High-Pressure Crystallography

DOI: 10.1002/ange.200502241

Staggered to Eclipsed Conformational Rearrangement of $[Co_2(CO)_6(PPh_3)_2]$ in the Solid State: An X-ray Diffraction Study at High Pressure and Low Temperature**

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Single-crystal high-pressure (HP) crystallography is a growing field, but studies on organometallics are relatively rare despite the many interesting behaviors inferred from HP spectroscopy.[1] Molecular solids, being held together by

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[**] We thank Prof. Bruni for the use of the spectrometer to perform the high-pressure measurements.

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

relatively weak forces, have high compressibilities; organometallics, in addition, have soft metal-centered bonds. Thus, at HP it should be possible to observe significant changes in both inter- and intramolecular distances.

We have recently discussed the nature of M–M bonds of metal carbonyl clusters using experimental and theoretical charge densities;[2] here we report the first attempt to "directly" observe the behavior of a M–M bonded system under pressure. As suggested by HP spectroscopy, $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, and $[MnRe(CO)_{10}]$ undergo a staggered to eclipsed conformational rearrangement of the equatorial carbonyl ligands,[3] which seems to be associated with a reconstructive phase transition (PT) and extensive crystal fragmentation.

To obtain "indirect" proof of this process we considered a related species, $[Co_2(CO)_6(PPh_3)_2]$ (**1**), which at room temperature and pressure (RT and RP) has an unsupported M–M bond and a staggered arrangement of equatorial CO ligands. In the solid state, **1** is isomorphous to $[Co_2(CO)_6(AsPh_3)_2]$ (**2**), which is known to undergo a reversible "crystal to crystal" PT (at $T \approx 200$ K) characterized by an incipient staggered to eclipsed rearrangement.[4] Thus, according to the well-known relationship between low-temperature (LT) and HP changes, **1** (as well as **2**) should be the ideal candidate for a single-crystal HP diffraction study of this process. Here we report the detailed crystallographic analysis of the structural behavior of **1** on lowering T (down to 28 K) and on raising P (up to 46 kbar).[5]

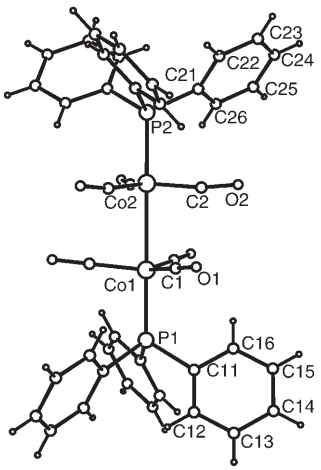

Figure 1. $[Co_2(CO)_6(PPh_3)_2]$ (**1**); independent atoms of the HP/LT phases are labeled. Before the transition the presence of an intramolecular inversion center halves the asymmetric unit and limits the significant degrees of freedom to a few angles (C11-P1-Co1-O1, C16-C11-P1-Co1, and Co2-Co1-C1) and bond lengths (Co1-Co2 and Co1-P1). After the transition the inversion center is lost, the CO-Co-Co-CO and Ph-P-P-Ph torsions are freed, and the above-mentioned parameters doubled.

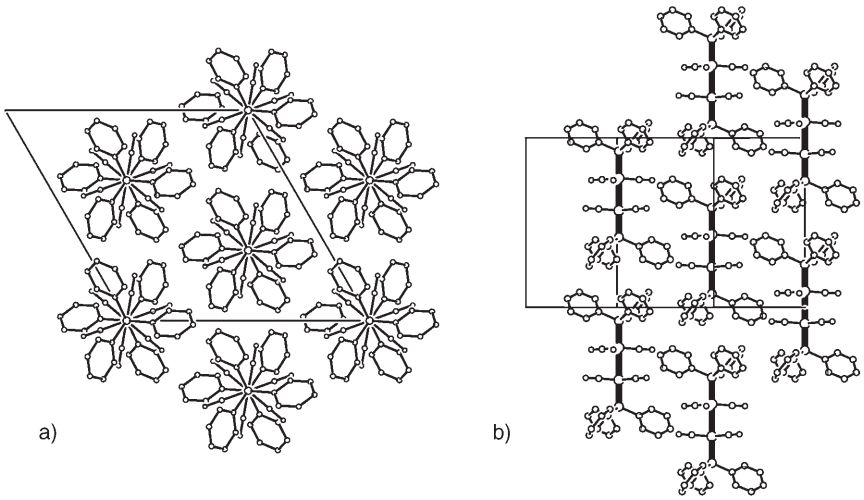

Figure 2. Crystal packing of **1** under ambient conditions. a) View normal to (001). b) View normal to (100).

