JOC Article

Insight into the Reactivity of Olefins in the Pauson−Khand Reaction

Theodorus J. M. de Bruin, Anne Milet,* Andrew E. Greene, and Yves Gimbert*

*Université Joseph Fourier de Grenoble, Chimie Recherche (LEDSS-UMR 5616) BP 53,
38041 Grenoble, France*

yves.gimbert@ujf-grenoble.fr; anne.milet@ujf-grenoble.fr

Received September 3, 2003

The reactivity of different $Co_2(CO)_6$−acetylene complexes in the Pauson−Khand reaction is strongly dependent on the nature of the olefin. Theoretical calculations at both the DFT and ONIOM levels are concordant with experimental observations and suggest how the olefin−cobalt interactions in the complex could have a major effect on the relative reactivity of the olefins. This study rationalizes for the first time the experimentally observed reactivity differences of cyclohexene, cyclopentene, and norbornene.

Introduction

The Pauson−Khand reaction,[1,2] a cobalt-mediated joining of an acetylene, an olefin, and CO that can produce a wide range of substituted cyclopentenones, is of considerable synthetic and theoretical interest.[3,4] The theoretical fascination with this reaction derives mainly from the gaps that persist in the understanding of various aspects of the transformation. One area that is particularly perplexing concerns the reactivity differences observed with certain olefins. Why do cyclohexene, cyclopentene, and norbornene, for example, experimentally manifest such large differences in reactivity (cyclohexene < cyclopentene < norbornene) in the intermolecular, thermal version of the Pauson−Khand reaction?[5] In this paper we address this question, specifically for these three common olefins and $Co_2(CO)_6$−propyne, through theoretical studies performed at the DFT and ONIOM levels.

Theoretical Methods

All geometry optimizations and frequency analyses were performed with the Gaussian 98 set of programs,[6] using Becke's three-parameter hybrid exchange functional,[7] in combination with the correlation functional of Lee−Yang−Parr.[8] This B3LYP functional was used with the effective core potential LANL2DZ[9] for Co; the D95 split valence basis set,[10] augmented with a set of *d* polarization functions for a correct description of CO,[11] was used for C and O; and the D95 split valence basis set was used for H. (This tailor-made basis set, which has proven to yield accurate geometries for these dicobalt complexes,[4b] will be denoted as LANL2DZ*.) All geometries have been fully optimized without any symmetry constraints and a frequency analysis subsequently effected to confirm the desired character of the stationary point. Atomic charges were computed from natural population analysis (NPA) with the NBO program at the same level of theory as for the optimizations.[12] Orbital analyses were performed on

---

* Corresponding author.

[1] (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 36. (b) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 975−977. (c) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977−981.

[2] For recent reviews, see: (a) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *Chem. Eur. J.* **2001**, *7*, 1589−1595. (b) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263−3283. (c) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657−1668. (d) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1995; Vol. 12, pp 703−739. (e) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911−914. (f) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341.

[3] (a) Verdaguer, 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. (b) Fonquerna, S.; Rios, R.; Moyano, A.; Pericàs, M. A.; Riera, A. *Eur. J. Org. Chem.* **1999**, 3459−3478. (c) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Alvarez-Larena, A.; Piniella, J.-F. *Organometallics* **1999**, *18*, 4275−4285. (d) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A.; Alvarez-Larena, A.; Piniella, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 7944−7952.

[4] (a) Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2001**, *123*, 1703−1708. (b) Robert, F.; Milet, A.; Gimbert, Y.; Konya, D.; Greene A. E. *J. Am. Chem. Soc.* **2001**, *123*, 5396−5400. (c) de Bruin, T. J. M.; Milet, A.; Robert, F.; Gimbert, Y.; Greene A. E. *J. Am. Chem. Soc.* **2001**, *123*, 7184−7185.

[5] In the thermal version of the Pauson−Khand reaction, generally, norbornene, norbornadiene, cyclopentene, cyclopentadiene, 2,5-dihydrofuran, and cyclobutene derivatives are good substrates, cycloheptene and cyclooctene moderately good substrates, and cyclohexene and acyclic olefins poor substrates. Norbornene gives only the exo-fused product.[1,2]

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; 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. G.; 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.

[7] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[8] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

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

[10] Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976, 1−28.

