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# Phase Transition in Metal-Organic Complex *trans*-$PtCl_2(PEt_3)_2$ under pressure – insights of molecular and crystal structure

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## Supplementary Information

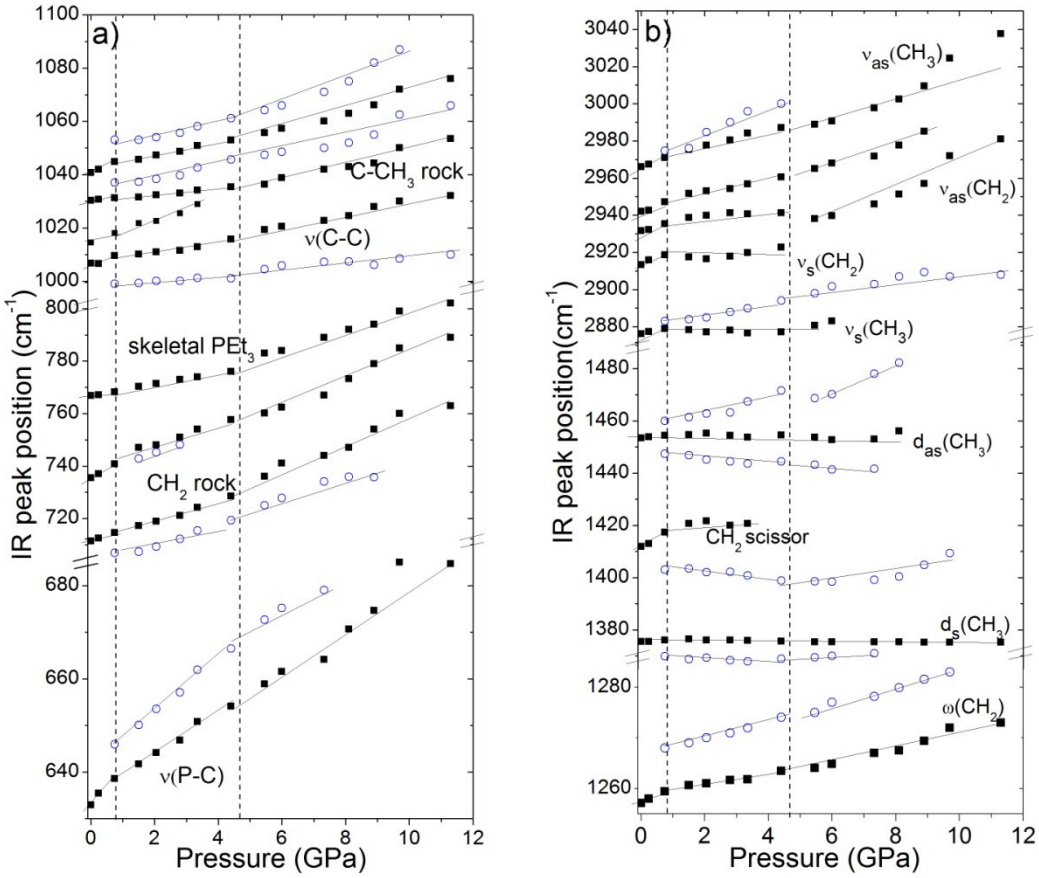


**Figure S1.** (color online) Variation of IR peak positions with pressure in *trans*-$PtCl_2(PEt_3)_2$ in the region **(a)** 630-1100 cm$^{-1}$ and **(b)** 1250-3050 cm$^{-1}$. Blue open circles represent new peaks emerged across 0.8 GPa.

