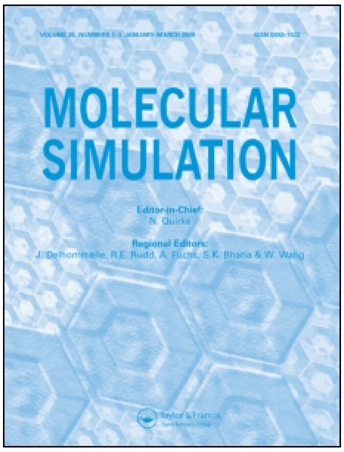

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A molecular mechanics investigation of the structures and energetics of two classes of Ru(II) complexes with applications in homogeneous catalysis

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A molecular mechanics investigation of the structures and energetics of two classes of Ru(II) complexes with applications in homogeneous catalysis

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We have used the extensible systematic forcefield (ESFF) to model two classes of chiral organometallic complexes with Ru(II) centres, both complexes having been shown to have excellent catalytic performance with respect to asymmetric ketone hydrogenation. Our results compare favourably with all available experimental data for these complexes, illustrating that the ESFF can be applied successfully to these systems. The results we obtain are useful and relevant in connection with the study of these complexes as catalysts and in turn the results support the further use of the ESFF for modelling other organometallic complexes.

Keywords: Organometallic complex; Ruthenium(II); Homogeneous catalysis; Molecular mechanics simulations; ESFF

1. Introduction

Certain classes of organometallic Ru(II) complexes have important applications as catalysts for the asymmetric hydrogenation of ketones. This process is of crucial importance to the pharmaceutical industry, being for example an essential step in the manufacture of certain anti-depressants, antihistamines, antibiotics and anti-inflammatories [1]. It is known that enantiomers of a given molecule may respectively show beneficial and detrimental physiological behaviour, and in this context, it is important for ketone hydrogenation catalysts to exhibit high enantioselectivity (i.e. produce the desirable enantiomer in significant excess of the undesirable enantiomer). For economic reasons, the catalysts should also effect a high yield of the desired product.

This study has investigated the structures and energetics of two classes of organometallic Ru(II) complexes by a molecular mechanics simulation approach, using the extensible systematic forcefield (ESFF), which has been used successfully in the past to model transition-metal-bearing species such as BEDT-TTF salts [2] and poly(ferrocenylsilanes) [3]. The two complexes we study in this work are illustrated in figure 1. Complex 1 (figure 1(a)) is the well-known Noyori catalyst (e.g. [1,4]), consisting of a Ru(II) centre coordinated by a bidentate phosphine ligand and a bidentate diamine ligand and two other monodentate ligands in *trans* formation. Complex 2 (figure 1(b)) is structurally reminiscent of the salen catalysts, consisting of the tetradentate ligand N,N'-*bis*-[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine (or related species with different substituents at the P atoms) coordinating a Ru(II) centre with two monodentate ligands in *trans* formation. It has been shown to be an excellent catalytic precursor in asymmetric transfer hydrogenation [5]. We will refer to these complexes as “class 1” and “class 2” throughout this paper.

The broad purpose of this investigation is to use computational methods to gain useful insights into the catalytic behaviour of these complexes. Firstly, a consistent model must be developed for the systems being studied. To this end, we compare our simulation results with experimental data, where such data exist. We also present the structure (determined by X-ray diffraction) of a class 1 complex not previously reported in the literature and use it along with other experimental data as

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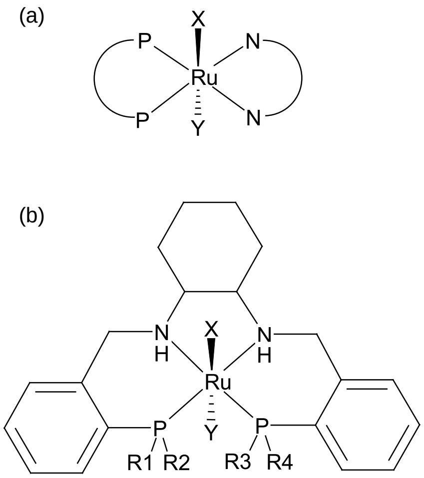

Figure 1. The two complexes studied in this work. (a) Class 1 (Noyori) complex. (b) Class 2 (salen-like) complex. X and Y represent monodentate ligands which may or may not be identical.

a point of comparison. Then, once our model is established, we show that it can be used to investigate both structural and energetic variations in the complexes, according to their chirality and the nature of the ligands used.

2. Method

2.1 Forcefield details

This work has used the ESFF, supplied as part of the Accelrys Cerius^2 and Materials Studio software [6]. The forcefield is described in detail elsewhere [7], so here, we simply give an introduction to the forcefield setup and underlying principles.

The ESFF uses a rule-based algorithm to determine a set of potential parameters for a given system. These potential parameters depend on a set of atomic parameters, which were determined by density functional theory (DFT) calculations, fitting experimental data and fitting crystal structures and properties. The parameters calculated by DFT are electronegativity, $\chi = \partial H/\partial q|_{q=0}$, hardness, $\eta = \partial^2 H/\partial q^2|_{q=0}$ and ionisation potential, $\mathrm{IP} = H(+1) - H(0)$, where H is the atomic energy and q the atomic charge. These were determined for each possible atom type according to its hybridisation and electronic configuration. The assumption is made that the atomic energy for an atom in a given valence state can be approximated by a truncated Taylor expansion about the atomic charge:

$$H(q) \approx H(0) + \chi q + \frac{1}{2}\eta q^2 \tag{1}$$

The van der Waals atomic parameters were then generated by fitting to crystal lattice parameters (and properties such as sublimation energies, where available) whilst keeping the internal coordinates frozen. The atomic force constant parameters were derived by fitting the available data for bond dissociation energies, spectroscopic data and force constant data. The remaining parameters were then determined by minimising the force on all atoms in a set of several hundred experimental organic and organometallic crystal structures (and some inorganics), which had been selected for their variation in bonding chemistry.

ESFF atom types are assigned according to a set of rules pertaining to the numbers and types of adjacent atoms. For example, the Ru centre in the complexes studied here is assigned the “Ru026” type—that is, Ru with a 2+ charge and six-fold coordination. The P atoms, which are tetrahedrally-coordinated, are assigned the generic “p” type; none of the more specific atom types for P is suitable—atom types involving “phosphorus with four bonds” permitted incorrect symmetries at P (e.g. square planar). The N atoms are assigned the “na” type (“sp^3 nitrogen in amines”). The full set of atom type assignments used in this work is given in table 1. Certain atom types are considered as equivalent for the computation of some parameters. For example, a “cp” atom at the centre of an angle is considered as equivalent to the “c=” type (“generic sp^2 carbon”). The equivalences relevant to this work are detailed in table 2.

The energy expression for the ESFF comprises terms for bond, angle, torsion, out-of-plane, van der Waals and electrostatic energies. The energy expression may thus be written as

$$E = E_\mathrm{b} + E_\mathrm{a} + E_\mathrm{t} + E_\mathrm{oop} + E_\mathrm{vdw} + E_\mathrm{el}, \tag{2}$$

Table 1. ESFF atom assignments for class 1 and class 2 complexes.

Atom	*ESFF atom type assigned*	*Description in forcefield information*
Aromatic C	cp	“sp^2 aromatic carbon with partial double bond”
sp^3 C	c	“Generic sp^3 carbon”
H bonded to C, Ru and B	h	“Generic hydrogen”
Bridging H in Ru–BH$_4$ group	hb	“Bridge hydrogen”
H bonded to N	h*	“Hydrogen bonded to nitrogen, oxygen”
All Ru	Ru026	“Ruthenium with 6 coordinations”
B in BH$_4$ complex	b	“Boron sp^3 atom”
Diamine N	na	“sp^3 nitrogen in amines”
N in PPhos and related ligands	np (class 1 only)	“sp^2 (4sp^{2}1p) nitrogen in 5-membered ring”
All P	p	“General phosphorus atom”
All Cl	cl	“Chlorine atom”
All O	o	“generic sp^3 oxygen in alcohol, ether,or acid group”

Note that the “Description” is not necessarily exhaustive for the atom type—for example, “np” atoms can also occur in 6-membered rings (as is the case in this work).

Table 2. Atom type equivalences for the atom types used in this work. Where an atom type is not already listed in table 1, its description in the forcefield information is given here.

Atom type	*Bond*	*Angle end*	*Angle centre*	*Torsion*	*Out-of-plane*	*Description in forcefield information*
cp	cp	cp	c=	cp	cp	c=—"generic sp^2 carbon"
c	c	c	c	c	c	
h	h	h	h	h	c	
hb	hb	hb	h*	h*	c	
h*	h*	h*	h*	h*	c	
Ru026	Ru026	Ru026	Ru026	Ko	Ko	Ko—"potassium atom"
b	b	b	b	b	c	
na	na	na	na	na	c	
np (class 1 only)	np	np	n=	np	np	n=—"sp^2 nitrogen in neutral arginine"
p	p	p	p	p	c	
cl	cl	cl	cl	cl	c	
o	o	o	o	o	c	

Note that the "Description" is not necessarily exhaustive for the atom type—for example, "n=" atoms can occur in compounds other than arginine, as is the case in this work.

with each of these energy terms being itself the sum of the individual energies:

$$E_k = \sum_{i=1}^{N_k} E_{ki}, \tag{3}$$

where there are N_k individual energies contributing to energy type k.

The bond energy has a Morse potential form:

$$E_\mathrm{b} = \sum_\mathrm{b} D_\mathrm{b}\left\{1 - \exp\left(1 + \alpha\left(r_\mathrm{b} - r_\mathrm{b}^\mathrm{o}\right)\right)\right\}^2, \tag{4}$$

in which D_b is the bond dissociation energy and α the anharmonicity parameter, and r_b^o is the reference bond length, and these three parameters are derived from atomic parameters such as covalent radii and ionisation potentials. Bond types are specified according to bond orders (single, double, triple, partial double, dative) and symmetry (axial or equatorial position).

The angle energy term depends on the type of angle under consideration:

$$E_\mathrm{a} = \begin{cases} \sum_\mathrm{a} \frac{K_\mathrm{a}}{\sin^2\theta_\mathrm{a}^\mathrm{o}}\left(\cos\theta_\mathrm{a} - \cos\theta_\mathrm{a}^\mathrm{o}\right)^2 & \text{normal} \\ \sum_\mathrm{a} 2K_\mathrm{a}(\cos\theta_\mathrm{a} + 1) & \text{linear} \\ \sum_\mathrm{a} K_\mathrm{a}\cos^2\theta_\mathrm{a} & \text{perpendicular} \\ \sum_\mathrm{a} \frac{2K_\mathrm{a}}{n^2}[1 - \cos(n\theta_\mathrm{a})] & \\ \quad + 2K_\mathrm{a}\exp[-\beta(r_{13} - \rho_\mathrm{a})] & \text{equatorial} \end{cases} \tag{5}$$

"Normal" angles comprise all angles that do not belong to the special angle types discussed below. θ^o is the reference angle and is determined from the angle atomic parameters of the three atoms subtending the angle. The atomic parameters for the terminal atoms in the angle depend on their atom types and bond orders and the atomic parameter for the central atom is determined according to its atom type and ring information ("exocyclic" angles having one bond in a particular ring, "endocyclic" angles having both bonds in a particular ring; unconstrained angles are denoted as "free"). K_a is the force constant and again is dependent on atom types and ionisation potentials of the atoms included in the angle.

The special cases are perpendicular, linear and equatorial angles. Perpendicular angles are restricted to metal centres and include angles between axial and equatorial ligands around a metal centre. Linear angles are those with central atoms having sp hybridization and angles between two axial ligands in a metal complex. Equatorial angles are those between two equatorial bonds in a metal complex. The second term in the expression for the equatorial angle energy acts as a barrier preventing two bonds from overlapping, since $\theta_\mathrm{a} = 0$ is a minimum for the first term. The n in the first term represents a particular symmetry (e.g. $n = 4$ for $D4h$ symmetry).

Torsion energy contributions are governed by the equation:

$$E_\mathrm{t} = \sum_\mathrm{t} D_\mathrm{t}\left(\frac{\sin^2\theta_1 \sin^2\theta_2}{\sin^2\theta_1^\mathrm{o} \sin^2\theta_2^\mathrm{o}} + \mathrm{sign}\frac{\sin^n\theta_1 \sin^n\theta_2}{\sin^n\theta_1^\mathrm{o} \sin^n\theta_2^\mathrm{o}}\cos[n\tau]\right), \tag{6}$$

in which τ is a torsion angle and θ_1 and θ_2 are bond angles. The inclusion of a sine term in this equation results in the torsion approaching zero smoothly if either bond angle approaches 0° or 180°, which is an improvement on traditional molecular mechanics torsion potentials. Moreover, in the second term, the numerator $\sin^n\theta_1 \sin^n\theta_2$ $\cos(n\tau)$ can be expressed as a function of $\cos^2\theta_1$, $\cos^2\theta_2$ and the function $F(\theta, \tau) = \sin\theta_1 \sin\theta_2 \cos\tau$, which in turn can be expressed as a product of the unit vectors along the 1–2, 2–3 and 3–4 bonds

$$\begin{aligned} F(\theta, \tau) &= (\hat{r}_{12} \times \hat{r}_{23})\cdot(\hat{r}_{23} \times \hat{r}_{34}) \\ &= (\hat{r}_{12}\cdot\hat{r}_{23})\cdot(\hat{r}_{23}\cdot\hat{r}_{34}) - (\hat{r}_{12}\cdot\hat{r}_{34}), \end{aligned} \tag{7}$$

meaning that it is possible to express the torsion energy in terms of scalar products of the unit vectors $\hat{r}_{12}$, $\hat{r}_{23}$ and $\hat{r}_{34}$, thereby simplifying considerably the calculation of torsions and their derivatives.

Out-of-plane contributions to the energy are given by

$$E_\mathrm{oop} = \sum_\mathrm{o} D_\mathrm{o}\phi^2 \tag{8}$$

where ϕ is the average of the three possible angles associated with the out-of-plane centre. The single parameter D_o associated with the central atom is a fitted quantity.

Non-bonding contributions to the energy comprise van der Waals and electrostatic parts, the former being given by:

$$E_{\mathrm{vdw}} = \sum_{i=1}^{N}\sum_{j\neq 1}^{N}\left(\frac{A_iB_j + A_jB_i}{r_{ij}^9} - 3\frac{B_iB_j}{r_{ij}^6}\right) \qquad (9)$$

with

$$A_i = \sqrt{\epsilon_i}r_i^{o6} \qquad (10)$$

and

$$B_i = \sqrt{\epsilon_i}r_i^{o3} \qquad (11)$$

and the latter being given by

$$E_{\mathrm{es}} = \sum_{i=1}^{N}\sum_{j\neq 1}^{N}\frac{q_iq_j}{r_{ij}} \qquad (12)$$

In equations (9) and (12), N is the number of atoms in the system under investigation and in equations (10) and (11), r_i^o and ϵ_i are the van der Waals radius and well depth for atom i. Van der Waals and electrostatic interactions are only calculated between 1–4 neighbours and higher.

