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# Regiochemistry in the Pauson−Khand Reaction: Has a Trans Effect Been Overlooked?

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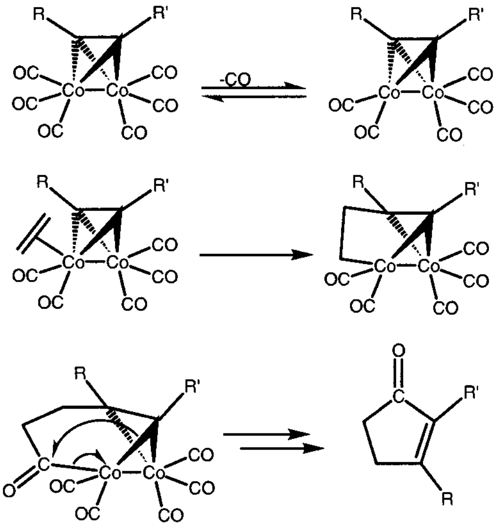
**Abstract:** Alkyne−dicobalt hexacarbonyl complexes have been studied by DFT to examine whether electronic differences in the acetylenic substituents could play a role in determining the regiochemical outcome in the Pauson−Khand reaction. It appears that in some instances the regiochemistry is, in fact, governed exclusively by the electronic nature of the acetylenic substituents through the discriminant loss of a carbon monoxide ligand.

## Introduction

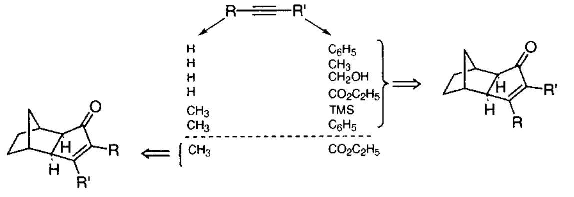
The Pauson−Khand (PK) reaction, thanks in part to gains in reactivity recently achieved in both the stoichiometric and catalytic versions, is now a useful transformation that is widely employed for the synthesis of complex organic compounds.[1] Although this reaction has been known for some 30 years, a full, supported mechanistic elucidation has, surprisingly, yet to be provided.[2] Nonetheless, it is now largely accepted that the alkyne−$Co_2(CO)_6$ complex, formed from an alkyne and $Co_2(CO)_8$, initially suffers the loss of a CO ligand,[3] and that this is followed by olefin coordination at one of the two enantiotopic Co atoms (Scheme 1). It has long been supposed, but with only empirical foundation, that in the intermolecular PK reaction the coordinating olefin for steric reasons positions itself adjacent to the less bulky acetylenic substituent and that the subsequent C−C bond formation occurs between an olefinic carbon and this closer acetylenic carbon. Indeed, but with few exceptions, the larger acetylenic substituent is found, following insertion of CO and reductive elimination, at the α position in the resulting cyclopentenone (Scheme 2).

There are some results, though, that are difficult to explain solely on the basis of steric effects: for example, and perhaps most saliently, ethyl propiolate[4] under PK conditions yields mainly an α-carbethoxy-substituted cyclopentenone, whereas ethyl butynoate[5] under similar conditions reacts to form only a *β*-carbethoxy-substituted derivative (Scheme 2). To rationalize this, it has been suggested polarization effects that result from electron density differences at the acetylenic carbons can combine with steric effects to determine the regiochemistry of the reaction. However, the manner in which these postulated electronic effects might influence the resulting regiochemistry of the PK reaction has nowhere been clearly indicated. Furthermore and more fundamentally, the occurrence of a specific vacant site in the alkyne−$Co_2(CO)_6$ complex on loss of carbon monoxide with attendant effect on the regiochemistry of the PK reaction is a possibility that has not to date been addressed. That electron effects engendered by different acetylenic substituents could in some way influence the position from which carbon monoxide is lost and ultimately the regiochemistry of the PK reaction seemed to be a possible unifying concept worthy of study. A theoretical study has been carried out to probe this idea.

