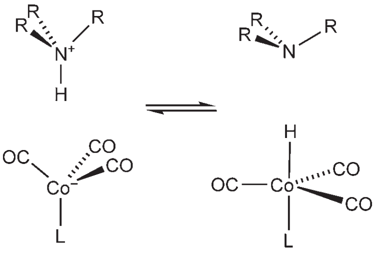
DOI: 10.1002/ange.200503597

Polyhedral Interconversion Coupled with Proton Transfer between an Ammonium Cation and the $[Co(CO)_4]^-$ Ion**

*David Casanova, Pere Alemany, and Santiago Alvarez**

Proton transfer between ammonium cations and $[CoL(CO)_3]^-$ ions ($L = CO$, PR_3) has been illustrated by Brammer et al.[1] through a series of crystal structures according to the structure-correlation principle, which states that “if a correlation can be found between two or more independent parameters describing the structure of a given fragment in a variety of environments, then the correlation function maps a minimum energy path in the corresponding parameter space”.[2] The two ends of the proton transfer reaction correspond to an ionic pair formed by an ammonium cation and the $[CoL(CO)_3]^-$ ion (**1a**) and independent amine and hydrido carbonyl complexes **1b**. The structures analyzed by Brammer et al. correspond to compounds with N–H···Co hydrogen bonds, a behavior consistent with the acidity of the hydrido carbonyl complex in water.[3] According to the structure-correlation principle, the variety of H···Co distances found (between 2.63 Å for a N–H···Co hydrogen-bonded species and 1.43 Å for the hydrido complex) should correspond to snapshots along the proton-transfer reaction coordinate. Since the coordination spheres of both the N and Co atoms are significantly affected by the progress of the proton-transfer reaction, these systems provide an excellent opportunity to test the applicability of the polyhedral-shape measures as reaction coordinates and to correlate the potential-energy surface with the structural evolution. Therefore, the aim of this communication is to show how DFT calculations provide an energy profile for such a reaction that accounts for the fine details of the distribution of structures along the path and how the proton transfer is coupled to changes in the coordination polyhedra of the N and Co atoms. An outcome of this study is that the energy and the stereochemical changes that accompany the proton transfer can be described as a function of a single parameter, the generalized polyhedral-interconversion coordinate[4] for the transformation of a $[CoL(CO)_3]^-$ (L = ligand) tetrahedron into a vacant trigonal bipyramid.



1a **1b**

To represent the general case of an ammonium cation, we took the NH_4^+ ion as the simplest example, whereas the family of the $[CoL(CO)_3]^-$ ions was represented in our calculations by the $[Co(CO)_4]^-$ ion. To explore the potential-energy surface, we calculated a linear-transit reaction coordinate for the $NH_4{\cdot}[CoL(CO)_3]$ aggregate keeping the Co···H distance fixed and optimizing the rest of the geometry.[5] The two minima and one maximum obtained were fully optimized and could be characterized as stationary points on the potential-energy surface through frequency analysis (geometries and frequencies for the three stationary points are provided in the Supporting Information). The two minima correspond to the two alternative hydrogen-bonding situations: a) N–H···Co, referred to herein as the ion pair, to avoid confusion with the second minimum, and b) N···H–Co, which we term the hydrogen-bonded complex. The maximum corresponds to a transition state with a delocalized hydrogen bond of the type N···H···Co. The isolated fragments $[Co(CO)_4]^-$, NH_4^+, NH_3, and $[HCo(CO)_4]$ were also optimized. The optimized structures are shown in Figure 1, those of the cobalt complexes are in good agreement with the experimentally determined structures for $[HCo(CO)_4]$[6] and a variety of salts of the $[Co(CO)_4]^-$ ion, as found in a structural database search.[7]