The first stage of computing the electrostatic energy in equation (12) is to determine the partial charges q_i on the individual atoms; this is performed by "electronegativity equalisation", i.e. minimising the electrostatic energy with respect to the partial charges, maintaining the constraint that the sum of the charges must be equal to the net charge on the molecule. The charges are derived from the hardness and electronegativity, which are in turn calculated using DFT. After electronegativity equalisation, some further adjustments may be necessary, e.g. for delocalised π systems. A full discussion of the derivation of partial charges can be found elsewhere [7].

2.2 Complexes investigated

For the class 1 complexes, we have considered the diamine 1,2-diphenylethylenediamine (DPEN, figure 2). This diamine is commonly used in experimental studies of the catalytic properties of these complexes (e.g. [8–11]). We have used the following monodentate ligands (see figure 1(a)): X = Y = Cl; X = H, Y = Cl; X = Y = H. Finally, we have also considered different diphosphines, having used 2,2′,6,6′-tetramethoxy-4,4′-bis(diphenylphosphino)-3,3′-bipyridine (PPhos, figure 3(a)), 4,12-bis(diphenylphosphino)-[2.2]-paracyclophane (PhanePhos, figure 3(b)) and 2,2′-bis(di-4-tolylphosphino)-1,1′-binaphthalene and 2,2′-bis(di-3,5-xylylphosphino)-1,1′-binaphthalene (TolBINAP and XylBINAP, figure 3(c)). These variations therefore amount to a sizable data set of simulations.

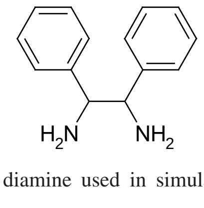

Figure 2. DPEN, the diamine used in simulation studies of class 1 complexes.

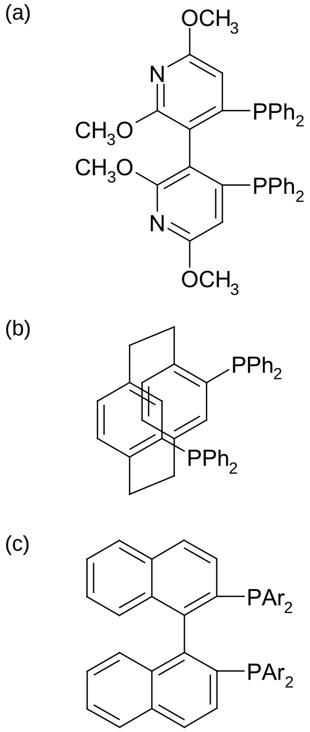

Figure 3. Different diphosphines used in simulation studies of class 1 complexes. (a) PPhos, (b) PhanePhos, (c) TolBINAP (Ar = 4-$CH_3C_6H_4$) and XylBINAP (Ar = 3,5-$(CH_3)_2C_6H_3$).

There are five crystal structures available in the literature for class 1 complexes; we will label them A–E for simplicity. They are A, *R*-TolBINAP–$RuCl_2$–*R*,*R*-DPEN [8]; B, *R*-TolBINAP–$RuCl_2$–*S*,*S*-DPEN [8]; C, *R*-TolBINAP–RuH(η^2-BH_4)–*R*,*R*-DPEN [10]; D, *R*-TolPPhos–$RuCl_2$–*R*,*R*-DPEN [11]; and E, *R*-BINAP–RuHCl–*R*,*R*-DPEN [12]. In addition, we present in this work the crystal structure of another class 1 complex, *S*-XylPPhos–$RuCl_2$–*S*,*S*-DPEN (see below), which we will label F. We have therefore modelled these six complexes as well as the data set discussed above, in order to make direct comparisons with experiment.

For the class 2 complexes, we investigated the dichlorides and dihydrides. We probed two types of variation in this class: (i) the variation in substituents at the P atoms and (ii) the variation in chirality at the six chiral centres (P, N, C, C, N, P). For (i), two cases were considered: 2a (R1 = R4 = Me, R2 = R3 = Ph) and 2b (R1 = R4 = *p*-MeOPh, R2 = R3 = Ph). For (ii), there are $2^6 = 64$ possible chirality combinations for six chiral centres (RRRRRR, RRRRRS, ... SSSSSS, labelled clockwise from P at bottom left of figure 1(b)). However, only 20 of these 64 configurations are distinct in energetic terms: the others are simply related by reflection or rotation; results are therefore presented for only the 20 unique configurations.

There is one directly-comparable crystal structure available in the literature for class 2 complexes: that of [RuCl$_2${(1*R*,2*R*)-*N*, *N'*-bis[*o*-(diphenylphosphino)benzyl]-cyclohexane-1,2-diamine}] [5]. We will refer to this as complex G.

2.3 Simulation details

All molecular structures were constructed with the Accelrys Materials Studio software. For C_2-symmetric molecules, care was taken to ensure that the starting structure for each calculation was C_2, but symmetry is unrestricted during optimisation. Structure optimisation was performed using the ESFF parameters, via a cascade of steepest descent, conjugate gradient and Newton–Raphson (BFGS) minimisers. The tolerance level for minimisation was 10^{-5} kcal mol^{-1} Å^{-1}. Coulomb and van der Waals contributions to the energy were summed over the whole molecule: no cutoffs were used. Potential parameters used in the simulations of class 1 and class 2 complexes are given in tables 3–12. Potential parameters used for the simulations of specific complexes A–G can be found in the supplementary information to this paper.

For complexes A–G, the ESFF was used to optimise the crystal structure, in addition to the single molecule. Two sets of optimisations were performed: in the first, only the atom positions were allowed to vary and in the second, the atom positions and cell parameters were allowed to vary. Regardless of the experimentally observed symmetry, ESFF crystal structure optimisations were performed with *P*1 symmetry—a requirement of the simulation engine—but in some minimisations, symmetry higher than *P*1 is nevertheless maintained during the course of the simulations. In some crystal structures, solvent molecules (e.g. tetrahydrofuran) are present; in such cases, simulations were performed both with and without these solvent molecules. Coulomb and van der Waals interactions were handled via the Ewald sum at ultra-fine accuracy (tolerance 10^{-4} kcal mol^{-1}).

2.4 X-ray structure determination of S*-XylPPhos–RuCl$_2$–*S,S*-DPEN*

Pale yellow single crystals of *S*-XylPPhos–RuCl$_2$–*S*,*S*-DPEN were grown by slow diffusion of diethylether into a dichloromethane solution of *S*-XylPPhos–RuCl$_2$–*S*,*S*-DPEN. A single crystal (size 0.23 × 0.16 × 0.10 mm) was placed in a capillary tube and mounted on a Nonius Kappa CCD X-ray diffractometer. Data were collected using Mo-K$_\alpha$ radiation at 180 K. The structure was solved using direct methods (SHELXl-97) and refined by full-matrix least-squares techniques.

Table 3. Parameters used for bond energies (equation (4)) in class 1 complexes.

Atom types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o *(Å)*
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
c—o	1	87.99588	2.07423	1.41763
cp—cp	1	92.84087	1.78338	1.47625
cp—cp	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
cp—np	1.5	127.15352	1.92564	1.33168
cp—o	1	86.61671	2.05812	1.35479
cp—p	1	68.55895	1.70576	1.83522
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
Ru026—cl†	1	76.21987	2.06388	2.40813
Ru026—h‡	1	92.27285	1.93883	1.76368
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

† Indicates parameters used only in simulations of dichlorides.
‡ Indicates parameters used only in simulations of dihydrides.

Table 4. Parameters used for angle energies (equation (5)) for class 1 complexes.

Atom types i—j—k	*i—j—k angle type*	K_a *(kcal mol^{-1})*	θ_a^o*(°)*
c—c—cp	Exocyclic	39.61136	113.3026
c—c—h	Exocyclic	36.72293	109.31218
c—c—h	Free	36.72293	109.09128
c—na—h*	Exocyclic	37.44733	111.81867
cl—Ru026—cl†	Planar	47.36236	N/A
cl—Ru026—p†	Planar	44.42497	N/A
cl—Ru026—p†	Perpendicular	44.42497	N/A
cp—c—c	Free	39.61136	113.10691
cp—c—h	Free	36.60359	110.15146
cp—c=c	Free	39.68756	120.40071
cp—c=—cp	Free	39.48518	120.69128
cp—c=—cp	Free	39.48518	121.43308
cp—c=—h	Free	36.17768	118.90658
cp—c=—np	Free	30.75736	119.76141
cp—c=—o	Free	48.82026	119.22076
cp—c=—p	Free	36.46393	118.36999
cp—n=—cp	Free	50.07563	111.64555
cp—o—c	Free	52.56115	110.68582
cp—p—cp	Free	32.65196	100.62694
h—c—h	Free	34.65328	107.29538
h—Ru026—h‡	Planar	42.64449	N/A
h—Ru026—p‡	Perpendicular	42.7183	N/A
h—Ru026—p‡	Planar	42.7183	N/A
h*—na—h*	Free	33.75864	106.33327
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—cl†	Perpendicular	52.00791	N/A
na—Ru026—cl†	Planar	52.00791	N/A
na—Ru026—h‡	Perpendicular	46.76726	N/A
na—Ru026—h‡	Planar	46.76726	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
na—Ru026—p	Perpendicular	47.0028	N/A
na—Ru026—p	Linear	47.0028	N/A
na—Ru026—p	Planar	47.0028	N/A
o—c—h	Free	42.10816	108.16316
o—c=—np	Free	32.40933	118.279
p—Ru026—p	Perpendicular	42.795	N/A
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—cp	Free	36.9934	114.82283

† Indicates parameters used only in simulations of dichlorides.
‡ Indicates parameters used only in simulations of dihydrides.

Table 5. Parameters used for torsion energies (equation (6)) in class 1 complexes.

Atom types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t *(kcal mol^{-1})*
c—c—cp—cp	1	Exocyclic	Free	0.10422
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—c—c—cp	1	Free	Free	0.15806
cp—c—c—h	1	Free	Free	0.15806
cp—cp—c—c	1	Free	Free	0.10422
cp—cp—c—h	1	Free	Free	0.10422
cp—cp—cp—c	1.5	Free	Free	3.16825
cp—cp—cp—cp	1	Free	Free	0.895
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—p	1.5	Free	Free	3.16825
cp—cp—np—cp	1.5	Free	Free	5.16825
cp—cp—o—c	1	Free	Free	0.9975
cp—cp—p—cp	1	Free	Free	0.11898
cp—cp—p—Ko	1	Free	Free	0.11898
cp—o—c—h	1	Free	Free	0.30542
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—cp	1	Exocyclic	Exocyclic	0.15806
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—c—h	1	Free	Free	0.15806
h—c—cp—cp	1	Free	Free	0.10422
h—cp—cp—c	1.5	Free	Free	3.16825
h—cp—cp—cp	1.5	Free	Free	3.16825
h—cp—cp—h	1.5	Free	Free	3.16825
h—cp—cp—p	1.5	Free	Free	3.16825
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
np—cp—cp—cp	1.5	Free	Free	3.16825
np—cp—cp—h	1.5	Free	Free	3.16825
np—cp—o—c	1	Free	Free	0.9975
o—cp—cp—cp	1.5	Free	Free	3.16825
o—cp—cp—h	1.5	Free	Free	3.16825
o—cp—np—cp	1.5	Free	Free	5.16825
p—cp—cp—c	1.5	Free	Free	3.16825

3. Results

3.1 *Structure of* S-*XylPPhos–RuCl$_2$–*S,S-*DPEN*

The crystal of *S*-XylPPhos–RuCl$_2$–*S*,*S*-DPEN studied is monoclinic, with space group $C2$, $a = 25.6496(4)$, $b = 13.0965(2)$, $c = 20.6949(4)$ Å, $U = 6776.1(2)$ Å^3 and $Z = 4$. The chemical formula is $C_{69}H_{88}Cl_4N_4O_6P_2Ru$ and the formula weight $M = 1374$. At $T = 180$ K, using Mo-K$_\alpha$ radiation (absorption coefficient μ (Mo-K$_\alpha$) $= 0.490$ mm^{-1}), 13,150 reflections were measured, 11,952 unique ($R_{\text{int}} = 0.0642$) which were used in all calculations. The refinement of F^2 was based on all reflections and the final weighted *R*-factor, *wR*, based on F^2, was 0.1503.

Table 6. Parameters used for out-of-plane energies (equation (8)) for class 1 complexes.

Atom type (centre atom)	D_o *(kcal mol^{-1})*
cp	16

Selected bond lengths (Å) and angles (°) in the molecular structure of *S*-XylPPhos–RuCl$_2$–*S*,*S*-DPEN were measured as follows: Ru—N1 2.162(5), Ru—N2 2.157(4), Ru—P1 2.2822(12), Ru—P2 2.2800(14), Ru—Cl1 2.4197(14), Ru—Cl2 2.4240(13), N1—Ru—N2 78.67(16), P1—Ru—P2 92.30(5), Cl1—Ru—Cl2 162.09(4). This structure has been deposited with the Cambridge Crystallographic Data Centre (see website: http://www.ccdc.cam.ac.uk) with deposition number CCDC 290484. A crystallographic information file (.cif) of the structure is also available as supplementary material to this paper.

3.2 *Simulations of class 1 complexes*

Figures 4–7 show some examples of the optimised crystal and molecular structures of the class 1 complexes

Table 7. van der Waals parameters used in simulations of class 1 complexes.

Atom type	r_0	ϵ_0	Additional notes
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.973013	0.062367	cp bonded to nitrogen (np) and oxygen (o) (PPhos only)
cp	3.998049	0.062367	cp bonded to carbon (cp)
c	4.036373	0.051134	c bridging in paracyclophane group (PhanePhos only)
c	4.022160	0.051134	c in DPEN
c	4.025547	0.051134	c in OMe group of PPhos ligand (PPhos only)
c	4.040293	0.051134	c in Me of tolyl and xylyl groups (TolBINAP and XylBINAP only)
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (c)
h‡	3.094482	0.020223	Hydride: h bonded to Ru026
h*	1.575370	0.015836	
Ru026	3.952810	0.447049	
na	3.809074	0.072656	
np	3.754782	0.067728	(PPhos only)
p	4.488726	0.209681	
cl†	4.181166	0.214743	
o	3.648581	0.078033	(PPhos only)

† Indicates parameters used only in simulations of dichlorides.
‡ Indicates parameters used only in simulations of dihydrides.

A–F. Each structure is overlaid with the experimentally determined structure as obtained from the literature (or, for complex F, this work). Tables 13 and 14 compare experimental and simulated values for bond lengths and bond angles for complexes A and F (data for complexes B–E may be found in tables A1–A4 in the Appendix). Simulated structures of both crystals and isolated molecules are compared with the experimental data.