[11] Calculated (and experimental) values: r(C−O) = 1.14 (1.13) Å, ω = 2186 (2170) cm^{-1}, and dipole moment = 0.146 (0.122) debye.

[12] *NBO*, version 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. (sold by Gaussian, Inc., as part of *Gaussian 98*, revision A.6).

10.1021/jo035294w CCC: $27.50

the canonical Kohn−Sham orbitals. The ONIOM calculations[13] were also performed with the Gaussian 98 set of programs. The different $Co_2(CO)_5$−propyne−olefin complexes have been fully optimized at the ONIOM (B3LYP/lanl2z*/UFF) level, with $Co_2(CO)_5$−propyne-ethylene being treated by quantum mechanics. The molecular mechanics calculations were performed with the UFF force field;[14] the validity of such calculations for transition-metal complexes has been well demonstrated (e.g., by Eisenstein et al.[15]). The nature of the extrema was determined through computation of the vibrational frequencies.

The charge decomposition analysis (CDA) program[16] was used to calculate the amount of donation and back-donation.

Results and Discussion

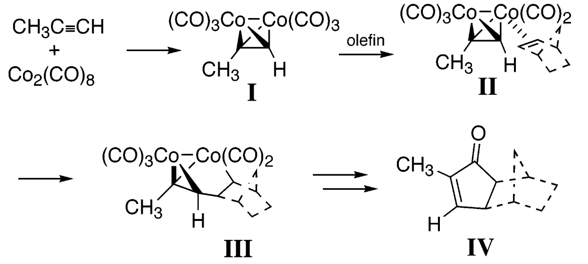
To understand the reactivity differences of cyclohexene, cyclopentene, and norbornene, the structure and the electronic nature of the corresponding $Co_2(CO)_5$−propyne−olefin complexes **II**, as well as the transition-state barriers connecting **II** to **III** (C−C bond formation), need to be analyzed in detail, since the ease of formation of the intermediates **II** from **I** and the facility of the ensuing insertion (→ **III**) should be determining factors (Scheme 1).

Published work[4c,17] strongly suggests that olefins react preferentially from an axial position (see Figure 1), and this has been accepted for the present study. The optimized structures of the complexes of $Co_2(CO)_5$−propyne with cyclohexene (**2a**), cyclopentene (**2b**, **2b′**), and norbornene (**2c**, **2c′**) are depicted in Figure 2. It should be noted that with cyclopentene and norbornene, two different olefin orientations have been found.

The above structures appear to be quite similar; however, inspection of Table 1 reveals some remarkable differences in the interatomic distances. Significantly, there is a much shorter C(1)−C(3) distance in the cyclopentene complex **2b** and in the norbornene complex **2c** than in the three other olefin complexes. The relative shortness of this key distance does not appear to be principally a result of Coulombic interactions. As can be seen in Table 2, the differences in the NPA charges on C(1) and C(3) in the complexes do not correlate with the corresponding C(1)−C(3) distances (Table 1), as would be expected were Coulombic interactions significant, but show in fact the opposite behavior. For example, the charge difference is 0.202 in **2a** and 0.131 in **2c**, whereas the C(1)−C(3) distances are 2.910 and 2.800, respectively.

The C(1)−C(3) distance derives from both the Co−olefin distance, least in the case of **2c**, and the olefin tilt, most pronounced in **2b** and **2c**, the steric interaction of the CH_2 group with the two proximate carbonyls ligands in **2b′** and **2c′** forbidding a comparable tilt. With cyclohexene (**2a**), a sizable tilt (2.910 vs 3.325 Å for the C(1)−C(3) and C(2)−C(4) bond distances, respectively) is overwhelmed by the relatively long Co−olefin distance (ca. 2.31 vs 2.27 and 2.22 Å in **2b** and **2c**, respectively). It should be pointed out, however, that tilt appears to be governed by steric factors and, thus, its degree may vary with the substituents on the alkyne and/or the ligands on cobalt.

SCHEME 1. Magnus Pathway for the PK Reaction



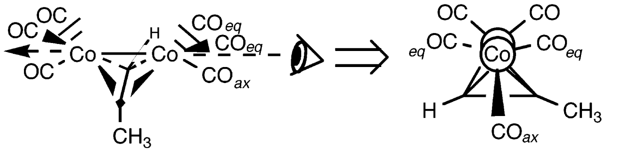


FIGURE 1. Designation of COs in the $Co_2(CO)_6$−propyne complex.