**Scheme 1.** Supposed Mechanism of the PK Reaction



**Scheme 2.** The Regiochemical Outcome of the PK Reaction of Diversely Substituted Acetylenes and Norbornene



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(1) For recent reviews, see: Geis, O.; Schmalz, H. G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911−914. Jeong, N. *Trans. Met. Org. Synth.* **1998**, *1*, 560−577. Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341.

(2) Magnus, P.; Exon, C.; Albough-Robertson, P. *Tetrahedron* **1985**, *41*, 5861−5869.

(3) Gordon, G. M.; Kiszka, M.; Dunkin, I. R.; Kerr, W. J.; Scott, J. S.; Gebicki, J. *J. Organomet. Chem.* **1988**, *554*, 147−154.

(4) Krafft, M. E.; Romero, R. H.; Scott, I. L. *Synlett* **1995**, 677−678.

(5) Krafft, M. E.; Romero, R. H.; Scott, I. L. *J. Org. Chem.* **1992**, *57*, 5277−5278. For other reactions with 2-alkynoates, see: Fonquerna, S.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 4239−4254.

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## Results and Discussion

A number of published spectroscopic studies have indicated that the nature of the acetylenic substituents can markedly affect electronic properties within the alkyne−$Co_2(CO)_6$ complex.

Carbon-13 NMR analysis of $Co_2(CO)_6(RC{\equiv}CR')$ complexes shows that the nature of the R and R′ groups, as before coordination, but generally more so in the complex, impacts on the chemical shifts of the acetylenic carbons.[6] Assuming that the observed acetylenic carbon-13 chemical shifts reflect electron density,[7] then it is apparent that dissymmetry in the acetylene induces an electronic distortion or polarization.[8] Carbon-13 NMR analysis of the CO carbons in the $Co_2(CO)_6(RC{\equiv}CR')$ complexes indicates that these too are affected by the nature of the R and R′ groups; however, the chemical shift variations are smaller than those above. An increase in the electron donating ability of the substituents results in downfield shifts of the CO resonances. NMR, while not as useful as infrared spectroscopy[9] for gaging the effect of the R and R′ groups on the electronic nature of the Co−CO association, nonetheless clearly demonstrates a qualitative dependence of the $\delta_{CO}$ on the electronic properties of these groups.[10]

The infrared spectra of $Co_2(CO)_6(RC{\equiv}CR')$ complexes show 5 or 6 absorptions in the carbonyl region (2000−2100 $cm^{-1}$), which shift as a function of the R and R′ substituents,[11] an increase in the vibrational frequence $\upsilon_{CO}$ being observed with an increase in the electronegativity of R and R′. Electronegative substituents on the acetylene could be expected to strengthen the acceptor properties of the bridging ligand, which would result in reduced electron back-donation from the metal into the $\pi^*$ orbitals of the carbonyls and produce the observed shift.[12,13]

The spectroscopic findings are supportive of the possibility that the acetylenic substituents may cause through transmitted electronic effects the departure of a unique carbon monoxide from the complex, and that this departure in turn governs the regiochemical outcome of the PK reaction. The carbon−carbon triple bond in a dissymmetric alkyne is most certainly polarized due to the dissimilar electronic effects exerted on the acetylenic carbons by the different substituents, and on coordination the polarization appears to become more substantial. *This difference in electron density on the two acetylenic carbons in the complex we believe to be responsable for a discriminant loss of CO.* A relative accumulation of density on one of these carbon atoms should lead to discharge, via the metal atoms, to the strongly $\pi$-accepting CO ligands, this back-donation serving to strengthen the Co−CO bonds. Orbital symmetry considerations, though, lead to the conclusion that the 6 carbon monoxide ligands will not participate equally in this redistribution of electron density. The pseudoequatorial, *trans-positioned* (with respect to $C(\delta^-)$) carbon monoxide ligands should be the most receptive to back-donation, which would then make the pseudoequatorial, *cis-positioned* ligands labile in comparison (Figure 1).[14] The olefin should then occupy the position of a labile CO and, consequently, the A group should be found at the α position in the resulting cyclopentenone. A Density Functional Theory (DFT) study[15] has now been carried out to examine this novel proposal that differences in the electron density at the acetylenic carbons can translate into regiochemical preferences in the PK reaction.

