Supplementary Information

Parameterisation of Force Field

The first stage of this work was the addition of parameters to the MM+ force field to enable the bite angle to be calculated. Parameters are generally obtained from X-ray crystallography structures or quantum mechanics studies and require equilibrium values and force constants for bonds, angles and torsions. To calculate the bite angle, one atom type must be added to the force field, that of the metal and a series of corrections and modifications must be made to other parameters for those atoms that interact directly with the metal centre. This work was done in stages to ensure that only those parameters that were necessary were added to the force field to avoid creating a large number of variables each requiring testing and modifying. To simplify matters further, three dendrimers were picked for this work with closely related structures (figure S1).

Figure S1: Three small ligands used for parameter development. Dppe – Bis-diphenylphosphinoethane, Dppp – Bis-diphenylphosphinopropane, Dppb – Bis-diphenylphosphinobutane.

The parameters were developed using a trial and error approach with a series of small molecules (figure S1) for which both the X-ray crystal structure had been reported in literature(1) as well as previous bite angle calculation values. A successful set of parameters was defined as those that could reproduce the same trends in series of ligands and were within ± 4 º of the values calculated by X-ray diffraction.

The first attempt to model rhodium diphosphine complexes with the Hyperchem Program was made using the MM+ forcefield with no modifications because it automatically assigns the atom type ** to elements for which no atom type exists (such as rhodium) and creates values for bond stretches, bond angles, torsions and non-bonded interactions that are not found in the parameters based on a series of rules.

Table S1: Atom types present within MM+ force field

Element	Atom Type	Notes
Carbon	C_4	Aliphatic carbon, sp3
Carbon	Ca	Aromatic carbon
Hydrogen	H	Hydrogen atom singly bonded
Phosphorus	P	General phosphorus atom

Generic	**	Unassigned atom
Rhodium	rh	Rhodium
Phosphorus	pa	4 coordinate P

Basic force field parameters were added to the MM+ force field, based on Casey 's work. An atom type rh for Rhodium (mass: 102.906 amu, atom type 73.) was added as well as a selection of bond stretches and angle bends.

In keeping with the method of Casey, the force constant for the P-Rh-P bend was set to zero and no equilibrium value was entered. Values were entered for Rh-P-C bends and the P-Rh bond length was set to a standard value of 2.315 Å with a very high force constant to ensure it did not deviate.

In order to refine the parameters, another atom type was added to the force field, this time for tetrahedral phosphorus (pa, atom type no. 74). The parameters for this were derived from Casey *et al.* (2) (3,4)and Gleich *et al.* (5,6) and also from modifying pre-existing parameters for phosphorus-carbon bonds to include the new phosphorus atom type. While this meant that a large number of parameters were created, most of them did not have 'new' values. Bonds and angles including rhodium were created (similar to the second approximation) from various sources.

Table S2: Bond Stretches added MM+, entries in italics refer to parameters that were modified by changing the atom type from p to pa, entries in bold were added. Note the very high force constant for the pa-rh bond is designed to restrain that bond length. T_1 – atom 1, T_2 – atom 2 in bond, K_r – force constant, r_0 equilibrium bond distance (Å)

T_1	T_2	K_r	r_0	DIPOLE
rh	pa	201	2.315	0
c3	*pa*	*2.91*	*1.828*	*1.04*
c4	*pa*	*2.91*	*1.856*	*0.83*

ca	*pa*	*2.91*	*1.828*	*1.04*

Table S3: Angle Bends added to MM+, entries in Italics refer to parameters that were modified by changing the atom type from p to pa, entries in Bold were added and entries in standard script were modified both by changing the atom type from p to pa and by altering the equilibrium value to reflect the tetrahedral phosphorus. T_1, T_2, T_3 – three atoms in angle, K_θ – force constant, θ_o – equilibrium angle.

T_1	T_2	T_3	K_θ	Θ_0
pa	rh	pa	0	0
rh	pa	c4	0.4	109.2
rh	pa	ca	0.7	117
c4	c4	pa	0.48	109.5
c4	pa	c4	0.576	96
c4	pa	ca	0.7	109.5
ca	*ca*	*pa*	*0.38*	*120*
h	c4	pa	0.36	109.5

Table S4: Torsion parameters added to MM+, entries in Italics refer to parameters that were modified by changing the atom type from p to pa, entries in Bold were added and entries in standard script were modified both by changing the atom type from p to pa and by altering the equilibrium value to reflect the tetrahedral phosphorus. T_1, T_2, T_3, T_4 – four atoms in torsion, V_1, V_2, V_3, - what the hell are these values?