The changes in the coordination spheres of the N and Co atoms can be monitored by using continuous-shape measures (CShM).[8,9] In short, a shape measure is a dimensionless continuous function that calibrates the degree of distortion of a set of atoms from a predetermined shape (typically a polyhedron), thus yielding zero for those structures that exactly match the reference shape and increasingly higher values as the distortions are more pronounced. As a rule of thumb, small but chemically significant distortions give shape measures of the order of 0.1 units, whereas values of 1 unit or more indicate important-to-severe distortions. In Figure 2, we represent the evolution of different shape measures as a function of the Co···H distance: 1) that of the NH_3 group relative to a vacant tetrahedron and those of the $\{Co(CO)_4\}$ fragment relative to 2) the tetrahedron and 3) the vacant trigonal bipyramid (a trigonal bipyramid with one axial ligand missing, termed vTBP herein). The stereochemistry around the Co atom, which is perfectly tetrahedral at the early stages of the reaction (Co···H ≈2.4 Å), is gradually distorted as the

---

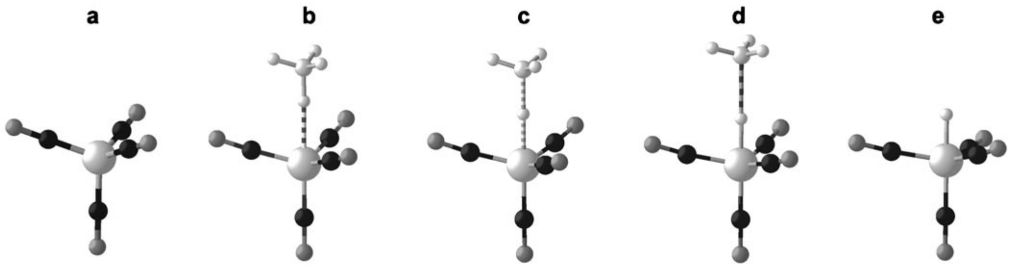
[*] D. Casanova, Prof. S. Alvarez
Departament de Química Inorgànica and
Centre de Recerca en Química Teòrica
Universitat de Barcelona
Martí i Franquès 1–11, 08028 Barcelona (Spain)
Fax: (+34) 93-4907725
E-mail: santiago.alvarez@qi.ub.es

Dr. P. Alemany
Departament de Química Física and
Centre de Recerca en Química Teòrica
Universitat de Barcelona (Spain)

[**] Work supported by the Dirección General de Investigación (MCyT), projects CTQ2005-08123-C02-01/BQU, and −02/BQU.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



$\varphi(T_d$–vTBP)	0 %	22 %	34 %	42 %	54 %
Co···H (Å)	-	2.09	1.70	1.52	1.49
N···H (Å)	-	1.12	1.49	2.09	-

Figure 1. Structures along the path for proton transfer between the NH_4^+ and $[Co(CO)_4]^-$ moieties: a) Isolated $[Co(CO)_4]^-$ ion, b) ion pair with an N–H···Co bond, c) transition state, d) hydrogen-bonded species with N···H–Co bond, and e) isolated $[HCo(CO)_4]$. The generalized coordinates along the interconversion path from the tetrahedron to the vTBP, $\varphi(T_d$–vTBP), are given alongside each optimized structure.

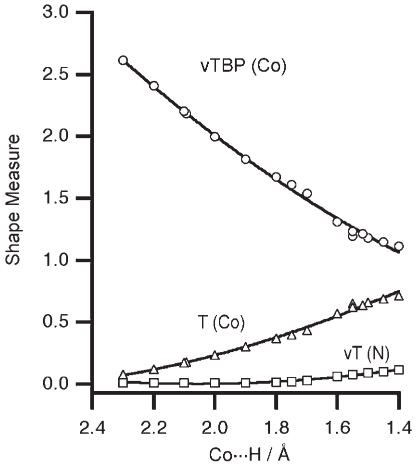


Figure 2. Evolution of the polyhedral measures of the N and Co coordination spheres along the proton-transfer reaction, vacant tetrahedron (vT) for NH_3 (squares), tetrahedron (T; triangles), and vacant trigonal bipyramid (vTBP; circles) for the $\{Co(CO)_4\}$ fragment.