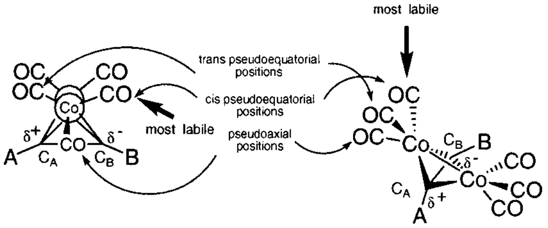

**Figure 1.** Lability of the carbon monoxide ligands (the cis and trans positions are defined with respect to the position of substituent B).

In this study, all geometries were fully optimized through analytic gradient calculations using the hybrid Hartree−Fock DFT approach B3LYP.[16] The basis sets used in these optimizations were as follows: the 10 innermost core electrons of the cobalt atom were described by the non-relativistic pseudopotential of Hay and Wadt[17] and the remaining outer core and valence electrons by a (8,5,5) ⟨3,3,2⟩ basis set. For the first row atoms and hydrogen atoms the split valence basis sets of Dunning were used.[18] A d polarization function was added to the first row atoms ($\alpha_{dO} = 0.85$, $\alpha_{dC} = 0.75$). Population analysis was computed through the NBO scheme.[19] All calcula-

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[6] (a) Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, L. *Inorg. Chim. Acta* **1977**, *22*, 135−139. (b) Happ, B.; Bartik, T.; Zucchi, C.; Rossi, M.-C.; Ghelfi, F.; Palyi, G.; Varadi, G.; Szalontai, G.; Horvath, I. T.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1995**, *14*, 809−819. (c) Baxter, R. J.; Knox, G. R.; McLaughlin, M.; Pauson, P. L.; Spicer, M. D. *J. Organomet. Chem.* **1999**, *579*, 83−89.

[7] Although the C-13 chemical shifts are influenced by several factors, comparison within a family is thought to allow a qualitative evaluation of this property.[6b]

[8] The interactions between R and R′ and $C_2Co_2(CO)_6$ should be governed by not only the donor/acceptor character of these groups but also their orbital symmetry.[6b]

[9] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

[10] Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335−1354.

[11] Dickson, R. S.; Yawney, D. B. W. *Aust. J. Chem.* **1968**, *21*, 1077−1082. Bor, G.; Kettle, S. F. A.; Stanghellini, L. *Inorg. Chim. Acta* **1976**, *18*, L18−L20.

[12] For a similar analysis with bisphosphinoamine ligands, see: Gimbert, Y.; Robert, F.; Durif, A.; Averbuch, M.-T.; Kann, N.; Greene, A. E. *J. Org. Chem.* **1999**, *64*, 3492−3497.

[13] $Co_2(CO)_6(RC{\equiv}CR')$ complexes can undergo alkyne exchange, which is also influenced by the substituents and supports this interpretation. The alkynes bearing the more electronegative R and R′ groups are preferentially incorporated, which can be explained by an increase in the alkyne−cobalt bond strength through enhanced electron back-donation from the d orbitals of the cobalt into the $\pi^*$ orbitals of the preferred alkyne. See: Cetini, G.; Gambino, O.; Rosseti, R.; Sappa, E. *J. Organomet. Chem.* **1967**, *8*, 149−154.

[14] Cis-labilization has precedent in hexacoordinated, trigonal bipyramid metal complexes. See: Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160−3166.

[15] To the best of our knowledge, no such theoretical studies have been performed to date on PK complexes; those that have been reported were carried out at the semiempirical (PM3) level, followed at times by single point calculations at the DFT level to improve the accuracy of the energy differences among the various structures. See: Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A.; Alvarez-Larena, A.; Piniella, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 7944−7952. Fonquerna, S.; Rios, R.; Moyano, A.; Pericàs, M. A.; Riera, A. *Eur. J. Org. Chem.* **1999**, *64*, 3459−3478. Breczinski, P. M.; Stumpf, A.; Hope, H.; Krafft, M. E.; Casalnuovo, J. A.; Schore, N. E. *Tetrahedron* **1999**, *55*, 6797−6813. Verdager, X.; Vázquez, J.; Fuster, G.; Bernardes-Génisson, V.; Greene, A. E.; Moyano, A.; Pericàs, M. A.; Riera, A. *J. Org. Chem.* **1998**, *63*, 7037−7052. Recently, a DFT optimization of complex **1a** has appeared: Balsells, J.; Vázquez, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *J. Org. Chem.* **2000**, *65*, 7291−7302. (Note added in proof: A DFT study of the PK reaction pathway has just been published: Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2001**, *123*, 1703−1708.)

