The conformational analysis of phosphine ligands in organometallic complexes. Part 2. Triphenylphosphine coordinated to achiral and prochiral octahedral metal centres[1]

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The novel concept of nadir energy planes has been used to illuminate the principles governing the preferred orientation of rings **A**–**C** in PPh$_3$ **1**, coordinated to achiral octahedral metal complexes of the type [M(PPh$_3$)L$_{1-5}$] **2a**–**d**, and prochiral octahedral metal complexes of the type [M(η^5-C$_5$H$_5$)(PPh$_3$)L$_2$] **3**, and [M(η^6-C$_6$H$_6$)(PPh$_3$)L$_2$] **4**. An achiral arrangement of complex-bound **1** (reminiscent of the transition state for the one-ring flip stereoisomerisation process) orients all three ring apices proximal to three of the four orthogonal nadir energy planes associated with an octahedral metal centre. From this achiral arrangement, the favoured, degenerate conformations of complex-bound **1** may be subsequently derived by applying the following principles (in descending order of priority), (i) *superimpose the vertical ring* **A** *of the achiral conformer onto the least encumbered nadir plane*, (ii) *allow ring* **B** *to tilt onto the least encumbered nadir plane orthogonal to the vertical ring* **A**, and (iii) *tilt ring* **B** *in a manner which orients the flatter ring* **C** *beneath the smallest ligand.* These principles are wholly consistent with 60 X-ray crystal structures, and detailed conformational analyses. The phenomenon of PPh$_3$ ligand tilting, consistent with intramolecular steric strain, is characterised.

Conformational analysis has revolutionised organic chemistry[2] such that it is now routinely used to explain and predict the outcome of stereoselective reactions. Organometallic complexes form a major class of compounds of interest both intrinsically and as reagents and catalysts for organic synthesis.[3] Highly stereoselective reactions of these complexes continue to be discovered, yet relatively little consideration has been given to the influence of conformation on reactivity and selectivity. As ligands, phosphines provide a versatile tool for the control of both the structure and reactivity of transition metal complexes. Triphenylphosphine **1** is a ligand ubiquitous in organometallic chemistry, and a general model for predicting the preferred conformations of this molecule when coordinated to metal centres should provide a valuable contribution to the development of improved reagents and catalysts for organic synthesis.[4] Although structural correlations,[5–8] molecular mechanics calculations[9] and NMR studies[10] have been reported, limited progress has been made towards achieving this goal.

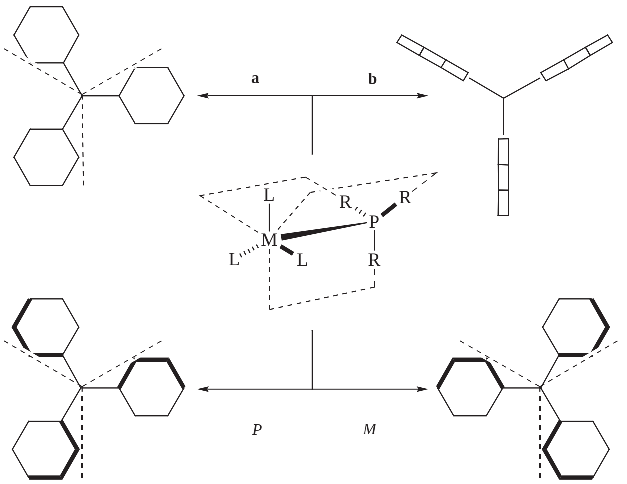


Fig. 1 A sawhorse projection demonstrating the nadir energy planes associated with the ligands L attached to a C_3 symmetric metal centre. Newman projections (as viewed along the M–P bond axis) demonstrating the complementarity between C_3 symmetric nadir planes and the achiral (**a**/**b**) and chiral (*M*/*P*) conformations of **1**.

A sawhorse projection of a generic trialkylphosphine (PR$_3$) coordinated to a C_3 symmetric achiral metal centre is shown in Fig. 1. The potential energy of the complex is primarily a function of the dihedral angle L–M–P–R, the barrier to rotation being occasioned by the fact that eclipsing groups incur the maximum steric compression. A given R group upon the P atom will prefer to be oriented proximal to the region of minimum vicinal steric compression which bisects any two geminal ligands L. Indeed, a continuum of minimum steric compression, delimited by the M–P bond axis, exists at all points within the plane bisecting any two geminal ligands L. We have termed[1] a plane incorporating all points of minimum steric compression the *plane of nadir energy*. In the case of **1** (R = Ph), the atoms associated with a phenyl ring apex (*i.e.* H$_o$/C$_o$) will prefer to be orientated proximal to a nadir plane; the ring apices and not the P–C bonds will be staggered with respect to the M–L bonds. Indeed, the C_3 symmetry of the nadir planes complement the disposition of the ring apices of **1**. Consider the two high energy *achiral* (C_{3v}) conformations of **1**, in which the plane of each phenyl ring may: (**a**) lie approximately orthogonal to,[11a] or (**b**) include[11c] the M and P atoms of the M–P bond (Fig. 1). For conformations (**a**) and (**b**), the ring apices of the phenyl rings may be oriented proximal to the C_3 symmetrically disposed nadir energy planes. The achiral conformations **a** and **b** incur repulsive inter ring–ring (C$_o$/H$_o\cdots$H$_o$), and inter ring–ligand (C$_o$/H$_o\cdots$L) interactions, respectively. Therefore, in order to minimise these interactions, a correlated feathering of the phenyl rings occurs. Each phenyl group twists about the P–C$_i$ bond in the same sense such that the basic framework possesses

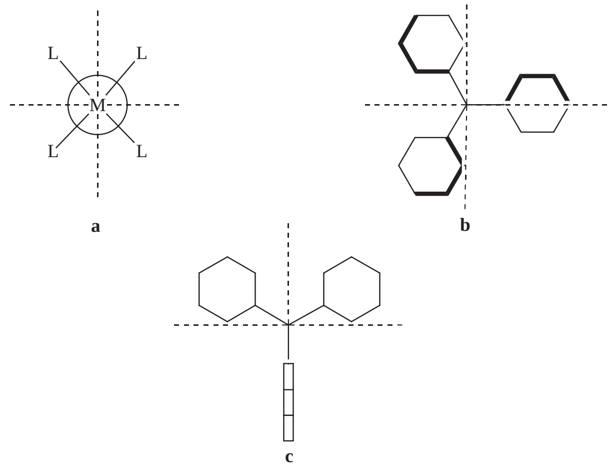
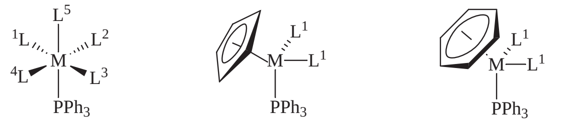


Fig. 2 Coordination of chiral (**b**) and achiral (**c**) conformations of **1** to an octahedral metal complex.



2a ($L^1 = L^2 = L^3 = L^4$)
2b ($L^1 = L^3$; $L^2 = L^4$)
2c ($L^1 = L^4$; $L^2 = L^3$)
2d ($L^1 = L^3 = L^4$)
3
4

Fig. 3 The generic achiral and prochiral octahedral complexes **2**(**a**–**d**)–**4**.

C_3 symmetry. As a result of phenyl ring feathering, the axis coincident upon the M–P bond is thus recognised as being chiral. The chirality in **1** can be described[12] therefore in terms of two enantiomeric configurations, *i.e.*, *clockwise* (*P*) and *anti-clockwise* (*M*), respectively (Fig. 1). Importantly, all three ring apices remain proximal to a nadir energy plane. Therefore, the degenerate correlated conformations *P*-**1** and *M*-**1**, represent a compromise between the two high energy achiral arrangements **a** and **b** (Fig. 1).