At the ONIOM level, the same general trends are observed; however, there is now little difference between **2a** and **2b**, which is primarily due to the longer Co−olefin distance in **2b**. The relatively short Co−olefin and C(1)−C(3) calculated distances in **2c** are again consistent with the reactivity difference observed with norbornene vs cyclopentene and cyclohexene in the Pauson−Khand reaction.[18]

The reactivity of these complexes toward C(1)−C(3) bond formation has been studied, and the results are gathered in Table 3 (energy data) and in Table 4 and Figure 3 (transition-state structures). Inspection of Table 3 shows clearly that calculations at both the B3LYP and ONIOM levels are in accord with experimental observations. The cyclohexene complex **2a** exhibits the highest barrier (ca. 15 kcal/mol) and a slightly endothermic reaction (ca. 1 kcal/mol). The two cyclopentene-coordinated complexes **2b** and **2b′** react with an average barrier of ca. 11 kcal/mol, whereas the norbornene complex **2c** confronts a considerably smaller barrier (ca. 6 kcal/mol) and reacts highly exothermically.[19] Good agreement is observed between the DFT and ONIOM calculations, with a deviation of only ca. 1 kcal/mol, except for complexes **2c** and **2c′**. The reason for these exceptions is not clear. Inspection of the transition-state structures (Table 4) does not show unexpected results for **2c** and **2c′**; they are, in fact, in good agreement with the energy figures. The transition state from **2a** is the latest structure and has the shortest C(1)−C(3) distance (1.88 Å). At the opposite extreme is the transition state resulting from complex **2c**, which is the earliest structure

---

[13] Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357−19363.

[14] Rappe, A. K.; Casewitt, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024−10035.

[15] Clot, E.; Eisenstein, O.; Dubé, T.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 575−580.

[16] Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352−9362.

[17] (a) Derdau, V.; Laschat, S.; Jones, P. G. *Eur. J. Org. Chem.* **2000**, *4*, 681−689. (b) Gimbert, Y.; Robert, F.; Durif, A.; Averbuch, M.-T.; Kann, N.; Greene, A. E. *J. Org. Chem.* **1999**, *64*, 3492.

[18] It is interesting to note that there is *not* a general shortening or lengthening of the cobalt−olefin distances, as usually observed on going from one level of theory to another. However, the characteristics and differences of the olefins are well maintained and homogenization of the key distances is not observed, even when only the double bond of the olefin is included in the DFT part of the calculations. Moreover, as in the purely QM calculations, the differences in the cobalt−olefin distances are reflected in the C(1)−C(2) distances: a shortening of the cobalt−olefin distance gives rise to an increase in the C(1)−C(2) distance (and vice-versa).

[19] It can also be seen in Table 3 that differences in reaction reversibility do not determine the relative reactivities.