[16] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. This B3LYP functional has previously been found to be of a suitable theoretical level for the study of the binding energy of ligands, especially between carbon monoxide and transition metals. Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173−9177. Bomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. J. *J. Chem. Phys.* **1996**, *104*, 9546−9554. Ricca, A.; Bauschliber, C. W., Jr. *J. Phys. Chem. A* **1997**, *101*, 8949−8955. Siegbahn, P. E. M.; Bomberg, M. R. A. *Chem. Rev.* **2000**, *100*, 421−437.

[17] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283.

[18] Dunning, T. H., Jr.; Hay, P. J. *Method of Electronic Structure Theory*; Plenum Press: New York, 1977.

[19] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

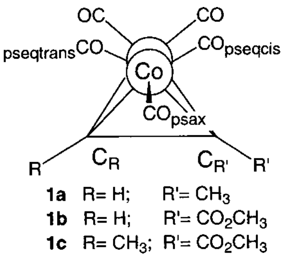


**Figure 2.** Complexes **1a**−**c**.

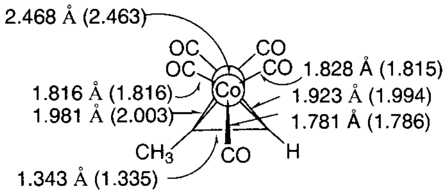


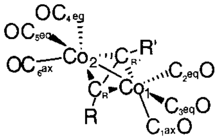
**Figure 3.** Comparison of calculated bond lengths in **1a** with those (given in parentheses) derived from X-ray of the di-*tert*-butyl acetylene−dicobalt hexacarbonyl complex.

tions were carried out using the Gaussian 98 program package.[20] The study was effected on the complex **1a** derived from propyne, taken as a typical alkyne, and on the complexes **1b** and **1c** derived from methyl propiolate and methyl butynoate, the results with which (ethyl esters) are arguably the most puzzling in PK chemistry (see above) (Figure 2).[21]

The calculated geometry of **1a** is in excellent agreement with that found through X-ray diffraction analysis of similar complexes.[22] This concordance can be seen in Figure 3, in which the calculated bond lengths in **1a** are compared with the X-ray-based bond lengths in the closely related di-*tert*-butylacetylene−dicobalt hexacarbonyl complex (indicated in parentheses).[22b]

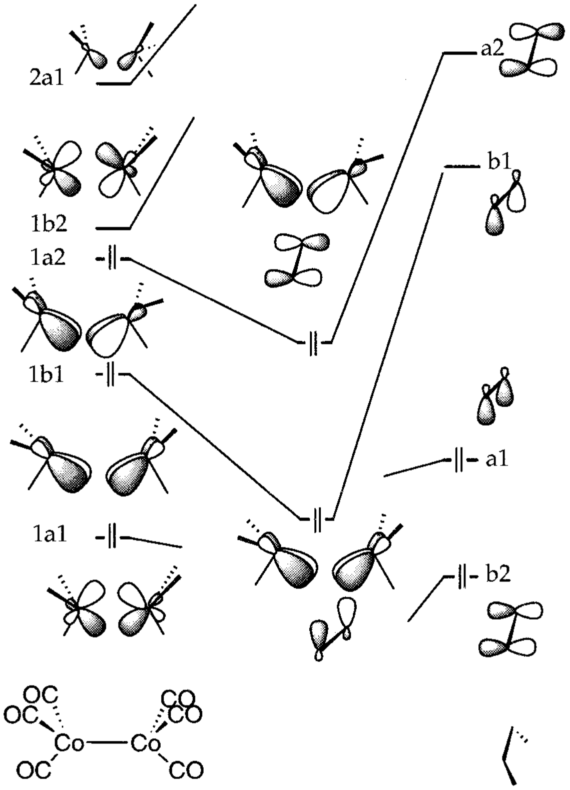
With this assurance as to the validity of the calculations, the $Co_2(CO)_6(RC{\equiv}CR')$ complexes **1b** and **1c** were next similarly optimized. Like complex **1a**, complexes **1b** and **1c** exhibit a bent, perpendicular acetylene, as found and discussed by Hoffmann and co-workers.[23] The different geometrical features such as acetylene association, interatomic Co−Co distances, and Co−CO bond lengths are in very good agreement with the X-ray data of similar complexes. The most striking feature of the Co−CO bond lengths is the calculated difference between the pseudoaxial (apical) and pseudoequatorial (basal) values. This revealing difference is observed for all three of the $Co_2(CO)_6(RC{\equiv}CR')$ complexes (see Table 1, entry 2−7), and is also found in the crystallography-based structures that are available.[22]