In an octahedral complex possessing C_4 symmetry about the metal centre, all four L–M–L interstices, and the associated planes of nadir energy, will be orthogonal and equivalent (Newman projection, Fig. 2a). Consider coordination of the C_3 symmetric conformation of *P*-**1** for example, to a C_4 symmetric metal centre. Fig. 2b depicts the lowest energy arrangement of the C_3 symmetric conformation of *P*-**1**, superimposed upon C_4 symmetrically disposed nadir energy planes. Clearly, this does not represent the optimum possible arrangement as only *one* of the three ring apices lies proximal to a nadir energy plane. By a series of M–P and P–C_i bond rotations, it is possible to orient all three ring apices of **1** proximal to a nadir plane. The resultant achiral arrangement[11b] is depicted in Fig. 2c. Any advantage derived from orienting all three apices proximal to a plane of nadir energy will be off-set by inter ring–ring and ring–ligand interactions. Nevertheless, the achiral arrangement depicted in Fig. 2c is pivotal to understanding the principles which govern the preferred conformations adopted by **1** in achiral and prochiral octahedral metal complexes.

We have previously demonstrated that in organometallic complexes containing **1**, the conformation of the three phenyl rings in the crystal is primarily determined by a balance between inter ring–ring and ring–ligand steric repulsive interactions.[1] Computational studies[13] using van der Waals interaction energy calculations[14] have proven remarkably successful in determining the accessible conformations of **1** in organometallic complexes. For simplicity, achiral (**2a**–**d**, Fig. 3) and prochiral (**3**–**4**, Fig. 3) octahedral metal complexes are considered where the ligands L^{1-4} possess the highest symmetry possible (*e.g.*, CO, NO, halide *etc.*).† Unless stated otherwise, $L^5 = PPh_3$ (Tables 2–4).

Results and discussion ‡

1 Triphenylphosphine coordinated to an achiral octahedral metal centre

1.1 Complexes of type 2a [$L^1 = L^2 = L^3 = L^4$]. In order to illuminate the principles governing the preferred conformations of **1** bound to an octahedral metal centre, C_4 symmetrical octahedral complexes of type **2a**, where $L^1 = L^2 = L^3 = L^4$ (Fig. 3) are considered. Taking the fragment $Re(CO)_4PPh_3$ (CADKAT, Table 1) to be a representative example of **1** bound to such an octahedral complex, calculations were performed upon an idealised (*i.e.* $\angle$L–M–L = 90 and 180°, M–P–C_i = 114° and C_i–P–C_i = 104°) structure derived from CADKAT. The initial investigation was focused upon determining the relative energies of the chiral and achiral arrangements depicted in Fig. 2b and 2c, respectively. The torsion angles ω_{A-C} were adjusted to those of the lowest energy arrangement of C_3 symmetric complex-bound **1** (*i.e.* $\omega_{A-C} = -40°$).[1] The M–P bond was allowed to minimise until the default energy convergence criteria were achieved. For reference purposes, the resultant conformation (Fig. 2b) is designated to be of zero energy. Similarly, the torsion angles ω_{A-C} within the idealised fragment CADKAT were adjusted to those of the achiral arrangement (*i.e.*, $\omega_A = 0°$, $\omega_{B/C} = 90°$).[11b] The M–P bond was allowed to minimise, affording an arrangement (Fig. 2c) which orients the *vertical* ring **A** coincident upon a plane of nadir energy [*i.e.*, L–M–P–C_i (hereon referred to as θC_i) = 45°]. As expected, the achiral conformation of **1** ($E = +74$ kJ mol^{-1}, Fig. 4a) invokes a greater degree of intramolecular strain within an octahedral complex than the corresponding C_3 arrangement ($E = 0$ kJ mol^{-1}).

Attention was now focused upon determining the thermodynamically preferred conformation of **1** within complexes of type **2a**. The minimum energy conformation was determined by driving the torsion angles ω_{A-C} through the range 0→180° (20 increments). At each increment, the van der Waals interaction energy of the structure was allowed to minimise by independent rotations about the M–P and P–C_i bonds. The degenerate minimum energy conformations are depicted pictorially in Fig. 4d. The corresponding values of ω_{A-C} are presented within Table 1. Importantly, the degenerate conformations of **1** (Fig. 4d) possess considerably less intramolecular strain than the achiral (Fig. 4a) and C_3 symmetric arrangements (Fig. 2b). The calculated minimum energy conformation (Table 1) is in excellent agreement with previously reported crystallographic and molecular mechanics studies[15] upon analogous systems. How-

Table 1 Crystallographic data for an octahedral complex of type **2a**

Structure (refcode)	M	L^1	ω/° A	ω/° B	ω/° C	E^a
2a (CADKAT)^b	Re	CO	−25	−51	−70	**−226**
2a (calculated)	Re	CO	−43	−57	−65	**−229**

^{a} Calculated energy in kJ mol^{-1}. ^{b} $L^5 = SnBr_2[Re(CO)_4(PPh_3)]$.

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† This study considers all available data consistent with these criteria.

‡ It is convenient to describe the orientation of the phenyl ring attached to the phosphorus atom in **1** with the torsion angle M–P–C_i–C_o (hereon referred to as ω). The torsion angle ω = 0° when the M–P and C_i–C_o bonds are eclipsed. The correlated *clockwise* or *anti-clockwise* deviation of the torsion ω from 0° determines the helical chirality of the triphenylphosphine rotor. A negative value for ω corresponds to a *clockwise* torsion and therefore *clockwise* (*P*) helical chirality. For correlated systems, values of ω_{A-C} have been normalised to the *P* (−ω) propeller sense (see Tables 1–6).

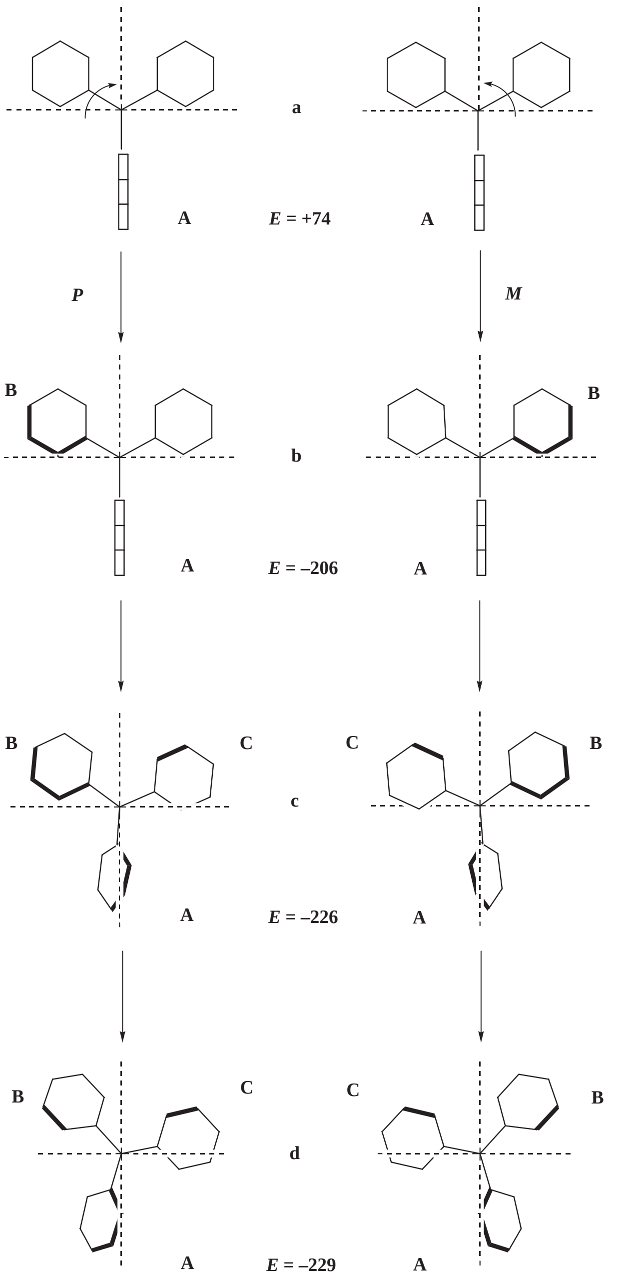

Fig. 4 Predicting the preferred conformation of **1** within octahedral metal complexes of type **2a** ($L^1 = L^2 = L^3 = L^4$) (energy in kJ mol^{-1}, relative to the achiral arrangement, depicted in Fig. 2b).

ever, the observed solid state conformation of the fragment $[Re(CO)_4PPh_3]$, which is characterised by a near vertical ring **A** (depicted pictorially in Fig. 4c) is higher in energy (3 kJ mol^{-1}, Table 1) than the calculated global minimum (Fig. 4d). Indeed, in the crystal, two general types§ of conformation are adopted by **1**, which are characterised by a more (Fig. 4c) or less (Fig. 4d) vertical orientation of ring **A**. Calculations upon the idealised structure infer that the latter arrangement is favoured. This apparent anomaly is considered at the end of section 1.

