regiochemistry is influenced by the polarization of the acetylenic bond, which arises from the different substituents. The initial C–C bond is preferentially formed with the acetylenic carbon that has the greater electron density: with propyne, this leads to a cyclopentenone having the methyl group in the α -position; with methyl 2-butynoate, to a cyclopentenone with the CO₂Me in the β -position; with methyl propiolate, which is virtually unpolarized in the complex, to a cyclopentenone with the CO₂Me in the α -position (a result of steric effects). These theoretical results are concordant with those observed experimentally with norbornene. The question of axial versus equatorial reactive positions for the coordinated olefin is also addressed and a kinetic simulation is presented.

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Keywords: Pauson–Khand reaction; DFT studies; Triple-bond polarization; Olefin insertion

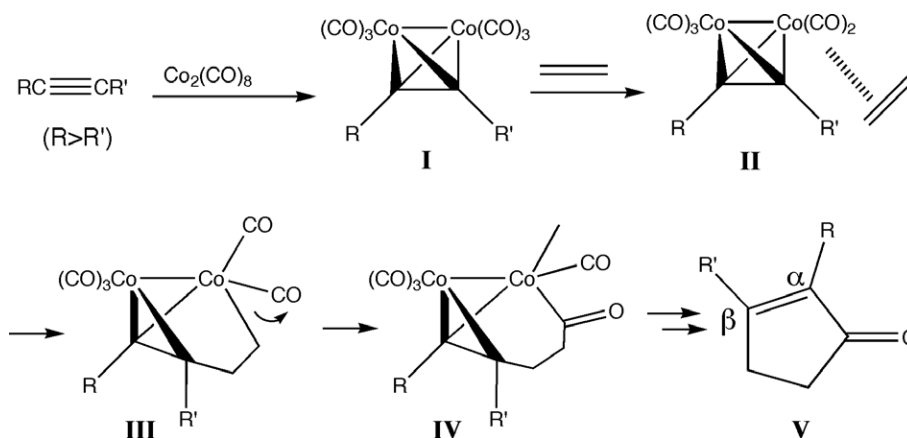
1. Introduction

Discovered in the early seventies [1], the Pauson–Khand reaction has become important for the synthesis of cyclopentenone derivatives and is now often used for the preparation of natural products [2]. This novel transformation, formally a [2 + 2 + 1] cycloaddition of an alkyne, alkene, and carbon monoxide, can be effected with either stoichiometric or catalytic amounts of dicobalt octacarbonyl (Eq. (1)).



Over the years, numerous modifications of the Pauson–Khand reaction have been studied that have greatly improved its efficiency [3]. In contrast to this progress, the mechanistic understanding of this reaction remains today incomplete, and only recently has the pathway initially proposed in 1985 by Magnus *et al.* [4] received serious study. In the Magnus mechanism (Scheme 1), it is assumed that C–C bond formation leading to cobaltacycle **III** occurs at the less hindered acetylenic carbon. While this is generally consistent with the regiochemical outcome of the reaction, the observation of Krafft *et al.* that with ethyl 2-butynoate and norbornene the CO₂Et group of the resultant cyclopentenone resides exclusively in the β -position [5] has been difficult to explain. In that the scheme proposed by Magnus would predict, on the basis of steric impediment, the α -position, there must be at least one

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Scheme 1. Pauson–Khand mechanism proposed by Magnus.

other factor that influences regiochemistry in the Pauson–Khand reaction. Although experimental studies have suggested that, in addition to steric effects, electronic factors can somehow also play a role in determining the regiochemistry, insight into how this might occur has only recently been published [6].

The first full quantum mechanical investigation of the Pauson–Khand reaction (a DFT study), published in 2001 by Yamanaka and Nakamura [7], offered support for the Magnus pathway. However, the authors only considered equatorial coordination of the olefin, although experimental data at the time suggested that axial olefin coordination could be involved (see Fig. 1 for nomenclature) [8]. We later showed that in cases where pseudorotation of the olefin is relatively facile, the olefin insertion takes place, in fact, mainly from an axial position; it was also pointed out at the time that strong polarization of the “acetylenic” carbon–carbon bond [9] existed in the complex with propyne, and offered that polarization might have an important effect on the outcome of the Pauson–Khand reaction [10]. Given these two new parameters, i.e., axial binding and acetylenic bond polarization, a study of polarization effects, as well as steric effects, on cobalt-cycle formation from the different Co coordination sites seemed appropriate.