**Table 1.** Selected Bond Lengths (in Å) and Angles (in deg) in the Optimized Complexes **1a**−**c** and X-ray-Derived Values for the Di-*tert*-butylacetylene−Dicobalt Hexacarbonyl Complex[22b]



| entry | X−Y | **1a** | **1b** | **1c** | X-ray[22b] |
|---|---|---|---|---|---|
| 1 | Co1−Co2 | 2.468 | 2.470 | 2.465 | 2.463(1) |
| 2 | Co1−C1ax | 1.780 | 1.796 | 1.792 | 1.786(5) |
| 3 | Co1−C2eq | 1.818 | 1.828 | 1.832 | 1.816(4) |
| 4 | Co1−C3eq | 1.827 | 1.823 | 1.815 | 1.815(5) |
| 5 | Co2−C6ax | 1.780 | 1.790 | 1.783 | 1.786(5) |
| 6 | Co2−C4eq | 1.818 | 1.827 | 1.833 | 1.803(5) |
| 7 | Co2−C5eq | 1.827 | 1.824 | 1.821 | 1.823(5) |
| 8 | $C_R$–$C_{R'}$ | 1.342 | 1.355 | 1.352 | 1.335(6) |
| 9 | Co1−$C_R$ | 1.965 | 1.944 | 1.962 | 1.994(4) |
| 10 | Co1−$C_{R'}$ | 1.979 | 1.956 | 1.966 | 2.003(4) |
| 11 | Co2−$C_R$ | 1.965 | 1.955 | 1.976 | 1.992(4) |
| 12 | Co2−$C_{R'}$ | 1.979 | 1.949 | 1.943 | 1.995(4) |
| 13 | R−$C_R$–$C_{R'}$ | 142.6 | 140.0 | 141.6 | 144.8(4) |
| 14 | R′-$C_{R'}$–$C_{R'}$ | 143.8 | 138.8 | 138.6 | 144.5(4) |

**Chart 1.** MO Correlation Diagram for $(CO)_3CoCo(CO)_3$ with $C_2H_2$



The bonding between the bent acetylene fragment and $Co_2(CO)_6$ is derived primarily from the stabilizing interaction between the empty $\pi$* orbitals of the acetylene and the bonding and antibonding combination of the $d_{x^2-y^2}$ orbitals of cobalt, i.e., through back-donation to the acetylene (Chart 1). These same d orbitals, however, are also involved in the $\sigma$-antibonding to the equatorial CO ligands. Thus, back-donation to the acetylene effectively increases the Co−$CO_{pseq}$ distances.

The atomic charges on the acetylenic carbon atoms have been calculated using natural population analysis and these "natural charges" are presented in Table 2. It can be seen that the different substituents on the acetylene give rise to different

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[20] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

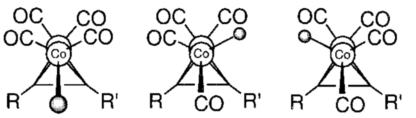
[21] The methyl esters were studied in place of the ethyl esters to simplify the calculations.