As previously outlined, the achiral conformation of **1** (Fig. 4a)[11b] may be derived from the chiral arrangement depicted in Fig. 2b by a series of M–P and P–C_i bond rotations. The achiral arrangement is accompanied by sterically demanding inter ring–ring and inter ring–ligand interactions which may be relieved by allowing *one* of the two degenerate flat rings to *tilt*, *via* P–C_i bond rotation (*i.e.*, Fig. 4a→Fig. 4b). It is important to note that the helical configuration of **1** is ultimately determined by the sense in which a given ring *tilts*. In the case of the achiral conformation of the free ligand **1**, a given flat ring may *tilt* in either one of two directions as both processes are degenerate. Thus, an *anti-clockwise* tilt (*i.e.* $-\omega_B$) affords the *P* configuration; conversely, a *clockwise* tilt (*i.e.* $+\omega_B$) affords the *M* configuration. However, for complex-bound **1** (Fig. 4a), the directions in which a given flat ring may *tilt* are no longer degenerate. The sense in which a ring *tilts* (*i.e.* $\pm\omega_B$) may orient the apex of ring **B** either proximal or distal to a plane of nadir energy; the former process is clearly favoured. A simple calculation mimicking the favoured process demonstrates that ring *tilting* relieves a considerable degree of steric strain ($\Delta E_{a-b} = 280$ kJ mol^{-1}, Fig. 4). Further relaxation (*via* M–P and P–C_i bond rotations) of the degenerate ring *tilted* conformers of **1** (Fig. 4b) occurs in order to minimise both inter ring–ligand and inter ring–ring interactions. This process of relaxation ultimately affords a fully correlated system as depicted in Fig. 4c–d. The optimum conformation of **1** may therefore be characterised as: (i) a near *vertical* ring **A**, and a *tilted* ring **B**, where the apices of both lie proximal to orthogonal nadir planes, and (ii) a *flatter* ring **C**, the apex of which lies distal to a nadir plane. The corollary of the previous discussion constitutes a principle which governs the preferred conformations adopted by **1** in octahedral metal complexes *i.e.*, *allow ring* **B** *to tilt onto the nadir plane orthogonal to the vertical ring* **A**.

It should be pointed out that for the achiral arrangement depicted in Fig. 4a, the *vertical* ring **A** may lie upon any one of the four available degenerate planes of nadir energy. For each of these arrangements, there are two degenerate nadir planes orthogonal to ring **A**, onto which ring **B** may *tilt*, thereby affording the arrangements depicted in Fig. 4b. Therefore, within complexes of type **2a**, the ligand **1** may adopt any one of eight (*i.e.* 4 × *M*/*P* pairs) degenerate stereoisomeric conformations.

1.2 Complexes of type 2b ($L^1 = L^3$ and $L^2 = L^4$).

Complexes of type **2b** (*i.e.*, $L^1 = L^3$ and $L^2 = L^4$, Fig. 3) in which identical ligands are *trans* disposed and the size of $L^2 > L^1$ (Newman projection, Fig. 5) are now considered. Although $L^2 \neq L^1$, all four ligand interstices, and therefore all of the corresponding nadir energy planes are degenerate. Therefore, it is immaterial into which interstice we choose to orient the vertical ring **A** of

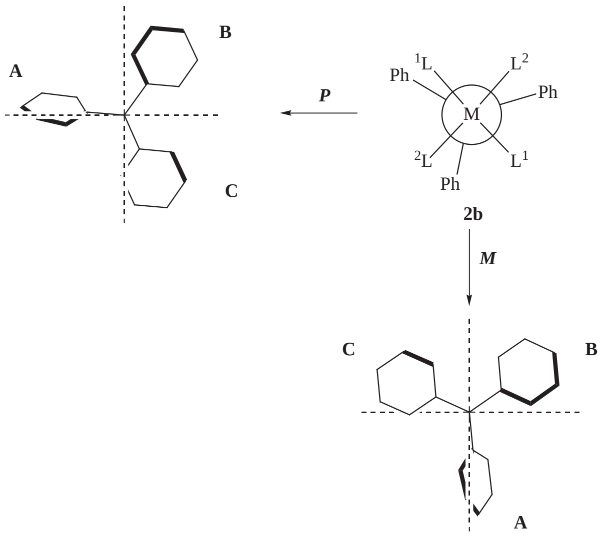

Fig. 5 Predicting the preferred conformation of **1** within octahedral complexes of type **2b** ($L^1 = L^3$ and $L^2 = L^4$, where $L^2 > L^1$).

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§ Refcodes for complexes of type **2a**; as depicted in Fig. 4d (BEKHII, BIFLIL, CMSPMN, DAFNED, HEWYOX, HIGXEA, JEZLEF, LABBIZ, NAVLUR) and Fig. 4c (BOJNOD, CADKAT, DAFMUS, DAFNAZ, DILJOX, PINJOL, PSNMNP10, REXSES, RIBWAA, ZEMGUT).

Table 2 Crystallographic data for octahedral complexes of type **2b**

Structure (refcode)	M	L^1	L^2	ω/°		
				A	B	C
2b (GIHWAV)	Os	CO	Br	2	−59	−65
2b (COPMUP)	Re	$-NCCH_3$	$-CN^tBu$	−17	−49	−80

the achiral conformation[11b] of **1**. However, in contrast to the previous case, the ligand **1** may adopt only four degenerate stereoisomeric conformations within complexes of type **2b**. To illustrate this statement, firstly recall the principle highlighted in the previous section, namely: *allow ring* **B** *to tilt onto the nadir plane orthogonal to the vertical ring* **A**. It is instructive to examine the degeneracy (or otherwise) associated with the process of *tilting* ring **B**.

Consider the manner in which one might derive the *P* configuration of **1** within a complex of type **2b** (Fig. 5). Tilting ring **B** enforces the flatter ring **C** to lie beneath the smaller ligand L^1. Assuming that the position of the vertical ring **A** remains unaltered, the alternative *M* configuration of **1** would enforce the flatter ring **C** to lie beneath the larger ligand L^2. Clearly, inter ring–ligand interactions are minimised by allowing ring **C** to lie beneath the smaller ligand L^1. A similar analysis may be applied to the *M* configuration of **1** (Fig. 5). Thus, for complexes of type **2b**, the *tilting* of ring **B** is a non-degenerate process. Only two X-ray crystal structures of complexes of type **2b** have been reported, and the conformations adopted by **1** are entirely consistent with the above analysis (*i.e.*, ω_{A-C}, Table 2). Using an idealised structure based upon the X-ray crystal structure of GIHWAV, non-degenerate configurations of **1** were calculated to differ in energy by 8 kJ mol^{-1}. Therefore, a second principle governing the preferred conformations of **1** in octahedral metal complexes can be formulated: *tilt ring* **B** *in a manner which orients the flatter ring* **C** *beneath the smallest ligand.*

1.3 Complexes of type 2c (L^1 = L^4 and L^2 = L^3). Next, complexes of type **2c** (*i.e.*, $L^1 = L^4$ and $L^2 = L^3$, Fig. 3) in which identical ligands are *cis* disposed and $L^2 > L^1$ (Newman projection, Fig. 6) are considered. In contrast to complexes of type **2b**, a *cis* arrangement of ligands L^1 and L^2 renders two *trans* disposed interstices equivalent; consequently, one must choose which one of the three unique interstices will accommodate the vertical ring **A** of the achiral conformation of **1**. Given that the size of $L^2 > L^1$, the steric compression exerted by the three resulting, non-identical interstices *decreases* in the order, L^2–M–L^2 > L^2–M–L^1 > L^1–M–L^1. It is reasonable to assume that the apex of a vertical ring **A** will be oriented within the largest interstice thereby minimising inter ring–ligand interactions. Therefore, the vertical ring **A** is oriented proximal to the nadir within the interstice L^1–M–L^1 (Fig. 6).

