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ARTICLE

Conformational chiral polymorphism in *cis*-bis-triphenylphosphine complexes of transition metals

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The structure of *cis*-$[Mo(CO)_4(PPh_3)_2]$ **1** was determined by Cotton et al. in 1982,[1] with the space group P-1. A second polymorph **2** is reported here, with the space group $P2_1/c$. The compounds differ in the relation between the conformational chiral triphenylphosphine groups. In **1** there is a $\pi-\pi$ stacking between adjacent phenyl groups whereas in **2** there are $\sigma-\pi$ interactions instead. Search of the Cambridge Structural Database reveals that this is a relatively frequent occurrence in *cis*-bis-triphenylphosphine complexes and the phenomenon can be analysed by the C(ipso)-P-M-P torsion angles. The majority of compounds fall in the $\pi-\pi$ stacking data area with torsion angles 10-15° and 55-60°, however for octahedral-coordinated metals the optimum is a $\sigma-\pi$ interaction at 40° and 40°. This corresponds well to the values in **2**: 46°, 40° but for **1** we instead find the torsion angles 11° and 18°. There is indeed a small tendency for these values as well in the data, and it appears that for **1** this conformation is stabilised by weak CO…H-C hydrogen bonds. Density Functional Theory (DFT) calculations indicate that **1** is the more stable polymorph by 72 kJ/mol but that the strain of the complexes (the difference between a relaxed molecule in the respective conformation and the structure in the crystal) is larger for **1** than for **2**, further indicating that a special intermolecular interaction is responsible for the stability of this polymorph. In both polymorphs the triphenylphosphines have the same conformational chirality, consistent with single-molecule calculations that predict racemic conformations to be substantially higher in energy for both $\sigma-\pi$ interactions (+17 kJ/mol) and $\pi-\pi$ stacking (+30 kJ/mol).

1. Introduction

Triarylphosphines are ubiquitous in organometallic chemistry. Already in 1948 Reppe used $[NiBr_2(PPh_3)_2]$,[2] and ever since the preparation of Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, in 1965,[3] and the subsequent employment of triphenyl phosphine and its derivatives as ligands to transition metal catalysts in industrial processes, for example hydroformylation,[4] they have been trustworthy work horses for the organometallic and catalysis community.[5]

PPh_3 continues to this day to play an important role in catalysis, examples including use of $[Pd(PPh_3)_4]$ in classical cross-coupling reactions with aryl halides,[6] as well as applications of diphosphine complexes such as $[PdCl_2(PPh_3)_2]$ in carbonylative Sonogashira reactions,[7, 8] and a $[RuCl(phenpy\text{-}OH)(PPh_3)_2]PF_6$ catalyst in the β-alkylation of secondary alcohols with primary alcohols.[9] Looking at other metal-PPh_3 complexes, iron catalysts such as $[Fe(H)(CO)(NO)(PPh_3)_2]$ and $[Fe(CO)Cp(PPh_3)I]$ have been applied in the hydrosilylation of alkynes[10] and acetophenone,[11] respectively, while cobalt complexes like $[Co(H)(N_2)(PPh_3)_3]$ or $[CoH_3(PPh_3)_3]$ can effect CH-activation of aromatic compounds.[12] A recent application of interest involves the dual use of $[Ph_3PAuCl]$ and visible light to achieve the synthesis of biarylic compounds via a Suzuki-type coupling.[13] Triphenylphosphine has also been employed in itself as an organocatalyst in reactions of allenes with electrophiles,[14] as well as in [2+2+2]-annulations to form dihydropyridine structures.[15]

That triarylphosphines are conformationally chiral was realised long ago,[16, 17] and has been subject to detailed studies,[18] but such analysis of bis-triphenylphosphine complexes are scarce. In this communication we report on a new polymorph of *cis*-$[Mo(CO)_4(PPh_3)_2]$ in space group $P2_1/c$ **2** distinct from the earlier reported P-1 polymorph **1** both in terms of phosphine configurations and intermolecular interactions. We have also placed this finding into a broader

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† Electronic Supplementary Information (ESI) available: Figure S1. CCDC 1499384 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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context by analysing diphosphine complexes in the Cambridge Structural Database (CSD) and performing quantum chemical calculations on both crystals and single molecules.