In this paper, the potential energy surface for this crucial, regiochemistry determining step will be detailed. Propyne, methyl propiolate, and methyl 2-butynoate are used as the acetylenes and ethylene as the reacting olefin for this theoretical study. Propyne and ethyl propiolate with norbornene experimentally yield cyclopentenones in which

the larger substituent is in the α position, whereas ethyl 2-butynoate, as mentioned above, produces a cyclopentenone with the larger substituent in the β position. Additionally relevant is that propyne and methyl 2-butynoate have opposite polarizations, i.e., the acetylenic carbon atom with larger substituent has in propyne the smaller electron density, while in methyl 2-butynoate it has the larger electron density; methyl propiolate, in contrast, is virtually devoid of polarization [6]. Thus, these three examples, taken together, are useful for probing the relative importance of steric and electronic factors in determining the geometrical orientation of the coordinated olefin and the regiochemical outcome of the Pauson–Khand reaction.

2. Theoretical methods

All calculations were performed with the Gaussian 98 suite of programs [11], using Becke’s three-parameter hybrid exchange functional [12], in combination with the correlation functional of Lee–Yang–Parr [13]. This B3LYP functional was used with the non-relativistic effective core potential LANL2DZ [14] for cobalt, the D95 split valence basis set [15] for C and O augmented with a set of d polarization functions for a correct description of CO [16], and the D95 split valence basis set for H. This tailor-made basis set has proven to yield accurate geometries for these dicobalt complexes and will be denoted as LANL2DZ*. All geometries were fully optimized without any symmetry constraint and subsequently followed by frequency analysis to determine the nature of the stationary point. In addition, all energy comparisons were derived from the zero-point corrected total energies. Net atomic charges have been calculated using natural population analysis from the NBO program at the same level of theory as for the optimizations [17]. Orbital analyses were performed on the Kohn–Sham orbitals without any localization procedure.

The kinetic study was carried out using the RRKM approximation. Calculations were performed with the freely available MassKinetics program [18]. (The algorithm was originally developed for modeling complex reaction

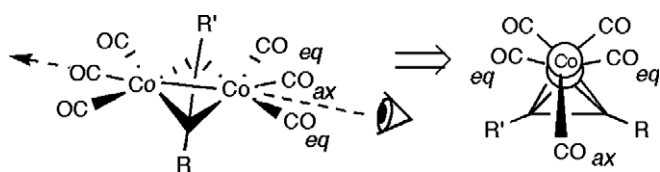


Fig. 1. Nomenclature for the different olefin coordination sites: pseudo-equatorial and pseudo-axial.

kinetic systems for mass spectrometry [19], i.e., for non-thermal, non-equilibrium situations, but can be used for thermal systems as well.) Energy differences and molecular frequencies necessary for RRKM were extracted from the DFT calculations.

3. Results and discussion

3.1. Propyne

The optimized structures of the dicobalt pentacarbonyl–propyne–ethylene complex for the two possible modes of equatorial olefin coordination (perpendicular and parallel) and an axial mode are shown in Fig. 2.

It can be seen that for both *cis* and *trans* equatorial binding, the distance $r(\text{Co}-\text{C}_{\text{ethylene}})$ is significantly shorter for the perpendicular mode of coordination (**2a** and **2c**) than the parallel mode (**2b** and **2d**). An analysis of the orbitals involved in the binding of ethylene to cobalt shows that the amount of “back-donation” [20] (Co electrons \rightarrow olefin empty π^* -orbital) is significantly smaller in parallel coordination than in perpendicular coordination, which explains the relative distances. The increased amount of back-donation in the perpendicular coordination is also reflected in the longer interatomic distance between the two carbon atoms of the olefin: 1.376 Å (**2a**) and 1.377 Å (**2c**) in case of perpendicular coordination versus 1.367 Å (**2b**) and 1.370 Å (**2d**) for parallel coordination. The interatomic dis-

