

Electronic Supplementary Information

Direct evidence of a polycentre halogen bond: unexpected contraction of the P-XXX-P fragment in triphenylphosphine dihalides

Kirill Nikitin, Helge Müller-Bunz, Declan Gilheany

General methods: All reactions were carried out under a nitrogen atmosphere in Schlenk-type reaction vessels. Dry degassed solvents were stored in Young-type flasks over molecular sieves 4A. NMR spectra were acquired on a Varian VNMRS 400 MHz spectrometer at 30 °C. Assignments were based on standard ^1H - ^1H and ^1H - ^{13}C two-dimensional techniques.

Chlorotriphenylphosphonium chloride (1C). To a solution of triphenylphosphine oxide (0.28 g, 1 mmol) in DCM (2 mL) oxalyl chloride (0.16 mL, 2 mmol) was added *via* a syringe. Upon the evolution of gases the reaction mixture was slowly concentrated under reduced pressure to furnish **1C** ($\text{Ph}_3\text{PCl}_2 \cdot \text{CH}_2\text{Cl}_2$, 415 mg, 98%) as colourless cubic crystals. ^1H NMR (CD_2Cl_2 , 400 MHz, numbering in accord with Figure S1): δ 8.00 (3H, t, $J = 8$ Hz, 4-H), 7.80 (6H, dd, $J = 8$ Hz, $J = 16$ Hz, 2-H), 7.85 (6H, m, $J = 8$ Hz, 3-H); ^{31}P NMR (161 MHz): δ 62.1; ^{13}C NMR (100 MHz): δ 137.2 ($J = 3$ Hz, 4-C), 133.5 ($J = 13$ Hz, 2-C), 130.8 ($J = 14$ Hz, 3-C), 119.2 ($J = 95$ Hz, 1-C). **Crystal data:** cubic, $a = 15.995$ Å, identical to the previously published $[\text{Ph}_3\text{P}-\text{Cl}-\text{C}-\text{Cl}-\text{PPh}_3]\text{Cl} \cdot 2\text{CH}_2\text{Cl}_2$ (Ref. 7a of the main text; CCDC 717813).

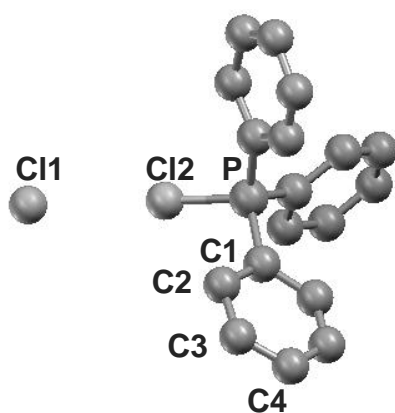


Fig. S1. Atom numbering in the structure of **1C**.

Bromotriphenylphosphonium bromide (2C). To a solution of triphenylphosphine oxide (0.14 g, 0.5 mmol) in DCM (2 mL) oxalyl bromide (0.1 mL, 1.1 mmol) was added *via* a syringe. Upon the evolution of gases was complete the reaction mixture was slowly concentrated under reduced pressure to furnish **2C** ($\text{Ph}_3\text{PBr}_2 \cdot \text{CH}_2\text{Cl}_2$, 490 mg, 97%) as yellow cubic crystals. ^1H NMR (CD_2Cl_2 , 400 MHz, numbering in accord with Figure S1): δ 7.70 (3H, m, 4-H), 7.69 (6H, m, 2-H), 7.43 (6H, m, 3-H); ^{31}P NMR (161 MHz): δ 51.1; ^{13}C NMR (100 MHz): δ 134.8 ($J = 3$ Hz, 4-C), 133.1 ($J = 12$ Hz, 2-C), 129.3 ($J = 13$ Hz, 3-C), 123.6 ($J = 108$ Hz, 1-C). **Crystal data.** molecular formula $[\text{C}_{18}\text{H}_{15}\text{PBr}]^+[\text{Br}]^-\cdot\text{CH}_2\text{Cl}_2$; cubic $a = b = c = 16.1626(2)$, $\alpha = \gamma = \beta = 90^\circ$, $U = 4222.15(9) \text{ \AA}^3$, $T = 100$ K, space group $Pa-3$, $Z = 8$, independent reflections 1127, $R_{\text{int}} = 0.0458$, R indices (all data) $R_1 = 0.0454$, $wR_2 = 0.1294$.

Chlorotriphenylphosphonium bromide (3C). To a DCM solution of **1C** (0.17 g, 0.4 mmol) a solution of **2C** (0.1 g, 0.2 mmol) in DCM was added *via* a syringe. The reaction mixture was slowly concentrated under reduced pressure until precipitation of the product began. Separation of the mother liquor gave **3C** ($\text{Ph}_3\text{PCl}_{1.31}\text{Br}_{0.69} \cdot \text{CH}_2\text{Cl}_2$, 72 mg, 0.16 mmol, 26%) as a pale yellow crystalline material. **Crystal data.** Molecular formula $[\text{C}_{19}\text{H}_{17}\text{PCl}]^+[\text{Cl}]^{-0.31}[\text{Br}]^{-0.69} \cdot \text{CH}_2\text{Cl}_2$; cubic $a = b = c = 15.9738(2)$, $\alpha = \gamma = \beta = 90^\circ$, $U = 4075.91(9) \text{ \AA}^3$, $T = 100$ K, space group $Pa-3$, $Z = 8$, Independent reflections 1773, $R_{\text{int}} = 0.0277$, R indices (all data) $R_1 = 0.0548$, $wR_2 = 0.1180$.

