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Bowing to the Pressure of $\pi\cdots\pi$ Interactions: Bending of Phenyl Rings in a Palladium(II) Thioether Crown Complex**

Henry L. S. Wong, David R. Allan, Neil R. Champness, Jonathan McMaster, Martin Schröder, and Alexander J. Blake**

Aromatic $\pi\cdots\pi$ interactions[1] are found in many biologically important systems including proteins and DNA where they influence profoundly both structure and function.[2–5] These interactions also underpin many supramolecular systems,[5–7] and thus an increased understanding of weak, noncovalent molecular interactions is essential not only to gain insight into the roles that these interactions play, but also to engineer new polyfunctional materials.[7–10] High-pressure crystallography affords a method for directly manipulating molecules in the solid state, and allows exploration of potential-energy surfaces[11] by mechanically forcing molecules together under pressure, thereby modulating and controlling $\pi\cdots\pi$ interactions.

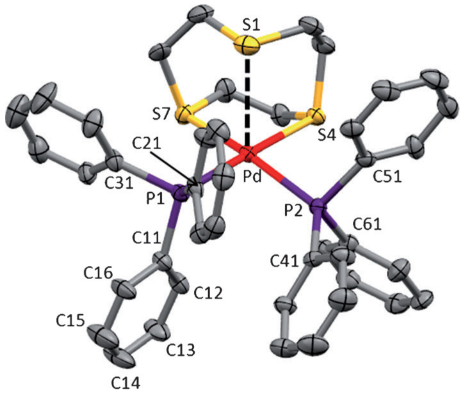


Figure 1. Structure of the cation in **1** at ambient pressure with H atoms omitted for clarity. Pd···S1 = 2.868(2) Å is shown as a dashed line, and displacement ellipsoids are drawn at 30% probability level.

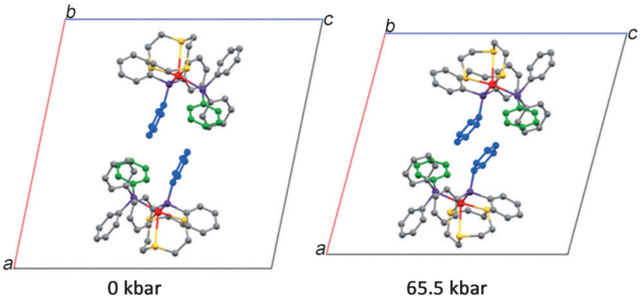
Variable-pressure structural studies have been growing in number,[12–14] but there are still relatively few on metal–ligand complexes (see Table S1 in the Supporting Information). In this study we set out to investigate the behavior under compression of **1**, in which the Pd^{II} center adopts a [4+1]

$[Pd([9]aneS_3)(PPh_3)_2](PF_6)_2$ **1** ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

coordination environment in the solid state (Figure 1):[15] The Pd^{II} center is bound to a P_2S_2 donor set in the equatorial plane, with the remaining S center interacting[16] through an apical Pd···S1 contact of 2.868(2) Å. The length of this contact depends on the co-ligands at the Pd^{II} center: π-donating Cl^- ligands afford long axial Pd···S1 distances (e.g., Pd···S1 = 3.140(2) Å in $[PdCl_2([9]aneS_3)]$[17]), while π-acceptor ligands such as phosphines give short Pd···S1 distances of ca. 2.8 Å.[16] A notable feature of **1** is the presence of PPh_3 ligands that can participate in both face-to-face and edge-to-face $\pi\cdots\pi$ interactions through phenyl embraces.[18] Thus, it appeared that **1** was an ideal candidate for studying the interplay of intermolecular $\pi\cdots\pi$ interactions and intramolecular Pd···S interactions under variable compression.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with the cations arranged such that two phenyl rings on one cation can potentially interact with two rings on another cation through a parallel four-fold phenyl embrace.[18] Each such embrace involves one face-to-face parallel interaction and two edge-to-face interactions (Figure 2, 0 kbar). The face-to-face interaction can be described as slipped-parallel,[1] involving aromatic rings which are parallel and separated by a perpendicular distance of 3.5–4.0 Å.

At ambient pressure (Figure 2, 0 kbar), there is virtually no overlap between the inversion-related rings in **1**, as confirmed by the centroid–centroid distance *B* and the



0 kbar 65.5 kbar

Figure 2. Structure of the cation in **1** at ambient pressure (0 kbar) and at 65.5 kbar with hydrogen atoms omitted for clarity. The phenyl rings forming part of the phenyl embrace are highlighted: face-to-face interactions occur between pairs of blue rings and edge-to-face interactions between blue/green pairs.