In principle, one could envisage four different ways in which these molecules could vary in their conformations. We could think of either $\sigma-\pi$ interactions or $\pi-\pi$ stacking as potentially being the most favoured intramolecular interaction between the closest phenyl groups of the two triphenylphosphine units. Added to this is the possibility of having either homo ($\Delta\Delta$ or $\Lambda\Lambda$) or heterochiral triphenyl phosphines, giving in total four possible conformers: $\sigma\pi-\Delta\Delta$, $\sigma\pi-\Delta\Lambda$, $\pi\pi-\Delta\Delta$, and $\pi\pi-\Delta\Lambda$. Considering also the possibility of different packings, the potential for polymorphism seems rather large. However, it is quite possible that some of the conformers have too high energies to be accessible, even if a favoured packing can be arranged.

2. Experimental

2.1 Materials and methods

2.1.1 X-ray Crystallography Intensity data were collected on a Bruker Apex II diffractometer with Mo Kα radiation (λ=0.7107Å). Unit cell determinations were carried out both at ambient temperature (294 ± 2 K) as well as low temperature (173 ± 2 K) in order to test whether there were any phase changes during the cooling process; none was evident. The structure of **2** was solved routinely using SHELXS-64 and refined against F^2 with SHELXL-64.[19]

Structure determination details are found in Table 1 and an ORTEP type drawing for the molecular unit is shown in Figure 1.

2.1.2 Searching the Cambridge Crystallographic Database The CSD database 5.38 was used as of February 2017. In all runs the Conquest software (version 1.19) was used with the restrictions that all retrieved structures would have R values <10% and be error and disorder free. No powder structures were included.

2.1.3 Computational details Density functional theory (DFT) simulations were applied using the Crystal14 software developed Dovesi and coworkers.[20] We used the PBESOL0 functional[21] in conjunction with the POB triple-zeta valence + polarization basis set for C, O, P, H elements,[22] and Mo was treated with small-core effective-core pseudopotential of the Hay-Wadt type described by Corà *et al*.[23] The geometries of the single molecules and crystal structures were optimized using default convergence criteria. Optimizations of the crystal structures included relaxing both atomic coordinates and the parameters of the cell. Lattice energy is defined by the difference energy between the crystal and the free molecule, in its relaxed form. Packing energy is calculated by the difference in energy between the crystal and the individual molecule, in the same conformation it has in the crystal. The difference between lattice energy and packing energy is defined as the strain energy which is attributed to the deformation of the molecule within the lattice. The geometries of the single molecules and crystal structures were optimized using default convergence criteria and shrink parameter was set to 2 2. Input files for the calculations and optimized structures can be found online at https://github.com/fxcoudert/citable-data

2.2 Synthesis

2.2.1 Synthesis of 2, *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$] in space group P2$_1$/c To a 250 mL two neck round bottom flask equipped with a stirrer bar was put [Mo(CO)$_3$(1,3,5-trimethylbenzene)] (0.2919 g, 0.9773 mmol) and PPh$_3$ (0.8813g, 3.364 mmol) under a nitrogen atmosphere. THF (in 50 mL) was added and the solution was kept under reflux for 1 hour. The reaction mixture turned from the initial colour of yellow to dark orange. The product was obtained as light yellow crystals after reducing the volume of the solution to ~ 10 mL, then adding 20 mL of petroleum ether (60-80 °C) and collecting the crystals of **2** by suction filtration. Yield: 58%. FT-IR (Nujol, cm^{-1}): ν(C≡O) 2013, 1899, and 1877. ^{1}H NMR (CD$_2$Cl$_2$, 300.13 MHz) δ: 7.26-7.41 (m, 30 H, Ph) ppm. ^{31}P NMR (CD$_2$Cl$_2$, 75.47 MHz); δ = 37.7 ppm. Single crystals of the compound, suitable for X-ray crystallographic analysis, were obtained by slow diffusion of hexane into a solution of **2** in dichloromethane for a period of one week. The crystals were sent to University of Cape Town for X-ray crystallographic analysis.