Figures 4–7 and tables 13 and 14 show that there is good agreement between observed and simulated parameters. The Ru—N bond lengths are accurate to within 2%, Ru—P to within 4%. The least accurate Ru—Cl bond length is in the RuHCl complex (table A4), with 7% accuracy; others are accurate to within 1%. Ru—H bond lengths, in the Ru(H)(η^1-BH_4) and RuHCl complexes (tables A2 and A4), show very poor agreement; however, X-ray diffraction does not permit the accurate location of hydrogen atoms and so the calculated bond lengths are likely to be more accurate than the experimentally-determined ones. P—Ru—P angles are accurate to within 4%, N—Ru—N angles to within 5% and X—Ru—Y angles (where X and Y may be H and H, H and Cl, or Cl and Cl, depending on the complex) to within 8%.

Table 8. Parameters used for bond energies (equation (4)) in class 2 complexes.

Atom types i—j	*Bond order*	D_b *(kcal mol^{-1})*	*α (Å^{-1})*	*r_b^o (Å)*
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
cp—cp	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
p—c	1	65.97093	1.71563	1.85949
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl†	1	76.21987	2.06388	2.40813
Ru026—h‡	1	92.27285	1.93883	1.76368
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

† Indicates parameters used only in dichloride simulations.
‡ Indicates parameters used only in dihydride simulations.

For the complexes whose crystal structures do not contain solvent molecules (A, B, D), the best agreement for cell parameters was obtained for B, whose cell parameters are accurate to within 3%. In A, all cell parameters are accurate to within 2% (except *c*, to 6%), and in D, all cell parameters are accurate to within 3% (except *a*, to 7%). The crystal structure of D contains solvent molecules, but these are disordered, so cannot be included in this simulation; this discrepancy means that the cell parameters are accurate to within 6%. The crystal structures of E and F also contain solvent molecules and when these are included in the simulations, the cell parameters are accurate to within 2% (E) and 4% (F).

Figure 8 shows the optimised total energies of the dihydride and dichloride complexes, for both matching (R/RR and S/SS) and mismatching (R/SS and S/RR) pairs (RuHCl complexes not shown). Figure 9 compares the energies of the matching and mismatching dihydrides and dichlorides with the corresponding RuHCl complexes. Figure 10 compares the energy components from all three sets of complexes.

3.3 *Simulations of class 2 complexes*

Figure 11 compares the optimized crystal structure of complex G with the original experimental structure [5]. Figure 12 compares the molecular structures. Table 15 compares experimental and simulated crystal structures in

Table 9. Parameters used for angle energies (equation (5)) in class 2 complexes.

Atom types i — j — k	*i — j — k angle type*	K_a *(kcal mol^{-1})*	θ_a^o *(°)*
c—c—c	Exocyclic	39.7881	112.45814
c—c—c	Free	39.7881	112.26629
c—c—h	Exocyclic	36.72293	109.31218
c—c—h	Free	36.72293	109.09128
c—c=—cp	Free	39.68756	120.40071
c—na—c	Exocyclic	51.04868	114.24467
c—na—h*	Free	37.44733	107.29783
c—na—h*	Exocyclic	37.44733	111.81867
cl—Ru026—cl†	Planar	47.36236	N/A
cp—c—h	Free	36.60359	110.15146
cp—c=—cp	Free	39.48518	120.69128
cp—c=—h	Free	36.17768	118.90658
cp—p—c	Free	32.79276	100.18783
cp—p—cp	Free	32.65196	100.62694
h—c—h	Free	34.65328	107.29538
h—c—p	Free	34.82206	107.24831
h—Ru026—h‡	Planar	42.64449	N/A
na—c—c	Endocyclic	50.68569	105.47161
na—c—c	Exocyclic	50.68569	112.19548
na—c—cp	Free	50.30486	112.86668
na—c—h	Free	44.08114	108.99985
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—cl[†,¶]	Perpendicular	52.00791	N/A
na—Ru026—cl[†,§]	Planar	52.00791	N/A
na—Ru026—h[‡,¶]	Perpendicular	46.76726	N/A
na—Ru026—h[‡,§]	Planar	46.76726	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
na—Ru026—p[‖]	Linear	47.0028	N/A
na—Ru026—p[#]	Perpendicular	47.0028	N/A
na—Ru026—p[**]	Planar	47.0028	N/A
p—c=—cp	Free	36.46393	118.36999
p—Ru026—cl[†,††]	Perpendicular	44.42497	N/A
p—Ru026—cl[†,‡‡]	Planar	44.42497	N/A
p—Ru026—h[‡,††]	Perpendicular	42.7183	N/A
p—Ru026—h[‡,‡‡]	Planar	42.7183	N/A
p—Ru026—p	Perpendicular	42.795	N/A
Ru026—na—c	Exocyclic	61.47563	116.11432
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—c	Free	37.21706	114.3113
Ru026—p—cp	Free	36.9934	114.82283

[†] Indicates parameters used only in dichloride simulations.
[‡] Indicates parameters used only in dihydride simulations.
[¶] N1—Ru1—X1 and N1—Ru1—X2, where X = H or Cl.
[§] N2—Ru1—X1 and N2—Ru1—X2, where X = H or Cl.
[‖] N1—Ru1—P1.
[#] N1—Ru1—P2 and N2—Ru1—P1.
[**] N2—Ru1—P2.
[††] P1—Ru1—X1 and P1—Ru1—X2, where X = H or Cl.
[‡‡] P2—Ru1—X1 and P2—Ru1—X2, where X = H or Cl.

terms of bond lengths, bond angles and crystallographic parameters. As was the case for the class 1 complexes, simulations were performed with and without solvent molecules. Ru—N, Ru—P and Ru—Cl bond lengths are accurate to within 2% (except one Ru—P in S3 at 2.2%), N—Ru—N angles to 1% (except one in S5 at 1.3%), P—Ru—P angles to 4% and Cl—Ru—Cl angles to 6% (except one in S1 at 6.4%).

For the simulation including the solvent molecules and allowing the cell parameters to change, the simulated cell parameter values were accurate to within 4% and the original space group symmetry is maintained.

Figure 13 shows the MM-computed total energies of the 2a and 2b complexes and figure 14 shows the components of the internal energies (bond, angle, torsion, out-of-plane), plus the nonbond energy, which is a sum of van der Waals and electrostatic components.

4. Discussion

The favourable comparison of our simulation results with experimentally determined structures illustrates that the ESFF is an excellent forcefield for modelling the organometallic complexes relevant to this work on ketone hydrogenation. Not only are the experimental crystal and molecular structures reproduced well by the model, but also several useful insights have been gained into the structural and energetic behaviour of these molecules.

Table 10. Parameters used for torsion energies (equation (6)) for class 2 complexes.

Atom types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t *(kcal mol^{-1})*
c—c—c—c	1	Exocyclic	Exocyclic	0.15806
c—c—c—h	1	Exocyclic	Exocyclic	0.15806
c—c—c—c	1	Exocyclic	Free	0.15806
c—c—c—h	1	Exocyclic	Free	0.15806
c—c—c—c	1	Free	Free	0.15806
c—cp—cp—cp	1.5	Free	Free	3.16825
c—cp—cp—h	1.5	Free	Free	3.16825
c—cp—cp—p	1.5	Free	Free	3.16825
c—na—c—cp	1	Exocyclic	Free	0.23688
c—na—c—h	1	Exocyclic	Free	0.23688
c—na—c—c	1	Exocyclic	Endocyclic	0.23688
c—na—c—c	1	Exocyclic	Exocyclic	0.23688
c—na—c—h	1	Exocyclic	Exocyclic	0.23688
c—p—cp—cp	1	Free	Free	0.11898
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—p	1.5	Free	Free	3.16825
cp—p—c—h	1	Free	Free	0.1375
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—c—c	1	Free	Free	0.15806
h—c—c—h	1	Free	Free	0.15806
h—c—cp—cp	1	Free	Free	0.10422
h—cp—cp—h	1.5	Free	Free	3.16825
h—cp—cp—p	1.5	Free	Free	3.16825
h—na—c—cp	1	Free	Free	0.23688
h—na—c—h	1	Free	Free	0.23688
h—na—c—c	1	Exocyclic	Endocyclic	0.23688
h—na—c—c	1	Exocyclic	Exocyclic	0.23688
h—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—cp	1	Exocyclic	Free	0.23688
Ko—na—c—h	1	Exocyclic	Free	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—p—c—h	1	Free	Free	0.1375
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—c	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—c—c	1	Exocyclic	Free	0.15806
na—c—c—h	1	Exocyclic	Free	0.15806
na—c—cp—cp	1	Free	Free	0.10422

4.1 Structure and energetics of class 1 complexes

The first point of interest concerns the fact that, for the TolBINAP, XylBINAP and PPhos catalysts, matching pairs (e.g. R/RR) give rise to better enantioselectivity, (e.g. XylPPhos/DPEN complex with acetophenone [11]: S/RR 78% e.e., R/RR 99% e.e. for otherwise identical conditions), but for PhanePhos complexes it is the mismatching pairs (e.g. R/SS) whose performance is better (e.g. PhanePhos/DPEN complex with acetophenone [9]: S/SS 43% e.e. after 1.25h, S/RR 98% e.e. after 0.5 h; XylPhanePhos/DPEN complex with acetophenone [9]: S/SS 41% e.e. after 1 h, R/SS 99% e.e. after 0.5 h [9]). From figure 8, we can compare the behaviour of the dichloride precatalyst molecules and the dihydride molecules. In all cases except PhanePhos, the total energies of matching pairs are lower than those of the corresponding mismatching pairs. In PhanePhos, this result is obtained for the dichlorides, but for the dihydrides, the behaviour is reversed and the total energies of the matching pairs become higher than those of the mismatching pairs. Whilst it is not directly appropriate to relate catalytic activity and selectivity to these MM-determined energies (they are energy minima, whereas the relative catalytic performance of stereoisomers is likely to be related to maxima in the energy surface), this is nevertheless a striking result. It could have predictive use, i.e. by performing simulations of matching and mismatching complexes containing a new ligand, it could be possible to predict the most selective catalyst by comparing the energies, but this would be rather a bold conclusion to draw from having studied only four ligands!

Secondly, from figures 9 and 10, we can examine the energy differences in the class 1 complexes with respect to matching/mismatching pairs and with respect to the

Table 11. van der Waals parameters used in simulation of class 2 complexes.

Atom type	r_0	ϵ_0	*Additional notes*
c	4.041159	0.051134	c in Me group
c	4.039090	0.051134	c in cyclohexane (not bonded to N)
c	4.024956	0.051134	c in cyclohexane (bonded to N)
c	4.026192	0.051134	c bonded to na and cp
c[†]	4.025547	0.051134	c in Me of *p*-PhOMe
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp[†]	3.982368	0.062367	cp bonded to o in *p*-PhOMe
h	2.987406	0.020223	h bonded to carbon (c)
h	2.955159	0.020223	h bonded to carbon (cp)
h[‡]	3.094482	0.019896	Hydride h (hydrides only)
h*	1.575370	0.015836	
cl[¶]	4.181166	0.214743	
na[¶]	3.806958	0.072656	
na[‡]	3.815723	0.070776	
o[†]	3.648581	0.078033	o in *p*-PhOMe
p[¶]	4.491418	0.209681	
p[‡]	4.507496	0.201000	
Ru026[¶]	3.952810	0.447049	
Ru026[‡]	4.077176	0.408006	

[†] Indicates parameters used only in simulations of 2b complexes.
[‡] Indicates parameters used only in simulations of hydrides.
[¶] Indicates parameters used only in simulations of chlorides.

different ligands around the Ru centre. Figure 9 shows that, interestingly, there is not always an obvious trend in total energy going from $RuCl_2 \rightarrow RuHCl \rightarrow RuH_2$ complexes. In most complexes, the total energy decreases, but in the matching PhanePhos and mismatching PPhos systems, there is no such trend, with the dihydrides having higher total energies than the HCl complexes. Comparing the energy contributions in figure 10 for matching/mismatching PhanePhos (black and red bars) and PPhos (green and blue bars), we can observe that the energy components apparently responsible for this difference are the angle and nonbond components for PhanePhos and the torsion and nonbond components for PPhos. In the PhanePhos H_2 complex, there is a noticeably larger difference between matching and mismatching angle energies than there is for the Cl_2 and HCl complexes and the nonbond energy of the mismatching complex is larger than that of the matching complex, whereas the reverse is true for the Cl_2 and HCl complexes. In the PPhos HCl complex, the torsion energy is smaller and the nonbond energy larger, than those of the H_2 and Cl_2 complexes.

Visual examination of the structures of these complexes reveals that the differences are likely to be due to slight differences between the structures of the matching and mismatching complexes in each series. The structures of the matching PPhos complexes are very similar, but in the mismatching HCl complex, there is some rotation of the PPhos ligand that is absent from the mismatching Cl_2 and H_2 complexes. Analogous rotations of the PhanePhos ligand occur in the matching HCl complex but not the other matching complexes and in the mismatching H_2 complex, but not the other mismatching complexes. These subtle differences in structure and energetic behaviour between series of complexes may have implications for reactions in which dichlorides or HCl precursor complexes are converted into dihydrides *in situ*.

Table 12. Parameters used for out-of-plane energies (equation (8)) for class 2 complexes.

Atom type (centre atom)	D_o (*kcal mol*$^{-1}$)
cp	16

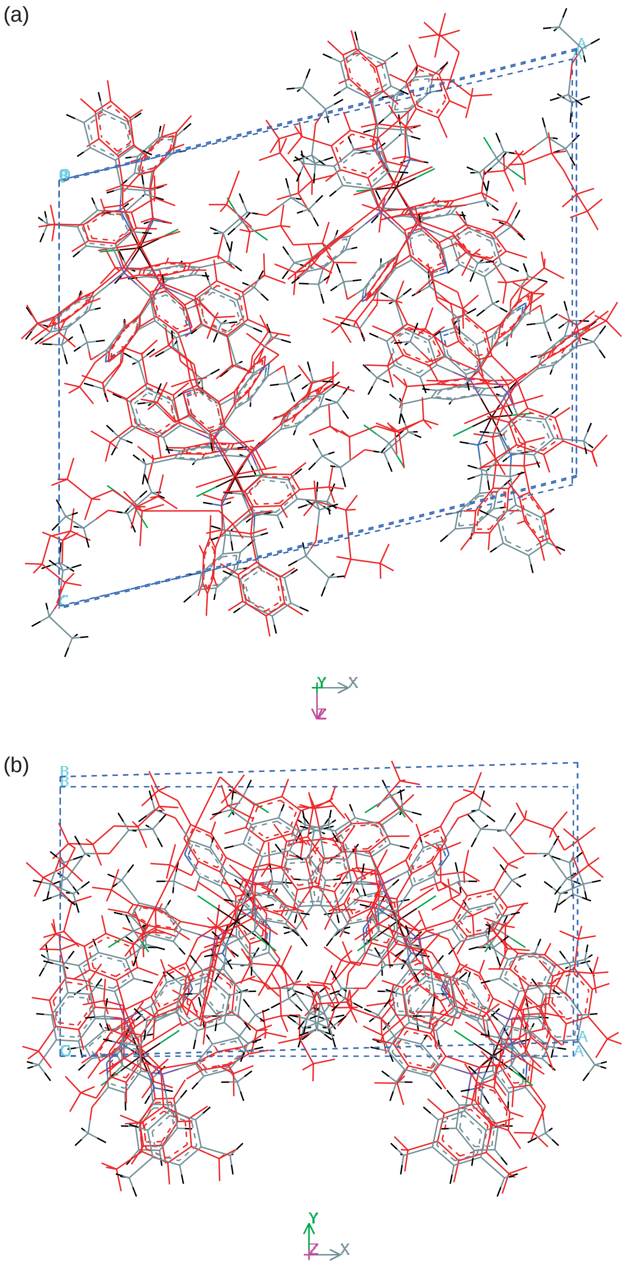

Figure 4. Crystal structure of the class 1 complex F. Optimised simulated structure shown in red. In experimental structure: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; and brown, Ru. Dotted lines indicate unit cells. (a) View along the *y*-axis, (b) view along the *z*-axis.