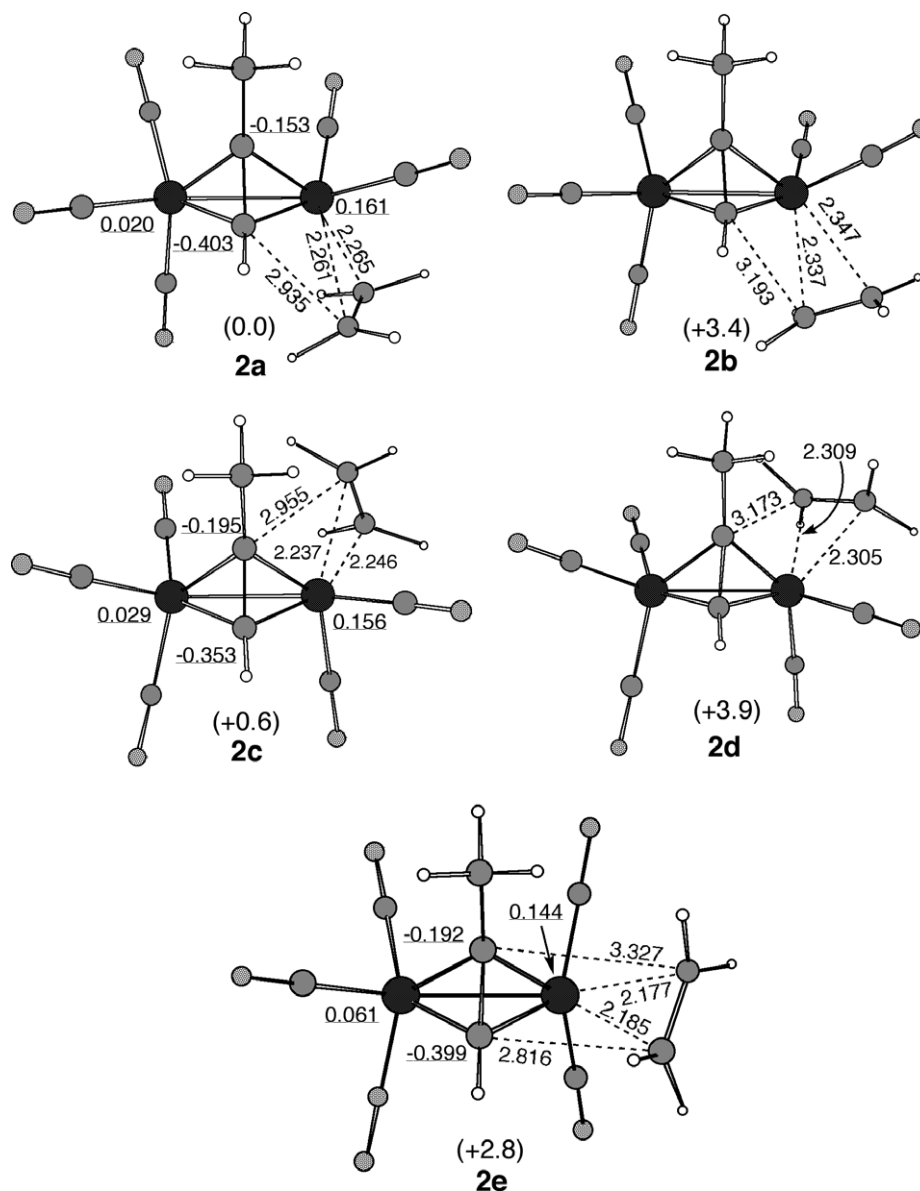


Fig. 2. Localized minima of the olefin-coordinated dicobalt pentacarbonyl–propyne complexes at the B3LYP/LANL2DZ* level. Interatomic distances are in Å and relative energies (kcal mol⁻¹) are with respect to structure **2a**. Natural populations (e⁻) are underlined.

tances between the carbon atoms that are involved in the formation of the cobaltacycle product are significantly longer and therefore less favorable in the parallel mode: $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{H}}) = 3.193$ in **2b** versus 2.935 \AA in **2a** and $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{Me}}) = 3.173$ in **2d** versus 2.955 \AA in **2c**. Not surprisingly, perpendicular coordination is, energetically, clearly favored over parallel (by 3.4 and $3.3 \text{ kcal mol}^{-1}$). The parallel structures, therefore, will not be further considered.

Only one coordination mode could be found for axial association of the olefin (**2e**). Although this complex displays shorter $r(\text{Co}-\text{C}_{\text{ethylene}})$ distances as compared to, for example, **2a** ($2.177/2.185 \text{ \AA}$ versus $2.261/2.265 \text{ \AA}$, respectively), its energy is higher by $2.8 \text{ kcal mol}^{-1}$. These relatively short $\text{Co}-\text{C}_{\text{ethylene}}$ distances for axial coordination most likely result from the fact that the $d_{x^2-y^2}$ orbital (z taken as the $\text{Co}-\text{Co}$ axis and x and y as the $\text{Co}-\text{CO}$ equatorial bonds), which is important for the description of the back-donation of electrons from the filled Co d-orbitals into the empty π^* -orbitals of the acetylene, is also involved in the back-donation of electrons from the Co into the empty π^* -orbital of ethylene. This back-donation component is significantly smaller in case of equatorial binding, the major binding contribution coming from the donation of π -electrons from ethylene into the empty d-orbitals, and this most probably explains the longer $r(\text{Co}-\text{C}_{\text{ethylene}})$ distances. This increased back-donation in axial coordination is also reflected in the longer carbon–

carbon distance in the olefin of 1.388 \AA , as compared to 1.376 \AA (**2a**) and 1.377 \AA (**2c**). It should be noted that axially coordinated ethylene is not symmetrically bound to the cobalt, i.e., a substantial tilt is observed: $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{H}}) = 2.816 \text{ \AA}$ and $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{Me}}) = 3.327 \text{ \AA}$ [21].