T_1	T_2	T_3	T_4	V_1	V_2	V_3
c4	pa	rh	pa	0.2	0	0
rh	pa	c4	c4	0.2	0	0
rh	pa	c4	c4	0.2	0	0
rh	pa	ca	ca	0.2	0	0
rh	pa	ca	ca	0.2	0	0
ca	*ca*	*ca*	*pa*	*0*	*16.25*	*0*
ca	*ca*	*pa*	*c4*	*0*	*0*	*0.4*
ca	*ca*	*pa*	*ca*	*0*	*0*	*0.33*
ca	*pa*	*rh*	*pa*	*0.2*	*0*	*0*
h	*c4*	*c4*	*pa*	*0*	*0*	*0.33*
h	*c4*	*pa*	*ca*	*0.05*	*0*	*0.2*

h	c4	pa	h	0	0	0.428
h	ca	ca	pa	0	16.25	0

For comparison purposes, the data obtained for the three small test compounds is shown (table X), comparing the average bite angle, bite angle from XRD data and the natural bite angle calculated from a minimum energy structure. The trends between the three data sets are the same with the largest angles and the largest flexibility being found for the most flexible ligand. The bite angle calculated from the minimum energy structure is within approximately 3 º of that obtained by x-ray diffraction while that obtained from dynamics at 300 K is between 2 and 14 º higher than the x-ray value. This is to be expected, as at 300 K there is more energy in the system available for overcoming energy barriers, which leads to an increase in the number of energetically accessible conformations. In general, the addition of a CH_2 group increases the average bite angle by approximately 8 – 13 º and raises the flexibility range accordingly. The increase in size of ring formed on coordination also broadens the flexibility range.

Table S5: The bite angle calculated from the minimum energy structure (β_n), average bite angle (β_d) and flexibility calculated at 300 K with an average of 210000 frames of data. XRD data from (1)

| Molecule	Calculated P-M-P /º	X-ray Average Value P-M-P / º	Molecular Modelling	β_n (º)	β_d (º)	Flexibility (º)
7	85.03 (3.11)	82.55 (3.65)	78.1, 84.4	81.20	86.3	70.0 – 98.0
8	91.08 (4.00)	91.56 (3.70)	86.2	88.94	94.5	79.5 – 116.8
9	97.70 (5.15)	97.07 (2.84)	98.6	96.49	107.1	85.0 – 135.8

β_n is calculated with our parameters finding a minimum energy structure. The values are within +- 3 deg of the x-ray values, substantially better than the previous modelling values, and better than the

calculated PMP angles. Need to elaborate on differences between beta n and beta d. beta d correlates

with x-ray diffraction data, which is collected at room temperature. Do I have beta d complex for these

ligands?

Restraints

In order to gain additional insight into the dendrimer-metal complex, modelling simulations of the dendrimer with a rhodium complex attached at one branch was attempted.

Figure S2: Rhodium complex attached to G1-16ethylPPh$_2$ by diequatorial binding. The phenyl rings have been omitted for clarity.
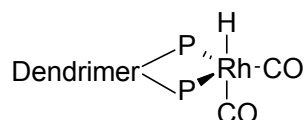
Adding parameters to an empirical force field for transition metal complexes is extremely difficult especially when required to define specific positions of binding such as axial or equatorial. This is best appreciated when considering the two carbonyls in the complex (figure S2). The axial carbonyl would require very different parameters in terms of angles with such as HRhC = 180 º and PRhC = 90 º, compared to the equatorial carbonyl HRhC = 90 º and PRhC = undefined. It would not be possible to add values for PRhC for an equatorial coordinated carbonyl because defining those two angles with high force constants to enforce trigonal bipyramidal geometry at the metal centre would define the third angle, PRhP. The problem is mainly to do with getting the computer program to recognize two identical atoms in two subtly different environments and no way could be found to solve this by adding parameters to the force field.

Table S6: Bond length restraints used for simulation of metal complex.

Bond	R_0 (Å)	K_b Hard	K_b Soft
Rh-H	1.65	7	5
Rh-Ca	1.90	7	5
Rh-Ce	1.90	7	5
Ca-Oa	1.18	7	5
Ce-Oe	1.18	7	5

Table S7: Angle bend restraints used for simulation of metal complex.

Angle	R_0 (°)	K_θ Hard	K_θ Soft
P_1RhCa	90	125	5
P_2RhCa	90	125	5
HRhCa	180	125	25
HRhCe	90	125	25
RhCaOa	180	125	25
RhCeOe	180	125	25
$HRhP_1$	90	125	5
$HRhP_2$	90	125	5

Hyperchem offers the use of restraints to set lengths, angles and torsions to fixed values to keep part of a molecule in a specific orientation and this offered the best route for modelling a rhodium-dendrimer complex. Hard restraints were used in the first instance, creating extremely rigid geometry around the metal centre to allow the molecule to be heated to a high enough temperature to overcome any energy barriers induced by these restraints. The hard restraints are detailed in tables S6 and S7 and include high force constants. The dendrimer complexes were heated to 1500 K then cooled to 300 K. At this point, the restraints were reduced to allow more freedom of motion. Angles that included the phosphorus atoms were reduced to very low values to enable calculation of the bite angle and the others were reduced to moderately low values. The dendrimer complex was cooled to 0 K and equilibrated at the 300 K after a short period of energy minimisation.

References:

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