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[*] H. L. S. Wong, Prof. Dr. N. R. Champness, Dr. J. McMaster, Prof. Dr. M. Schröder, Prof. Dr. A. J. Blake
School of Chemistry, The University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
E-mail: m.schroder@nottingham.ac.uk
a.j.blake@nottingham.ac.uk
Dr. D. R. Allan
Diamond Light Source, Harwell Science and Innovation Campus
Didcot (UK)

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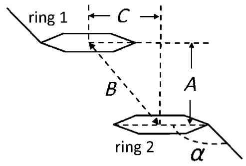


Scheme 1. Definition of the parameters in Table 1. A: perpendicular distance between the two ring planes; B: distance between the centroids of the two rings; C: slippage distance, defined as the distance between the centroid of ring 1 and the perpendicular projection of the centroid of ring 2 onto the plane of ring 1; α: P–C11⋯C14 angle.

Table 1: Observed experimental values for parameters defined in Scheme 1 for **1** as a function of pressure.

Pressure [kbar]	A [Å]	B [Å]	C [Å]	α [°]
0	3.058(13)	5.192(6)	4.195(10)	169.6(4)
10.5	2.96(2)	4.864(12)	3.861(18)	164.7(6)
28.8	3.01(4)	4.467(15)	3.30(3)	156.7(12)
36.7	2.819(18)	4.074(11)	2.941(18)	155.1(7)
40.2	3.016(13)	4.069(9)	2.731(13)	155.1(5)
55.7	2.996(17)	3.596(13)	1.99(2)	149.8(8)
65.5	3.016(15)	3.568(11)	1.906(18)	149.1(7)

slippage distance C (Scheme 1 and Table 1). The P–C11⋯C14 angle (α) is 169.6(4)°, which lies towards the lower end of the normal range for such angles in unstrained molecules at ambient pressure, as confirmed by entries in the Cambridge Structural Database[19] (Figure S1 in the Supporting Information). When **1** is placed under pressure[20] the cations are, as expected, forced into closer proximity and the unit cell is compressed, its volume reducing linearly (Figure 3) from 4554(2) Å^3 to 3482(7) Å^3, representing a 23.5% decrease in volume.[21] The parallel four-fold phenyl embrace is particularly affected by pressure, especially in the face-to-face phenyl ring interactions (colored blue in Figure 2). The distances B and C as well as the angle α contract linearly over the pressure range studied (Figure 3), but the interplanar distance A is essentially invariant throughout. At 28.8 kbar, a major increase in the ring overlap is already apparent, with C at 3.30(3) Å; significant bowing at C11 (see Figure 1) is seen as the value of α decreases to 156.7(12)°, well below the normal range of values for this angle. Ring overlap continues to increase up to 55.7 kbar as a consequence of decreases in both C and B, as does the degree of bowing at C11, indicated by a value of 149.8(8)° for α. The final pressure increment to 65.5 kbar affects only the slippage distance C which reaches a value of 1.906(18) Å, indicating further overlap of the phenyl rings (Figure 2, 65.5 kbar). Although it was not possible to collect viable datasets beyond 65.5 kbar (see the Supporting Information) it does appear that a limit or a plateau has been reached for all parameters other than C: for this reason we anticipate that the application of higher pressures would result primarily in further reduction of this distance.

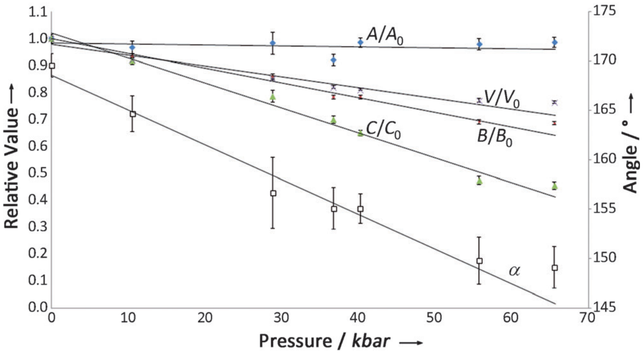
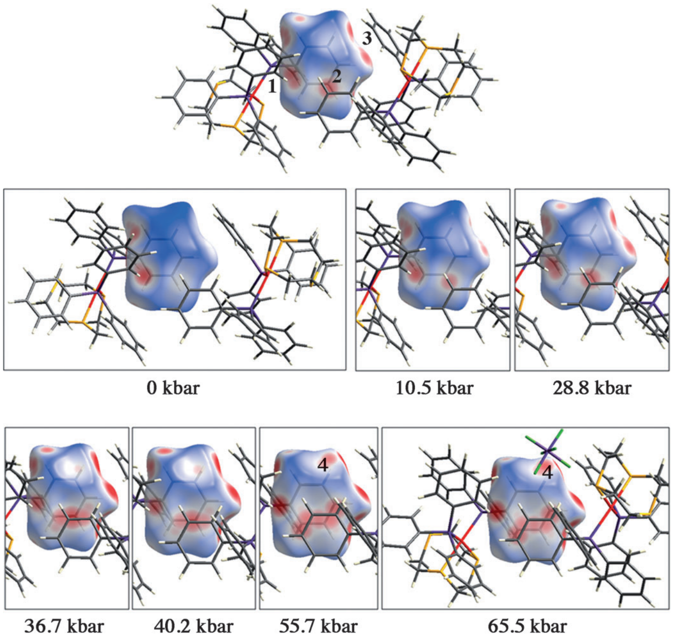


Figure 3. Plots of A, B, C, and the unit-cell volume V relative to the corresponding original values (left vertical axis) and of α (right vertical axis) show these values decreasing linearly as a function of pressure but leveling off between 55.7 and 65.5 kbar. Error bars indicate 3σ limits.