Fig. 3 displays the energy diagram for the formation of the two possible cobaltacycle products, starting from the two equatorially (perpendicular) (**2a** and **2c**) and one axially (**2e**) coordinated ethylene structures. It is readily seen in Fig. 2 that axially coordinated ethylene (**2e**) can potentially react with either acetylenic carbon and thereby yield the two cobaltacycles. In contrast, the equatorially coordinated olefin can reasonably react only with the closer acetylenic carbon, thus yielding just one of the two possible cobaltacycle products. Complex **2e** is less stable than **2a** and **2c**, but reacts more readily than either, as evidenced by the energy barriers: 11.0 and 14.4 versus 15.2 and $16.8 \text{ kcal mol}^{-1}$, respectively. In the coordinated structures, **2e** has a relatively short distance (Fig. 2, 2.816 \AA), but in the corresponding **TS1**, the distance is relatively long (Fig. 3, **TS1**, 1.953) [22]. With respect to the reaction coordinate for the C–C bond formation, the transition state (**TS1**) thus arrives relatively quickly, which is usually associated with a lower energy barrier, as observed.

The interatomic distance between the reacting carbons appears, however, not to be the only parameter closely associated with the energy barrier. The distances in the reacting structures **2a** and **2c** are nearly equal (2.935 and

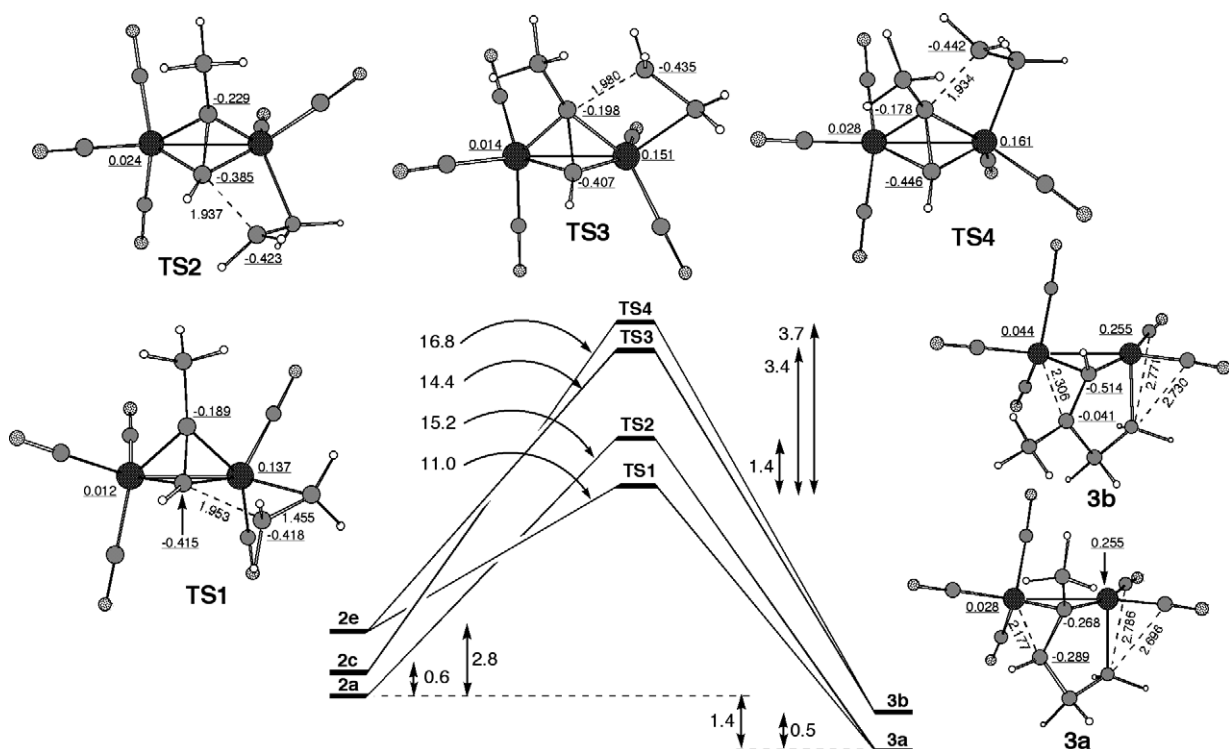


Fig. 3. B3LYP/LANL2DZ* potential energy surface for the formation of the two cobaltacycle products from the dicobalt pentacarbonyl-propyne-ethylene complex. Distances are in \AA and energies are in kcal mol^{-1} . Natural populations (e^-) are underlined.

2.955 Å, respectively), as are the distances in the corresponding transition state structures **TS2** and **TS4** (1.937 and 1.934 Å, respectively), yet there is a difference of almost 2 kcal mol⁻¹ between the two barriers: 15.2 and 16.8 kcal mol⁻¹. Natural population analysis shows that the acetylenic carbon with the hydrogen has a larger electron density than that with the methyl (**Fig. 3**, **TS2** and **TS4**). A strong polarization of propyne, with the C_H negatively charged, has previously been observed, both experimentally and computationally [6], and the role of electronic factors in determining the regiochemistry of the insertion of unsymmetrical alkynes in a different organometallic process has already been discussed [9].