Table 1 Crystallographic parameters for **1** (Cotton ref. 1.) and **2** (this work)

	1*	**2**
Empirical formula	C40 H30 Mo O4 P2	C40 H30 Mo O4 P2
Molecular mass (g.mol-1)	732.52	732.52
Crystal size (mm)		0.03 x 0.09 x 0.16
Temperature of data collection	298	173(2)
Crystal symmetry	Triclinic	Monoclinic
Empirical formula	C40 H30 Mo O4 P2	C40 H30 Mo O4 P2
Space group	P-1	P2$_1$/c
a (Å)	11.522(1)	9.4289(7)
b (Å)	16.909(3)	38.395(3)
c (Å)	9.633(2)	9.9447(7)
α (°)	98.05(2)	90
β (°)	110.29(1)	107.876(1)
γ (°)	99.95(1)	90
Z	2	4
Volume (Å^3)	1692.73(4)	3426.4(4)
Density$_{calc}$ (g.cm^{-3})	1.437	1.420
2θ range scanned (°)		2.12-27.95
F(000)		1496
No. of reflections collected		57328
No. of unique reflections		8215
No. of reflections with I > 2θ		6229
Goodness of fit, S		1.016
R$_1$ (I > 2σI)	0.043	0.0392
Final wR$_2$ (all data)		0.0857
Min, Max e density / e		-0.470, 0.540

* Cotton et al. ref. 1.

3. Results and discussion

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3.1 Synthesis

Crystals of *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$] in space group P2$_1$/c **2** were obtained when attempting the synthesis of *fac*-[Mo(CO)$_3$(PPh$_3$)$_3$] by the method for preparing *fac*-[Cr(CO)$_3$(PPh$_3$)$_3$] reported by Nicholls and Whiting.[24] Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of hexane into a solution of **2** in dichloromethane for a period of one week. It should be noted that the previously reported crystals **1** of *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$] in space group P-1 were obtained by recrystallizations from chloroform/methanol mixture at 0°C.[1] This underpins the important role of the solvent during crystallisation.

3.2 X-ray crystallography structure analysis

Structure determination details are displayed in Table 1 and an ORTEP type drawing for the molecular unit is shown in Fig. 1.

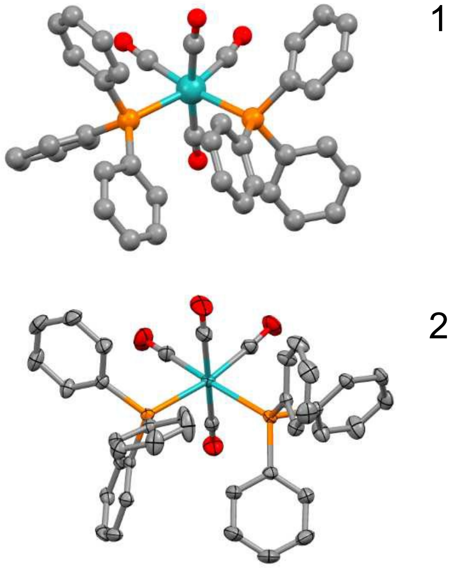

Fig. 1 Drawings of the molecular units of **1** (top, ball-and-stick) and **2** (bottom ORTEP type**)**. Hydrogen atoms omitted for clarity.

On the bonding level **1** and **2** are very similar as the Mo-C and Mo-P bonds are close (Mo-P 2.58 Å vs. 2.58 Å, Mo-C 1.98-2.04 Å vs. 1.97-2.06 Å) but the configuration of the closest phenyl contacts between triphenyl phosphine ligands are distinctively different as shown schematically in Fig, 2, corresponding to the $\pi\pi-$ and $\sigma\pi-$case.

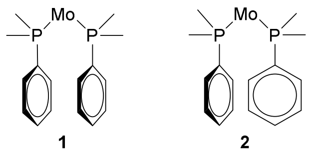

Fig. 2 Schematic difference between the bis-phosphine units in **1** and **2**.

However, this is not a question of the two polymorphs having in one case the same configurational chirality on the phosphine ligands and the other one having opposing chirality. In both cases, as far as that can be quantified, the chirality is the same for the two phosphine ligands, but in neither case the propeller-like chirality is perfect. Thus, what we have are the $\sigma\pi-\Delta\Delta$ and $\pi\pi-\Delta\Delta$ conformers. In fact, judging from physical balls-and-spokes molecular models, it seems difficult to have different chirality on the two PPh$_3$ ligands and turn these to a sensible conformation that does not generate too close contacts. This, however, needs to be quantified and confirmed by quantum chemical calculations.

3.3 Structure calculations

To gain some insight into the factors playing a role in this polymorphism case, DFT calculations were performed, both with periodic boundary conditions on the two crystal systems, single molecule calculations for the chiral conformers in **1** and **2**, and the corresponding hypothetical non-chiral conformers **3** and **4**.