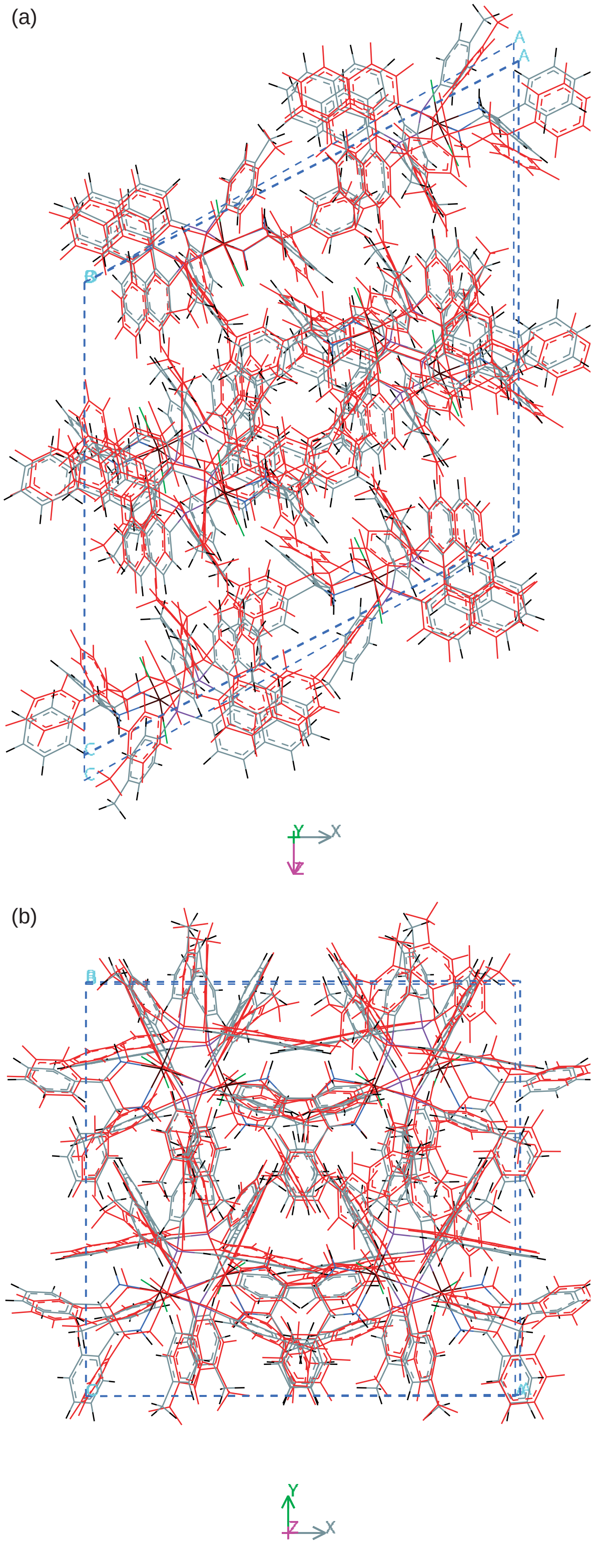

Figure 5. Crystal structure of the class 1 complex A. Optimised simulated structure shown in red. In experimental structure: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; and brown, Ru. Dotted lines indicate unit cells. (a) View along the *y*-axis, (b) view along the *z*-axis.

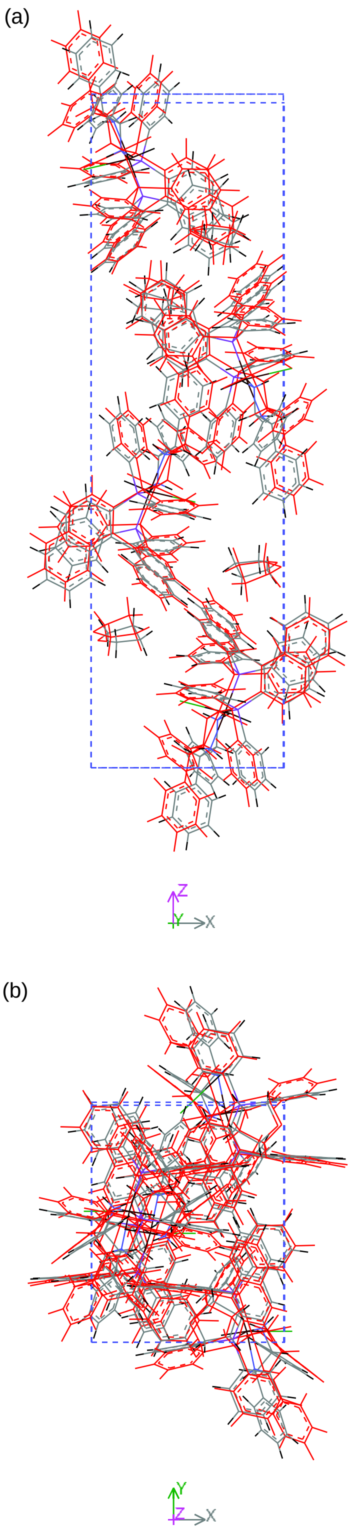

Figure 6. Crystal structure of the class 1 complex E. Optimised simulated structure shown in red. In experimental structure: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; and brown, Ru. Dotted lines indicate unit cells. (a) View along the *y*-axis, (b) view along the *z*-axis.

We can also consider more obvious variations in energetic behaviour. For example, from figure 10, it can be seen that there are significant contributions to the total energy of PhanePhos complexes from the torsion and out-of-plane energies, which is due to the PhanePhos ligand itself, whose novel structure is significantly

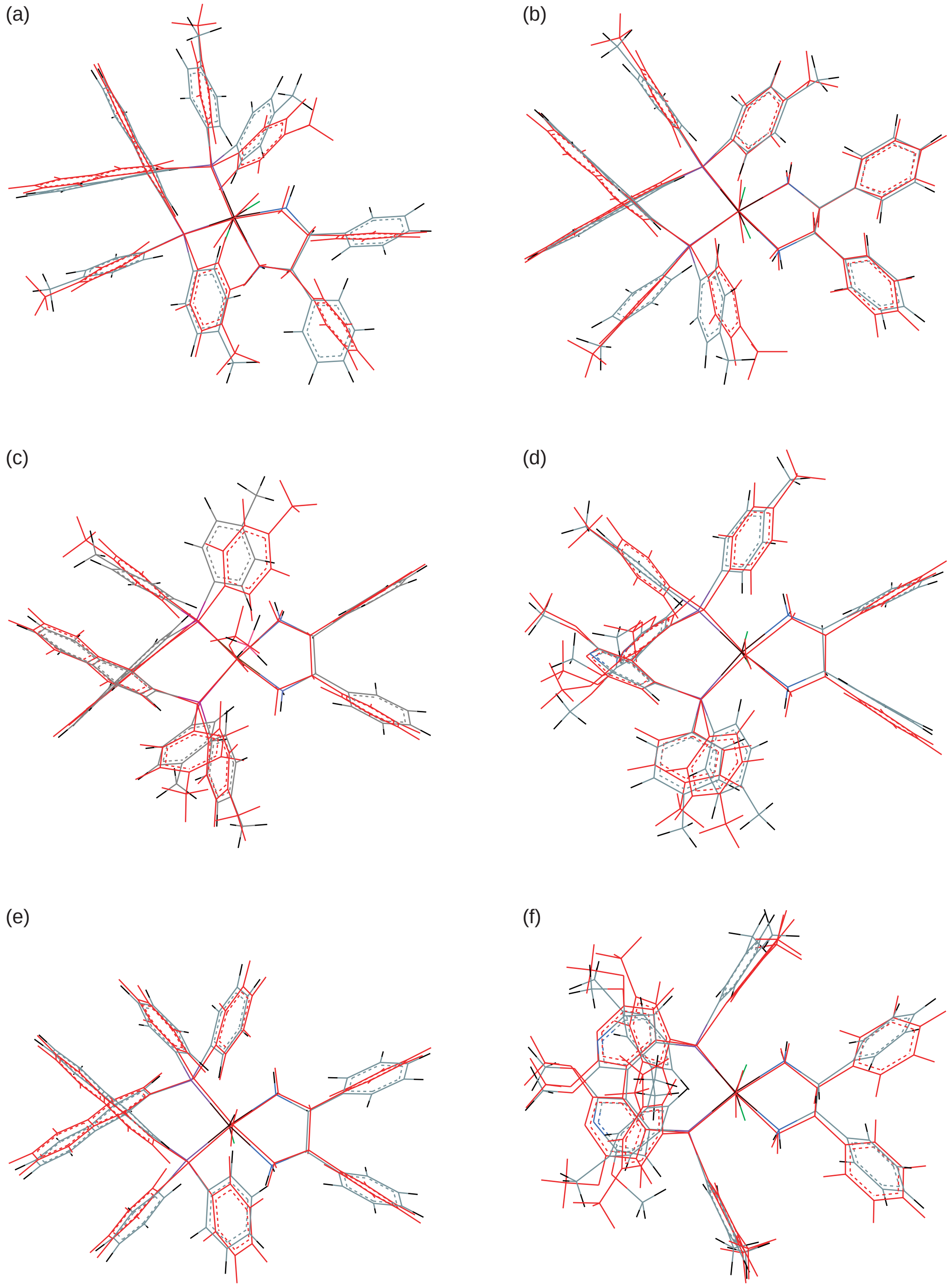

Figure 7. Molecular structures of class 1 complexes A–F. Simulated structures are shown in red. The experimental structures are simply those of the molecules as extracted from the crystal structures and are coloured as follows: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; pink, B; and brown, Ru.

strained with respect to the equilibrium environments of sp^2 and sp^3 carbon atoms. Also, the PPhos complexes appear to have very large nonbonding components; examination of the separate van der Waals and electrostatic components of the nonbonding energy (not shown here) reveals that this is mostly due to the electrostatic contribution, the magnitude of which is almost twice that of the van der Waals contribution (though opposite in sign).

4.2 *Structure and energetics of class 2 complexes*

We can comment on the relative energetics of the class 2 complexes as a function of chirality. It can be noted from figure 13 that the complexes with higher total energies generally have opposite chiralities at the two C atoms of the cyclohexane group, e.g. RR**RS**SS, whilst those with lower total energies generally have both C atoms of the cyclohexane group with the same chirality, e.g. RR**SS**RR.

Table 13. Comparison of experimentally observed and simulated structural parameters for complex A.

Parameter	*Experiment [8]*	*S1*	*S2*	*S3*	*%diff S1*	*%diff S2*	*%diff S3*
Symmetry	$C2$	C_2	$C2$	$P1$			
a	24.5	–	–	24.28264	–	–	−0.9
b	20.533	–	–	20.63401	–	–	0.5
c	24.8	–	–	23.54333	–	–	−5.1
α	90	–	–	90.08948	–	–	0.1
β	119.2	–	–	117.04145	–	–	−1.8
γ	90	–	–	89.80333	–	–	−0.2
Ru1—N1	2.196	2.152	2.152	*2.147*	−2.0	−2.0	−2.2
Ru1—N2	2.185	2.152	2.158	*2.158*	−1.5	−1.2	−1.2
Ru2—N3	2.183		2.151	*2.150*		−1.5	−1.5
Ru2—N4	2.188		2.157	*2.157*		−1.4	−1.4
Ru1—P1	2.282	2.308	2.306	*2.309*	1.1	1.1	1.2
Ru1—P2	2.274	2.308	2.316	*2.311*	1.5	1.8	1.6
Ru2—P3	2.28		2.315	*2.304*		1.5	1.1
Ru2—P4	2.27		2.314	*2.320*		1.9	2.2
Ru1—Cl1	2.42	2.406	2.404	*2.401*	−0.6	−0.7	−0.8
Ru1—Cl2	2.42	2.406	2.401	*2.401*	−0.6	−0.8	−0.8
Ru2—Cl3	2.426		2.401	*2.403*		−1.0	−0.9
Ru2—Cl4	2.409		2.401	*2.402*		−0.3	−0.3
N1—Ru1—N2	77.647	79.716	79.103	*79.328*	2.7	1.9	2.2
N3—Ru2—N4	78.073		79.797	*79.271*		2.2	1.5
P1—Ru1—P2	92.233	94.627	94.738	*95.120*	2.6	2.7	3.1
P3—Ru2—P4	92.472		93.755	*95.064*		1.4	2.8
Cl1—Ru1—Cl2	162.958	173.592	173.439	*174.635*	6.5	6.4	7.2
Cl3—Ru2—Cl4	162.939		172.658	*174.464*		6.0	7.1

Key to simulations: S1, single molecule; S2, crystal (unit cell not relaxed); and S3, crystal (unit cell relaxed). There are no solvent molecules present in this crystal structure. Bond lengths are quoted in Å to 3 d.p., bond angles in ° to 3 d.p., cell parameters in Å to the computed accuracy (5 d.p.). Molecular point group symmetry (for S1) and crystal space group symmetry (for S2 and S3) are computed with a tolerance of 0.01 Å. Italic values are averages of parameters that were formerly equivalent before the $P1$ symmetry was enforced to facilitate simulation with the ESFF.

It is also possible to make some general comments by considering some of the individual energy components in figure 14. For example, highest bond energies are usually found in configurations with like chiralities at the N and C atoms, e.g. R**SSSS**R, with lowest bond energies in configurations like R**SRRS**R where the N chirality is opposite to that at the C atoms. Angle energies are at their highest in complexes such as R**RRSS**R, where each N—C pairing is of like chirality, but opposite to the other; and also in complexes such as R**RRRR**R where the chirality is the same at each of the C and N centres.