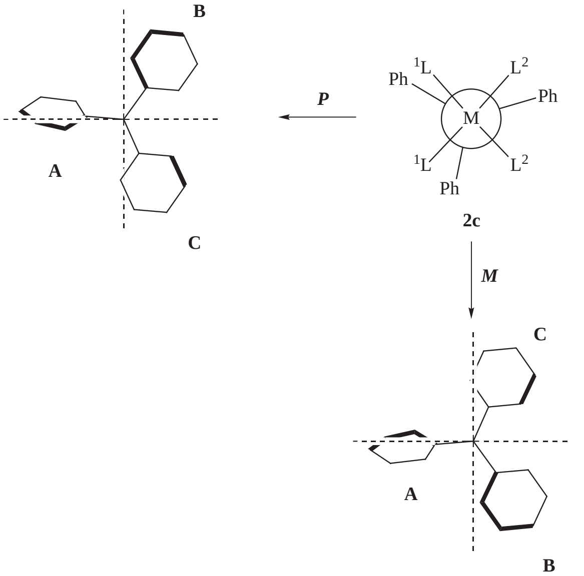


Fig. 6 Predicting the preferred conformation of **1** in octahedral metal complexes of type **2c** (L^1 = L^4 and L^2 = L^3, where L^2 > L^1).

Table 3 Crystallographic data for octahedral complexes of type **2c**

Structure (refcode)	M	L^1	L^2	ω/°		
				A	B	C
2c (HELREV)	Ru	Cl	CO	6	−31	−69
2c (PIGGER)[a]	Ru	CO	$-NCCH_3$	−3	−44	−75

[a] Ru–Ru dimer.

Following the above proposal: *ring* **B** *tilts onto the nadir plane orthogonal to the vertical ring* **A**. As the interstices orthogonal to the vertical ring **A** are identical, *tilting* one or other ring **B** affords degenerate *M* or *P* configurations. Unlike the previous case for complexes of type **2b**, ring **C** is compelled to lie beneath L^2 irrespective of the configuration adopted by **1**. Therefore, within achiral octahedral complexes of type **2c**, the ligand **1** may adopt only two (*i.e.*, *M* and *P*) degenerate stereoisomeric conformations. Several crystal structures[¶] of complexes of type **2c** have been reported, and torsion angles ω_{A-C} for representative examples are presented in Table 3. The solid-state structures are entirely consistent with this analysis. The relative orientation of the $[Ru(CO)_2(NCCH_3)_2PPh_3]$ fragments within the Ru–Ru dimer (PIGGER, Table 3) merit comment, as our analysis assumes that $-NCCH_3$ > CO (*i.e.* $L^2 > L^1$). It is anticipated that the larger $-NCCH_3$ ligands upon one metal fragment will be oriented proximal to the least sterically encumbered nadir planes upon the second metal fragment (*i.e.* OC–Ru–CO and OC–Ru–$NCCH_3$). This is found to be the case. Therefore, a third principle can be proposed which governs the preferred conformations of **1** in octahedral metal complexes: *superimpose the vertical ring* **A** *of the achiral conformer onto the least encumbered nadir.*

1.4 Complexes of type 2d [L^1 = L^3 = L^4]. We now consider complexes of type **2d** which contain three identical ligands (*i.e.*, $L^1 = L^3 = L^4$, Fig. 3) where $L^2 > L^1$ (Newman projection, Fig. 7). The steric compression exerted upon the two unique inter-

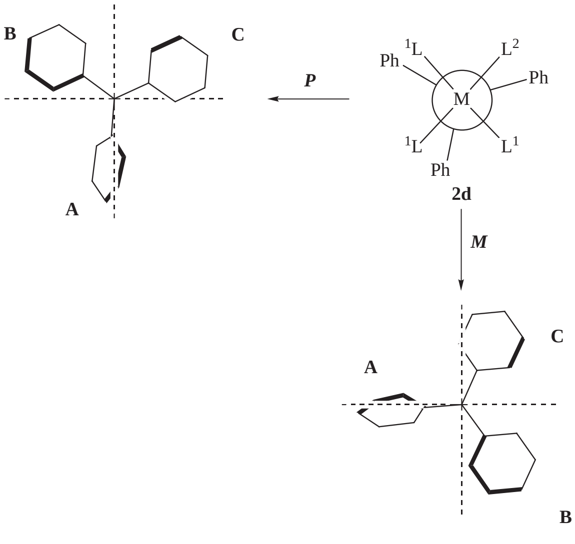


Fig. 7 Predicting the preferred conformation of **1** within octahedral metal complexes of type **2d** (L^1 = L^3 = L^4, where L^2 > L^1).

[¶] Refcodes for complexes of type **2c**: CCNPOS, FEZVIP, FOGROI, HELREV, PIGGER.

Table 4 Crystallographic data for octahedral complexes of type **2d**

Structure (refcode)	M	L^1	L^2	ω/° A	ω/° B	ω/° C
2d (KIPMOL)	Tc	Cl	CO	4	−58	−65
2d (CESNET)	Os	Cl	NS	5	−61	−70
2d (TCNTRU)	Ru	Cl	NO	4	−64	−65
2d* (YASLOT)	Re	CO	Cl	4	−50	−72

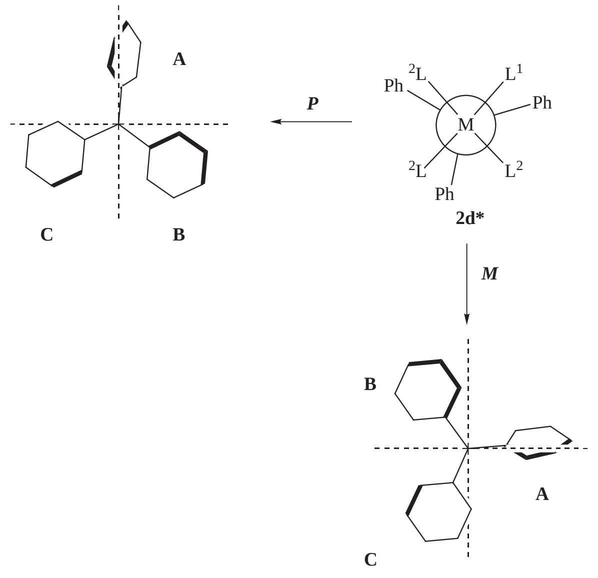


Fig. 8 Predicting the preferred conformation of **1** within octahedral metal complexes of type **2d*** ($L^2 > L^1$).