[22] (a) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323−377. (b) Cotton, F. A.; Jamerson, J. D.; Stulb, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774−1779. See also: Baert, F.; Guelzim, A.; Poblet, J. M.; Wiest, R.; Demuynck, J.; Bénard, M. *Inorg. Chem.* **1986**, *25*, 1830−1841. (c) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 2972−2984.

[23] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858−3875.

**Table 2.** Atomic Charges ($e^-$) Based on Natural Population Analysis of the "Acetylenic" Carbons in Compounds **1a**−**c**

| entry | complex | $q(C_R)$ | $q(C_{R'})$ | $\Delta q$ |
|---|---|---|---|---|
| 1 | **1a** | −0.31 | −0.18 | −0.23 |
| 2 | **1b** | −0.36 | −0.33 | −0.03 |
| 3 | **1c** | −0.14 | −0.34 | +0.20 |



**2**, psax **3**, pseq$_{cis}$ **4**, pseq$_{trans}$

**Figure 4.** Different complexes missing a CO (the cis and trans positions are defined with respect to the position of substituent R′).

electronic densities on its carbon atoms, $C_R$ and $C_{R'}$, which results in polarization of the $C_R-C_{R'}$ bond. Neither the intensity nor the sign of this polarization is constant. Significantly, the calculated values are in qualitative agreement with what could be predicted based on the free alkynes. It could be reasoned, for example, that in the alkyne of complex **1a**, due to the donating effect of the methyl group, the carbon atom ($C_R$) bonded to the hydrogen should have a larger electron density than the carbon atom ($C_{R'}$) that is methyl substituted, and indeed this reflects what is calculated for the complex. It might, however, initially appear doubtful that the propiolate of complex **1b,** for which calculations indicate an absence of polarization, could be devoid of polarization. Although the ester group is electronegative and thus has a tendency to polarize a carbon−carbon triple bond, the acetylene does not carry a second substituent capable of participating in polarization of the bond, hydrogen's 1s orbital having no electronic interaction with such a $\pi$ system, and therefore very little or no polarization should, in fact, exist. The situation is different, however, with the butynoate, where the corresponding $C_R-C_{R'}$ bond in the complex is clearly polarized. In this case, the methyl group overlaps to a degree with the $\pi$ system and enriches it electronically; in conjunction with the electronegative ester group, a significant polarization could be expected. The relevance of the orbital symmetry of acetylenic substitutents on their capacity to interact with the acetylenic system has previously been discussed.[6b]

In the $Co_2(CO)_6(RC{\equiv}CR')$ complexes, three different carbon monoxide ligands can dissociate: loss of $CO_{psax}$ will lead to **2**, whereas departure of the two equatorial ligands, $CO_{pseq,cis}$ and $CO_{pseq,trans}$, will produce **3** and **4**, respectively (Figure 4).

Type **2** complexes exhibit relatively nondeformed structures in comparison with the parent complexes, $Co_6(CO)_6(RC{\equiv}CR')$. In contrast, for the complexes **3** and **4**, which have suffered the loss of an equatorial CO, large structural changes have been calculated: most significantly, a shortening of the Co−Co bond, the acetylene−cobalt bonds, and the two remaining Co−CO bonds of the involved cobalt. Energetically, the calculated values are in reasonable agreement with available experimental and calculated values for CO dissociation in mononuclear complexes (Table 3).[24] It is noteworthy that type **2** complexes are found to be about 10 kcal/mol higher in energy than the two others, which is consistent with the shorter $Co-CO_{ax}$ bond lengths. Also clear from the results in this table is that the fate of

**Table 3.** First Carbonyl Bond Dissociation Energies (kcal/mol) of Complexes **1a**−**c**

| entry | initial complex | 2 | 3 | 4 |
|---|---|---|---|---|
| 1 | **1a** | *a* | *b* | 24.2 |
| 2 | **1b** | 37.1 | 26.4 | 26.7 |
| 3 | **1c** | 37.9 | 24.5 | *c* |

[a] Optimized structure (38.5 kcal/mol) exhibits a small imaginary frequency and reoptimization yields **4a**. [b] Optimization of this structure yields **4a**. [c] Optimization of this structure yields **3a**.

complexes **3** and **4** depends on the particular acetylenic substituents. For each of the initial complexes **1a** and **1c**, only one complex lacking a $CO_{pseq}$ could be optimized.