Torsional energies are greatest where there is unlike chirality at the C atoms, e.g. RR**RS**SR, and in x**RSRS**x and x**SRSR**x complexes (x = R or S) where there are several chirality changes along the N—C—C—N linkage and the Ns are of opposite chirality to each other, as are the Cs. They are lowest where chirality at the C atoms is the same (e.g. RR**RR**SS) and where there are changes along the N—C—C—N linkage but the Ns are of identical

Table 14. Comparison of experimentally observed and simulated structural parameters for complex F.

Parameter	*Experiment*	*S1*	*S2*	*S3*	*S4*†	*S5*†	*%diff S1*	*%diff S2*	*%diff S3*	*%diff S4*	*%diff S5*
Symmetry	$C2$	C_1	$P2_1$	$P1$	$P1$	$P1$					
a	25.6496	–	–	24.60912	–	25.97651	–	–	−4.1	–	1.3
b	13.0965	–	–	12.88884	–	13.58087	–	–	−1.6	–	3.7
c	20.6948	–	–	19.7461	–	20.74557	–	–	−4.6	–	0.2
α	90	–	–	84.22465	–	89.68184	–	–	−6.4	–	−0.4
β	103.273	–	–	95.28435	–	104.25953	–	–	−7.7	–	1.0
γ	90	–	–	96.95478	–	88.57028	–	–	7.7	–	−1.6
Ru—N1	2.162	2.152	*2.152*	*2.154*	*2.149*	*2.150*	−0.5	−0.5	−0.4	−0.6	−0.6
Ru—N2	2.157	2.152	*2.152*	*2.146*	*2.152*	*2.147*	−0.2	−0.3	−0.5	−0.2	−0.5
Ru—P1	2.282	2.307	*2.316*	*2.306*	*2.314*	*2.319*	1.1	1.5	1.1	1.4	1.6
Ru—P2	2.28	2.307	*2.310*	*2.311*	*2.308*	*2.311*	1.2	1.3	1.4	1.2	1.3
Ru—Cl1	2.422	2.405	*2.404*	*2.404*	*2.404*	*2.405*	−0.7	−0.8	−0.8	−0.7	−0.7
Ru—Cl2	2.424	2.405	*2.404*	*2.404*	*2.400*	*2.401*	−0.8	−0.8	−0.8	−1.0	−0.9
N1—Ru—N2	78.67	79.767	*80.158*	*80.124*	*79.224*	*79.187*	1.4	1.9	1.8	0.7	0.7
P1—Ru—P2	92.3	94.209	*93.635*	*92.955*	*93.932*	*94.717*	2.1	1.4	0.7	1.8	2.6
Cl1—Ru—Cl2	162.09	173.578	*172.453*	*172.498*	*173.562*	*173.770*	7.1	6.4	6.4	7.1	7.2

Key to simulations: S1, single molecule; S2, crystal (unit cell not relaxed); S3, crystal (unit cell relaxed); S4, crystal including solvent molecules (unit cell not relaxed); and S5, crystal including solvent molecules (unit cell relaxed). Bond lengths are quoted in Å to 3 d.p., bond angles in ° to 3 d.p., cell parameters in Å to the computed accuracy (5 d.p.). Molecular point group symmetry (for S1) and crystal space group symmetry (for S2–S5) are computed with a tolerance of 0.01 Å. Italic values are averages of parameters that were formerly equivalent before the $P1$ symmetry was enforced to facilitate simulation with the ESFF.

†Solvents present: dichloromethane and diethylether.

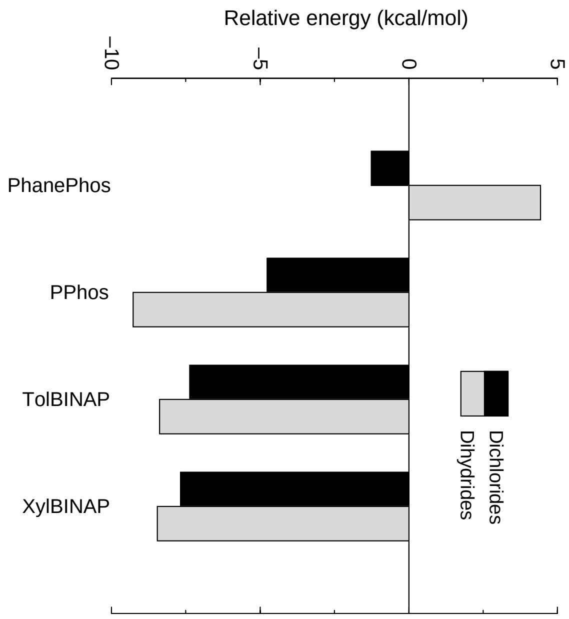

Figure 8. Relative energies of matching class 1 dichlorides and dihydrides (R/RR and S/SS) with respect to the analogous mismatching complex (R/SS and S/RR).

chirality, as are the Cs, i.e. x**RSSR**x and x**SRRS**x complexes. Further work is in progress to examine these trends.

5. Conclusion

We have shown in this paper that the ESFF can be used to provide accurate information about the structures and energetics of ground-state organometallic complexes. Whilst higher-level calculations using a quantum-mechanical description will be necessary for a full investigation of reaction pathways and transition states, molecular modelling with the ESFF is a high-throughput method

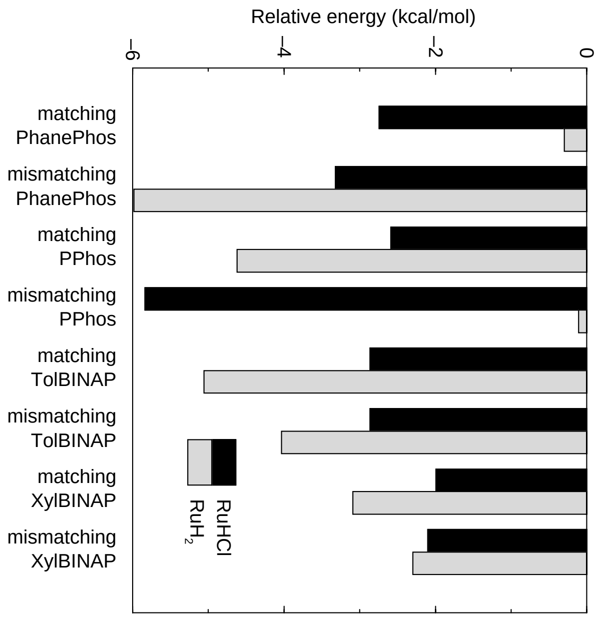

Figure 9. Energies of RuHCl and RuH_2 complexes relative to that of the corresponding $RuCl_2$ complex.

Table 15. Comparison of experimentally observed and simulated structural parameters for complex G.

Parameter	*Experiment [5]*	*S1*	*S2*	*S3*	*S4*†	*S5*†	*% diff S1*	*% diff S2*	*% diff S3*	*% diff S4*	*% diff S5*
Symmetry	$P2_12_12_1$	C_1	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$					
a	12.946	–	–	12.69926	–	12.94522	–	–	−1.9	–	0.0
b	34.8	–	–	33.88715	–	33.66742	–	–	−2.6	–	−3.3
c	9.994	–	–	9.94906	–	10.15424	–	–	−0.4	–	1.6
α	90	–	–	88.33176	–	89.99999	–	–	−1.9	–	0.0
β	90	–	–	91.56357	–	89.99999	–	–	1.7	–	0.0
γ	90	–	–	90.2087	–	90	–	–	0.2	–	0.0
Ru—N1	2.14	2.167	2.166	2.165	2.165	2.165	1.3	1.2	1.2	1.2	1.2
Ru—N2	2.164	2.167	2.167	2.169	2.164	2.164	0.1	0.1	0.2	0.0	0.0
Ru—P1	2.297	2.327	2.344	2.347	2.341	2.339	1.3	2.0	2.2	1.9	1.8
Ru—P2	2.29	2.32	2.317	2.314	2.318	2.318	1.3	1.2	1.0	1.2	1.2
Ru—Cl1	2.409	2.41	2.408	2.407	2.407	2.407	0.0	0.0	−0.1	−0.1	−0.1
Ru—Cl2	2.43	2.41	2.407	2.408	2.403	2.402	−0.8	−0.9	−0.9	−1.1	−1.2
N1—Ru—N2	80.347	80.713	*80.918*	*80.550*	81.152	81.387	0.5	0.7	0.3	1.0	1.3
P1—Ru—P2	98.539	95.27	*95.477*	*95.850*	94.910	94.994	−3.3	−3.1	−2.7	−3.7	−3.6
Cl1—Ru—Cl2	164.213	174.774	*173.129*	*173.771*	172.437	172.354	6.4	5.4	5.8	5.0	5.0

Key to simulations: S1, single molecule; S2, crystal (unit cell not relaxed); S3, crystal (unit cell relaxed); S4, crystal including solvent molecules (unit cell not relaxed); and S5, crystal including solvent molecules (unit cell relaxed). Bond lengths are quoted in Å to 3 d.p., bond angles in ° to 3 d.p., cell parameters in Å to the computed accuracy (5 d.p.). Molecular point group symmetry (for S1) and crystal space group symmetry (for S2–S5) are computed with a tolerance of 0.01 Å. Italic values are averages of parameters that were formerly equivalent before the $P1$ symmetry was enforced to facilitate simulation with the ESFF.

† Solvent present: toluene.

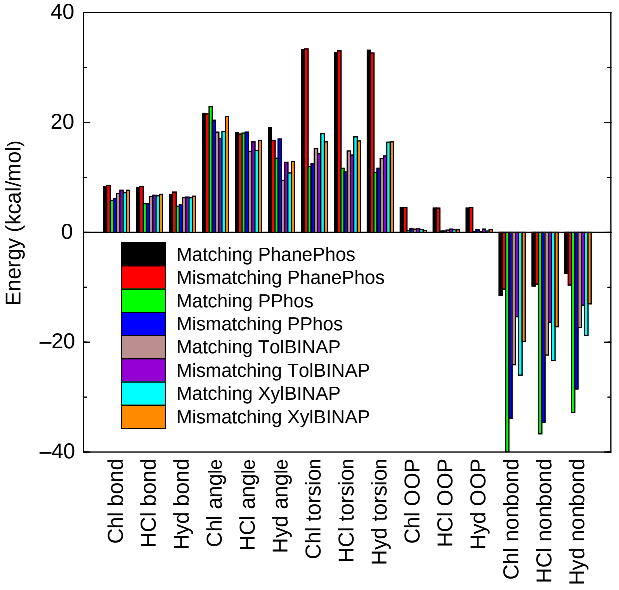

Figure 10. Comparison of energy components in $RuCl_2$ (Chl), RuHCl (HCl) and RuH_2 (Hyd) complexes.

upon which further calculations at the quantum-mechanical level may be based. We envisage that such calculations will be the subject of a future paper.

Acknowledgements

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A Data tables

Tables A1–A4: Comparison of experimentally observed and simulated structural parameters for Ru-based homogeneous catalyst precursors. Key to simulations: S1, single molecule; S2, crystal (unit cell not relaxed); S3, crystal (unit cell relaxed); S4, crystal including solvent molecules (unit cell not relaxed); and S5, crystal including solvent molecules (unit cell relaxed). Where no parameters are quoted for S4 and S5, there are no solvent molecules present in the crystal structure. Bond lengths are quoted in Å to 3 d.p., bond angles in ° to 3 d.p., cell parameters in Å to the computed accuracy (5 d.p.). Molecular point group symmetry (for S1) and crystal space group symmetry (for S2–5) are computed with a tolerance of 0.01 Å. Italic values are averages of parameters that were formerly equivalent before the *P*1 symmetry was enforced to facilitate simulation with the ESFF.

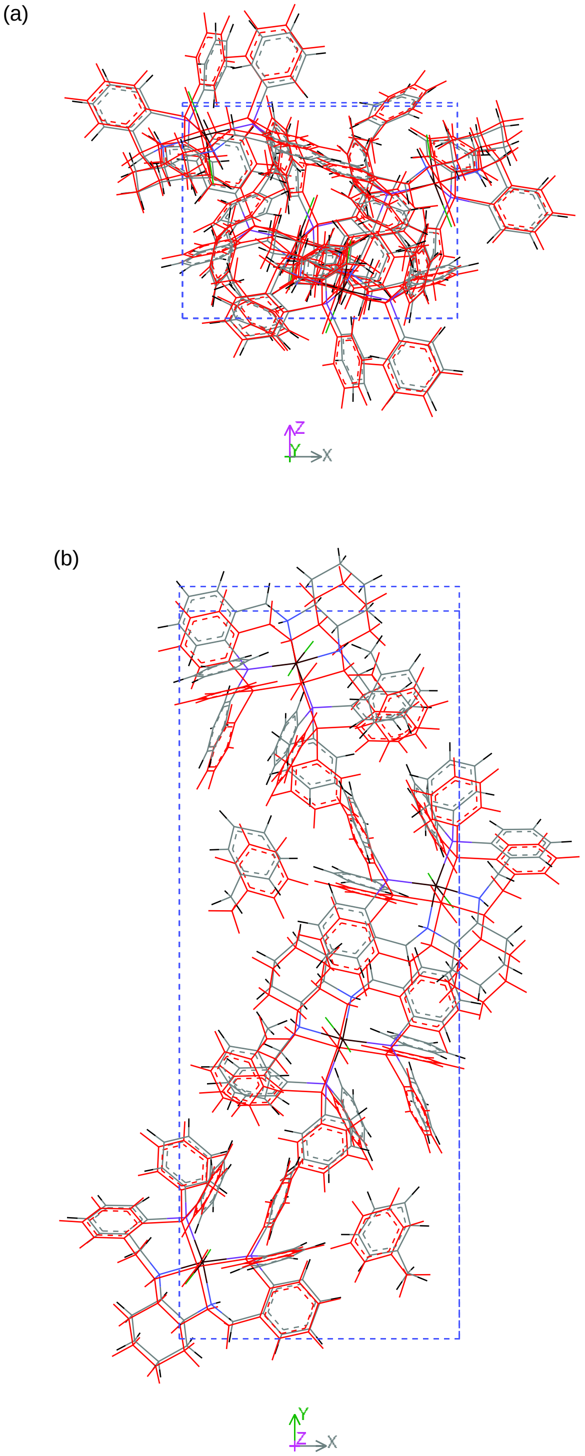


Figure 11. Crystal structure of the class 2 complex G. Optimised simulated structure shown in red. In experimental structure: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; and brown, Ru. Dotted lines indicate unit cells.