stices will *decrease* in the order: L^1–M–L^2 > L^1–M–L^1. Now consider the origins of the *P* configuration of **1** within a complex of type **2d**. Firstly, apply the principle associated with ring **A**, *i.e.*, *superimpose the vertical ring of the achiral conformer onto the least encumbered nadir* (*i.e.* L^1–M–L^1, Newman projection Fig. 7). Secondly, apply the principle associated with ring **B**, *i.e.*, *allow one flat ring to tilt onto the nadir plane orthogonal to the vertical ring*. One notes that the nadir planes orthogonal to the vertical ring **A** (*i.e.*, those defined by the interstices L^1–M–L^1 and L^1–M–L^2) are non-degenerate. Thus, *tilting* one or other rings of type **B** will afford non-degenerate configurations. Clearly, ring **B** will prefer to be *tilted* onto the least encumbered nadir (defined by L^1–M–L^1). A similar analysis may be applied to the degenerate *M* configuration of **1** (Newman projection Fig. 7). Several X-ray crystal structures of complexes of type **2d** have been reported,|| and values of ω_{A-C} for selected structures are presented in Table 4. Once again, the solid-state structures are entirely consistent with this analysis. To accommodate the previous discussion, it is necessary to modify the principle associated with ring **B**, *i.e.*, *allow ring* **B** *to tilt onto the least encumbered nadir plane orthogonal to the vertical ring* **A**. In complexes of type **2d**, the principle governing the preferred orientation of ring **C** (*i.e*, *tilt ring* **B** *in a manner which orients the flatter ring* **C** *beneath the smallest ligand*) is violated, as the flatter ring is forced to lie beneath the largest ligand L^2 (Fig. 7). It is reasonable to expect that the magnitude of inter ring–ligand interactions decreases in the order **A** > **B** > **C**. Therefore, the corresponding principles governing the preferred orientations of rings **A**–**C** in **1** will also decrease in the same order.

Finally, consider metal complexes of type **2d***, possessing an identical geometric disposition of ligands as the case above

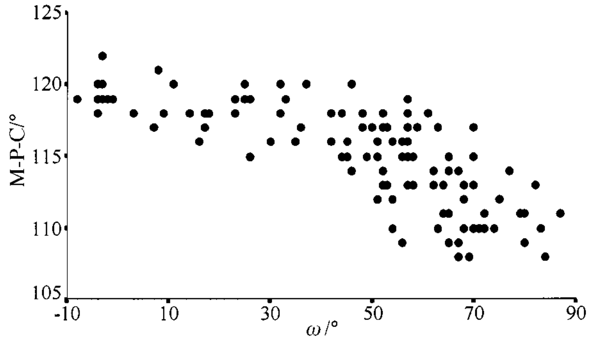


Fig. 9 Scatter-plot of the torsion angle ω/° *vs.* ∠M–P–C_i/° for complexes of type **2a**–**d***.

(Newman projection, Fig. 8). The steric compression exerted upon the two non-degenerate interstices *decreases* in the order: L^2–M–L^2 > L^1–M–L^2. Therefore, if one considers the *P* configuration of **1**, the least encumbered nadir plane orthogonal to the vertical ring is that defined by the interstice L^1–M–L^2. Clearly, ring **B** will prefer to be *tilted* onto this nadir. The corresponding degenerate *M* configuration of **1** may be derived using a similar argument. Only three X-ray structures corresponding to complexes of type **2d*** have been reported,** and values of ω_{A-C} for one of these are presented in Table 4. Again, the solid-state structures are consistent with this analysis. It is noteworthy that within complexes of type **2d**/**2d***, the ligand **1** may adopt only two (*i.e.*, *M* and *P*) degenerate stereoisomeric conformations.

The relationship between the torsion angle ω, and the bond angle M–P–C_i for the **A**–**C** rings in complexes of type **2a**–**d*** is presented in Fig. 9. Clearly, as the torsion angle ω increases, the angle M–P–C_i decreases. This observation is consistent with the ligand **1** tilting in response to the repulsive inter ring–ligand interactions accompanying the vertical orientation of ring **A**. The phenomenon of phosphine tilting has been noted previously, both in the solid state,[16] and in the course of molecular mechanics studies.[17] Consequently, we consider phosphine tilting to be a manifestation of the relative flexibility of metal–ligand bond lengths and angles towards intramolecular steric compression.

In conclusion, three principles are proposed which govern the preferred orientations of rings **A**–**C** in **1** namely, and in descending order of priority (i) *superimpose the vertical ring* **A** *of the achiral conformer onto the least encumbered nadir*, (ii) *allow ring* **B** *to tilt onto the least encumbered nadir plane orthogonal to the vertical ring* **A**, and (iii) *tilt ring* **B** *in a manner which orients the flatter ring* **C** *beneath the smallest ligand.*

2 Triphenylphosphine coordinated to a prochiral octahedral metal centre possessing an unsaturated cyclic π-ligand

Applying the principles governing the preferred orientation of rings **A**–**C** *in* **1**: The principles developed in the previous section can be used to predict the preferred orientation of rings **A**–**C** in **1** attached to prochiral octahedral complexes containing unsaturated cyclic π-ligands. The geometry of metal complexes of the form (η^5-C_5H_5)ML_3 and (η^6-C_6H_6)ML_3 is appropriately described as pseudo-octahedral.[18] All three ligands L are essentially orthogonal to each other, and occupy the adjacent coordination sites of an octahedron. The π-ligand occupies the three remaining coordination sites. Newman projections (viewed along the M–P bond) of prochiral complexes of the type (η^5-C_5H_5)M(L^1)$_2$$PPh_3$ **3** and (η^6-C_6H_6)M(L^1)$_2$$PPh_3$ **4** are presented in Fig. 10. The η^5-C_5H_5 and η^6-C_6H_6 ligands are formally considered to be terdentate, and are thus regarded as being small with respect to three monodentate ligands.[19] It is reasonable to suggest therefore, that within the *square plane*

|| Refcodes for complexes of type **2d**: ANREPS01, CAFREG, CESNET, CNPHOS, COKHOZ, COZZOG, HAGMUX, KIPMOL, KOVSUJ, JECZUM, TCNTRU, TCTPOS, TIZJER.

** Refcodes for complexes of type **2d***: CMNPHP, JOWKIP, YASLOT.

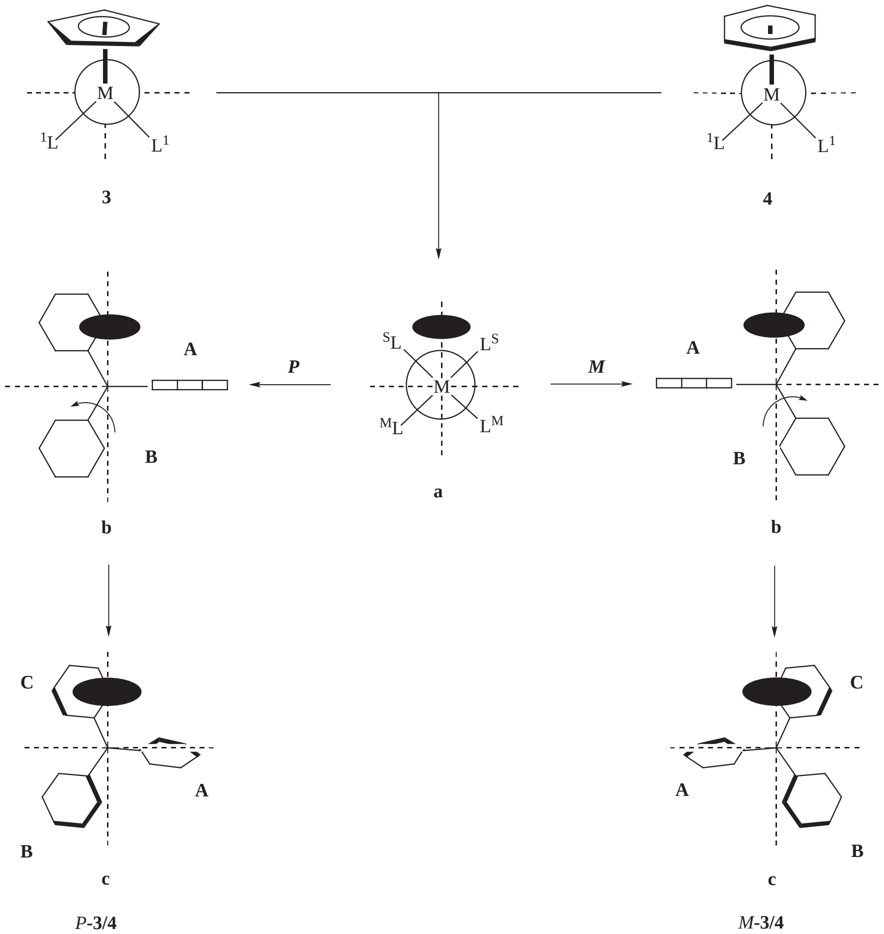


Fig. 10 Predicting the preferred conformation of **1** within pseudo-octahedral metal complexes of type **3** and **4**.