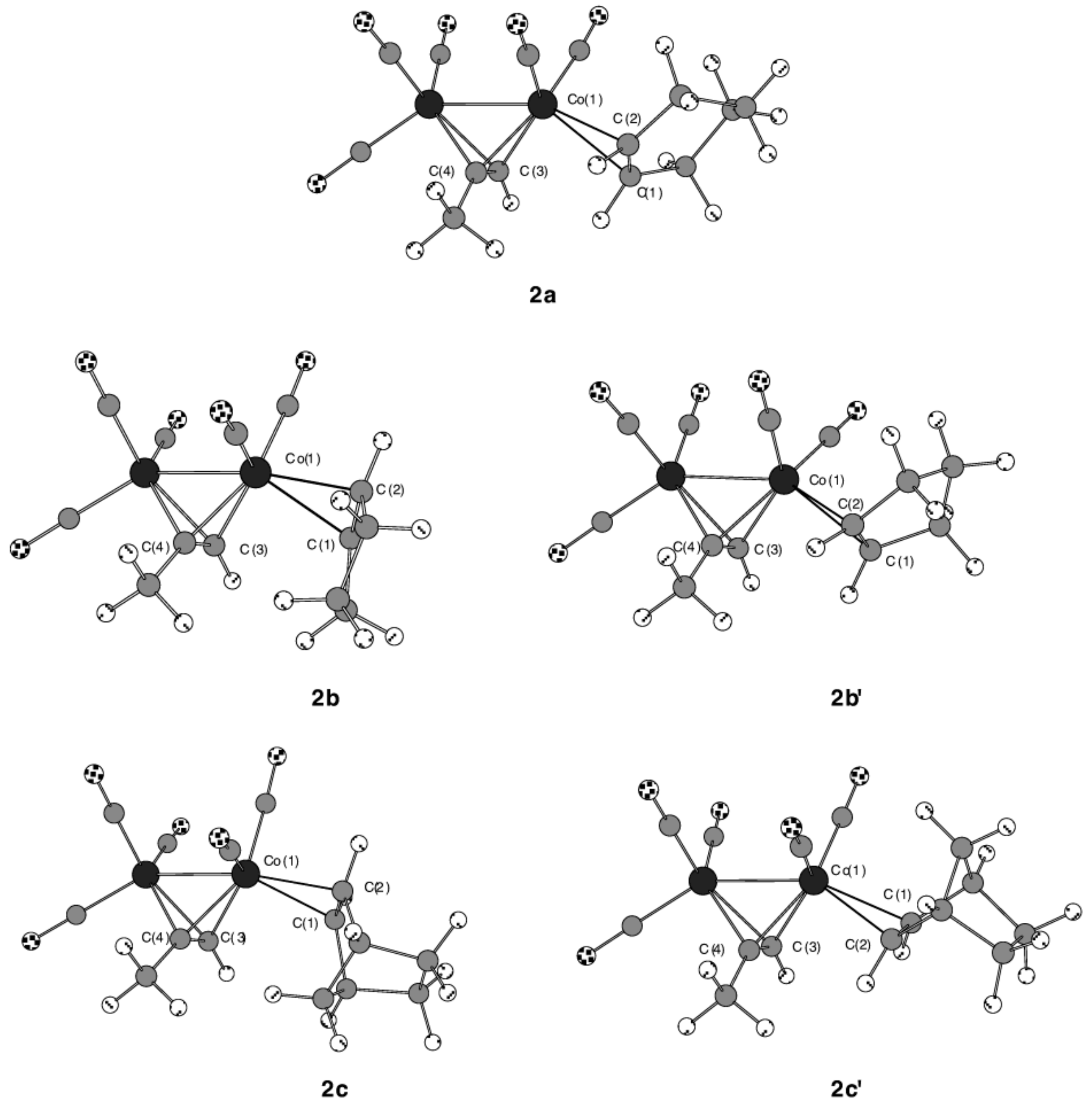


FIGURE 2. B3LYP/LANL2DZ*-optimized structures of the complexes of $Co_2(CO)_5$−propyne with olefins.

TABLE 1. Distances (Å) in the $Co_2(CO)_5$−Olefin Complexes (Results from ONIOM Calculations in Parentheses)[a]

	2a	2b	2b′	2c	2c′
Co(1)−C(1)	2.308 (2.281)	2.282 (2.319)	2.258 (2.302)	2.230 (2.155)	2.231 (2.214)
Co(1)−C(2)	2.309 (2.300)	2.267 (2.288)	2.258 (2.268)	2.208 (2.180)	2.207 (2.166)
C(1)−C(3)	2.910 (2.903)	2.840 (2.927)	2.968 (2.971)	2.800 (2.845)	3.013 (2.976)
C(2)−C(4)	3.325 (3.292)	3.681 (3.726)	3.145 (3.142)	3.674 (3.726)	3.046 (3.025)
C(1)−C(2)	1.380 (1.387) $\Delta = 0.036$	1.384 (1.379) $\Delta = 0.042$	1.386 (1.381) $\Delta = 0.044$	1.399 (1.422) $\Delta = 0.050$	1.396 (1.414) $\Delta = 0.047$

[a] Value of Δ is the difference in the C(1)−C(2) bond length in the complexed and uncomplexed olefins.

and that with the longest C(1)−C(3) distance (2.05 Å), consistent with its having the smallest activation energy and the highest exothermicity. The ONIOM transition-state structures are similar to those derived from the DFT calculations; however, the norbornene transition states are earlier with the ONIOM calculations, whereas the cyclopentene transition states are later.