The results of this theoretical study are consistent with those of the above-mentioned spectroscopic studies[25] and fully support the proposal that electronic effects caused by different acetylenic substituents can influence the position from which carbon monoxide is lost and ultimately the regiochemistry of the PK reaction. It bears repeating that the loss of carbon monoxide from the $Co_2(CO)_6(RC{\equiv}CR')$ complex provides for the incoming alkene a coordination site, the position of which is assumed to fix the regiochemistry of the resulting cyclopentenone adduct. Let us now consider separately the complexes **1a**−**c**.

In complex **1a**, the $C_R-C_{R'}$ bond must be strongly polarized (Table 2, entry 1). The larger charge density is found on $C_R$ and the longer $Co-CO_{pseq}$ bond length is calculated for the carbon monoxides that are *trans*-positioned with respect to R′ (Table 1, entries 3 and 4). Therefore, it is reasonable to expect these carbon monoxide ligands to dissociate more easily, an expectation that is supported by the calculated bond dissociation energies (Table 3, entry 1). The olefin (norbonene) then occupies the vacant coordination site, which leads to the observed α-methylcyclopentenone. Importantly, the calculations show that even if one of the strongly bound $CO_{psax}$ ligands were to dissociate from the complex and thus create a vacant site that could, potentially, also produce the observed cycloadduct, a migration of a $CO_{pseq,trans}$ to the axial position would result to give once again a vacant trans pseudoequatorial coordination site.[26]

In complex **1b**, where the $C_R-C_{R'}$ bond appears to lack significant polarization (Table 2, entry 2), the $Co-CO_{pseq}$ bond lengths and bond dissociation energies should be nearly identical, and this is exactly what the calculations indicate (Table 1, entries 3 and 4; Table 3, entry 2). The $CO_{pseq}$ ligands should thus be able to dissociate with equal facility, and therefore steric effects, as opposed to electronic ones, should now play the decisive role. In the absence of significant electronic effects, the larger substituent on an acetylene should ultimately be found at the α position in the cyclopentenone, and the bigger ester group, in the present case, is indeed found there.

Finally, in complex **1c**, in which the R and R′ substituents are sterically similar, the $C_R-C_{R'}$ bond should again be strongly polarized, but with $C_{R'}$ in this case having the higher electron density (Table 2, entry 3). Thus it is now a $CO_{pseq,cis}$ that would

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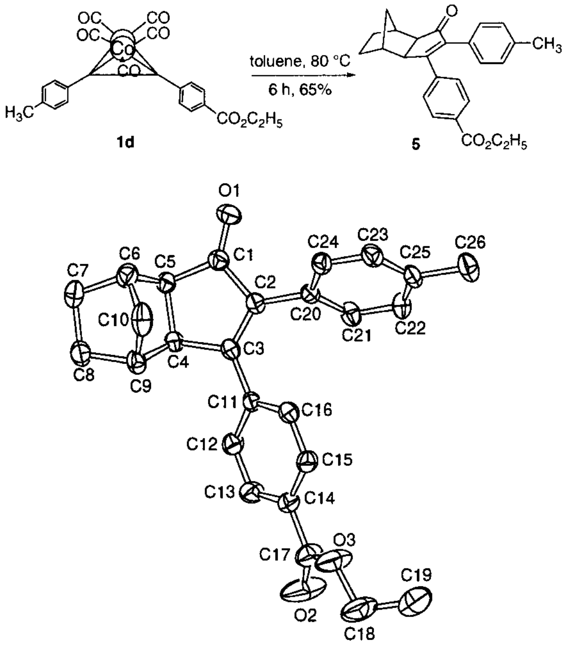
(24) For example, the experimental value of the first dissociation energy for $Mo(CO)_6$ is 34 kcal/mol. (Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514−1520). Good agreement is found between the calculated and experimental values for the dissociation energy of CO in complexes in which acetylene and CO are on the same metal atom. (Decker, S. A.; Klobukowski, M. *J. Am. Chem. Soc.* **1998**, *120*, 9342−9355.)