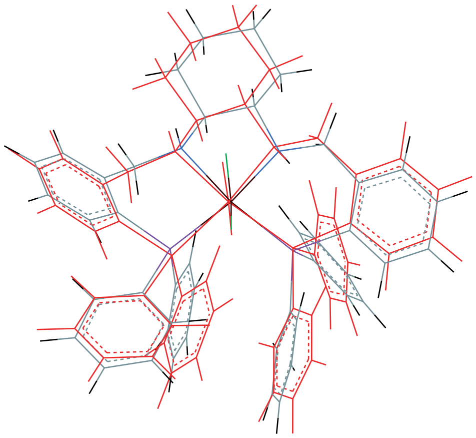
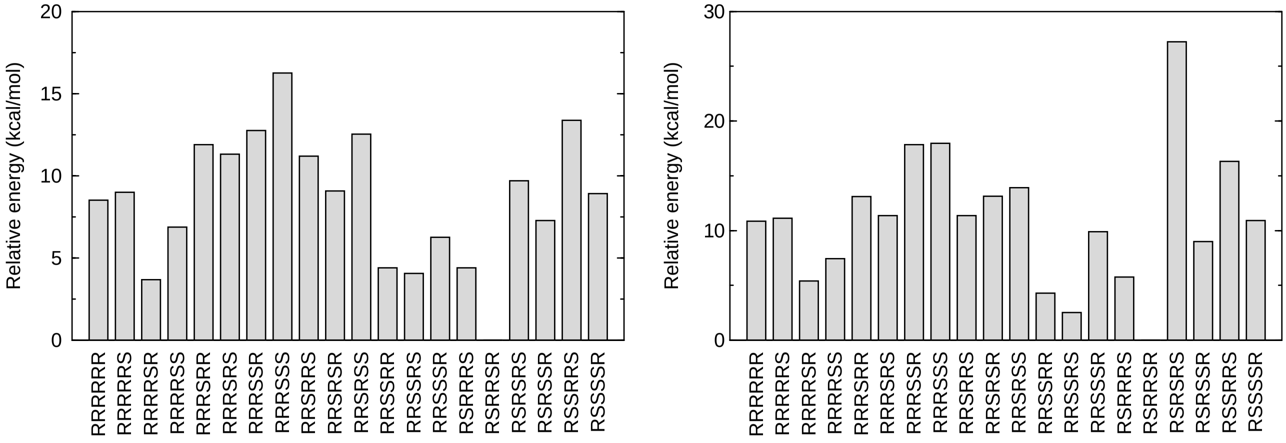
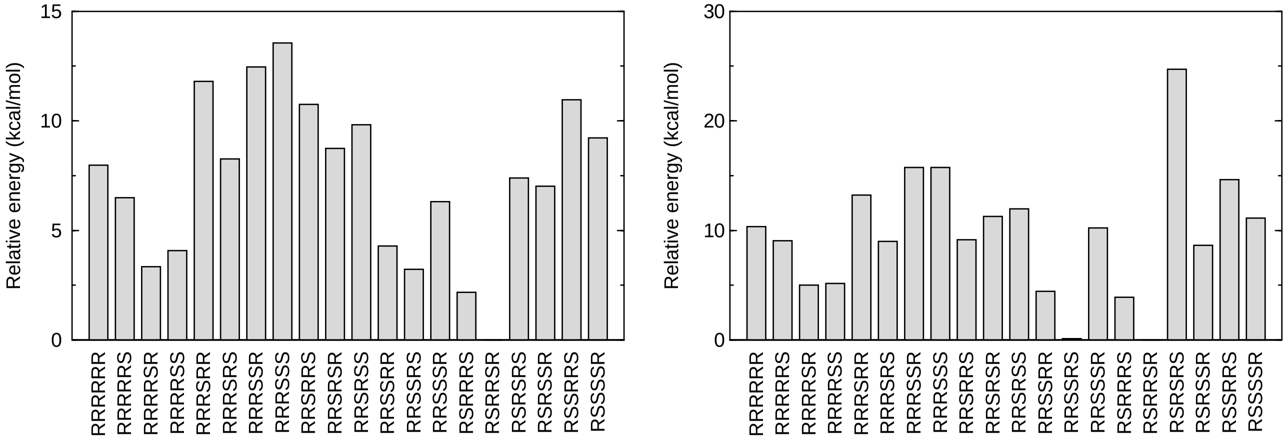


Figure 12. Molecular structure of the class 2 complex G. Simulated structure shown in red. The experimental structure is simply that of the molecule as extracted from the crystal structure and is coloured as follows: black, H; grey, C; red, O; blue, N; purple, P; green, Cl; and brown, Ru.



(a) 2a—dihydrides

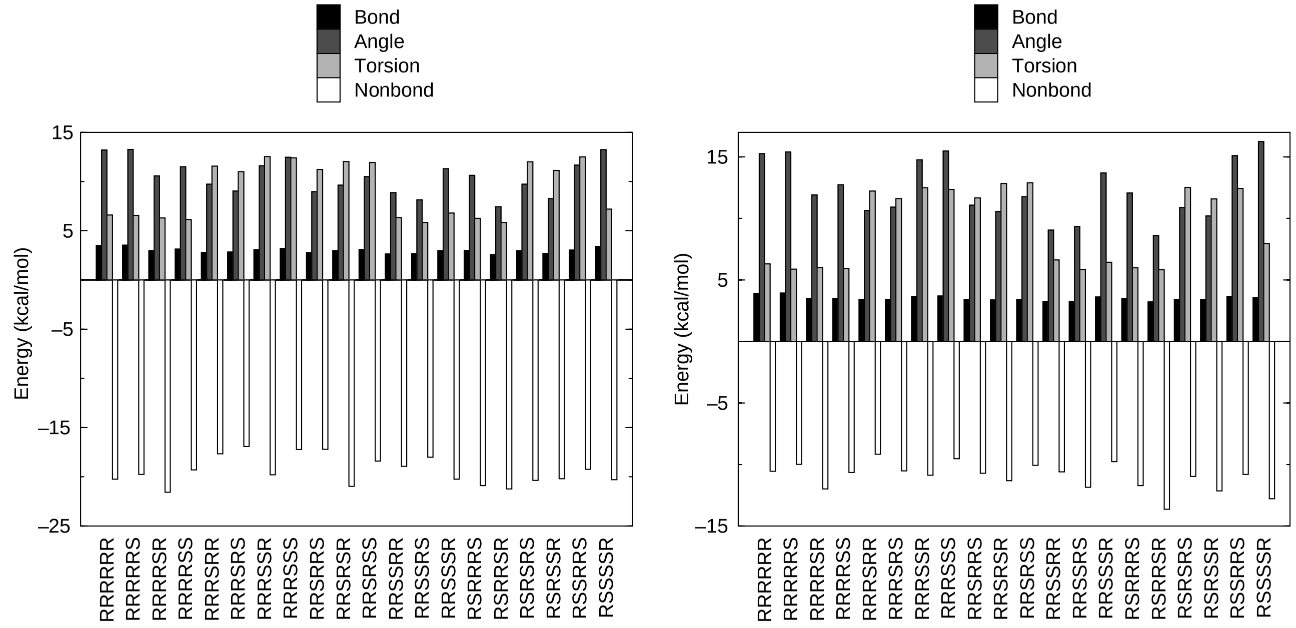
(b) 2a—dichlorides



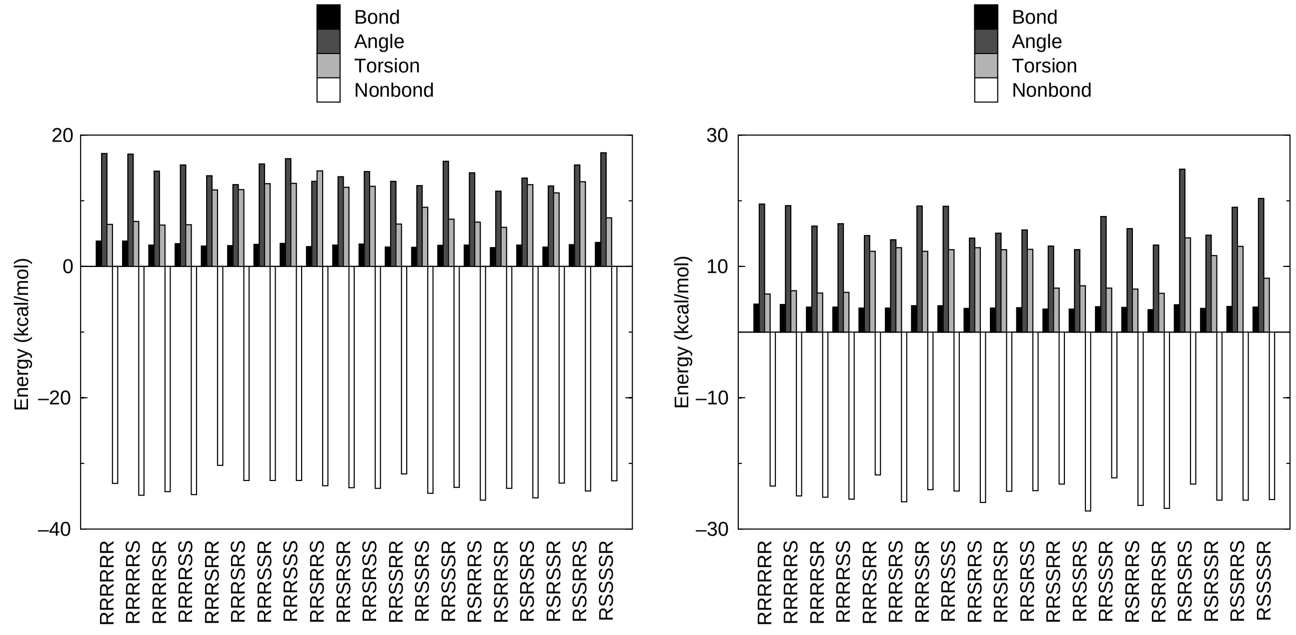
(c) 2b—dihydrides

(d) 2b—dichlorides

Figure 13. Energies of 2a and 2b complexes relative to the relevant RSRRSR (lowest-energy) complex.



(a) 2a—dihydrides (b) 2a—dichlorides



(c) 2b—dihydrides (d) 2b—dichlorides

Figure 14. Bonding (bond, angle, torsion) and nonbonding (= van der Waals + electrostatic) energy components of 2a and 2b complexes. Out-of-plane energies are negligible and thus not plotted. (a) 2a, dihydrides; (b) 2a, dichlorides; (c) 2b, dihydrides; and (d) 2b, dichlorides.

Table A1. Complex B.

Parameter	*Experiment* [8]	*S1*	*S2*	*S3*	*%diff S1*	*%diff S2*	*%diff S3*
Symmetry	*C*2	C_2	*C*2	*C*2			
a	24.74	–	–	24.6725	–	–	− 0.3
b	20.49	–	–	20.85462	–	–	1.8
c	25.04	–	–	24.81514	–	–	− 0.9
α	90	–	–	90.00163	–	–	0.0
β	120.79	–	–	123.7184	–	–	2.4
γ	90	–	–	89.99876	–	–	0.0
Ru1—N1	2.141	2.153	2.149	2.147	0.6	0.4	0.3
Ru1—N2	2.189	2.153	2.159	2.161	− 1.6	− 1.4	− 1.3
Ru2—N3	2.187		2.157	2.158		− 1.4	− 1.3
Ru2—N4	2.140		2.150	2.151		0.5	0.5
Ru1—P1	2.276	2.309	2.316	2.316	1.4	1.8	1.8
Ru1—P2	2.296	2.309	2.314	2.312	0.6	0.8	0.7
Ru2—P3	2.301		2.322	2.324		0.9	1.0
Ru2—P4	2.275		2.312	2.308		1.6	1.5
Ru1—Cl1	2.408	2.406	2.401	2.400	− 0.1	− 0.3	− 0.3
Ru1—Cl2	2.426	2.406	2.403	2.401	− 0.8	− 0.9	− 1.0
Ru2—Cl3	2.412		2.402	2.402		− 0.4	− 0.4
Ru2—Cl4	2.416		2.403	2.401		− 0.5	− 0.6
N1—Ru1—N2	77.991	79.672	79.726	79.517	2.2	2.2	2.0
N3—Ru2—N4	78.375		79.696	79.554		1.7	1.5
P1—Ru1—P2	91.500	94.420	93.774	93.947	3.2	2.5	2.7
P3—Ru2—P4	91.377		93.861	94.285		2.7	3.2
Cl1—Ru1—Cl2	163.230	173.563	172.653	173.168	6.3	5.8	6.1
Cl3—Ru2—Cl4	163.002		172.520	173.167		5.8	6.2

Table A2. Complex C.

Parameter	*Experiment* [10]	*S1*	*S2*	*S3*	*%diff 1*	*%diff 2*	*%diff 3*
Symmetry	$P2_12_12_1$	C_1	$P2_12_12_1$	$P2_12_12_1$			
a	15.722	–	–	15.18768	–	–	− 3.4
b	27.7418	–	–	26.31049	–	–	− 5.2
c	30.0706	–	–	29.74026	–	–	− 1.1
α	90	–	–	90.00045	–	–	0.0
β	90	–	–	90.00091	–	–	0.0
γ	90	–	–	90.00075	–	–	0.0
Ru1—N1	2.159	2.153	2.147	2.144	− 0.3	− 0.6	− 0.7
Ru1—N2	2.182	2.144	2.155	2.154	− 1.7	− 1.2	− 1.3
Ru2—N3	2.14		2.145	2.140		0.2	0.0
Ru2—N4	2.163		2.149	2.148		− 0.6	− 0.7
Ru1—P1	2.233	2.288	2.294	2.287	2.5	2.7	2.4
Ru1—P2	2.24	2.289	2.297	2.301	2.2	2.5	2.7
Ru2—P3	2.219		2.299	2.289		3.6	3.2
Ru2—P4	2.233		2.290	2.291		2.6	2.6
Ru1—H(nbr)[†]	1.576	1.763	1.770	1.768	11.9	12.3	12.2
Ru1—H(br)[†]	1.734	1.864	1.876	1.873	7.5	8.2	8.0
Ru2—H(nbr)[†]	1.521		1.767	1.768		16.2	16.2
Ru2—H(br)[†]	1.736		1.874	1.869		7.9	7.7
N1—Ru1—N2	78.001	79.58	79.395	79.215	2.0	1.8	1.6
N3—Ru2—N4	76.862		79.713	80.168		3.7	4.3
P1—Ru1—P2	90.661	93.783	93.090	93.109	3.4	2.7	2.7
P3—Ru2—P4	91.865		93.965	94.854		2.3	3.3
H(br)—Ru1—H(nbr)[†]	167.875	175.047	176.061	176.609	4.3	4.9	5.2
H(br)—Ru2—H(nbr)[†]	172.635		175.331	175.849		1.6	1.9

Note: There are hexane and THF solvent molecules present in the crystal structure, but the hexane molecules are disordered over two positions and there is insufficient information available from experiment to enable the structure to be simulated with solvents included.

[†] nbr, non-bridging hydrogen; br, bridging hydrogen; and Ru-H bond lengths poorly constrained by experiment.

Table A3. Complex D.