(defined by the metal atom M, and the ligands L^1), the L^1 ligands (which formally occupy a single coordination site) may be regarded as being large with respect to the π-ligands (which only partially occupy single coordination sites). Consequently, within the square plane, we have assigned the η^5-C_5H_5 and η^6-C_6H_6 ligands (represented by a shaded oval) to be small (L^S) with respect to the L^1 ligands (L^M) (Newman projection, Fig. 10a). Consistent with our previous analyses of octahedral complexes, orthogonal nadir energy planes have been superimposed upon this Newman projection.

To predict the preferred orientations of rings **A**–**C** in **1**, the principle of highest priority associated with ring **A** namely, (i) *superimpose the vertical ring* **A** *of the achiral conformer onto the least encumbered nadir,* is applied. Complexes of the type **3** and **4** possess two unique nadir planes defined by L^1–M–L^1 (*i.e.* L^M/L^M), and L^1–M–π-ligand (*i.e.* L^M/L^S); the latter being least encumbered (Fig. 10b). A simple calculation confirms that the degenerate interstices exert the least steric pressure. The phenylphosphine complexes (η^5-C_5H_5)Fe(CO)$_2$PH$_2$Ph and (η^6-C_6H_6)Ru(CO)$_2$PH$_2$Ph were derived from X-ray data of appropriate triphenylphosphine analogues (ZEGJOK and MBZCRP, respectively). The torsion angle ω was adjusted to 0°, and the vertical phenyl ring was placed (*via* M–P bond rotation) within the interstices defined by the ligands, (a) CO/CO (*i.e.* L^M/L^M), and (b) CO/π-ligand (*i.e.* L^M/L^S). The M–P and M–[η-C_{5-6}-(cent.)] bonds were allowed to minimise until the default energy convergence criteria were achieved. In the case of (a), the lowest energy arrangement ($E = 0$ kJ mol^{-1}) placed the vertical ring equidistant from adjacent CO ligands ($\theta C_i = 45°$, coincident upon the nadir energy plane). In the case of (b) however, the lowest energy arrangement ($E \ll 0$ kJ mol^{-1}) placed the vertical ring 12° away from the idealised nadir plane, towards the π-ligand. The relative energies of (a) and (b) demonstrate that degenerate CO/π-ligand interstices exert the least steric pressure; the observed displacement of the nadir plane towards the smaller π-ligand being consistent with this assertion. However, for the purposes of developing a predictive model, all planes of nadir energy are considered to be orthogonal, differing only in the degree of steric pressure exerted upon them by flanking ligands.

Finally, recall the principle of second priority associated with ring **B** (*i.e.*, *tilt onto the least encumbered nadir plane orthogonal to the vertical ring* **A**). Inspection of Fig. 10b reveals that one of the nadir planes orthogonal to the vertical ring **A** is actually blocked by the π-ligand, thereby rendering it unavailable for occupation by a ring apex. Clearly, ring **B** must *tilt* onto the alternative nadir plane flanked by the ligands L^M/L^M. In doing so, one derives the preferred degenerate conformations *M*-**3/4** and *P*-**3/4** (Fig. 10c). Finally, it should be noted that the principle associated with ring **C** (*i.e.*, *tilt ring* **B** *in a manner which orients the flatter ring* **C** *beneath the smallest ligand*) is valid.

2.1 Complexes of type 3, possessing η^5-C_5H_5 as ligand.

Next, attention turns to investigating the thermodynamically preferred conformation of **1** within complexes of type **3**. We consider [(η^5-C_5H_5)Fe(CO)$_2$PPh$_3$]$^+$ (ZEGJOK, Table 5) to be a representative example of **1** bound to a complex of type **3**. All calculations were performed upon the idealised structure using averaged bond lengths. The torsion angles ω_{A-C} were driven through the range $0 \rightarrow -180°$ (20 increments) with concomitant minimisation of all rotatable bonds at each increment. The calculated values of ω_{A-C} associated with the minimum energy conformation are presented in Table 5. Except for ω_A (*vide infra*), the torsion angles for the calculated and solid-state structures are in close agreement. Importantly, the orientations adopted by rings **A**–**C** in the calculation and solid-state are entirely consistent with the principles delineated at the beginning of this section.

Table 5 Crystallographic data for all pseudo-octahedral complexes of type **3**

Structure (refcode)	M	L^1	ω/° A	ω/° B	ω/° C
3 (ZEGJOK)	Fe^+	CO	−33	−49	−55
3 (calculation)	Fe	CO	−22	−44	−60
3 (TITYOK)	Fe^+	CO	−46	−49	−56
3 (PFECYP)	Fe^+	CO	−18	−75	−53
3 (CPCPMN)	Mn	CO	−23	−59	−51
3 (FAKYEV)	Cr	CO	−28	−55	−47

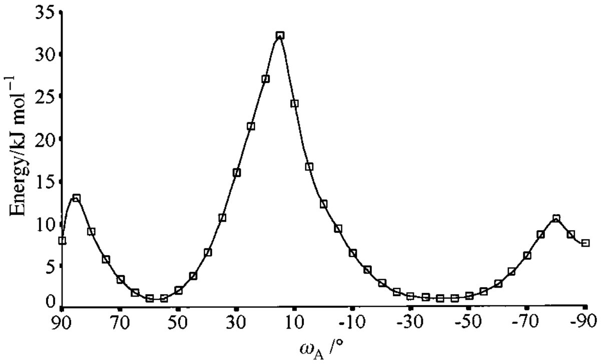
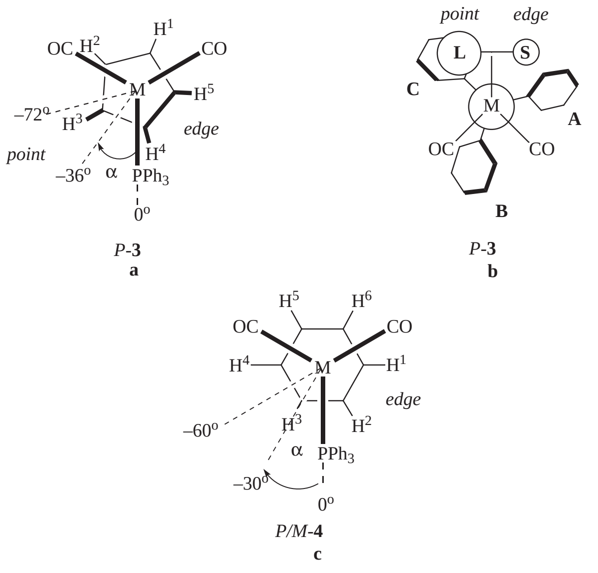


Fig. 11 The conformational energy associated with complexes of type **3** (M = Fe^+) as ω_A is driven through 90→0° and 0→−90° (equivalent to rings **C** and **A**, respectively).