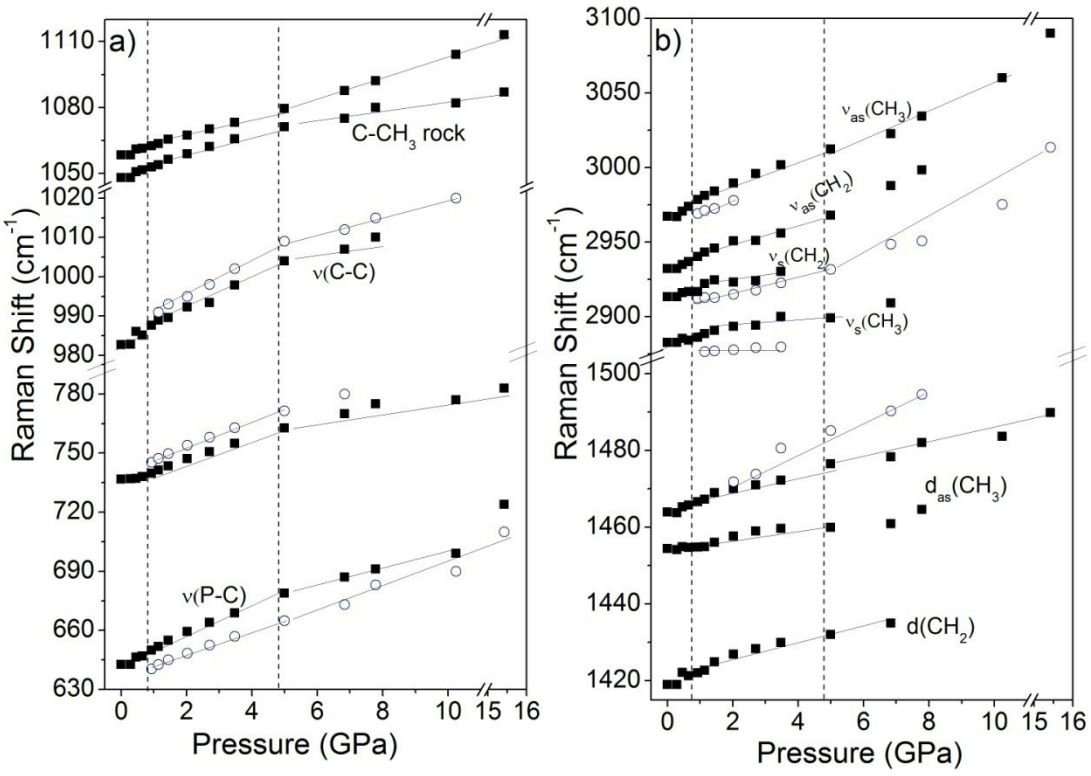


**Figure S2.** (color online) Variation of Raman mode positions with pressure in *trans*-$PtCl_2(PEt_3)_2$ in the spectral range **(a)** 630-1120 $cm^{-1}$ **(b)** 1410-3100 $cm^{-1}$. The new peaks emerged during high pressure are shown with blue empty circles.

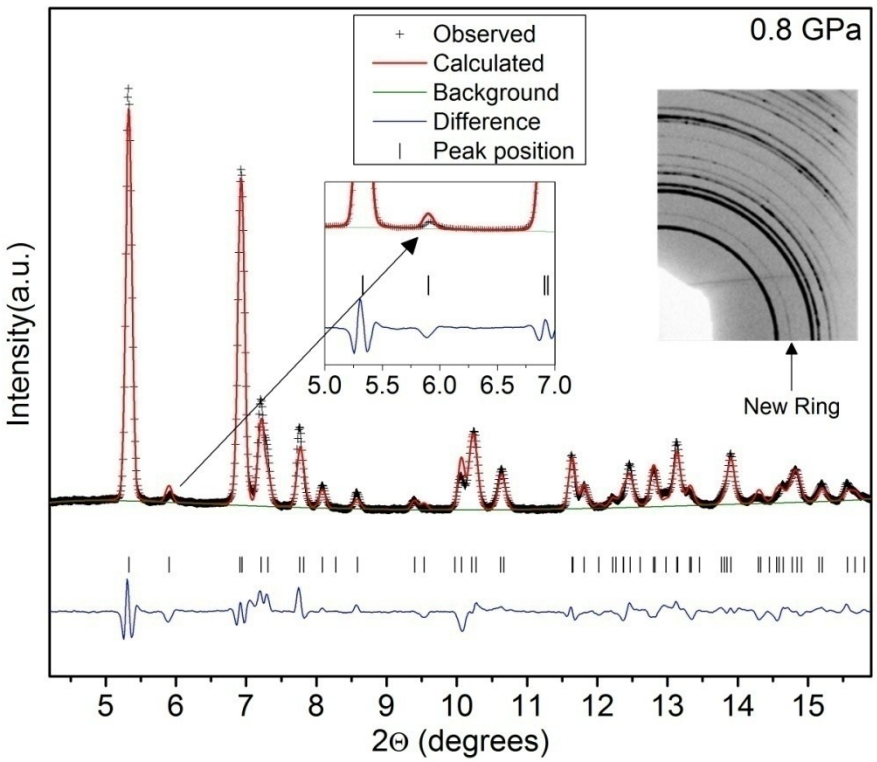


**Figure S3.** Rietveld refinement of *trans*-$PtCl_2(PEt_3)_2$ at 0.8 GPa (Phase 2) pressure using relaxed structure obtained from DFT calculations at this pressure. Inset: (Left) Enlarged view of the Rietveld refinement of XRD pattern in the region of appearance of the new peak in Phase 2, (Right) Typical 2D pattern obtained in the new phase above 0.8 GPa.