Parameter	*Experiment* [11]	*S1*	*S2*	*S3*	*%diff S1*	*%diff S2*	*%diff S3*
Symmetry	$C2$	C_1	$C2$	$C2$			
a	25.073	–	–	23.43335	–	–	−6.5
b	17.012	–	–	17.46209	–	–	2.6
c	13.935	–	–	14.04595	–	–	0.8
α	90	–	–	90.00001	–	–	0.0
β	91.307	–	–	90.71463	–	–	−0.6
γ	90	–	–	90.0002	–	–	0.0
Ru—N1	2.141	2.153	2.155	2.156	0.6	0.7	0.7
Ru—N2	2.179	2.153	2.151	2.149	−1.2	−1.3	−1.4
Ru—P1	2.267	2.312	2.31	2.306	2.0	1.9	1.7
Ru—P2	2.277	2.304	2.309	2.305	1.2	1.4	1.2
Ru—Cl1	2.406	2.408	2.404	2.402	0.1	−0.1	−0.2
Ru—Cl2	2.429	2.406	2.407	2.408	−0.9	−0.9	−0.9
N1—Ru—N2	77.82	79.512	79.395	79.461	2.2	2.0	2.1
P1—Ru—P2	94.36	93.898	94.567	95.088	−0.5	0.2	0.8
Cl1—Ru—Cl2	166.06	173.308	175.764	176.109	5.6	5.8	6.1

Table A4. Complex E.

Parameter	*Experiment* [12]	*S1*	*S2*	*S3*	*S4*†	*S5*†	*%diff S1*	*%diff S2*	*%diff S3*	*%diff S4*
Symmetry	$P2_12_12_1$	C_1	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$				
a	10.6219	–	–	10.96125	–	10.58275	–	–	3.2	–
b	13.2088	–	–	13.14907	–	13.04588	–	–	−0.5	–
c	36.5984	–	–	34.66105	–	37.07671	–	–	−5.3	–
α	90	–	–	89.99999	–	90.00019	–	–	0.0	–
β	90	–	–	89.99999	–	90.00006	–	–	0.0	–
γ	90	–	–	89.99442	–	90.00001	–	–	0.0	–
Ru—N1	2.164	2.15	*2.148*	2.148	2.145	2.145	−0.6	−0.7	−0.7	−0.9
Ru—N2	2.198	2.154	*2.159*	2.159	2.158	2.158	−2.0	−1.8	−1.8	−1.8
Ru—P1	2.224	2.301	*2.291*	2.288	2.291	2.291	3.5	3.0	2.9	3.0
Ru—P2	2.238	2.296	*2.311*	2.308	2.308	2.306	2.6	3.3	3.1	3.1
Ru—H‡	1.55	1.76	*1.759*	1.759	1.760	1.760	13.5	13.5	13.5	13.5
Ru—Cl	2.571	2.405	*2.403*	2.403	2.404	2.405	−6.5	−6.5	−6.5	−6.5
N—Ru—N	78.22	79.818	*79.373*	79.405	79.822	79.765	2.0	1.5	1.5	2.0
P—Ru—P	92.25	94.457	*94.723*	94.711	94.287	94.083	2.4	2.7	2.7	2.2
H—Ru—Cl	167.7	175.863	*175.594*	175.895	177.498	177.717	4.9	4.7	4.9	5.8

† Solvent present: THF.

‡ Ru—H bond length poorly constrained by experiment.

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Supplementary information for paper "A molecular mechanics investigation of the structures and energetics of two classes of Ru(II) complexes with applications in homogeneous catalysis" (Palin et al.)

For atom equivalences in angle and torsion terms, see table 2 in the main part of this paper. Labels for complexes are identical to those in the main paper .

Table S-1. Bond parameters for simulation of A and B.

Atoms types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o *(Å)*
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
cp—cp[†]	1	92.84087	1.78338	1.47625
cp—cp[‡]	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl	1	76.21987	2.06388	2.40813
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

[†] cp—cp bond joining naphthyl groups in BINAP.
[‡] All other cp—cp bonds.

Table S-2. Angle parameters for simulation of A and B.

Atoms types i—j—k	*i—j—k angle type*	K_a *(kcal mol^{-1})*	θ_a^o (°)
c—c—cp	Exocyclic	39.61136	113.3026
c—c—h	Exocyclic	36.72293	109.31218
c—c=—cp	Free	39.68756	120.40071
c—na—h*	Exocyclic	37.44733	111.81867
c—na—Ru026	Endocyclic	61.47563	112.27731
cl—Ru026—cl	Linear	47.36236	N/A
cl—Ru026—na	Perpendicular	52.00791	N/A
cl—Ru026—p	Perpendicular	44.42497	N/A
cp—c—h	Free	36.60359	110.15146
cp—c=—cp[†]	Free	39.48518	120.69128
cp—c=—cp[‡]	Free	39.48518	121.43308
cp—c=—h	Free	36.17768	118.90658
cp—p—cp	Free	32.65196	100.62694
h—c—h	Free	34.65328	107.29538
h*—na—h*	Free	33.75864	106.33327
h*—na—Ru026	Exocyclic	40.27512	111.74849
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—na	Endocyclic	59.92359	84.72708
p—c=—cp	Free	36.46393	118.36999
p—Ru026—na	Planar	47.0028	N/A
p—Ru026—p	Planar	42.795	N/A
Ru026—p—cp	Free	36.9934	114.82283

[†] All angles of this type except those involving central BINAP bond.
[‡] Angles of this type involving central BINAP bond.

Table S-3. Torsion parameters for simulation of A and B.

Atoms types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t (kcal mol^{-1})
Ko—p—cp—cp	1	Free	Free	0.11898
cp—p—cp—cp	1	Free	Free	0.11898
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—c—c—h	1	Exocyclic	Exocyclic	0.15806
cp—cp—cp—cp	1	Free	Free	0.895
c—c—cp—cp	1	Exocyclic	Free	0.10422
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—cp—cp	1	Free	Free	0.10422
c—cp—cp—cp	1.5	Free	Free	3.16825
c—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
h—cp—cp—h	1.5	Free	Free	3.16825
p—cp—cp—cp	1.5	Free	Free	3.16825
p—cp—cp—h	1.5	Free	Free	3.16825

Table S-4. van der Waals parameters for A and B.

Atom type	ϵ_0	r_0	*Notes*
c	4.022160	0.051134	c in DPEN
c	4.040293	0.051134	c in Me of tolyl and xylyl groups
cl	4.181166	0.214743	
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.998049	0.062367	cp bonded to carbon (cp)
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (c)
h*	1.575370	0.015836	
na	3.809074	0.072656	
p	4.488726	0.209681	
Ru026	3.952810	0.447049	

Table S-5. Bond parameters for simulation of C.

Atoms types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o *(Å)*
b—h	1	80.02574	1.732	1.20603
b—hb	1	81.76959	1.75275	1.29496
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
cp—cp†	1	92.84087	1.78338	1.47625
cp—cp‡	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
p—cp	1	68.55895	1.70576	1.83522
Ru026—h	1	92.27285	1.93883	1.76368
Ru026—hb	dative	89.80118	1.95599	1.87511
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

† cp—cp bond joining naphthyl groups in BINAP.
‡ All other cp—cp bonds.

Table S-6. Angle parameters for simulations of C.

Atoms types i—j—k	*i—j—k angle type*	K_a *(kcal mol^{-1})*	θ_a^o *(°)*
c—c—cp	Exocyclic	39.61136	113.3026
c—c—h	Exocyclic	36.72293	109.31218
c—c═—cp	Free	39.68756	120.40071
c—na—h*	Exocyclic	37.44733	111.81867
cp—c—h	Free	36.60359	110.15146
cp—c═—cp	Free	39.48518	120.69128
cp—c═—h	Free	36.17768	118.90658
cp—p—cp	Free	32.65196	100.62694
h—b—h	Free	63.04148	105.64188
h—b—hb	Free	61.91486	107.02155
h—c—h	Free	34.65328	107.29538
h—Ru026—hb	Planar	41.51865	N/A
h*—na—h*	Free	33.75864	106.33327
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—h	Perpendicular	46.76726	N/A
na—Ru026—hb	Perpendicular	43.17456	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
p—c═—cp	Free	36.46393	118.36999
p—Ru026—h†	Planar	42.7183	N/A
p—Ru026—h‡	Perpendicular	42.7183	N/A
p—Ru026—hb†	Planar	41.5483	N/A
p—Ru026—hb‡	Perpendicular	41.5483	N/A
p—Ru026—na¶	Perpendicular	47.0028	N/A
p—Ru026—na§	Planar	47.0028	N/A
p—Ru026—na‖	Linear	47.0028	N/A
p—Ru026—p	Perpendicular	42.795	N/A
Ru026—h*—b	Free	38.9549	180
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—cp	Free	36.9934	114.82283

† Angles of this type involving P1 atom.
‡ Angles of this type involving P2 atom.
¶ P1—Ru—N1 angle.
§ P1—Ru—N2 angle.
‖ P2—Ru—N1 angle.

Table S-7. Torsion parameters for simulation of C.

Atoms types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t *(kcal mol^{-1})*
c—c—cp—cp	1	Exocyclic	Free	0.10422
c—cp—cp—cp	1.5	Free	Free	3.16825
c—cp—cp—h	1.5	Free	Free	3.16825
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—c—c—h	1	Exocyclic	Exocyclic	0.15806
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—cp	1	Free	Free	0.895
cp—p—cp—cp	1	Free	Free	0.11898
h—b—h*—Ko	1	Free	Free	0.35563
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—cp—cp	1	Free	Free	0.10422
h—cp–cp—h	1.5	Free	Free	3.16825
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
p—cp—cp—cp	1.5	Free	Free	3.16825
p—cp—cp—h	1.5	Free	Free	3.16825

Table S-8. van der Waals parameters for simulation of C.

Atom type	ϵ_0	r_0	*Notes*
c	4.022160	0.051134	c in DPEN
c	4.040293	0.051134	c in Me of tolyl and xylyl groups
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.998049	0.062367	cp bonded to carbon (cp)
h	3.493428	0.016475	h (i.e. non—bridging) in BH_4 group
h	2.745430	0.023386	Hydride: h bonded to Ru026
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (c)
hb	1.835219	0.014139	
h*	1.575370	0.015836	
Ru026	3.819128	0.495826	
na	3.793288	0.074991	
b	4.386683	0.032232	
p	4.460263	0.220460	

Table S-9. Bond parameters for simulation of D.

Atoms types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o *(Å)*
c—c	1	87.5	1.80771	1.52825
c—h	1	96.58211	1.84395	1.10628
cp—c	1	90.51843	1.79546	1.50174
cp—cp[†]	1	92.84087	1.78338	1.47625
cp—cp[‡]	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
np—cp	1.5	127.15352	1.92564	1.33168
o—c	1	87.99588	2.07423	1.41763
o—cp	1	86.61671	2.05812	1.35479
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl	1	76.21987	2.06388	2.40813
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.1691	1.94405	2.28213

[†] cp—cp bond joining naphthyl groups in BINAP.
[‡] All other cp—cp bonds.

Table S-10. Angle parameters for simulation of D.

Atoms types i—j—k	*i—j—k angle type*	K_a (*kcal mol^{-1}*)	θ_a^o (°)
c—c—cp	Exocyclic	39.61136	113.3026
c—na—Ru026	Endocyclic	61.47563	112.27731
cl—Ru026—cl	Linear	47.36236	N/A
cl—Ru026—na	Perpendicular	52.00791	N/A
cl—Ru026—p	Perpendicular	44.42497	N/A
cp—c—h	Free	36.60359	110.15146
cp—c=—c	Free	39.68756	120.40071
cp—c=—cp[†]	Free	39.48518	120.69128
cp—c=—cp[‡]	Free	39.48518	121.43308
cp—c=—h	Free	36.17768	118.90658
cp—c=—np	Free	30.75736	119.76141
cp—n=—cp	Free	50.07563	111.64555
cp—o—c	Free	52.56115	110.68582
cp—p—cp	Free	32.65196	100.62694
cp—p—Ru026	Free	36.9934	114.82283
h—c—c	Exocyclic	36.72293	109.31218
h—c—h	Free	34.65328	107.29538
h*—na—c	Exocyclic	37.44733	111.81867
h*—na—h*	Free	33.75864	106.33327
h*—na—Ru026	Exocyclic	40.27512	111.74849
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—na	Endocyclic	59.92359	84.72708
o—c—h	Free	42.10816	108.16316
o—c=—cp	Free	48.82026	119.22076
o—c=—np	Free	32.40933	118.279
p—c=—cp	Free	36.46393	118.36999
p—Ru026—na	Planar	47.0028	N/A
p—Ru026—p	Planar	42.795	N/A

[†] All angles of this type except those involving central BINAP bond.
[‡] Angles of this type involving central BINAP bond.

Table S-11. Torsion parameters for simulation of D.

Atoms types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t (*kcal mol^{-1}*)
c—c—cp—cp	1	Exocyclic	Free	0.10422
c—o—cp—cp	1	Free	Free	0.9975
c—o—cp—np	1	Free	Free	0.9975
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—cp—c—h	1	Free	Free	0.10422
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—o	1.5	Free	Free	3.16825
cp—cp—cp—np	1.5	Free	Free	3.16825
cp—cp—cp—cp	1	Free	Free	0.895
cp—cp—cp—c	1.5	Free	Free	3.16825
cp—np—cp—o	1.5	Free	Free	5.16825
cp—np—cp—cp	1.5	Free	Free	5.16825
cp—o—c—h	1	Free	Free	0.30542
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—c—cp	1	Exocyclic	Exocyclic	0.15806
h—cp—cp—o	1.5	Free	Free	3.16825
h—cp—cp—np	1.5	Free	Free	3.16825
h—cp—cp—h	1.5	Free	Free	3.16825
h—cp—cp—c	1.5	Free	Free	3.16825
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
p—cp—cp—h	1.5	Free	Free	3.16825
p—cp—cp—cp	1.5	Free	Free	3.16825

Table S-12. van der Waals parameters for simulations of D.

Atom type	ϵ_0	r_0	*Notes*
c	4.02216	0.051134	c in DPEN
c	4.025547	0.051134	c in OMe group of PPhos
c	4.040293	0.051134	c in Me of tolyl group
cl	4.181166	0.214743	
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.973013	0.062367	cp bonded to nitrogen (np) and oxygen (o) in PPhos
cp	3.998049	0.062367	cp bonded to carbon (cp)
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (cp)
h*	1.57537	0.015836	
na	3.809074	0.072656	
np	3.754782	0.067728	
o	3.648581	0.078033	
p	4.488726	0.209681	
Ru026	3.95281	0.447049	

Table S-13. Bond parameters for simulation of E.

Atom types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o *(Å)*
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
cp—cp†	1	92.84087	1.78338	1.47625
cp—cp‡	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
o—c¶	1	87.99588	2.07423	1.41763
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl	1	76.21987	2.06388	2.40813
Ru026—h	1	92.27285	1.93883	1.76368
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

† cp—cp bond joining naphthyl groups in BINAP.
‡ All other cp—cp bonds.
¶ Indicates parameters used only in simulations including solvent molecules.

Table S-14. Angle parameters for simulation of E.