The above geometric interpretation of the evolution of the slipped-parallel interaction with pressure is confirmed by an analysis based on visualization of the intermolecular contacts using Hirshfeld surfaces (Figure 4).[22] These surfaces can be used to map intermolecular interactions directly onto the molecule and thereby facilitate and clarify their assessment and analysis. Combining the geometric and Hirshfeld analyses has allowed us to follow more clearly the evolution of the π⋯π interaction and to understand what is happening to the supramolecular contacts as the two cations approach one another. Figure 4 (top) illustrates the Hirshfeld surface at 28.8 kbar for phenyl ring C11–C16 involved in the slipped-parallel interaction; it indicates a short intermolecular contact on the face of the phenyl ring, shown as a red area (labelled as 2 in Figure 4). On electrostatic grounds, this is a favorable interaction between the aromatic carbon and hydrogen atoms from the slipped-parallel neighboring phenyl ring. Examination of the Hirshfeld surfaces at higher pressures reveals that this red area changes and becomes more diffuse as phenyl–phenyl overlap increases. The Hirshfeld surface in Figure 4 also shows one of the edge-to-face interactions of the parallel four-fold phenyl embrace (labelled as 3). This interaction becomes increasingly red, indicating shortening intermolecular distances and destabilizing strain energy. The interaction plays a key role in the approach path of the two cations, and is responsible for the decrease in C from 4.195(10) Å at 0 kbar to 1.906(18) Å at 65.5 kbar.

Although geometric deformations in related ligands can be enforced by bulky *tert*-butyl groups within the same molecule, a search of the Cambridge Structural Database[19] confirms that the mode of pyramidalization at C11 (Table 1) is unprecedented. This pyramidalization occurs concomitantly with the induction of π⋯π stacking interactions. An idealized structural model derived from the 65.5 kbar structure, but with the deformation of the C11–C16 phenyl ring removed, showed that very short, highly repulsive H⋯H contacts[23] of 1.742 Å occur between the C11–C16 phenyl ring and the C41–C46 and C61–C66 rings of the symmetry-related cation. Between ambient pressure and 65.5 kbar the compression of the axial Pd⋯S1 contact is only 0.033(13) Å, suggesting that induction of π⋯π interactions and pyramidalization at the bridgehead *ipso* carbon center are more facile processes. The above analysis is supported further by density functional



0 kbar — 10.5 kbar — 28.8 kbar

36.7 kbar — 40.2 kbar — 55.7 kbar — 65.5 kbar

Figure 4. The Hirshfeld surface of the unique phenyl ring at 28.8 kbar (top) and as a function of pressure with intermolecular distances represented by a color scale: red areas: short contacts as defined by overlapping van der Waals radii; white: van der Waals contacts which are close but non-overlapping; blue: contacts longer than the sum of the van der Waals radii. New close contacts are formed with increasing pressure. Four interactions are observed: 1) an intramolecular contact with the neighboring phenyl substituent present at ambient pressure; 2) a face-to-face interaction; 3) an edge-to-face interaction with an onset at 10.5 kbar, which could aid in drawing the two PPh_3 ligands together; 4) a close contact between a phenyl ring and an adjacent PF_6^- anion which appears at 55.7 kbar and 65.5 kbar, suggesting that at the highest pressures the PF_6^- anion ceases to be purely a spectator ion.

calculations and by natural bond order analysis (see the Supporting Information).

Herein we have demonstrated that high-pressure crystallography can be used to directly control and monitor the degree of π⋯π interactions as measured by the perpendicular distance between the two ring planes (A) and the centroid–centroid distance between two adjacent phenyl rings (B) in **1**, thus providing a detailed crystallographic profile of their evolution as a function of applied pressure. We have also shown that the application of pressure can sweep distance B across the range of significance (3.3–5.2 Å) for π⋯π interactions within the Cambridge Structural Database (see Figure S4 in the Supporting Information). The changes in the parameters describing the π⋯π interactions occur concomitantly with those describing the unprecedented deformation of one phenyl ring.[24] We are currently investigating related complexes with a view to elucidating and quantifying further the interactions underlying these various processes and distortions.

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[20] The use of a diamond anvil cell for high-pressure structure determination severely limits the fraction of total diffraction data that can be accessed, in this case to 21.5–31.4%. The consequences of this include the need for extensive constraints and restraints during refinement (see the Supporting Information) and for particular care in interpreting the resulting geometric parameters and their precision.

[21] A decrease in unit-cell volume of approximately 25% over a pressure range of about 75 kbar appears to be typical for coordination complexes (see for example entries 14, 22 and 28 in Table S1 of the Supporting Information).

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