One might now ask the fundamental question: why are there such clear differences with these three olefins, which, to a first approximation, are somewhat similar? The best explanation for the differences in interatomic distances (and reactivity) would appear to be one based on molecular orbital (MO) considerations. The increase in the C(1)−C(2) bond length on coordination reflects

TABLE 2. NPA Charges (Electrons; NPA Charges in the Optimized Uncoordinated Olefin in Parentheses)

	2a	2b	2b′	2c	2c′
Co(1)	+0.175	+0.171	+0.157	+0.168	+0.156
C(1)	−0.215 (−0.205)	−0.229 (−0.200)	−0.222 (−0.200)	−0.252 (−0.211)	−0.246 (−0.211)
C(2)	−0.238 (−0.205)	−0.228 (−0.200)	−0.235 (−0.200)	−0.269 (−0.211)	−0.259 (−0.211)
C(3)	−0.417	−0.404	−0.411	−0.383	−0.407
C(4)	−0.204	−0.202	−0.201	−0.205	−0.196

TABLE 3. Activation Energies ($\Delta E^{\ddagger}$) and Energy Differences (ΔE) between Complexes 2 and Cobaltacycle Intermediates, in kcal/mol^{-1} (Corrected ZPE Values in Parentheses)

	2a	2b	2b′	2c	2c′
$\Delta E^{\ddagger}_{\text{B3LYP}}$	14.5 (15.2)	9.5 (10.0)	12.4 (12.7)	5.6 (6.2)	10.8 (11.2)
$\Delta E^{\ddagger}_{\text{ONIOM}}$	15.4	10.6	11.7	2.5	6.6
ΔE_{B3LYP}	0.7 (2.5)	−6.9 (−5.2)	0.7 (1.2)	−13.0 (−10.9)	−1.7 (0.4)
ΔE_{ONIOM}	−3.0	−10.0	1.1	−13.9	1.8

TABLE 4. Transition-State Distances (Å) in the $Co_2(CO)_5$−Olefin Complexes (ONIOM Values in Parentheses)

	2a	2b	2b′	2c	2c′
Co(1)−C(1)	2.002 (2.004)	2.007 (2.005)	2.016 (1.999)	2.019 (2.014)	2.035 (2.030)
Co(1)−C(2)	2.247 (2.268)	2.262 (2.286)	2.249 (2.239)	2.248 (2.290)	2.268 (2.297)
C(1)−C(3)	1.884 (1.893)	1.997 (1.938)	1.964 (1.948)	2.057 (2.119)	2.051 (2.121)
C(1)−C(2)	1.476 (1.486)	1.463 (1.475)	1.457 (1.462)	1.457 (1.473)	1.448 (1.463)

TABLE 5. CDA Results

	2a	2b	2b′	2c	2c′
q[d] (e−)	0.506	0.430	0.441	0.456	0.479
q[b] (e−)	0.096	0.141	0.125	0.181	0.143
q[r] (e−)	−0.311	−0.297	−0.328	−0.309	−0.339
q[s] (e−)	−0.070	−0.084	−0.084	−0.095	−0.094

TABLE 6. LUMO Energies of Free and Coordinated Olefins and HOMO Levels of the $Co_2(CO)_5$ Complexes (eV)

	2a	2b	2b′	2c	2c′
LUMO (free)[a]	+0.715	+0.631	+0.631	+0.423	+0.423
LUMO (coord)[b]	+0.336	+0.203	+0.168	−0.087	−0.053
HOMO[c]	−6.347	−6.261	−6.319	−6.100	−6.286
$E_{\text{HOMO}} - E_{\text{LUMO(coord)}}$	−6.683	−6.463	−6.487	−6.013	−6.233

[a] Energy of LUMO of optimized uncoordinated olefin. [b] Energy of LUMO of olefin with geometry as in complex. [c] Energy of the HOMO of the $Co_2(CO)_5$−propyne complex with a geometry as if the corresponding olefin were present.

back-donation of electrons from the filled *d*-orbitals of Co into the empty π^*-orbitals of the olefin. If the changes in the interatomic distance between the two ethylenic carbons, C(1) and C(2), on coordination are compared, the largest change is found with norbornene, $\Delta = 0.050$ Å (Table 1). Back-donation should also produce proportionally shorter Co(1)−C(1/2) distances, and indeed, norbornene has the shortest such distance. To quantify this hypothesis, CDA calculations have been carried out, and the results are consistent with this analysis (Table 5).