Atom types i—j—k	*i—j—k angle type*	K_a *(kcal mol^{-1})*	θ_a^o (°)
c—c—cp	Exocyclic	39.61136	113.3026
c—c—h	Exocyclic	36.72293	109.31218
c—c═—cp	Free	39.68756	120.40071
c—na—h*	Exocyclic	37.44733	111.81867
c—o—¶	Endocyclic	52.91066	109.47978
cp—c—h	Free	36.60359	110.15146
cp—c═—cp†	Free	39.48518	120.69128
cp—c═—cp‡	Free	39.48518	121.43308
cp—c═—h	Free	36.17768	118.90658
cp—p—cp	Free	32.65196	100.62694
h—Ru026—cl	Linear	44.28674	N/A
h*—na—h*	Free	33.75864	106.33327
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—cl	Perpendicular	52.00791	N/A
na—Ru026—h	Perpendicular	46.76726	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
o—c—c¶	Endocyclic	47.76368	104.52967
o—c—h¶	Exocyclic	42.10816	108.38818
p—c═—cp	Free	36.46393	118.36999
p—Ru026—cl	Perpendicular	44.42497	N/A
p—Ru026—h	Perpendicular	42.7183	N/A
p—Ru026—na	Planar	47.0028	N/A
p—Ru026—p	Planar	42.795	N/A
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—cp	Free	36.9934	114.82283

† All angles of this type except those involving central BINAP bond.
‡ Angles of this type involving central BINAP bond.
¶ Indicates parameters used only in simulations including solvent molecules.

Table S-15. Torsion parameters for E.

Atom types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t *(kcal mol^{-1})*
c—c—cp—cp	1	Exocyclic	Free	0.10422
c—cp—cp—cp	1.5	Free	Free	3.16825
c—cp—cp—h	1.5	Free	Free	3.16825
c—o—c—c†	1	Endocyclic	Endocyclic	0.30542
c—o—c—h†	1	Endocyclic	Exocyclic	0.30542
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—c—c—h	1	Exocyclic	Exocyclic	0.15806
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—cp	1	Free	Free	0.895
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—cp—cp	1	Free	Free	0.10422
h—cp—cp—h	1.5	Free	Free	3.16825
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
o—c—c—c†	1	Endocyclic	Endocyclic	0.15806
o—c—c—h†	1	Endocyclic	Exocyclic	0.15806
p—cp—cp—cp	1.5	Free	Free	3.16825
p—cp—cp—h	1.5	Free	Free	3.16825

† Indicates parameters used only in simulations including solvent molecules.

Table S-16. van der Waals parameters used in simulations of E.

Atom type	ϵ_0	r_0	*Notes*
c	4.022160	0.051134	c in DPEN
c	4.021510†	0.051134†	c adjacent to oxygen in THF
c	4.039090†	0.051134†	c not adjacent to oxygen in THF
cl	4.193871	0.206314	
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.998049	0.062367	cp bonded to carbon (cp)
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (c)
h	3.054029	0.020697	Hydride: h bonded to Ru026
h*	1.575370	0.015836	
na	3.813300	0.071744	
o	3.650095†	0.078033†	o in THF
p	4.496400	0.205467	
Ru026	4.011353	0.428093	

† Indicates parameters used only in simulations where solvents are included.

Table S-17. Bond parameters for simulation of F.

Atom types i—j	*Bond order*	D_b *(kcal mol^{-1})*	α *(Å^{-1})*	r_b^o (Å)
c—c	1	87.5	1.80771	1.52825
c—cl†	1	74.5553	1.85954	1.75743
c—h	1	96.58211	1.84395	1.10628
cp—c	1	90.51843	1.79546	1.50174
cp—cp‡	1	92.84087	1.78338	1.47625
cp—cp¶	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
cp—np	1.5	127.15352	1.92564	1.33168
cp—o	1	86.61671	2.05812	1.35479
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
o—c	1	87.99588	2.07423	1.41763
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl	1	76.21987	2.06388	2.40813
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

† Indicates parameters used only in simulations including solvent molecules.
‡ cp—cp bond joining naphthyl groups in BINAP.
¶ All other cp—cp bonds.

Table S-18. Angle parameters for simulation of F.

Atom types i—j—k	*i—j—k angle type*	K_a (*kcal mol^{-1}*)	θ_a^o (°)
c—c—h	Exocyclic	36.72293	109.31218
c—c—o[†]	Free	47.76368	111.10537
c—na—h*	Exocyclic	37.44733	111.81867
c—o—c†	Free	52.91066	110.04189
cl—c—cl[†]	Free	45.44201	110.11816
cl—c—h[†]	Free	38.40874	106.80281
cl—Ru026—cl	Linear	47.36236	N/A
cp—c—c	Exocyclic	39.61136	113.3026
cp—c—h	Free	36.60359	110.15146
cp—c═—c	Free	39.68756	120.40071
cp—c═—cp[‡]	Free	39.48518	120.69128
cp—c═—cp[¶]	Free	39.48518	121.43308
cp—c═—h	Free	36.17768	118.90658
cp—c═—np	Free	30.75736	119.76141
cp—c═—o	Free	48.82026	119.22076
cp—n═—cp	Free	50.07563	111.64555
cp—o—c	Free	52.56115	110.68582
cp—p—cp	Free	32.65196	100.62694
h—c—h	Free	34.65328	107.29538
h*—na—h*	Free	33.75864	106.33327
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Exocyclic	50.30486	113.06572
na—c—h	Exocyclic	44.08114	109.22397
na—Ru026—cl	Perpendicular	52.00791	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
na—Ru026—p	Planar	47.0028	N/A
np—c═—o	Free	32.40933	118.279
o—c—h	Free	42.10816	108.16316
p—c═—cp	Free	36.46393	118.36999
p—Ru026—cl	Perpendicular	44.42497	N/A
p—Ru026—p	Planar	42.795	N/A
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—cp	Free	36.9934	114.82283

[†] Indicates parameters used only in simulations including solvent molecules.
[‡] All angles of this type except those involving central BINAP bond.
[¶] Angles of this type involving central BINAP bond.

Table S-19. Torsion parameters for simulation of F.

Atom types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t (*kcal mol^{-1}*)
c—c—cp—cp	1	Exocyclic	Free	0.10422
c—c—o—c†	1	Free	Free	0.30542
cp—c—c—cp	1	Exocyclic	Exocyclic	0.15806
cp—c—c—h	1	Exocyclic	Exocyclic	0.15806
cp—cp—c—h	1	Free	Free	0.10422
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—c	1.5	Free	Free	3.16825
cp—cp—cp—np	1.5	Free	Free	3.16825
cp—cp—cp—o	1.5	Free	Free	3.16825
cp—cp—cp—cp	1	Free	Free	0.895
cp—cp—np—cp	1.5	Free	Free	5.16825
cp—cp—o—c	1	Free	Free	0.9975
cp—o—c—h	1	Free	Free	0.30542
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—c—o[†]	1	Free	Free	0.15806
h—c—o—c[†]	1	Free	Free	0.30542
h—cp—cp—c	1.5	Free	Free	3.16825
h—cp—cp—np	1.5	Free	Free	3.16825
h—cp—cp—o	1.5	Free	Free	3.16825
h—cp—cp—h	1.5	Free	Free	3.16825
h*—na—c—cp	1	Exocyclic	Exocyclic	0.23688
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
Ko—na—c—cp	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—cp	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Exocyclic	Free	0.10422
np—cp—o—c	1	Free	Free	0.9975
o—cp—np—cp	1.5	Free	Free	5.16825
p—cp—cp—cp	1.5	Free	Free	3.16825
p—cp—cp—h	1.5	Free	Free	3.16825

[†] Indicates parameters used only in simulations including solvent molecules.

Table S-20. van der Waals parameters in simulations of F.

Atom type	ϵ_0	r_0	*Notes*
c	4.022160	0.051134	c in DPEN
c	4.025547	0.051134	c in OMe group of PPhos
c	4.040293	0.051134	c in Me of xylyl group
c	4.030928[†]	0.051134[†]	c in dichloromethane
c	4.042989[†]	0.051134[†]	c not adjacent to oxygen in diethylether
c	4.021510[†]	0.051134[†]	c adjacent to oxygen in diethylether
cl	4.181166	0.214743	cl bonded to Ru026
cl	4.132412[†]	0.246367[†]	cl in dichloromethane
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
cp	3.973013	0.062367	cp bonded to nitrogen (np) and oxygen (o) in PPhos
cp	3.998049	0.062367	cp bonded to carbon (cp)
h	2.955159	0.020223	h bonded to carbon (cp)
h	2.987406	0.020223	h bonded to carbon (c)
h*	1.575370	0.015836	
na	3.809074	0.072656	
np	3.754782	0.067728	
o	3.648581	0.078033	o in PPhos
o	3.650095[†]	0.078033[†]	o in diethylether
p	4.488726	0.209681	
Ru026	3.952810	0.477049	

[†] Indicates parameters used only in simulations with solvents included.

Table S-21. Bond parameters for G.

Atom types i—j	*Bond order*	D_b *(kcal mol^{-1})*	*α (Å^{-1})*	r_b^o *(Å)*
c—c	1	87.5	1.80771	1.52825
c—cp	1	90.51843	1.79546	1.50174
c—h	1	96.58211	1.84395	1.10628
cp—cp	1.5	116.67511	1.78338	1.38891
cp—h	1	100.71035	1.83007	1.07879
na—c	1	75.89787	1.99972	1.46806
na—h*	1	91.13657	2.09385	1.00848
p—cp	1	68.55895	1.70576	1.83522
Ru026—cl	1	76.21987	2.06388	2.40813
Ru026—na	dative	69.58337	2.10577	2.16959
Ru026—p	dative	60.16913	1.94405	2.28213

Table S-22. Angle parameters for G.

Atom types i—j—k	*i—j—k angle type*	K_a *(kcal mol^{-1})*	θ^o_a *(°)*
c—c—c	Exocyclic	39.7881	112.45814
c—c—c	Free	39.7881	112.26629
c—c—h	Free	36.72293	109.09128
c—c—h	Exocyclic	36.72293	109.31218
c—c=—cp	Free	39.68756	120.40071
c—na—c	Exocyclic	51.04868	114.24467
c—na—h*	Exocyclic	37.44733	111.81867
c—na—h*	Free	37.44733	107.29783
cl—Ru026—cl	Linear	47.36236	N/A
cp—c—h	Free	36.60359	110.15146
cp—c=—cp	Free	39.48518	120.69128
cp—c=—h	Free	36.17768	118.90658
cp—p—cp	Free	32.65196	100.62694
h—c—h	Free	34.65328	107.29538
na—c—c	Exocyclic	50.68569	112.19548
na—c—c	Endocyclic	50.68569	105.47161
na—c—cp	Free	50.30486	112.86668
na—c—h	Exocyclic	44.08114	109.22397
na—c—h	Free	44.08114	108.99985
na—Ru026—cl	Perpendicular	52.00791	N/A
na—Ru026—na	Endocyclic	59.92359	84.72708
p—c=—cp	Free	36.46393	118.36999
p—Ru026—cl	Perpendicular	44.42497	N/A
p—Ru026—na	Planar	47.0028	N/A
p—Ru026—p	Planar	42.795	N/A
Ru026—na—c	Endocyclic	61.47563	112.27731
Ru026—na—c	Exocyclic	61.47563	116.11432
Ru026—na—h*	Exocyclic	40.27512	111.74849
Ru026—p—cp	Free	36.9934	114.82283

Table S-23. Torsion parameters for G.

Atom types i—j—k—l	*j—k bond order*	*i—j—k angle type*	*j—k—l angle type*	D_t *(kcal mol^{-1})*
c—c—c—c	1	Exocyclic	Free	0.15806
c—c—c—h	1	Exocyclic	Free	0.15806
c—c—c—c	1	Exocyclic	Exocyclic	0.15806
c—c—c—h	1	Exocyclic	Exocyclic	0.15806
c—c—c—c	1	Free	Free	0.15806
c—cp—cp—cp	1.5	Free	Free	3.16825
c—cp—cp—h	1.5	Free	Free	3.16825
c—cp—cp—p	1.5	Free	Free	3.16825
c—na—c—c	1	Exocyclic	Exocyclic	0.23688
c—na—c—c	1	Exocyclic	Endocyclic	0.23688
c—na—c—h	1	Exocyclic	Exocyclic	0.23688
c—na—c—cp	1	Exocyclic	Free	0.23688
c—na—c—h	1	Exocyclic	Free	0.23688
cp—cp—cp—cp	1	Free	Free	0.895
cp—cp—cp—cp	1.5	Free	Free	3.16825
cp—cp—cp—h	1.5	Free	Free	3.16825
cp—cp—cp—p	1.5	Free	Free	3.16825
cp—p—cp—cp	1	Free	Free	0.11898
h—c—c—c	1	Free	Free	0.15806
h—c—c—h	1	Free	Free	0.15806
h—c—c—h	1	Exocyclic	Exocyclic	0.15806
h—c—cp—cp	1	Free	Free	0.10422
h—cp—cp—h	1.5	Free	Free	3.16825
h—cp—cp—p	1.5	Free	Free	3.16825
h*—na—c—c	1	Exocyclic	Exocyclic	0.23688
h*—na—c—c	1	Exocyclic	Endocyclic	0.23688
h*—na—c—h	1	Exocyclic	Exocyclic	0.23688
h*—na—c—cp	1	Free	Free	0.23688
h*—na—c—h	1	Free	Free	0.23688
Ko—na—c—c	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—c	1	Endocyclic	Endocyclic	0.23688
Ko—na—c—h	1	Endocyclic	Exocyclic	0.23688
Ko—na—c—cp	1	Exocyclic	Free	0.23688
Ko—na—c—h	1	Exocyclic	Free	0.23688
Ko—p—cp—cp	1	Free	Free	0.11898
na—c—c—c	1	Exocyclic	Free	0.15806
na—c—c—h	1	Exocyclic	Free	0.15806
na—c—c—na	1	Endocyclic	Endocyclic	0.15806
na—c—c—c	1	Endocyclic	Exocyclic	0.15806
na—c—c—h	1	Endocyclic	Exocyclic	0.15806
na—c—cp—cp	1	Free	Free	0.10422

Table S-24. van der Waals parameters used in simulations of G.

Atom type	ϵ_0	r_0	*Notes*
c	4.024956	0.051134	c in cyclohexane (bonded to N)
c	4.039090	0.051134	c in cyclohexane (not bonded to N)
c	4.026192	0.051134	c bonded to na and cp
c	4.040293	0.051134	c in Me of toluene
cl	4.181166	0.214743	
cp	4.000845	0.062367	cp bonded to carbon (c)
cp	4.004649	0.062367	cp bonded to hydrogen (h)
cp	3.999249	0.062367	cp bonded to phosphorus (p)
h	2.987406	0.020223	h bonded to carbon (c)
h	2.955159	0.020223	h bonded to carbon (cp)
h*	1.575370	0.015836	
na	3.806958	0.072656	
p	4.488726	0.209681	
Ru026	3.952810	0.447049	