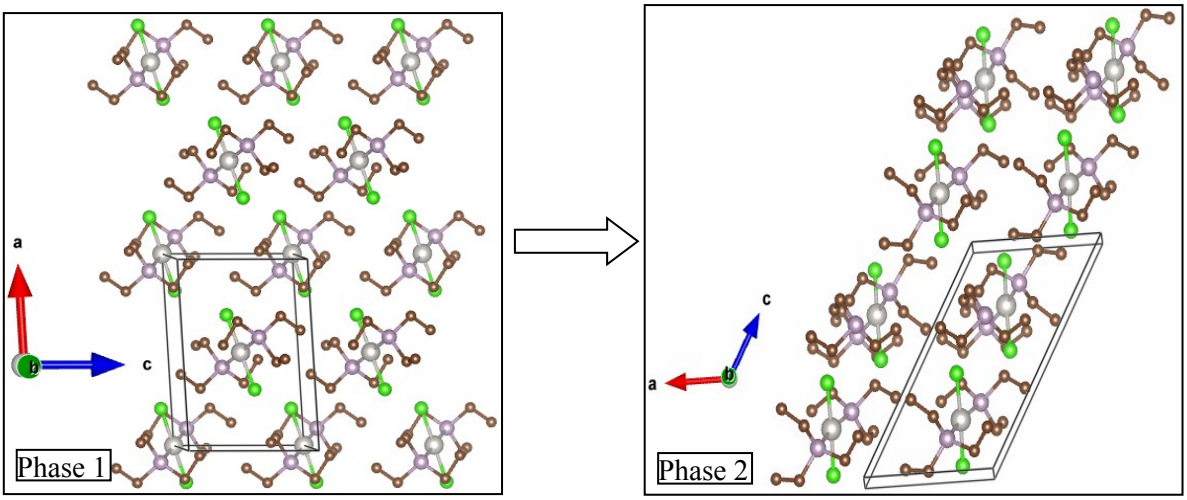


**Figure S4.** Unit cells of Phase 1 (ambient) and Phase 2 (0.8 GPa) in *trans*-$PtCl_2(PEt_3)_2$.

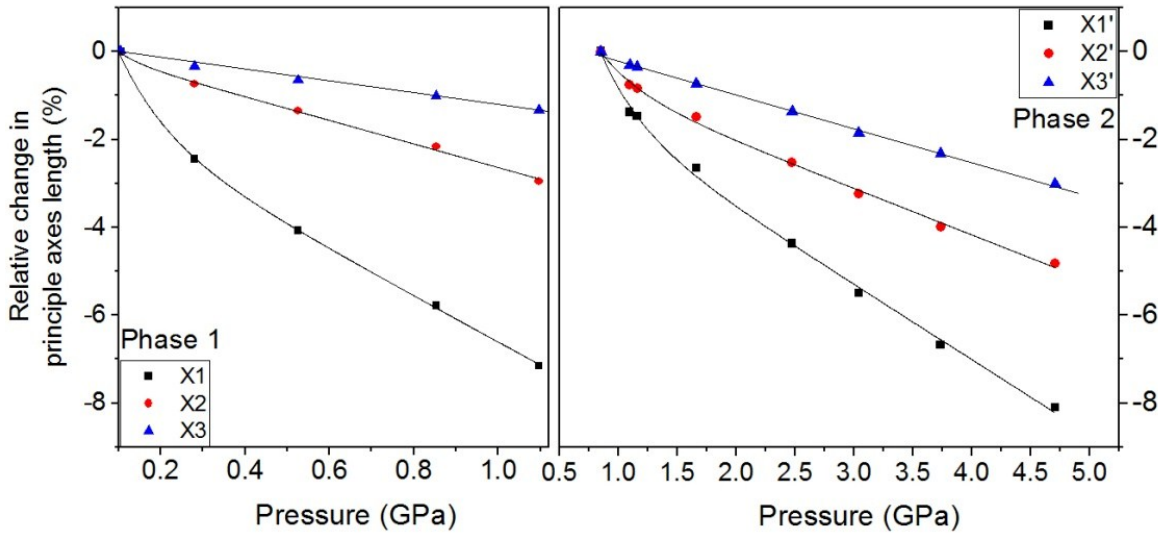


**Figure S5.** Principal axes evolution with pressure in *trans*-$PtCl_2(PEt_3)_2$ as obtained using the software PASCal.[58] The axis X3 coincides with the crystallographic *b*-axis, which shows the least compressibility with pressure.