At RT and RP, **1** crystallizes in the trigonal space group $R\bar{3}$ and lies about a $\bar{3}$ symmetry element (*b* in Wickoff notation). The molecule (Figure 1) consists of two trigonal-bipyramidal cobalt atoms linked by an unsupported Co–Co bond along the axial direction. The remaining axial site of each metal center is occupied by a PPh_3 group and three CO ligands are bound in the equatorial positions. Given the observed crystallographic symmetry the CO ligands are constrained to be exactly staggered, and the same occurs for the phenyl groups of the triphenylphosphane ligands. In the crystal, molecules of **1** stack on top of each other in columns (parallel to *c*, Figure 2a), the projections of which define a hexagonal motif in the *ab* plane (Figure 2b). The packing along the columns is dominated by the presence of "sextuple embraces" between opposite PPh_3 groups.[6] The six neighboring columns are shifted along the *c* axis by $\pm 1/3$ (three upwards, three downwards) to allow the optimization of "lateral" interactions (π stacking of phenyl groups and CH···O contacts).

On lowering the temperature below 120 K or on increasing the pressure above 13 kbar, we observed a reversible solid–solid PT,[7] in which doubling of the *c* axis reduces the molecular symmetry from $\bar{3}$ to 3 without losing the crystal symmetry class ($\bar{3}$). After the PT, the perfect staggering of the ligands no longer holds and different structural changes are observed, the most striking of which is the rapid progress toward eclipsing of the two sets of CO ligands.

Temperature-induced structural modifications are mainly due to reduced atomic motion and span a limited region of the molecular potential energy surface (at 28 K the OC-Co-Co-CO angle is ca. 56°), but larger effects are expected and found on increasing the pressure (at 46 kbar the OC-Co-Co-CO angle is as small as ca. 20°).

To estimate the energies associated with the observed molecular deformations, we performed a series of constrained DFT gas-phase optimizations of $[Co_2(CO)_6(PH_3)_2]$ (mimicking **1**, see Table 1), which showed a correlation between CO eclipsing and Co–Co elongation (the eclipsed conformer is ca. 0.2 Å longer and 10 kcal mol^{-1} less stable than the staggered one).[8] Further insight is offered by normal-mode analysis of the staggered conformer: H-P-P-H (33 cm^{-1}), OC-Co-Co-CO

Table 1: The main molecular and intermolecular distances [Å] and angles and torsion angles [°] of **1** as measured at different values of the independent variables *P* and *T* (experimentally) and of the carbonyl torsion (DFT calculations).

	OC-Co-Co-CO	Co-P-C-C		Co-Co-CO		Co-Co	Co-P		P···P	
P [kbar]										
0.001	60	43.9(5)		86.6(5)		2.67(1)	2.21(1)		6.80(3)	
8	60	43.2(11)		87.4(10)		2.61(3)	2.17(3)		6.76(6)	
13	46.1(5)	33.6(7)	49.1(9)	82.5(10)	89.6(11)	2.69(2)	2.18	2.16	7.00(4)	6.31(4)
26	24.5(3)	32.9(5)	48.8(6)	82.4(7)	95.3(7)	2.76(1)	2.22(2)	2.15(2)	6.99(4)	6.55(4)
34	22.5(3)	32.8(4)	50.2(5)	82.1(6)	96.6(5)	2.72(1)	2.20(1)	2.14(1)	6.96(3)	6.55(3)
46	21.6(3)	32.4(5)	50.4(6)	81.2(7)	96.2(6)	2.72(1)	2.20(2)	2.16(2)	6.91(3)	6.44(3)
T [K]										
298(2)[a]	60	43.8(1)		86.6(1)		2.6610(5)	2.1914(6)		6.853(1)	
120(2)	59.66(7)	42.86(8)	43.46(8)	86.2(1)	86.1(1)	2.6492(2)	2.1860(9)	2.1880(9)	6.839(1)	6.793(1)
90(2)	5750(2)	40.45(4)	45.43(4)	85.7(1)	86.6(1)	2.6494(4)	2.1886(5)	2.1868(5)	6.9454(9)	6.677(1)
60(2)	56.05(4)	39.17(6)	46.50(6)	85.5(1)	86.8(1)	2.6510(6)	2.1872(9)	2.1852(9)	7.007(1)	6.608(1)
28(2)	55.57(4)	38.56(6)	46.93(6)	85.3(1)	86.8(1)	2.6528(6)	2.1888(8)	2.1865(9)	7.034(1)	6.584(1)
E [kcal mol^{-1}][b]										
0.0	60.0	–	–	86.6		2.652	2.205		–	–
0.7	50.0	–	–	87.2	87.2	2.670	2.208	2.208	–	–
2.8	40.0	–	–	88.5	88.4	2.700	2.208	2.208	–	–
5.3	30.0	–	–	89.9	89.9	2.749	2.207	2.207	–	–
7.6	20.0	–	–	91.1	91.1	2.790	2.207	2.207	–	–
9.1	10.0	–	–	91.8	91.8	2.820	2.206	2.206	–	–
9.7	0.0	–	–	92.1		2.831	2.206		–	–

[a] Room temperature. [b] Relative energies for $[Co_2(CO)_6(PH_3)_2]$.