ammonium cation approaches, and such a loss of tetrahedricity is seen to correlate with a tendency to adopt a vTBP geometry. However, the final product of the proton transfer, $[HCo(CO)_4]$, is still far from being a perfect trigonal bipyramid, according to the nonzero value of the CShM of its $\{Co(CO)_4\}$ fragment relative to the vTBP, in good agreement with its experimental structure (calculated and experimental C_{ax}-Co-C_{eq} bond angles of 105 and 99°, respectively). The stereochemistry around the N atom, in contrast, varies very little at the early stages of the reaction, remaining nearly tetrahedral even at Co···H: 2.1 Å, the equilibrium geometry for the N–H···Co bonded ion pair. At Co···H distances of 1.8 Å or shorter, though, that shape measure increases gradually, thus reflecting the loss of the proton and the adjustment of the remaining H–N–H bond angles to the pyramidal geometry of ammonia. The rather small changes in shape measures of the NH_3 fragment relative to those experienced by the $\{Co(CO)_4\}$ unit reflects their different degree of geometrical change: while bond angles vary from 109.5° in NH_4^+ to 115.5° in NH_3, the C_{ax}-Co-C_{eq} bond angles change from 109.5° in $[Co(CO)_4]^-$ to 99.1° in $[CoH(CO)_4]$.

Not only are the shape measures correlated to the Co···H distance along the reaction path, but it is also seen that all the points in our linear transit pathway have shape measures for the $\{Co(CO)_4\}$ fragment that correspond to the minimal-distortion interconversion path between the tetrahedron and the vTBP according to the very small values of the path-deviation function.[10] For that reason, we can describe the proton-transfer reaction by means of the generalized reaction coordinate[4] that corresponds to the conversion of a $\{Co(CO)_4\}$ tetrahedron into a vTBP (Figure 3). Using such a coordinate, the independent reactants are represented by 0% of the polyhedral path, as the isolated $[Co(CO)_4]^-$ ion is perfectly tetrahedral. One hundred percent of the reaction coordinate would correspond to a vTBP shape for the $\{Co(CO)_4\}$ fragment. However, the products of the reaction, represented by the position of $[HCo(CO)_4]$ along the reaction coordinate, appear at 54% of the polyhedral-interconversion

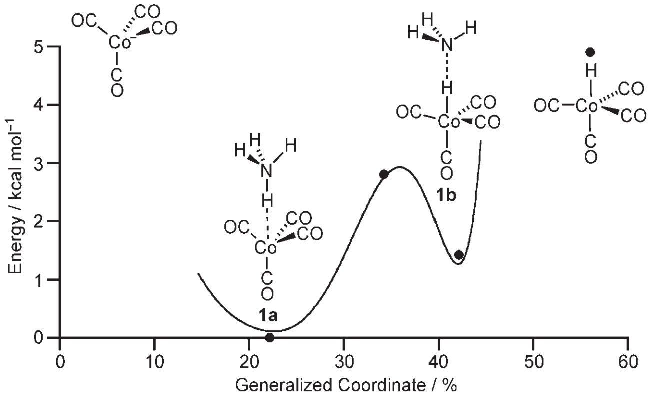


Figure 3. Calculated energy (gas phase) for the NH_4·$[Co(CO)_4]$ composite along the proton-transfer path, as a function of the generalized coordinate for the polyhedral rearrangement of the $\{Co(CO)_4\}$ fragment from a tetrahedral to vTBP shape. The continuous line represents the points along the linear transit pathway, the circles correspond to stationary points.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

path, as the hydrido carbonyl complex does not reach the trigonal bipyramidal shape (Figure 1e). In-between, we can see that the ion pair with N–H···Co bonding appears at 22%, the transition state at 35%, and the N···H-Co hydrogen-bonded complex at 42% of the polyhedral transformation around the Co atom. It is worth noting that the isolated $[HCo(CO)_4]$ complex is closer (54% of the path) to the vTBP than when hydrogen bonded (42%).