Quantum chemistry calculations were performed using SPARTAN 10.1.0 package on a Dell Precision T5500 workstation. Calculations of molecular geometries in vacuum were done at the HF or DFT B3LYP level using the 6-31G* basis set. Typically, calculations of the equilibrium geometry of $[\text{Ph}_3\text{PXXXPPh}_3]$ in **1C-3C** were carried out starting with the crystallographically determined geometry of this unit in the absence of solvent molecules and individual halide anions.

Structure	Level of theory and basis set	Computation time, h	Full energy, Hartrees
1C	HF 6-31G*	5	-3440.464483
1C	DFT B3LYP 6-31G*	1	-3453.016705
2C	HF 6-31G*	4	-9778.359007
2C	DFT B3LYP 6-31G*	3	-9794.101734
3C	HF 6-31G*	1	-5553.100850
3C	DFT B3LYP 6-31G*	4	-5566.713656

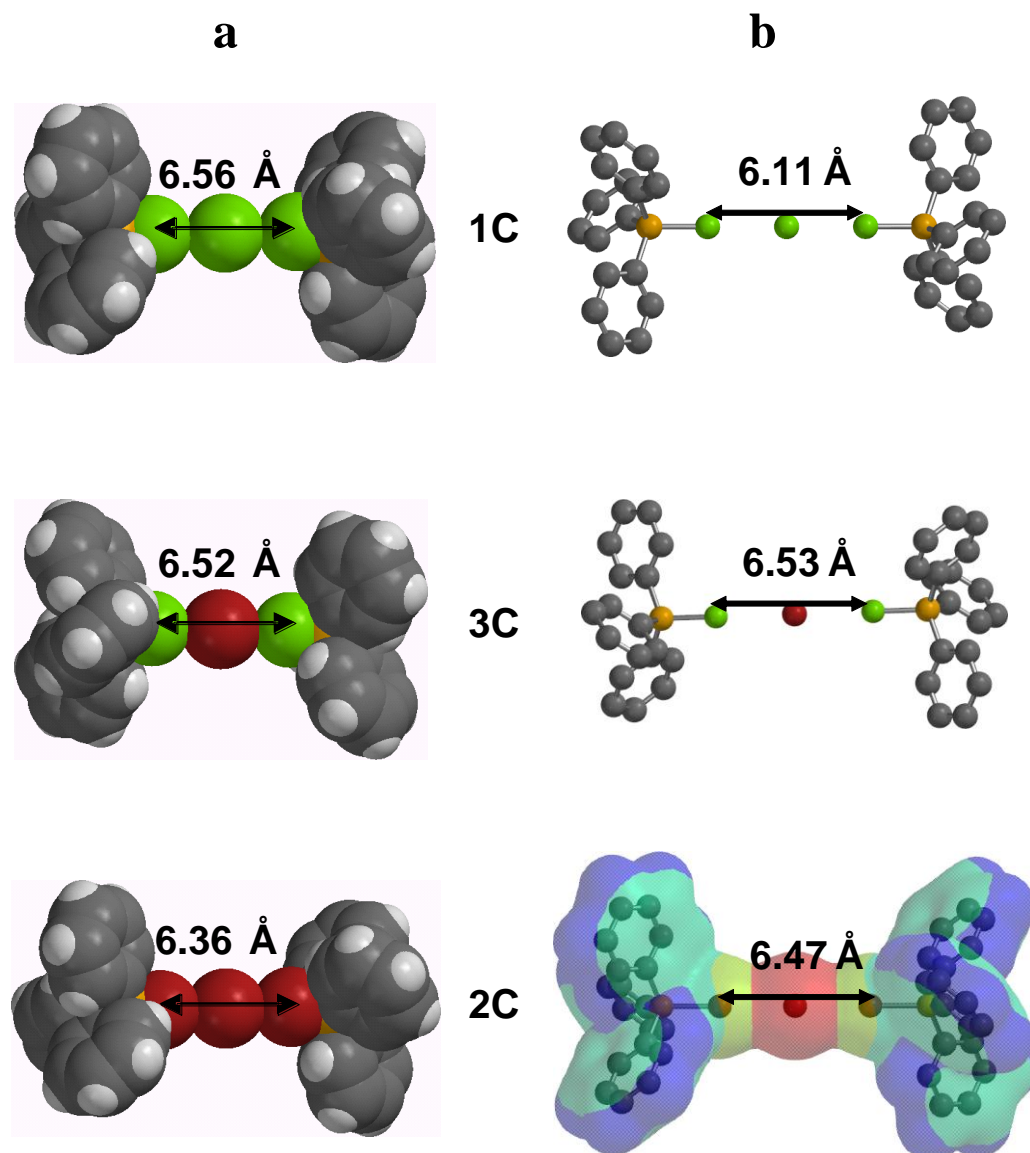


Fig. S2 Comparison of 1C-3C: a) gradual contraction of the XXX bridge in crystal structure; b) calculated geometry in vacuum (electrostatic potential density surface shown for 2C).

X-Ray measurements for 1-3: Crystal data were collected using an Agilent Technologies (former Oxford Diffraction) SuperNova A diffractometer. A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed.^{S1} The structures were solved by direct methods using SHELXS-97^{S2} and refined by full-matrix least-squares on F^2 for all data using SHELXL-97.^{S2} Hydrogen atoms were added at calculated positions and refined using a riding model. Their thermal displacement parameters were fixed to 1.2 times the equivalent one of their parent atoms. Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms. CCDC 887828 (**2C**) and 887829 (**3C**) contain the supplementary X-ray crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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References:

S1 Program CrysAlisPro Version 1.171.34.49, Agilent Technologies, 2011.

S2 G.M. Sheldrick, Acta Cryst. 2008, A64, 112.