(25) The $^{13}C$ NMR chemical shifts (in ppm) of the coordinated sp carbon atoms are: in **1a**,[6b] 73.0 (C-1) and 90.8 (C-2); in **1b**,[6b] 76.9 (C-2) and 73.5 (C-3); in **1c**, 80.0 (C-2) and 95.3 (C-3).

(26) However, axial complexation has been suggested: Derdau, V.; Laschat, S.; Jones, P. G. *Eur. J. Org. Chem.* **2000**, 681−689. Recent DFT results indicate that in certain cases axial complexation can, in fact, be produced by pseudorotation and that cobaltacycle formation can then occur through a low-energy pathway (see: de Bruin, T. J. M.; Milet, A.; Robert, F.; Gimbert, Y.; Greene, A. E. *J. Am. Chem. Soc.*, submitted for publication). In addition, preliminary DFT results indicate that the loss of a pseudoequatorial ligand can also lead to rearrangement of the coordination sphere to produce a CO-bridged structure. The formation of both intermediates, however, should also be subject to these electronic effects.

**Scheme 3.** Structure of the Cycloadduct Resulting from the PK Reaction of Complex **1d** and Norbornene and an ORTEP Representation (40% probability displacement ellipsoids)



be expected to dissociate, an expectation that is clearly supported by the calculations (Table 1, entries 3 and 4; Table 3, entry 3). Norbornene should coordinate to cobalt at a cis pseudoequatorial coordination site, which would then lead to the product cyclopentenone with the ester function at the $\beta$ position: this is precisely what is observed. Thus, the dichotomous PK results with ethyl propiolate and ethyl butynoate can now be understood.

What is the predictive power of this analysis? With an acetylene bearing substituents that sterically are virtually identical, but electronically different, can the regiochemical outcome of the PK reaction now be foreseen? Complex **1d** [27] is a good test case; gratifyingly, the tolyl group is found *exclusively* in the α position in the resultant cyclopentenone **5** (Scheme 3).[28]

In summary, a DFT study has been carried out on alkyne–dicobalt hexacarbonyl complexes to probe for the first time whether electronic differences in the acetylenic substituents could impact on the regiochemistry of the PK reaction. It has been found that the regiochemistry in certain cases appears, in fact, to be entirely governed by electronic differences in the acetylenic substituents, which translate, through discriminant carbon monoxide loss, into regioselective cyclopentenone formation. This new insight provides an alternative to the “steric rationale” for mechanistic interpretation of this important aspect of the PK reaction.

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**Supporting Information Available:** Tables of Cartesian coordinates for the theoretically optimized structures **1**–**4** and cristallographic data for cycloadduct **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] Ethyl 4-(4-methylphenylethynyl)benzoate was prepared from ethyl 4-iodobenzoate and 1-ethynyl-4-methylbenzene by using the Sonogashira procedure. See: Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCM: New York, 1997; Chapter 5. Complexation (80% yield) and the PK reaction (65% yield) were realized according to ref 12.

[28] Crystal data for $C_{26}H_{26}O_3$: colorless, triclinic, $P\bar{1}$, $a = 5.827(5)$, Å, $b = 9.154(6)$ Å, $c = 19.59(1)$ Å, $\alpha = 90.76(3)°$, $\beta = 92.54(3)°$, $\gamma = 81.82(3)°$, $V = 1033(1)$ Å$^3$, $Z = 2$, $d_{calc} = 1.242$ g/cm$^3$, $F(000) = 412$, $\mu$(Mo Kα) = 0.80 cm$^{-1}$, $\theta$ range 2–26° (Mo Kα), 4182 measured reflections on a Enraf-Nonius CAD4 diffractometer, 4055 independent reflections [$R$(int) = 0.021], the structure determination using direct methods (SIR92), $R$(F) = 0.062, $Rw = 0.057$ for 2012 reflections with $I > 2\sigma(I)$, GOF = 1.987.