In previous studies, we showed that the carbonyl–olefin ligand exchange did not proceed by a concerted pathway [23] and that the loss of a carbonyl from an equatorial position was less demanding than from an axial one by about 10 kcal/mol [6]. Thus, most probably, the olefin is initially coordinated in an equatorial position; however, the olefin can, through pseudo-rotation (when feasible), switch to an axial site [10]. Structure **2e** is quite easily accessible from **2a** or **2c** through low-lying transition states [24]. Reaction kinetic modeling (using the RRKM-based MassKinetics program [19]) indeed shows that near-equilibrium distribution among equatorial and axial positions is established very quickly (within 10⁻⁹ s). More significantly, though, reaction kinetic modeling of the possible routes to **3a** indicates that the reaction takes predominantly the pathway **2a** → **2c** → **2e** → **TS1** → **3a**, which is about 8 times faster than the more direct route **2a** → **TS2** → **3a**. (The branching ratio between these two reaction channels depends slightly on temperature; it is 9.1 at 60 °C, 8.2 at 80 °C, and 7.4 at 100 °C.)

The important conclusion to be drawn from above is that when the pseudorotation of the olefin is facile, the main route may well involve the axial position [25]. With the dicobalt pentacarbonyl–propyne–ethylene complex, the reaction pathway **2e** → **TS1** → **3a** is clearly the most favorable and, thus, the methyl group will be found in the α-position of the ultimately produced cyclopentenone.

3.2. Methyl 2-butynoate

As for propyne, with methyl 2-butynoate two modes of equatorial ethylene coordination are found. As before, the parallel associations are less stable than the perpendicular ones and, moreover, they have interatomic distances between the reactive carbon atoms that are considerably longer, and thus less favorable, for formation of the C–C bond leading to the cobaltacycle. Therefore, these parallel structures will again no longer be considered [26]. In addition to the localized stationary structures in which the ethylene is equatorially coordinated, there are now, in contrast to the case of propyne, two structures for the axially positioned olefin (**2h** and **2i**, **Fig. 4**). Ethylene shows a tilt toward either the carbon bearing the ester group [$r(\text{C}_{\text{ethylene}}\text{--C}_{\text{ester}}) = 3.035$; $r(\text{C}_{\text{ethylene}}\text{--C}_{\text{Me}}) = 3.115$ Å] in

the case of **2i** or the carbon with the methyl group [$r(\text{C}_{\text{ethylene}}\text{--C}_{\text{ester}}) = 3.255$; $r(\text{C}_{\text{ethylene}}\text{--C}_{\text{Me}}) = 2.904$ Å] in the case of **2h**. While in the latter case, the tilt is more pronounced, it is still significantly smaller than with propyne: $r(\text{C}_{\text{ethylene}}\text{--C}_{\text{H}}) = 2.816$ and $r(\text{C}_{\text{ethylene}}\text{--C}_{\text{Me}}) = 3.846$ Å. From these observations, it would seem that both electronic and steric effects play a role in the occurrence of this tilt. With propyne, the largest tilt is found and it is toward the carbon atom with the greater electron density, which also carries the smaller substituent. In case of methyl 2-butynoate, there is a tilt toward the carbon that bears the ester group, which also has the larger atomic charge; however, there is a larger tilt toward the other acetylenic carbon, which has the smaller electron density and is substituted with the smaller methyl group. From these results it would seem that both steric and electronic effects are operative and work in the same sense with propyne, but with methyl 2-butynoate, act in opposition. Because in the latter case the tilt is larger toward the smaller substituent, steric effects seem to have a greater influence than electronic effects on the tilt.

In **Fig. 4**, the four most important structures are displayed (**2f–2i**), together with the corresponding transition states (**TS8–TS5**), which lead to either cobaltacycle **3d** or **3c**. As in the propyne case, the structures with the ethylene axially coordinated (**2h** and **2i**) are energetically less favorable than the equatorial ones (**2f** and **2g**). The axial structure **2i** reacts most easily, however, as evidenced by the smallest energy barrier (13.5 kcal mol⁻¹), and yields cobaltacycle **3d**. This cobaltacycle ultimately yields the cyclopentenone with the ester group in the β-position, which is, in fact, formed experimentally with norbornene as the olefin.