In the CDA method, the MOs of the complex are expressed in terms of the MOs of appropriately chosen fragments, i.e., the Kohn−Sham orbitals of the complex are expressed as a linear combination of the MOs of the olefin ligand and the metal fragment. The orbitals are derived from: (1) the mixing of the occupied MOs of the olefin with the unoccupied MOs of the metal fragment (Co−olefin donation [d]); (2) the mixing of the unoccupied MOs of the olefin with the occupied MOs of the metal fragment (olefin−Co back-donation [b]); (3) the mixing of the occupied MOs of the olefin with the occupied MOs of the metal fragment (olefin−Co repulsive polarization [r]); and (4) the mixing of the unoccupied MOs of the olefin with the unoccupied MOs of the metal fragment (residual term [s]). In the case of norbornene, 0.181 and 0.143 electrons (**2c** and **2c′**, respectively) are involved in the back-donation, whereas with cyclohexene, only 0.096 is involved.

There is an excellent correlation between the level of back-donation and the barrier to cobaltacycle formation. For example, in the case of the cyclopentene and norbornene complexes **2b** and **2c′**, the same level of back-donation has been calculated, and indeed, the energies of activation are similar. With the norbornene complex **2c**, there is greater back-donation and a lower energy barrier. Finally, in the cyclohexene complex **2a**, in which there is relatively little back-donation, there is a correspondingly higher barrier to cobaltacycle formation. Thus, the important conclusion to be drawn is that the greater the back-donation, the higher the olefin's reactivity.

The LUMO (π^*-orbital) of the olefin is particularly important since it is involved in not only the olefin−Co back-donation but also the creation of the new carbon−carbon bond between C(1) and C(3). The HOMO of the $Co_2(CO)_5$−acetylene complex, which is involved in the Co−$C_{\text{acetylene}}$ bonding that is to be broken, is used with the π^*-orbital of the olefin for formation of the new C−C bond. The electrons in the HOMO of the olefin are involved in the new Co−C_{alkyl} bond (Figure 4). It can be seen that the HOMO levels of the $Co_2(CO)_5$−propyne complexes are, as expected, quite similar, between −6.100 and −6.347 eV (Table 6). Although the HOMO−LUMO energy gaps range only from 6.013 to 6.683 eV, the energy gap order for the three olefins does parallel their reactivity in the Pauson−Khand reaction: cyclohexene has the largest gap, followed by cyclopentene and norbornene, and reactivity increases on going from cyclohexene to cyclopentene to norbornene. The LUMOs of the free olefins also parallel this reactivity, as can be seen in Table 6, and thus *the LUMO of a free olefin should be generally useful as a first approximation of relative*