It is enlightening to consider the full conformational profile of rings **A** and **C** in **1**. This may be achieved by driving the torsion angle ω_A through the range 0→−180° (5° increments); the torsion angles $\omega_{B\text{–}C}$ were driven (0→−180°, 18 increments) with concomitant minimisation about all rotatable bonds (except ω_A) at each incremental step of ω_A. The calculated change in intramolecular energy associated with driving the torsion angle ω_A is presented in Fig. 11. In the range of torsion angles +90→0°, and 0→−90°, ω corresponds to ring **C** in *M*-**3** and ring **A** in *P*-**3**, respectively (Fig. 10c). As expected, two minima were identified, corresponding to the lowest energy arrangements of rings **C** ($\omega_C \approx +65 \rightarrow +55°$) and **A** ($\omega_A \approx -20 \rightarrow -55°$) in the degenerate conformations *M*-**3** and *P*-**3**, respectively. The broad energy minimum which corresponds to ring **A** indicates that a wide range of values for the torsion angle ω_A are energetically tolerable. This is consistent with our previous assertion that the more vertical ring **A** is accommodated within the least sterically encumbered interstice. In addition, the broad energy minimum is consistent with the equally wide range of values of the torsion angle ω_A observed in the crystal (*i.e.* $\omega_A = -18 \rightarrow -46°$, Table 5). The narrow energy minimum for ring **C** (*i.e.* $\omega_C = +60 \rightarrow +55°$, Fig. 11) is equally consistent with the corresponding narrow range of torsion angles observed in the crystal (*i.e.* $\omega_C = -47 \rightarrow -56°$, Table 5). The magnitude of the torsion angle ω_B in the crystal (*ca.* −45→−60°, Table 5) is similar to that observed for analogous systems in which ring **B** is flanked by CO ligands (*i.e.* **2a/c**, Tables 1/3); the exception being the structure PFECYP ($\omega_B = -75°$). For complexes of type **3**, the angle Fe–P–C_i = 114 ± 1°, except for PFECYP where the corresponding angles for rings **A/B** = 119 and 111°, respectively. Clearly, tilting of **1** occurs in response to the steric pressure accompanying the vertical orientation of ring **A** ($\omega_A = -18°$). A flatter orientation of ring **B** is therefore tolerated as a near vertical ring **A** alleviates inter ring **B** interactions.



P-**3**
a

P-**3**
b

P/M-**4**
c

Fig. 12 The manner in which the η^5-C_5H_5 ligand relaxes in order to accommodate the vertical ring of **1** in complexes of type *P*-**3**, viewed along the (a) M–C_5(cent.), (b) M–P bond and (c) M–C_6(cent.) axes.

For simplicity, the steric presence of the η^5-C_5H_5 ligand within the square plane is regarded as homogeneous (*i.e.* L^M, Fig. 10). This is an acceptable assumption to make when applying the principles governing the preferred conformations of rings **A**–**C** in **1**. A Newman projection of *P*-**3** [viewed along the M–C_5(cent.) axis] is presented in Fig. 12a. It is convenient to describe the orientation of the η^5-C_5H_5 ligand *via* the torsion angle H^3–C_5(cent.)–M–P (hereon referred to as *a*). When *a* = −36 or −72°, **3** possesses a local plane of symmetry which includes the atoms M, P, and the C_5 centroid. However, for all intermediate values of the torsion angle *a*, the local symmetry of **3** is broken insofar as the H^3 atom of the η^5-C_5H_5 ligand constitutes a *point*, and the H^4/H^5 atoms constitute an *edge*. Clearly, a *point* presents a greater steric infringement upon the adjacent interstice than an *edge*. A pictorial representation of the steric heterogeneity presented by the η^5-C_5H_5 ligand within the square plane is presented in Fig. 12b. Consistent with all computational and crystallographic studies (Table 5) upon complexes of type **3**, the η^5-C_5H_5 ligand presents the small *edge* (S) towards the interstice which accommodates the vertical ring **A**. Conversely, the ligand presents a large *point* (L) towards the interstice which would accommodate the flatter ring **C**. Thus, the L^1/π-ligand interstices are rendered non-degenerated because the π-ligand alleviates the steric compression attending the vertical orientation of ring **A**.

2.2 Complexes of type 4, possessing η^6-C_6H_6 as ligand. Attention now turns toward establishing the thermodynamically preferred conformation of **1** within complexes of the type **4** (Fig. 3). To our knowledge, only one unsubstituted arene complex of type **4** has been reported to date (ZESSAR, Table 6). However, in order to maintain continuity with the previous section, we consider a modified version of the complex (η^6-$C_6H_5CO_2CH_3$)$Cr(CO)_2PPh_3$ (MBZCRP, Table 6) to be representative of **1** bound to a complex of type (η^6-C_6H_6)$M(L^1)_2PPh_3$ **4**. Calcu-

Table 6 Crystallographic data for octahedral complexes of type **4**

Structure (refcode)	M	L^1	ω/° A	ω/° B	ω/° C
4b (ZESSAR)	Ru	Cl	2	−86	−54
4a (calculation)	Ru	Cl	−23	−53	−61
4c (ZESRUK)[a]	Ru	Cl	5	−48	−65
4a (MBZCRP)[b]	Cr	CO	−15	−55	−62
4a (calculation)	Cr	CO	−16	−42	−67
4b (FEZZIT)[c]	Cr	CO	12	−76	−56
4c (HETCRB10)[d]	Cr	CO	9	−52	−60

The η^6-C_6 ligand bears [a] *p,p′*-CH_2–C_6H_4–CH_2–, [b] –CO_2CH_3, [c] hexa –$CH_2CH_2CH_3$, and [d] hexa –CH_2CH_3 substituents.

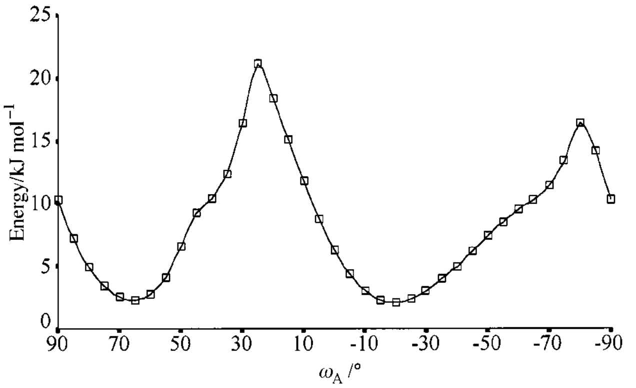


Fig. 13 The conformational energy associated with complexes of type **4** (M = Cr) as ω_A is driven through 90→0° and 0→−90° (equivalent to rings **C** and **A**, respectively).

lations were performed upon the idealised structure in a manner precisely analogous to that outlined previously for complexes of type **3**. The calculated values of $\omega_{A\text{–}C}$ associated with the minimum energy conformation are presented in Table 6. As expected, the calculated orientation of rings **A**–**C** are in complete accord with the principles outlined at the beginning of this section (Fig. 10). As suggested earlier, it is instructive to consider the full conformational profile of rings **A** and **C** in complex-bound **1**. The calculated change in intramolecular energy associated with the complex $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$ (derived from MBZCRP, Table 6), as the torsion angle ω_A is driven +90→0→−90°, is presented in Fig. 13. As expected, two minima were identified, corresponding to the lowest energy arrangement of rings **C** ($\omega_C \approx +70\rightarrow60°$) and **A** ($\omega_A \approx -15\rightarrow -25°$) in the degenerate conformations *M*-**4** and *P*-**4**, respectively (Fig. 10c). The broadest energy minimum corresponds to ring **A**, indicating that in comparison with ring **C**, a relatively wider range of ring orientations are energetically tolerable. This is consistent with the previous assertion that the more vertical ring **A** is accommodated within the least sterically encumbered interstice. However, the energy profile for ring **A** in complexes of type **3** [*i.e.*, $\omega_A \approx -18\rightarrow-46°$, Table 5 for $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}PPh_3$] is considerably broader than the corresponding energy profile observed for ring **A** within complexes of type **4** [*i.e.*, $\omega_A \approx -15\rightarrow-25°$, Table 6 for $(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3$]. The calculation is therefore consistent with the long-held assumption[19] that the $\eta^6\text{-}C_6H_6$ ligand is more sterically demanding than the $\eta^5\text{-}C_5H_5$ ligand. More specifically, the L^1/π-ligand interstice in complexes of type **4** is more sterically encumbered than the corresponding interstice within complexes of type **3**.