It can also be seen that the electron densities on the acetylenic carbons play an important role. The interatomic distances between the reacting atoms are clearly more favorable in **2h** [$r(\text{C}_{\text{ethylene}}\text{--C}_{\text{Me}}) = 2.904$ Å] than in **2i** [$r(\text{C}_{\text{ethylene}}\text{--C}_{\text{ester}}) = 3.035$ Å], but **2i** reacts significantly more easily, as judged from the energy barriers of 16.1 and 13.5 kcal mol⁻¹, respectively. As compared with the data for the propyne complex, where the carbon with the greater electron density also has the most favorable geometry, i.e., the shorter C–C distance, the data for methyl 2-butynoate suggest that steric effects, resulting from the interactions of the acetylene substituents, work in opposition to the electronic effects, but are dominated by them. In other words, the size of the ester substituent is not sufficient to override the electronic effects that result from the acetylene substituents.

Since with methyl 2-butynoate, the steric and electronic effects are in apparent opposition, it is not surprising that reactions that yield, via cobaltacycle **3c**, the cyclopentenone with the ester substituent in α-position are not markedly disfavored. The barriers for the reactions **2g** → **TS6** and **2h** → **TS7** are only 2.1 and 2.6 kcal mol⁻¹ higher than the barrier of 13.5 kcal mol⁻¹ for **2i** → **TS5**. Due to its relatively large barrier of 19.0 kcal mol⁻¹ [27], the reaction **2f** → **TS8** → **3d** seems highly unlikely. In spite of the large

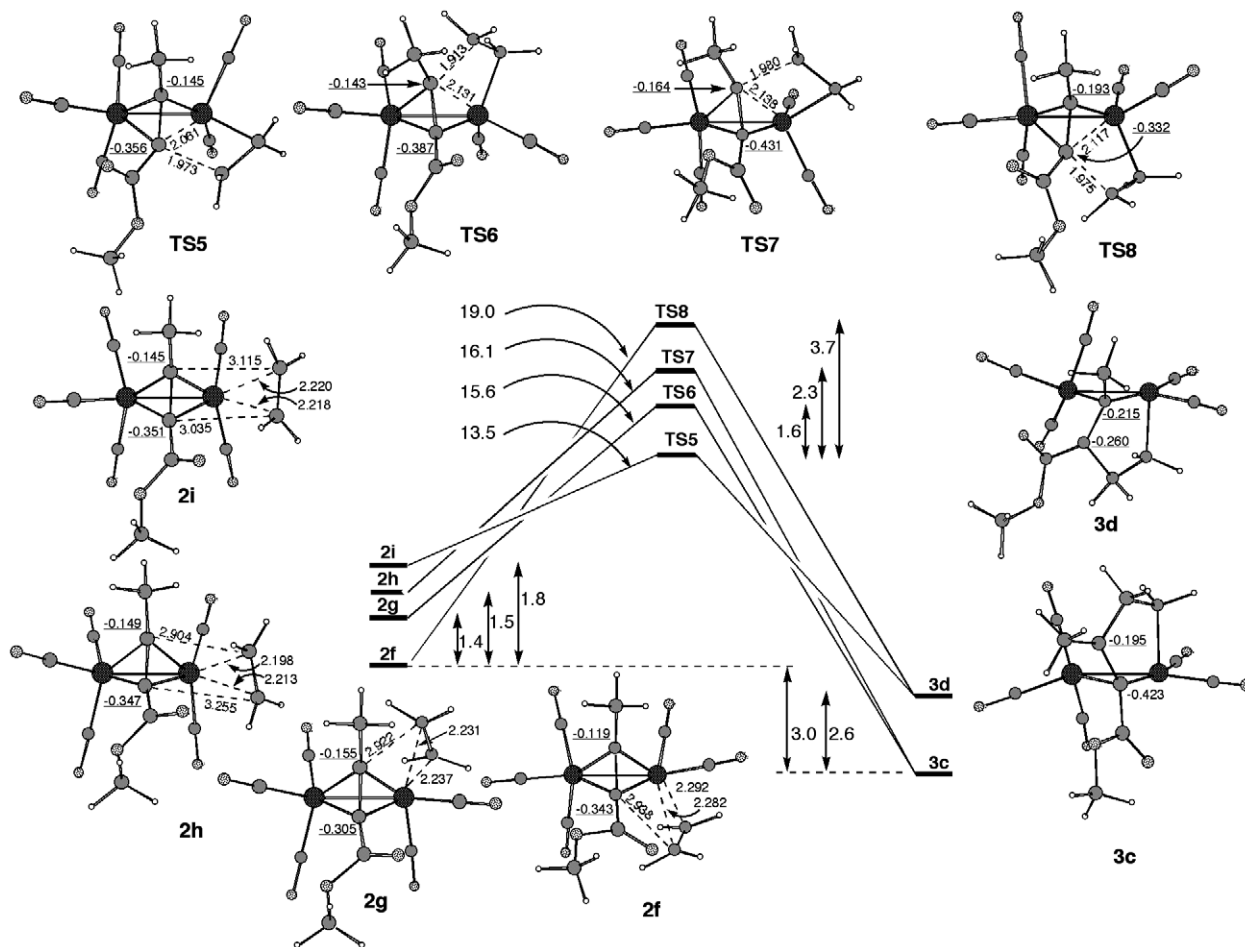


Fig. 4. B3LYP/LANL2DZ* potential energy surface for the formation of the two cobaltacycle products from the dicobalt pentacarbonyl-methyl 2-butynoate-ethylene complex. Distances are in Å and energies are in kcal mol⁻¹. Natural populations (e⁻) are underlined.