The results in terms of energy are summarised in Table 2. First, we note that the small difference on a single molecule level for **1** and **2** is just about significant, as the two configurations will differ only because of relatively weak interactions between the phenyl rings. Secondly, on a structural level, the two polymorphs are well reproduced by the calculations, see Fig. 3. The four molecular conformers **1**-**4** are displayed in Fig. 4.

Table 2 Energy calculations on the two polymorphs **1** and **2**, and the hypothetical single-molecule non-chiral conformers $\sigma\pi-\Delta\Lambda$ **3,** and $\pi\pi-\Delta\Lambda$ **4**.

	Space group	Conformation	Relative crystal energy (kJ mol^{-1})	Lattice energy^a (kJ mol^{-1})	Packing energy^b (kJ mol^{-1})	Molecular strain in crystal^c (kJ mol^{-1})	Single molecule energy difference (kJ mol^{-1})
1	P-1	$\pi\pi-\Delta\Delta$	0	-245.6	-282.9	37.3	0
2	P 21/c	$\sigma\pi-\Delta\Delta$	72.4	-235.6	-260.6	25.0	7.7
3	na	$\sigma\pi-\Delta\Lambda$					16.7
4	na	$\pi\pi-\Delta\Lambda$					30.3

[a] Lattice energy is the difference in energy between the crystal and the free molecule, in its relaxed form. [b] Packing energy is the difference in energy between the crystal and the individual molecule, in the same conformation it has in the crystal. [c] lattice energy = packing energy + strain energy from the deformation of the molecule to fit into the crystal lattice.

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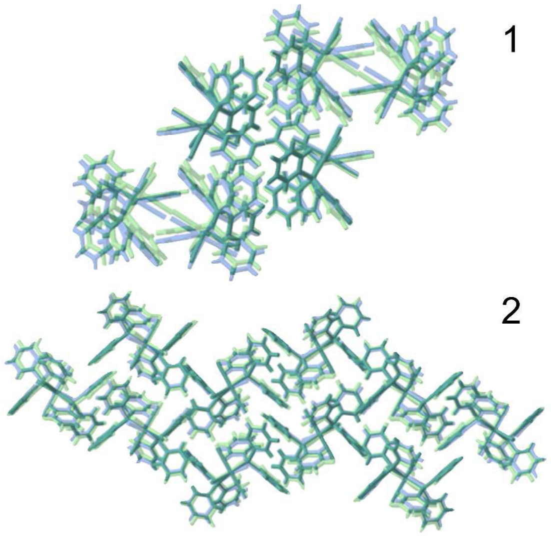

Fig. 3 Comparison of experimental (blue) and optimised structures (green) of **1** (top) and **2** (bottom).

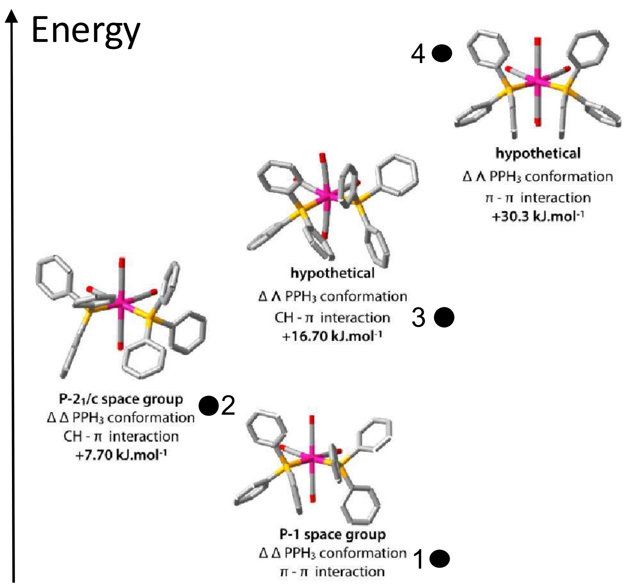

Fig. 4 Optimized structure of the four conformations of *cis*-[Mo(CO)$_4$(PPh$_3$)$_2$]. The two lowest energy conformers correspond to the experimentally observed compounds **1** and **2**.