**Table S1.** Experimental (ambient pressure – reported (column 2) and this study (column 3)) atomic coordinates and lattice parameters of *trans*-$PtCl_2(PEt_3)_2$ [$P2_1/n$ (14) – space group]. The experimentally obtained structure has been submitted to CCDC (1829359) by including H-atoms refined using the riding model. To further improve structure with H-atom positions, DFT-GGA calculated (at ambient pressure) equilibrium atomic positions have also been provided in the last column, obtained by including hydrogen atoms and optimizing single crystal XRD deduced experimental coordinates, the uncertainty in unit cell volume is found to be ~ 5%.

*Note: In this table, axes transformation of the single crystal structure, which has been deposited at CCDC after including H-atoms, have been carried out using PCW software for consistency in lattice parameter convention (*a* and *c*) with the reported values.[13]

| Atom (wyckoff positions) | Experimental positions (from ref. 13) | | | Experimental position (this study) (single crystal X-ray diffraction) (without H atoms) | | | Equilibrium atomic positions optimized using DFT-GGA calculations (this study) | | |
|---|---|---|---|---|---|---|---|---|---|
| Pt (2a) | 0.5000 | 0.5000 | 0.5000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Cl (4e) | 0.6980 | 0.4549 | 0.4604 | 0.7001 | 0.4539 | 0.4593 | 0.7054 | 0.4531 | 0.4666 |
| P (4e) | 0.4295 | 0.3314 | 0.3676 | 0.5705 | 0.6687 | 0.6373 | 0.5703 | 0.6709 | 0.6399 |
| C 1 (4e) | 0.3024 | 0.3623 | 0.1814 | 0.4556 | 0.7547 | 0.7441 | 0.4530 | 0.7596 | 0.7483 |
| C 2 (4e) | 0.3581 | 0.4299 | 0.0675 | 0.4970 | 0.8763 | 0.8120 | 0.4926 | 0.8819 | 0.8047 |
| C 3 (4e) | 0.3848 | 0.2393 | 0.6155 | 0.8578 | 0.2628 | 0.0251 | 0.8607 | 0.2656 | 0.0323 |
| C 4 (4e) | 0.4460 | 0.1930 | 0.5425 | 0.3054 | 0.3508 | 0.1870 | 0.3055 | 0.3479 | 0.1792 |
| C 5 (4e) | 0.5391 | 0.2797 | 0.2040 | 0.5424 | 0.8050 | 0.3250 | 0.5459 | 0.8087 | 0.3168 |
| C 6 (4e) | 0.5076 | 0.1158 | 0.1829 | 0.3330 | 0.4338 | 0.0460 | 0.3351 | 0.4350 | 0.0268 |
| H 1 (4e) | | | | | | | 0.4174 | 0.9267 | 0.8730 |
| H 2 (4e) | | | | | | | 0.5740 | 0.8828 | 0.9019 |
| H 3 (4e) | | | | | | | 0.5154 | 0.9339 | 0.6820 |
| H 4 (4e) | | | | | | | 0.3727 | 0.7605 | 0.6482 |
| H 5 (4e) | | | | | | | 0.4230 | 0.7096 | 0.8695 |
| H 6 (4e) | | | | | | | 0.2823 | 0.2618 | 0.1202 |
| H 7 (4e) | | | | | | | 0.2256 | 0.3773 | 0.2555 |
| H 8 (4e) | | | | | | | 0.3527 | 0.5211 | 0.0881 |
| H 9 (4e) | | | | | | | 0.4167 | 0.4102 | 0.9508 |
| H 10(4e) | | | | | | | 0.2585 | 0.4430 | 0.9211 |
| H 11(4e) | | | | | | | 0.4752 | 0.8639 | 0.3765 |
| H 12(4e) | | | | | | | 0.5922 | 0.8600 | 0.2117 |
| H 13(4e) | | | | | | | 0.4979 | 0.7358 | 0.2457 |
| H 14(4e) | | | | | | | 0.8143 | 0.3384 | 0.9581 |
| H 15(4e) | | | | | | | 0.7887 | 0.2132 | 0.0950 |
| Lattice parameters | | | | | | | | | |
| *a* (Å) | 11.00±0.02 | | | 10.9937(7)* | | | 10.861 | | |
| *b* (Å) | 11.52±0.02 | | | 11.5227(10) | | | 11.541 | | |
| *c* (Å) | 7.49±0.01 | | | 7.4499(5)* | | | 7.134 | | |
| *β* (°) | 93°0'±15' | | | 93.302(6) | | | 92.796 | | |
| Volume (Å$^3$) | 947.832 | | | 942.17(12) | | | 893.158 | | |