similarity between the geometries of **TS5** and **TS8** (in both structures the ester group is in the same position and the interatomic distances between the reacting carbons are 1.973 Å and 1.975 Å, respectively), there is a notable difference of 3.7 kcal mol⁻¹ between these transition states. The difference in the lengths of the Co–C bonds that are breaking in the transition states **TS5** and **TS8** (2.061 and 2.117 Å, respectively) seems to be in agreement with this energy difference.

Thus, with methyl 2-butynoate, the reaction should follow **2i** → **TS5** → **3d**, the pathway with the lowest energy barrier. As mentioned above, cobaltacycle **3d** affords the cyclopentenone with the ester group in β-position, the product that is experimentally observed with norbornene as the olefin.

3.3. Methyl propiolate

In contrast to the two other acetylenes, methyl propiolate exhibits a non-polarized triple bond (electronic charges: -0.360 (CH) versus -0.334 (CCOOMe)), but this bond bears two sterically very different substituents. It is

this steric difference that explains the generation of only one structure (**2i**) on axial olefin coordination. As in the above axial structures, the olefin is tilted and, not surprisingly, the tilt is toward the less sterically demanding substituent (H): $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{H}}) = 2.848$ Å versus $r(\text{C}_{\text{ethylene}}-\text{C}_{\text{ester}}) = 3.220$ Å (Fig. 5). The tilt is greater than in the case of the butynoate, where both steric and electronic effects are present.

With this alkyne, all of the starting structures are very close in energy (within 1 kcal mol⁻¹). As with methyl 2-butynoate, but to a lesser extent, the most stable structure (**2j**) is that with the olefin in the equatorial position *cis* to the ester group. The energy difference between the *trans* equatorial position (**2k**) and the axial position (**2l**) for the olefin is negligible.

The structures **2j** and **2l** lead to cobaltacycle **3e**, while **2k** and **2l** yield cobaltacycle **3f**. These last two reactive pathways display the smallest barriers and it is this cobaltacycle, **3f**, that will ultimately yield the cyclopentenone with the ester substituent in the α-position, in agreement with the experimental results with norbornene as the olefin. As before, the axial position is the most reactive one, with a