On a crystal level, **1** is the more stable polymorph, consistent with the higher density (Table 1). There may also be more specific interactions that evoke a more stable polymorph. Hirschfeld surface analysis[25-27] (Figure 5) indicates one fairly strong double CO...H interaction at 2.135 Å, O...C 3.190 Å, CHO 163.8° (calc). and 2.5404 Å, 3.490 Å, 177.7° (exp.). This is short, and the C...O (the best determined distance) very close to the optimum **C**-H...**O**C distance that is 3.48 Å according to an analysis of data in the CSD. However, the optimum angle is 116°, very far from the observed 177.7° (see ESI, Figure S1).

A fingerprint plot also reveals, higher H...H repulsion in **2** (the peaks pointing to the lower left along the diagonal). However, the strain induced in the two conformers going from the free single molecules to the crystal is larger by 12.3 kJmol^{-1} for **1**. This can be quantified also on a structural level as the total difference between the C$_{ipso}$-P-Mo-P torsion angles between the optimised free molecule and the molecule restricted in the crystal is almost double for **1** compared to **2**, see Table 3.

Table 3 Geometric data for the optimised structures **1** and **2**.

Comp.	Space gr.	In crystal		Free molecule		Total abs. diff. free crystal	Ph...Ph in crystal	Ph...Ph free molecule
		φ_1 (°)	φ_2 (°)	φ_1 (°)	φ_2 (°)		β (°)	β(°)
1	P-1	11.1	17.8	na	na		17.0	na
1	P-1 DFT	10.0	17.1	20.1	20.6	13.6	20.7	6.3
2	P 21/c	40.0	46.5	na	na		70.9	na
2	P 21/c DFT	37.6	45.2	39.0	39.6	7.0	63.9	39.0

3.4 Cambridge Structural Database analysis

These two C$_{ipso}$-P-M-P torsion angles (φ -angles) are also what we consider to be the best descriptors for the different conformations of the *cis*-M(PPh$_3$)$_2$-fragment when we searched the CSD to see which of these two conformations was the most common, or if there were indeed other ones to

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consider as well. Torsion angles were selected for all *cis*-bis-triphenylphosphine fragments (P-M-P angles 90-105°), first for all compounds, giving 1428 structures, and then with the restriction that the metal should be 6-coordinated just as the title compound, leaving us with 287 hits. The data are displayed in Figure 6.

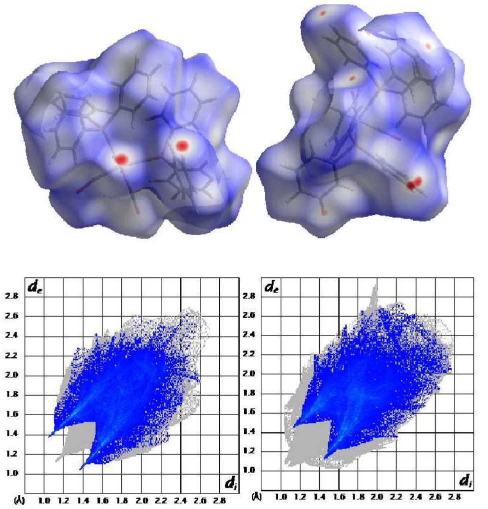

Fig. 5 Top Hirshfeld surface analysis **1** (left) **2** (right), Bottom: Hirshfeld surface analysis fingerprint plots **1** (left) **2** (right), O...H interactions are emphasised. The perspectives are different to show the major interactions for both compounds.

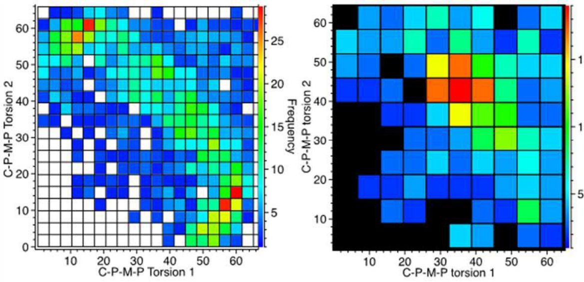

Fig. 6 CSD analysis of the C_{ipso}-P-M-P torsion angles for the *cis*-M(PPh_3)$_2$-fragment. Left all data, right with the restriction that M should be hexa-coordinated.

What emerges from this is that lower coordination numbers, as for cyclopentadienyl complexes for example, there is more space for the PPh_3 to spread around the metal ion and this seems to generate a clear preference for a 15°/60° conformation. With the more crowded octahedral complexes, like **1** and **2**, the most common is instead 40°/40° conformation. For six-coordinated compounds there is also a weak tendency towards 20°, 20°. This, however, does not tell us anything about if the closest phenyl rings make a π-stacking or a σ–π-interaction (Figure 2).