**Table S2.** Variation of dihedral angles of the ethyl group attached to phosphorous atoms on the two symmetrically opposite sides of Pt atom in *trans*-$PtCl_2(PEt_3)_2$ molecule with pressure.

| Dihedral Angles of ethyl groups (°) | Ambient pressure | | 0.8 GPa | |
|---|---|---|---|---|
| | One side | Other side | One side | Other side |
| Pt-P-C1-C4 | 52.67° | 52.67° | 62.42° | 56.23° |
| Pt-P-C2-C5 | 63.81° | 63.81° | 62.89° | 81.90° |
| Pt-P-C3-C6 | 170.95° | 170.95° | 160.59° | 57.64° |

**Table S3.** Projection of the three Principal axes (X1, X2, X3) on crystallographic axes (*a, b, c*) in *trans*-$PtCl_2(PEt_3)_2$ derived using PASCal software[58] with critical point at 0.85 GPa.

| Principal axes (Xn) | Compressibility K($TPa^{-1}$) | Error in Compressibility σK($TPa^{-1}$) | Projection of Xn on the unit cell axes | | |
|---|---|---|---|---|---|
| | | | *a* | *b* | *c* |
| Phase 1 | | | | | |
| X1 | 48.8612 | 4.8884 | -0.1425 | -0.0000 | 0.9898 |
| X2 | 25.9522 | 2.4928 | 0.9298 | 0.0000 | 0.3681 |
| X3 | 11.4934 | 1.0713 | 0.0000 | -1.0000 | 0.0000 |
| Phase 2 | | | | | |
| X1 | 17.3035 | 0.4974 | 0.9919 | -0.0000 | 0.1268 |
| X2 | 10.6181 | 0.3504 | -0.5115 | 0.0000 | -0.8593 |
| X3 | 7.3500 | 0.1454 | 0.0000 | -1.0000 | 0.0000 |

**Table S4.** Variation of Lattice parameters in Phase 1 and Phase 2.

| Phase 1 | | | | | |
|---|---|---|---|---|---|
| Pressure (GPa) | *a*(Å) | *b*(Å) | *c*(Å) | *β*(°) | Volume (Å$^3$) |
| ambient | 11.0048(15) | 11.5167(11) | 7.4802(7) | 93.483(9) | 946.3(2) |
| 0.15 | 11.0025(13) | 11.5156(10) | 7.4790(6) | 93.494(8) | 945.84(10) |
| 0.28 | 10.9073(15) | 11.4779(12) | 7.3063(7) | 92.988(10) | 913.46(11) |
| 0.52 | 10.8370(17) | 11.4422(14) | 7.1895(8) | 92.775(12) | 890.46(12) |
| 0.56 | 10.819(3) | 11.427(2) | 7.1577(11) | 92.749(16) | 883.86(19) |
| Phase 2 | | | | | |
| 0.8 | 7.067(5) | 11.4004(10) | 12.585(12) | 121.476(12) | 864.8(3) |
| 1.09 | 6.971(5) | 11.3649(12) | 12.476(15) | 121.379(15) | 843.78(10) |
| 1.16 | 6.965(6) | 11.3599(15) | 12.467(18) | 121.375(18) | 842.14(12) |
| 1.66 | 6.8843(58) | 11.3174(14) | 12.378(18) | 121.350(18) | 823.60(11) |
| 2.47 | 6.771(6) | 11.2455(14) | 12.247(17) | 121.376(17) | 796.13(11) |
| 3.04 | 6.697(6) | 11.1918(15) | 12.157(18) | 121.372(18) | 777.94(12) |
| 3.73 | 6.620(7) | 11.1392(16) | 12.062(19) | 121.382(19) | 759.29(13) |
| 4.7 | 6.530(12) | 11.062(4) | 11.96(4) | 121.44(4) | 737.2(3) |