For complexes of type **4**, three distinct arrangements for **1** in the solid state†† are observed, and these are depicted pictorially in Fig. 14. Type **4a** is entirely in accord with the principles outlined earlier which govern the preferred orientation of rings **A**–**C** in **1**, and includes the calculated minimum energy structure discussed earlier (Table 6). However, types **4b**–**c** contain an almost vertical ring **A**, which lies coincident upon the calculated nadir energy plane (*i.e.*, displaced +12° from the idealised nadir plane, towards the π-ligand). Type **4b** possesses a flatter ring **B**, and a *tilted* ring **C**; conversely, type **4c** possesses a *tilted* ring **B**, and a flatter ring **C**. For **1** within arrangements of type **4a** (*i.e.*, both the calculation and the solid), the angle M–P–C_i = 114 ± 1°. However, the corresponding angle associated with the phenyl rings in arrangements **4b**–**c** are **A** (115–120°), **B** (115–120°), **C** (110–116°). It would appear that within arrangements of the type **4b**–**c**, ligand **1** tilts away from the interstice which accommodates the vertical ring **A**. The phenomenon of ligand tilting appears to be more prevalent within complexes of type **4**, presumably because the L^1/π-ligand interstice is more sterically encumbered than the corresponding interstice within complexes of type **3**.

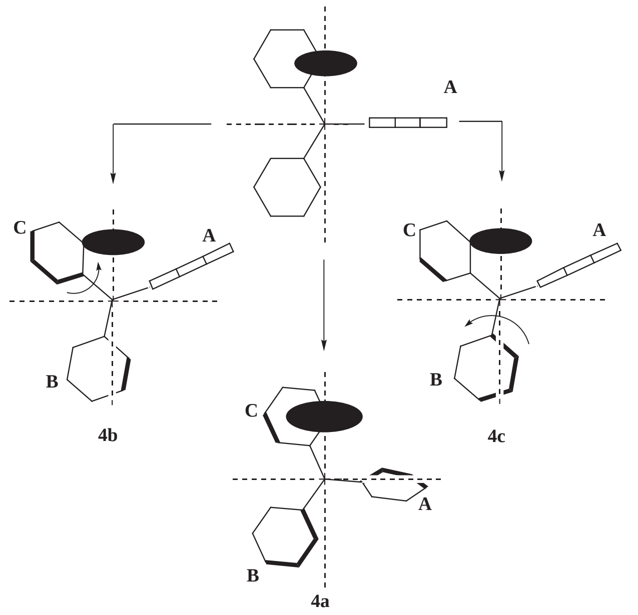


Fig. 14 The predicted (**a**) and solid-state (**a**–**c**) conformations of **1** in complexes of type **4**.

A Newman projection of *P*/*M*-**4** [viewed along the M–C_6-(cent.) axis] is presented in Fig. 12c. When the torsion angle *a* [H^3–C_6(cent.)–M–P] = −30 or −60°, **4** possesses a local plane of symmetry which includes the atoms M, P, and the C_6 centroid. At all intermediate values of the torsion angle *a*, the local symmetry of **4** is broken insofar as the H^3 atom constitutes a *point*, and the H^1/H^2 atoms constitute an *edge*. The calculated lowest energy conformation of the idealised structure demonstrates that the $\eta^6\text{-}C_6H_6$ ligand (D_{6h} symmetry) prefers to present two *edges* (*i.e.*, *a* = −30°) towards neighbouring interstices. This is in contrast to the $\eta^5\text{-}C_5H_5$ ligand (D_{5h} symmetry) in complexes of type **4**, which presents both an *edge* and a *point* towards neighbouring interstices. The higher symmetry of the $\eta^6\text{-}C_6H_6$ ligand appears to allow the ideal arrangement (*i.e.*, *edge*/*edge*) to occur. However, in the crystal, the unsubstituted complex $(\eta^6\text{-}C_6H_6)CrCl_2PPh_3$ (ZESSAR, type **4b**) possesses a torsion angle *a* of −60°; *i.e.* the $\eta^6\text{-}C_6H_6$ ligand presents two *points* towards neighbouring interstices. It is perhaps significant that this complex also possesses a tilted PPh_3 ligand. The phenomenon of ligand tilting and its effects upon neighbouring ligands are the subject of ongoing investigations in these laboratories.

In conclusion, principles governing the preferred orientations of rings **A**–**C** of **1** attached to achiral and prochiral octahedral complexes of type **2**–**4** have been derived using the concept of nadir energy planes. These principles are wholly consistent with van der Waals energy calculations and the solid state. The model is highly effective at predicting the preferred, degenerate conformations of **1**. Ligand tilting, which we believe to be an intramolecular phenomenon, leads to explicable distortions of the predicted conformers of **1**. An extension of this model to the comprehensive analysis of stereogenic pseudo-octahedral metal complexes will follow in due course.[4]

Experimental

Data retrieval

Crystal structures containing appropriate molecular fragments were located within the Cambridge Structural Database (CSD)

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†† Refcodes for complexes of type, **4a** MBZCRP, NAKROG; **4b** FEZZIT, TOMHOS, NAKRUM, ZESSAR; and **4c** CEDHUO, HETCRB, HETCRB10, KEDXOG, LANJOZ, TATCOG, ZESRUK.

using the QUEST program.[20] Data for these molecular structures were retrieved from the October 1998 release of the CSD in which the master data file contained 190,307 entries.

Molecular modelling calculations

All molecular modelling calculations were conducted using the *Chem-X* package (April 1998) supported on the *Windows NT* platform using a Pentium personal computer. The van der Waals energy (*E*vdW) calculation within *Chem-X* is a subset of the full molecular mechanics calculation which assumes that all bond lengths and angles are fixed and idealised and that the energy depends only upon the non-bonded (including 1,4) interactions. For all calculations, idealised structures have been used, with average bond lengths and angles being derived from the appropriate crystallographic data. Phenyl rings were treated as rigid bodies of D_{6h} symmetry, and for the PPh_3 ligand, $M–P–C_i = 114°$ and $C_i–P–C_i = 104°$ throughout. The van der Waals energy (*E*vdW) considers contributions from the torsion (*V*tor), electrostatic (*V*el), and non-bonded (*V*nb) terms [as defined in eqn. (1)], but without the range of functional forms and

$$E\text{vdW} = V\text{tor} + V\text{el} + V\text{nb} \quad (1)$$

parameters available in the full molecular mechanics calculation. Consequently, the calculations described herein can only be viewed as qualitative in nature.

Generic barrier constants were employed in the basic form of the torsion term (*V*tor). The electrostatic contribution (*V*el) is computed as a monopole–monopole interaction using Coulomb's law. The van der Waals interaction potential (*V*nb) within the software package is that of Del Re *et al.*,[21] and takes the form given in eqn. (2).

$$V\text{nb} = [A\exp(-Br)]r^{-D} - Cr^{-6} \quad (2)$$

In all calculations, steric contributions to *V*nb from the metal atom were not included because of the lack of adequate parameterisation. However, steric contributions from the metal centre upon the conformations of the triphenylphosphine ligand are considered to be negligible. The van der Waals energy was minimised for all conformations by independent rotations about all other single bonds (except those to L^1 ligands and hydrogen atoms) within the molecule. The π-ligands were treated as rigid bodies of D_{5h} or D_{6h} symmetry, and rotated about the axis from the centroid of the ring to the metal atom.

Acknowledgements

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