Therefore, we also searched for pairwise C-P-M-P torsion angles less than 65°, as these will correspond to the closest phenyls, and then calculated the angles between the corresponding phenyl planes (β angles). For every angle between planes, there will thus be two torsion angles so two plots are needed to display these data in Figure 7. These data show planar π-stacking for the 15°/60° combination and σ–π-interaction for the 40°/40° conformation. This corresponds well also for the data for both **1** and **2**, as can be seen from the β angles also tabulated in Table 3.

We note that the quantum chemical calculations indicate that the homochiral conformation is preferred. This means that it could be possible to crystallise conglomerates where individual crystals are enantiomerically pure, either ΔΔ or ΛΛ. If this would be the case, these compounds should crystallise in any of the Sohncke space groups (chiral space groups, that is without a centre of inversion). However, the most prominent space groups, accounting for 91% of the structures, are the non-Sohncke groups P-1 (#2) and P 2_1/c (#14), and the most occurring "chiral" space group, P $2_12_12_1$ is found only in 8 (3 %) of the 287 structures.

That both computational energy minima and distinct peaks in the CSD searcher are found means that the compounds fulfil the criteria for conformational polymorphism as discussed by Cruz-Cabeza and Bernstein.[28]

4. Conclusions

Analysis of CSD data indicates a multitude of possible bis triphenyl phosphine configurations and confirms the notion that both σ–π interactions and π–π stacking are possible.

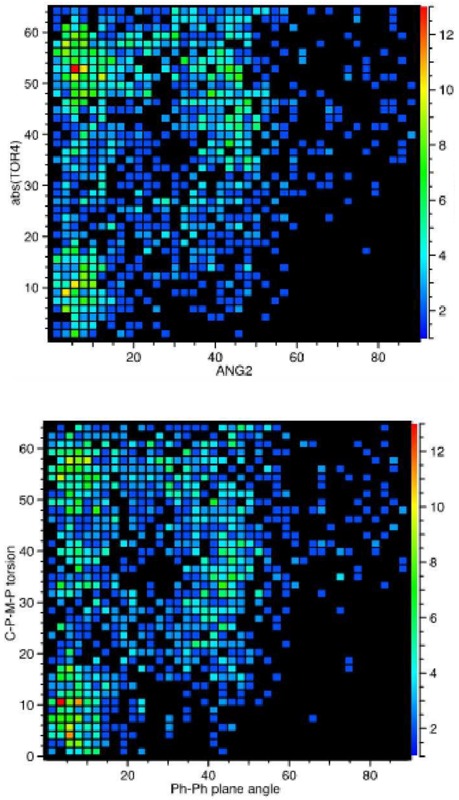

Fig. 7 CSD analysis of the C_{ipso}-P-M-P torsion angles for the *cis*-M(PPh_3)$_2$-fragment compared to the angle between the closest phenyl rings of the different PPh_3 ligands.

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However, quantum chemical calculations show that the heterochiral conformers are substantially higher in energy than the homochiral analogues.

Calculations on the entire crystal indicate, as expected, that the high density phase, **1** is indeed lower in energy than **2**, that has slightly lower density. Hirshfeld surface analysis indicate that a fairly strong double CO...H interaction may be one factor giving **1** the lower energy despite the fact that the conformation of the *cis*-$[Mo(CO)_4(PPh_3)_2]$ molecule in this structure is 12.3 kJ/mol more strained than in **2**.

Conflicts of interest

There are no conflicts to declare.

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Conformational chiral polymorphism in *cis*-bis-triphenylphosphine complexes of transition metals

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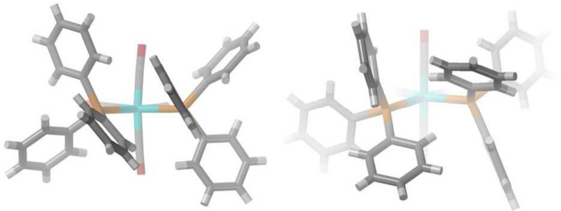

Analysis of conformation polymorphism in *cis*-bis-triphenylphosphine complexes points to the importance of coordination numbers and homochirality of the PPh_3 ligands.