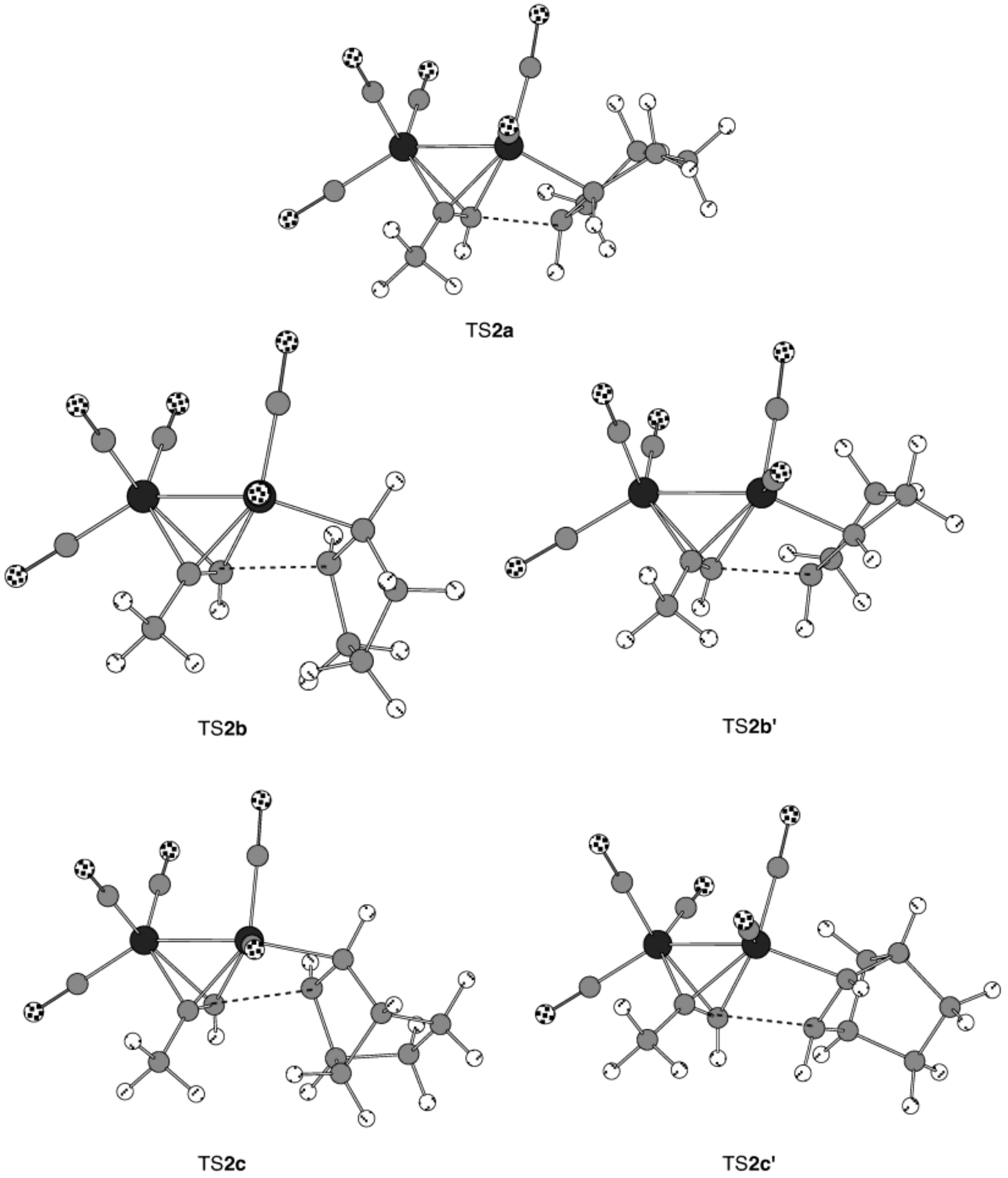


FIGURE 3. Optimized transition states for cobaltacycle formation.

TABLE 7. Thermodynamic Data (in kcal/mol)

	2a	**2b**	**2b′**	**2c**	**2c′**
$E_{\mathrm{int}}{}^{a}$	−18.90 (−23.98)	−20.78 (−25.74)	−22.17 (−27.14)	−24.89 (−30.06)	−24.64 (−30.26)
$D_{\mathrm{e}}{}^{b}$	+0.2	−0.4	−2.5	−1.8	−4.6
ΔE (geometry)^{c}	4.9	4.7	5.0	6.2	6.0

[a] Interaction energy in parentheses is not corrected for the basis set superposition error (bsse). [b] $D_e = E_H$ (complex) − E_H (Co_2CO_5) − E_H (olefin); E_H are ZPE-corrected energies. [c] Energy change on transforming the geometry of the olefin from that in the uncoordinated structure to that in the $Co_2(CO)_5$−propyne−olefin complex.

reactivity.[20] Pauson−Khand transformations found in the literature would seem to support this possibility: cyclohexadiene, for example, reacts in toluene at 70 °C to produce the expected adduct in 65% yield,[21] whereas cyclohexene, under the same conditions, affords a mere 3% yield of the expected cyclopentenone.[22] Likewise, ethyl vinyl ether (LUMO, 0.825 eV) and vinyl benzoate (LUMO, −1.648 eV), under essentially identical experimental conditions, produce the corresponding adducts in 43% yield (60 h) and 80% yield (16 h), respectively.[23,24]

The same trend can be seen in the thermodynamic data (Table 7). Norbornene has the largest interaction energy,

---

[20] It appears that a correlation exists between the C═C−C angle of the olefin (**2a**, 123°; **2b**, 112°; **2c**, 107°) and the energy level of its LUMO: the smaller the angle, the lower the LUMO energy. Calculation of the LUMO orbital energy of 3-hexene (bond angle = 128° and C═C bond distance = 1.346 Å) with the bond angle and C═C bond distance of norbornene (107° and 1.350 Å) shows a decrease of the LUMO energy of 0.369 eV.