($47\ cm^{-1}$); Co-Co-CO ($96\ cm^{-1}$); and Co–Co ($156\ cm^{-1}$), Co–P ($320\ cm^{-1}$) are the softer torsional, bending, and stretching modes, respectively.

These computations, although neglecting effects of crystal packing, clearly highlight the most accessible deformation modes of the molecule. However, before the PT, Ph-P-P-Ph and OC-Co-Co-CO torsions are locked in by the crystal symmetry; thus, other deformation modes must occur, even if associated with higher energies. Indeed, at 8 kbar we observed significant compression of the Co–Co and Co–P bonds.

After the PT, other intramolecular degrees of freedom become available (see legend to Figure 1) and the response of the molecule to the "external field" can be different. For example, the Co–Co bond elongates, that is, its stretching energy is released and redistributed over the softer deformation modes now available. However, using as reference the values calculated for the isolated molecule (at different OC-Co-Co-CO torsion angles) we were able to identify, above the PT, a continuous (relative) compression of the Co–Co bond, in spite of its actual (absolute) elongation (see Table 1 and Supporting Information).

As the pressure increases, the *ab* plane shrinks (see Supporting Information) and a series of concatenated deformations occurs. We suggest the following order of (major) events (see Figure 3): P2-bound phenyl groups come into contact with the neighboring Co1-bound CO ligands, which rotate about the threefold axis and bend toward the Co2-bound ones, which in turn are pushed away. At the same time, a translation along the *c* axis of the whole molecule generates an alternation of closely (P2···P2) and loosely (P1···P1) packed sextuple embraces (like a Peierls distortion), and thus the P2-bound phenyl groups are forced to become less parallel to the molecular axis, and the opposite behavior is exhibited by their P1-bound counterparts).

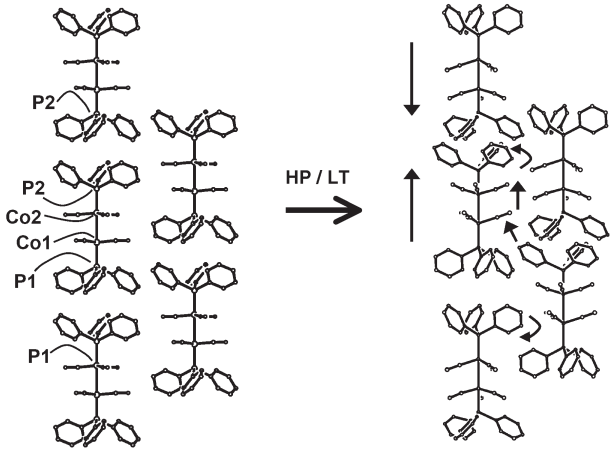

Figure 3. Schematic representation of the pressure-induced concatenated effects: bending of Co ligands, shifting of molecules, torsion of phenyl groups, and shortening of Co–P bonds.

Noteworthily, the shortening of the P2···P2 distance within the sextuple embrace is paralleled by shrinking of the related Co2–P2 bond. This is quite extraordinary as this deformation is associated with a rather deep energy well.

The interesting outcome of our experiments is that *T* and *P* induce not only modifications in the intermolecular packing but also a continuous variation of the molecular stereochemistry.

High-pressure (more than LT) crystallography is a very powerful tool for exploring the molecular potential energy surface quite far from the stationary points. Here, for

example, we could observe the previously undetected eclipsing of a staggered carbonyl metal dimer and the consequent "molecular response" (mainly Co–Co elongation), together with crystal effects leading to the compression of the more energetic Co–P bond.

As **2** undergoes the same transition as **1**, but at higher *T*, very likely it will also undergo a lower pressure PT. Presently we are performing HP experiments on **2**, to possibly take a wider picture of the molecular rearrangements.

Experimental Section

HP experiments were conducted on one side of a Merrill Basset diamond anvil cell equipped with 600 μm culet diamonds. The sample, a hexagonal single crystal of dimensions $0.18 \times 0.18 \times 0.1$ mm was loaded in a W gasket with a 300 μm hole pre-indented to 200 μm. Diffraction data at HP were collected on a Smart-APEX CCD Bruker diffractometer following literature methods.[9] Pressure was measured by the ruby fluorescence method, using a JASCO TRS-300 spectrometer equipped with a Kr laser source.

Details of the DFT calculations and crystallography can be found in the Supporting Information.

Received: June 25, 2005
Revised: September 1, 2005

Keywords: carbonyl ligands · high-pressure chemistry · phase transitions · X-ray diffraction

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[5] Details for all structures are available as Supporting Information. CCDC 276054–276064 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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