If we look now at the relative energies of the stationary points along the reaction path in the gas phase (relative energies at the B3LYP and CCSD(T) levels are given in the Supporting Information), we notice that the ion pair **1a** is much more stable than the independent ions (93 $kcal\,mol^{-1}$), the hydrogen-bonded species **1b** is nearly isoenergetic with **1a**, and the barrier for the proton transfer is about 2 $kcal\,mol^{-1}$. The dissociation of the hydrogen-bonded species into the two neutral molecules is calculated to cost some 3 $kcal\,mol^{-1}$. The fact that the ionicity of the species involved changes along the proton-transfer process made us worry about the effect of solvents of different polarities on the energy profile. Single-point calculations at the geometries optimized for the gas phase were carried out at the B3LYP level with the polarizable continuum model (PCM) approach, using dielectric constants that correspond to water, CH_2Cl_2, and CH_3Cl (energy profiles provided in the Supporting Information). As expected, the ionic forms are increasingly stabilized as the polarity of the solvent increases to the point that the independent ions become more stable than the ion pair **1a** for the case of water (by 2.5 $kcal\,mol^{-1}$). As a result, both the hydrogen-bonded species **1b** and the independent neutral molecules become unstable relative to the ion pair in the three solvents tested by more than 10 $kcal\,mol^{-1}$. Notice that the PCM model does not take into account possible bonding interactions between solvent molecules and the species that participate in the reaction, such as hydrogen bonding or weak coordination. Therefore, the energy profile given herein should not be taken as a quantitative representation of the corresponding proton-transfer reaction in solution.

Once we have a simple and clear description of the stereochemistry and the energetics of this proton-transfer process, we can go back to the structural correlation based on experimental distances and angles proposed by Brammer et al.[11] To that end, our theoretical results and some related experimental data plotted on shape maps are shown side by side in Figure 4.[9] There, the lower continuous line represents the minimal-distortion interconversion path between the tetrahedron and the vTBP; its two extremes correspond to these two ideal figures. All calculated points, both the optimized geometries (Figure 4, left) and the structures of the linear-transit reaction coordinate, are seen to follow the minimal distortion path.

The experimental structural data for the ternary ammonium salts of the $[Co(CO)_4]^-$ ion (Figure 4, right) are found in the shape map between the position predicted by calculations for the isolated anion and that of the ion pair, thus reflecting the shallowness of the potential well around the latter and the presence of steric hindrance in some cases that keeps the Co and N atoms at a relatively long distance (e.g., Co···H: 2.73 Å for the quinuclidinium salt[11]). The fact that all structurally characterized ammonium salts of the cobalt carbonylate present the ion-pair structure **1a**, while no hydrido carbonyl complex seems to exist in the presence of an amine, is consistent with our finding that the hydrido carbonyl complex is stable in the presence of an amine only in the gas phase. The experimental gas-phase structure of $[HCo(CO)_4]$ also occupies the position predicted along the minimal polyhedral distortion path. The absence of experimental structures in the region that corresponds to the transition state completes a rather accurate cross-section of the potential-energy surface.

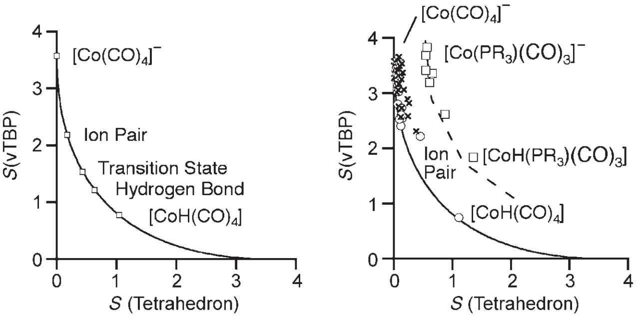
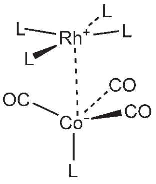


Figure 4. Calculated (left) and experimental (right) data on shape maps for tetracoordinate fragments in the tetrahedron–vTBP space, thus showing the minimal-distortion interconversion path (continuous line), and a distortion path with the axial ligand at a longer distance ($d'/d=1.27$) than the rest (dashed line in the right-hand-side plot). The theoretical data plotted are those of the optimized structures (left, squares). The experimental X-ray structural data shown (right) are those of the ternary ammonium salts of the $[Co(CO)_4]^-$ ion (circles), other salts of the same anion (crosses), $[HCo(CO)_4]$ and the phosphine substituted analogues, $[Co(PR_3)(CO)_3]^-$ and $[HCo(PR_3)(CO)_3]$ (squares).