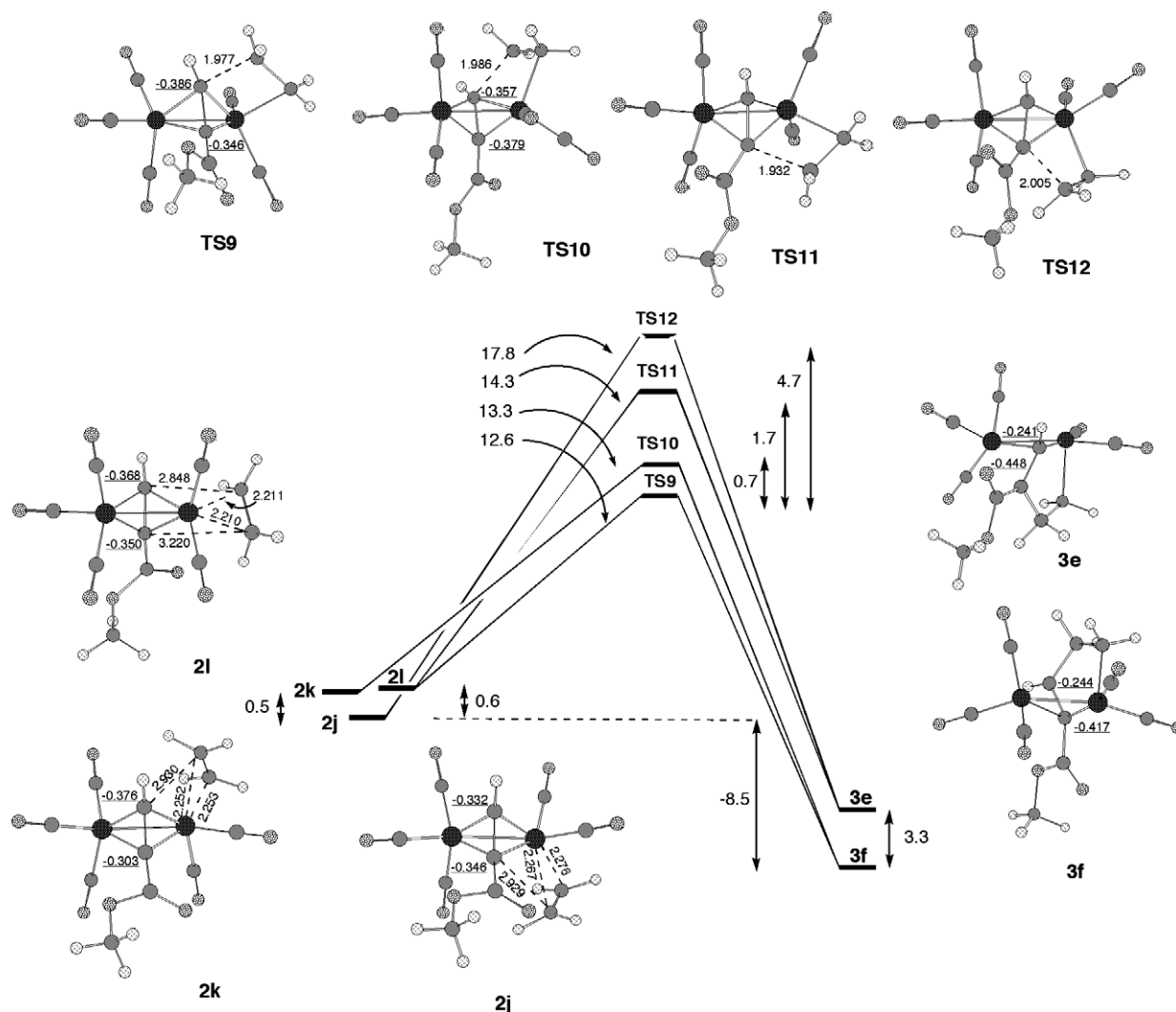


Fig. 5. B3LYP/LANL2DZ* potential energy surface for the formation of the two cobaltacycle products from the dicobalt pentacarbonyl–methyl propiolate–ethylene complex. Distances are in Å and energies are in kcal mol⁻¹. Natural populations (*e*⁻) are underlined.

barrier of 12.6 kcal mol⁻¹. The second most favorable pathway is the route **2k** → **TS10** → **3f**.

4. Conclusion

In conclusion, it has been shown with propyne, methyl 2-butynoate, and methyl propiolate, three acetylenes that differ in the polarization of the carbon–carbon triple bond and size of the substituents, that the electron density undoubtedly plays an important role in determining the regiochemical outcome of the Pauson–Khand reaction: the acetylenic carbon that carries the larger electron density will, in general, be that involved in forming the crucial C–C bond, even when geometrical factors are less favorable. A kinetic simulation, furthermore, has indicated with the model propyne–ethylene that a near-equilibrium distribution among equatorial and axial positions is established rapidly, which supports the idea that this C–C bond may be formed from the axial position.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.07.002](https://doi.org/10.1016/j.jorganchem.2006.07.002).

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- [18] L. Drahos, K. Vekey, *MassKinetics* computer program Version 1.5, 2004. Available from: <http://www.chemres.hu/ms/masskinetics>.
- [19] L. Drahos, K. Vekey, *J. Mass Spectrom.* 36 (2001) 237.
- [20] For the description of the bonding in olefin–metal complexes, the Dewar, Chatt, and Duncanson model has been used. See (a) M.J.S. Dewar, *Bull. Soc. Chim. Fr.* 18 (1951) C71;
(b) J. Chatt, L.A. Duncanson, *J. Chem. Soc.* (1953) 2939.
- [21] For the influence of electronic effects on olefin insertion, see D.L. Thorn, R. Hoffmann, *J. Am. Chem. Soc.* 100 (1978) 2079.
- [22] The interatomic distance is longer only in case of TS3 (1.980 Å), but this is mainly due to the exceptionally long distance already present in the reacting structure (3.237 Å).
- [23] Y. Gimbert, D. Lesage, A. Milet, F. Fournier, A.E. Greene, J.-C. Tabet, *Org. Lett.* 5 (2003) 4073.
- [24] The energy barrier for pseudorotation with ethylene in the conversion of **2a** into **2e** is only 5.7 kcal mol^{-1} . (The barrier for cobaltacycle formation is 11.0 kcal mol^{-1}).
- [25] It should be pointed out that an alternative pathway, involving bridged structures, exists for the generation of an axially coordinated olefin structure, which may be operative for axial coordination when pseudorotation is not feasible (C. Michel, A. Milet, unpublished results). Bridged structures are well known for dicobalt carbonyl complexes. See (a) P.C. Leung, P. Coppens, *Acta Crystallogr., Sect. B* 39 (1983) 535;
(b) G. Bor, K. Noack, *J. Chem. Soc., Chem. Commun.* (1976) 914.
- [26] For geometry details and total energy information, see [Supporting Information](#).
- [27] The reason for this abnormally high value, compare to TS5, TS6 and TS7, is not readily apparent.