[21] Khand, I. U.; Pauson, P. L.; Habid, M. J. A. *J. Chem. Res.* **1978**, 4401−4405.

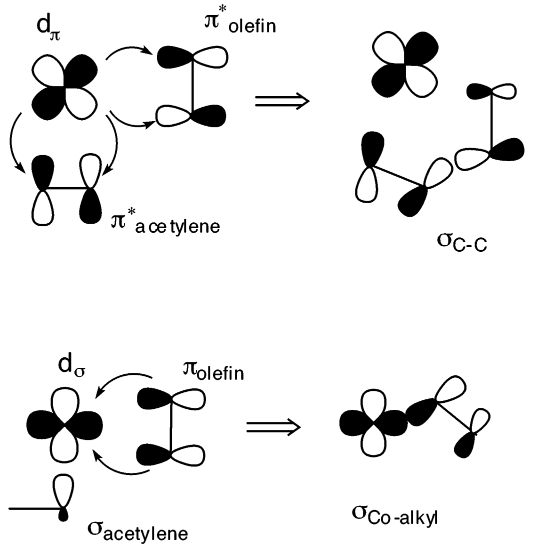


FIGURE 4. Schematic HOMO−LUMO orbital interaction.

followed by cyclopentene and then cyclohexene, paralleling the decrease in the back-donation in going from **2c** to **2a**. Likewise, the binding energy, calculated from $D_e = E_H$ (complex) − E_H (Co_2CO_5) − E_H (olefin), is exothermic for norbornene and cyclopentene, whereas for cyclohexene, which is practically unreactive in the Pauson−Khand reaction, a slightly endothermic value has been calculated. Steric decompression due to C−C lengthening does not seem to be involved, however, since in going from cyclohexene to norbornene there is a difference of merely ca. 1 kcal/mol.

In conclusion, the LUMO of the coordinated olefin appears to have a crucial role in olefin reactivity in the PK reaction. It determines to a large degree the back-donation in the complex, which impacts significantly the effectiveness of the LUMO overlap with the HOMO of the $Co_2(CO)_5$−acetylene complex, and it is this interaction that is key in the subsequent C−C bond formation. The surprising differences in reactivity of cyclohexene, cyclopentene, and norbornene thus find an explanation, one that can also be used to understand the behavior of other olefins and the effect of certain additives in this important transformation.

Acknowledgment. We thank Prof. R. Arnaud for fruitful discussions and the Université Joseph Fourier (UJF) and the centers IDRIS and CINES (Project 011219) and CECIC for providing computer facilities. We also express our gratitude to Dr. P. Vatton for the installation of the software programs. Financial support from the UJF and the CNRS (UMR 5616) and a postdoctoral fellowship to T. J. M. de Bruin from the CNRS are gratefully acknowledged.

Supporting Information Available: Cartesian coordinates of all optimized structures described in this publication. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035294W

---

(22) Khand, I. U.; Pauson, P. L. *J. Chem. Res., Miniprint* **1977**, 165−187.

(23) Kerr, W. K.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M. *J. Organomet. Chem.* **2001**, *630*, 104−117.

(24) Calculations performed on methyl vinyl ether (LUMO = −0.244 eV) and vinyl acetate (LUMO = −1.729 eV), olefins with similar electron-donating and electron-withdrawing substituents, indeed show that the reactive complex (type II) exhibits Co(1)−C(2) and C(1)−C(3) distances of 2.373 and 2.868 Å, respectively, for the former and 2.154 and 2.758 Å, respectively, for the latter. Likewise, the computed activation energy barriers are 12.0 (methyl vinyl ether) and 9.4 kcal/mol (vinyl acetate).