If we include the structures of salts of the same carbonylate anion with other cations in the shape map, we find them aligned along the expected reaction path as well. As the countercations in those cases are not proton donors, it is surprising at first sight to find such significant deviations of the $[Co(CO)_4]^-$ ion from the tetrahedron. Let us focus on the most extreme case to illustrate the usefulness of the shape map, that of a structure practically at the same position in which we find the ion pair with the shortest hydrogen bond: this structure corresponds to a carbonylate of the square planar $[Rh(CNR)_4]^+$ ion.[12] Since hydrogen bonding must be precluded in this case, the shape measures suggest that some sort of interaction between the two ions may drive the distortion of the tetrahedral carbonylate toward a trigonal bipyramid, as confirmed by a relatively short Co···Rh distance of 3.38 Å and a significant distortion of the Rh coordination sphere from square planar toward a square pyramid **2**. In other words, the rhodium center of the cationic complex is a Lewis acid that plays the role of the proton in the ammonium salts. Precedents of d^8 square-planar metals that act as Lewis acids are known,[13] and the existence of bonding that is as weak as the Co···Rh interaction found herein and the corresponding pyramidali-



2

zation of the metal coordination sphere have been explained with molecular-orbital arguments.

To show how the use of shape maps can provide further insight into the details of reaction pathways through structural correlations, we have separately analyzed the families of $[Co(PR_3)(CO)_3]^-$ and $[Co(PR_3)_4]^-$ ions. The former were included by Brammer et al. in the structural correlation of the cobalt carbonylate discussed above. The position of the mixed ligand complexes in the shape map (Figure 4, right, squares) shows that they follow a pathway parallel to the minimal distortion path as a result of the differences between Co–C and Co–P bond lengths with a product of the proton-transfer reaction, $[CoH(PR_3)(CO)_3]$, thus also presenting a geometry that is about halfway in the direction of the trigonal bipyramid. These similarities confirm the validity of the proposal of a common structural correlation for the two families of molecules at the qualitative level. Full substitution of carbonyls by phosphines in the $[Co(PR_3)_4]^-$ ions (not shown in Figure 4 for simplicity; see the Supporting Information) should bring us back to the minimal-distortion path, as all the bonds of the analyzed $\{CoP_4\}$ polyhedral fragment are practically identical. Even if no such anions have been structurally characterized, there is one hydrido derivative $[CoH(PR_3)_4]$[14] that appears right along the minimal distortion pathway. Analogous hydrido complexes with tripod tetradentate ligands present geometries much closer to the trigonal bipyramid,[15] as the tripod ligand enforces P_{axial}-Co-$P_{equatorial}$ bond angles much closer to 90°. The fact that the homoleptic phosphine complexes go back to the same path of the homoleptic carbonyl ones confirms that the changes in the reaction path upon substitution in the heteroleptic complexes are because of an asymmetric substitution pattern.

In summary, the present study of the proton transfer reaction between an ammonium cation and a cobalt carbonylate shows that the evolution of the polyhedral shape measure of the $\{Co(CO)_4\}$ fragment along the reaction path can be used as a reaction coordinate. Changes in bond distances and angles and the potential energy of the system can be adequately described by this reaction coordinate. The geometries of experimental structures of families of compounds with the general formulae $[Co(CO)_4]^-$, $[Co(PR_3)(CO)_3]^-$, $[CoH(CO)_4]$, $[CoH(PR_3)(CO)_3]$, and $[CoH(PR_3)_4]$ offer snapshots of the low-energy regions of the potential-energy surface for the proton-transfer reaction in the gas phase. Furthermore, there is a good correspondence between the optimized structures of the species that participate in this reaction and those found experimentally, thus providing an excellent illustration of the structure-correlation principle. Paradoxally, the proton-transfer reaction seems to be disfavored in solution and only the ion pair or the dissociated ions are expected to exist depending on the polarity of the solvent used.[16]

Received: October 11, 2005
Published online: January 20, 2006

Keywords: cobalt · continuous shape measures · coordination modes · proton transfer · reaction coordinates

---

[1] L. Brammer, J. C. Mareque Rivas, C. D. Spilling, *J. Organomet. Chem.* **2000**, *609*, 36.

[2] H.-B. Bürgi in *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Meerbach), Verlag Helvetica Chimica Acta, Basel, **1992**; H.-B. Bürgi, *Acta Crystallogr. Sect. A* **1998**, *54*, 873; P. Murray-Rust, H.-B. Bürgi, J. D. Dunitz, *J. Am. Chem. Soc.* **1975**, *97*, 921; H.-B. Bürgi, J. D. Dunitz, *Structure Correlations*, VCH, Weinheim, **1994**.

[3] W. Hieber, E. Lindner, *Chem. Ber.* **1961**, *94*, 1417.

[4] J. Cirera, S. Alvarez, *Chem. Eur. J.*, in press.

[5] DFT calculations at the B3LYP level were performed using the Ahlrichs triple-ζ all-electron basis set with two p-polarization functions at the Co atom. Interaction energies were corrected for the basis-set superposition error by means of the counterpoise method. All calculations were performed with the Gaussian package (Gaussian 03 Revision B.4), M. J. Frisch et al., Gaussian, Inc., Pittsburgh, PA, **2003**). Single-point calculations on the B3LYP-optimized geometries at the CCSD(T) level were also carried out (see the Supporting Information).

[6] E. A. McNeill, F. R. Scholer, *J. Am. Chem. Soc.* **1977**, *99*, 6243.

[7] Structural searches were carried out in the Cambridge Structural Database (F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31), version 5.26.

[8] H. Zabrodsky, S. Peleg, D. Avnir, *J. Am. Chem. Soc.* **1992**, *114*, 7843; D. Avnir, O. Katzenelson, S. Keinan, M. Pinsky, Y. Pinto, Y. Salomon, H. Zabrodsky Hel-Or in *Concepts in Chemistry: A Contemporary Challenge* (Ed.: D. H. Rouvray), Research Studies Press Ltd., Taunton, **1996**. All continuous shape measures and path-deviation functions reported herein were calculated with the *SHAPE* program (version 1.1): M. Llunell, D. Casanova, J. Cirera, J. M. Bofill, P. Alemany, S. Alvarez, M. Pinsky, D. Avnir, Barcelona, **2003**.

[9] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, *Coord. Chem. Rev.* **2005**, *249*, 1693.

[10] D. Casanova, J. Cirera, M. Llunell, P. Alemany, D. Avnir, S. Alvarez, *J. Am. Chem. Soc.* **2005**, *127*, 1755.

[11] L. Brammer, J. C. Mareque Rivas, D. Zhao, *Inorg. Chem.* **1998**, *37*, 5512.

[12] I. Ojima, N. Clos, R. J. Donovan, P. Ingallina, *Organometallics* **1991**, *10*, 3211.

[13] G. Aullón, S. Alvarez, *Inorg. Chem.* **1996**, *35*, 3137.

[14] J. D. Crane, N. Young, *Acta Crystallogr. Sect. E* **2004**, *60*, m487.

[15] C. A. Ghilardi, S. Midollini, L. Sacconi, *Inorg. Chem.* **1975**, *14*, 1790; C. Bianchini, D. Masi, C. Mealli, A. Meli, M. Sabat, *Gazz. Chim. Ital.* **1986**, *116*, 201; A. Orlandini, L. Sacconi, *Cryst. Struct. Commun.* **1975**, *4*, 157; A. Orlandini, L. Sacconi, *Inorg. Chim. Acta* **1976**, *19*, 61.

[16] See the Supporting Information for optimized atomic coordinates and calculated vibrational spectra for $[Co(CO)_4]^-$, $[CoH(CO)_4]$, ion pair, and N···H–Co hydrogen-bonded species; calculated B3LYP and CCSD(T) energies of the stationary points of the B3LYP potential energy surface; shape measures and CSD reference codes for the experimental structures of $[Co(CO)_4]^-$, $[CoH(CO)_4]$, $[Co(PR_3)(CO)_3]^-$, $[CoH(PR_3)(CO)_3]$, and $[CoH(PR_3)_4]$ complexes; plot of the B3LYP energy profile in different solvents and at the CCSD(T) level in the gas phase.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim