A Simple New Structural Force Field for the Computation of Linear Metallocenes

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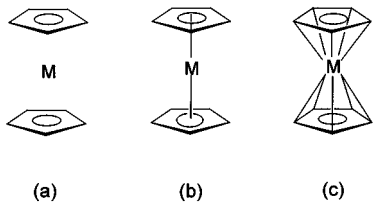
A new structural force field for metallocenes is presented, which involves harmonic bonding potentials from the metal center to each of the carbon atoms, no angular potentials around the metal ion, inter-ligand 1,3-non-bonded interactions, and transferable parameters for the ligand backbones. The model has been parameterized for ferrocene, ruthenocene, and osmocene derivatives and the force field has been validated with relevant structures from the CSD files (Fe: 34, Ru: 10, Os: 2). The conformational space [rotation of the Cp (cyclopentadienyl) rings] has been searched with a cartesian stochastic search routine and energy barriers have been computed by scanning the pseudo-torsional angles involving the centroids of the two Cp rings. The computed energy barriers are smaller than those determined experimentally, but the predicted increase in transition energy upon substitution of the Cp rings is in agreement with experiment and the torsional angles for the minimum structures are computed accurately. It is suggested that the underestimated barrier height is due to the neglect of solvation.

Introduction

Molecular mechanics is well established in organic chemistry,[1][2] force-field calculations are becoming increasingly important in biochemistry,[2−5] and there is an increasing number of well-balanced force fields enabling accurate prediction of the structures and properties of transition-metal coordination compounds.[6−8] However, there are still relatively few reports concerning force fields for organometallic compounds.[6][7] One of the reasons for this is that the connectivity and type of bonding is often rather ambiguous, especially for fluxional systems. For metallocenes, for example, the very manner in which these systems are drawn highlights the problem (Scheme 1). It should be borne in mind that, in general, the basis of molecular mechanics is not to use realistic bonding models.[6] However, the computed structures and, in favorable cases, some thermodynamic parameters (isomer distributions, dynamics) and vibrational spectroscopic parameters should reproduce the experimental data.[6] Thus, any of the models represented in Scheme 1 might be used, irrespective of the fact whether any particular metallocene has more ionic or more covalent bonding character, provided that the parameterization allows a reasonable modeling of structural parameters (metal−Cp ring distance, metal−carbon distance, angle between the Cp planes, torsional angle and barrier, i.e. eclipsed or staggered conformation, and the corresponding activation energy for the interconversion). In addition, it should be easy to extend the model to other classes of organometallic compounds, such as cyclopentadienyl−metal compounds with various other donors, transition-metal compounds with other classes of ligands such as benzene or allyl groups, and cyclopentadienyl−main-group element compounds.

The molecular mechanics approaches for dealing with metallocenes used to date[9−21] can be classified according to the structural plots depicted in Scheme 1: (a) purely electrostatic models, i.e. no covalent bonds (no harmonic but electrostatic and/or van der Waals potentials) between the Cp rings and the metal center;[11][16] (b) models in which the metal center is connected to dummy atoms at the centers of the Cp rings;[9−13,15,21] (c) models with covalent bonds between the metal center and either three carbon atoms per Cp ring[21] or each of the carbon atoms (10-coordinate metal center).[19][20]



Scheme 1

The most appealing approach reported to date involves interactionless dummy atoms, where the forces on the dummy atoms at the centroid of the five-membered rings are distributed among the Cp carbon atoms to avoid strain on the Cp rings.[12] This model allowed accurate computation of the structures and vibrational spectra of linear metallocene compounds.[12] The only obvious disadvantage is that this method needs a specific algorithm, which is not generally available in commercial programs. As yet, it has only been used for linear metallocenes and has not been extended to other similar problems such as the computation of metal−allyl compounds.

We now present a new structural force field for linear metallocenes (M = Fe, Ru, Os), which involves bonding of

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Table 1. Experimentally determined structures considered in this study

Type of ligand	Metal center	Ligand(s)[a]	CCDC No.	Ref.
Unbridged	Fe^{2+}	$(Cp)_2$	FEROC26	[28]
		$(MeCp)_2$	ENTRY'NOYSEZ	[30]
		$(Me_4Cp)_2$	JAROUB	[31]
		$(Me_5Cp)_2$	FODWEZH	[32]
		$(Et_4Cp)_2$	KOPJII	[33]
		$(Et_5Cp)_2$	KIYNIP	[34]
		$[1,2\text{-}(t\text{Bu})_2Cp]_2$	LIBFUX	[35]
		$[1,3\text{-}(t\text{Bu})_2Cp]_2$	TBUFER01	[36]
		$[1,2,4\text{-}(Cyh)_3Cp]_2$	HEZHUB	[37]
	Ru^{2+}	$(Cp)_2$	CYCPRU06	[38]
		$(1,3\text{-}Me_2Cp)_2$	HANYOK	[39]
		$(Me_4Cp)_2$	GIHGUH	[40]
		$(Me_5Cp)_2$	DATHIP	[41]
		$(Me_4EtCp)_2$	HAWPEA	[42]
	Os^{2+}	$(Cp)_2$	SINWER	[43]
		$(Me_5Cp)_2$	GENGUB	[44]
Mono-bridged	Fe^{2+}	$Cp-[1,1,2,2\text{-}(Me)_4Et]-Cp$	METFER	[45]
		$(3\text{-}t\text{BuCp})_2-1,1,2,2\text{-}(Me)_4Et$	TOGFAW	[46]
		$Cp-Prop-Cp$	FICJUW	[47]
		$(Cp-Me)_2-O$	FICKAD	[47]
		$(Cp-Me)_2-S$	FICKEH	[47]
		$Cp-Pent-Cp$	JIWGUR	[48]
	Ru^{2+}	$Cp-Et-Cp$	WEVKIR	[49]
		$Cp-Prop-Cp$	CEJLOS	[50]
		$Me_4Cp-Prop-CpMe_4$	YOSYIO	[51]
		$(Cyp)Cp-Prop-Cp$	DABDIT	[52]
		$Cp-But-Cp$	CEJLUY	[50]
Dibridged (sym.)	Fe^{2+}	$Cp-1,2\text{-}Et_2-Cp$	WICTIL	[53]
		$Cp-1,2\text{-}Prop_2-Cp$	YUMRAZ	[54]
		$Cp-1,2\text{-}Prop_2-Cp$	FICKIL	[47]
		$Cp-1,3\text{-}Prop_2-Cp$	TRMEFE01	[47]
		$(Cyp)Cp-1,2\text{-}Prop_2-Cp(Cyp)$	TTMFER	[55]
		$Cp-1,2\text{-}(Prop)(Me-O-Me)-Cp$	FICKORH	[47]
		$Cp-1,3\text{-}(Prop)(Me-O-Me)-Cp$	FICLAE	[47]
		$Cp-1,2\text{-}Bu_2-Cp$	COBSAN	[56]
		$Cp-1,3\text{-}Bu_2-Cp$	PEFGAI	[57]
Tribridged (sym.)	Fe^{2+}	$Cp-1,2,4\text{-}Prop_3-Cp$	YUMRIH	[54]
		$(Cyp)Cp-1,2,3\text{-}Prop_3-Cp(Cyp)$	PTMFER	[58]
		$Cp-1,2,4\text{-}Bu_3-Cp$	COBSER	[56]
		$Cp-1,2,4\text{-}Pent_3-Cp$	COBSIV	[56]
Tribridged (asym.)	Fe^{2+}	$Cp-1,1'\text{-}Prop-2,4',4,2'\text{-}Bu_2-Cp$	DUBJIT	[59]
Tetrabridged (sym.)	Fe^{2+}	$Cp-Pent_4-Cp$	SACVUN	[60]
Tetrabridged (asym.)	Fe^{2+}	$Cp-2\text{-}Prop-1,3,4\text{-}Bu_3-Cp$	FEROPI	[61]
		$Cp-1,3\text{-}Prop_2-2,4\text{-}Bu_2-Cp$	CEPWOJ	[62]
Pentabridged (sym.)	Fe^{2+}	$Cp-Bu_5-Cp$	DOMLIA10	[63]
Pentabridged (asym.)	Fe^{2+}	$Cp-Prop-Bu_4-Cp$	BETRUN	[64]

[a] Nomenclature: Cp = cyclopentadienyl, substructures in brackets in front of a Cp ring are substituents of the corresponding Cp; substructures between the two Cp rings are bridges; symmetrical bridges are only numbered at one Cp; Me = methylene, Et = ethylene, Prop = propylene, Bu = butylene, *t*Bu = *tert*-butylene, Pent = pentenyl, Cyh = cyclohexyl, Cyp = *n*, *n* + 1 propyl attached to a Cp ring.

all carbon atoms to the metal center (10-coordinate metal atom for MCp_2) and the replacement of valence angle terms around the metal center by inter-ligand 1,3-non-bonded interactions (modified points-on-a-sphere approach). Thus, the Cp rings are free to rotate about the centroid−metal−centroid axis without any need for defining dummy atoms, and there is no restriction in terms of a tilt between the two Cp planes. This approach is in agreement with simple MO considerations, i.e. the system is electronically degenerate with respect to the C_5 axis, which is also apparent from experiment. The points-on-a-sphere molecular mechanics model has been widely used for transition-metal coordination compounds[6,8,22,23] and is implemented in most commercially available programs. The only modification to generally available programs is the exclusion of 1,3-non-bonded interactions between covalently linked carbon atoms (intra-ligand 1,3-interactions), which has been simple to include in our software and force field. A similar but not identical approach to metallocene modeling has recently been developed for cyclopentadienyl−early transition-metal systems.[24]

Experimental Structural Data

The structural data considered in this study included selected X-ray-structural analyses of MCp_2 compounds with M = Fe, Ru, Os, where Cp_2 are two cyclopentadienyl rings or substituted Cp rings or where the two rings are bridged (substituents or bridges incorporating heteroatoms such as sulfur or silicon were not considered). The relevant structures (46 data sets; 34 Fe, 10 Ru, 2 Os), separated into simple and strapped sandwich compounds, are presented in Table 1.

Structural Parameters

The structural parameters considered here (average metal−carbon distance *b*; average distance *d* of the metal ion from the Cp planes; tilt angle α, torsional angle δ) are shown in Figure 1. The experimentally observed and computed parameters are given in Table 2 (the full set of structural data, experimental and computed, of all structures is available as Supporting Information). Note that, for some compounds, various experimental data sets are available. This is particularly true in the case of ferrocene, for which various polymorphic modifications are known and intermolecular interactions, polymorphism, disorder, gas-phase structures, and dynamics have been discussed extensively.[25−28] The fact that the computed and experimentally determined activation energies for the Cp ring rotations of the non-strapped metallocenes are generally small (see be-

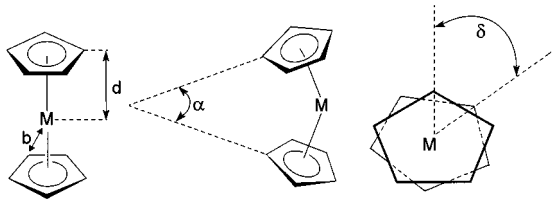

Figure 1. Definition of the structural parameters [torsion angle δ has the periodicity (360/5°), except for unsymmetrically substituted Cp rings; staggered: δ = 36°; eclipsed: δ = 0°]

Table 2. Averages of observed and computed structural parameters of metallocenes[a]

Structure		b[b] [Å]		d [Å]		α [°]		δ [°]	
		Observed	Computed	Observed	Computed	Observed	Computed	Observed	Computed
Fe	$(Cp)_2$	2.02(1)	2.04(0)	1.64	1.66	0.0	0.0	36.0	35.9
Fe	$(MeCp)_2$	2.08(2)	2.04(0)	1.70	1.66	6.1	0.2	1.5	30.6
Fe	$(Me_4Cp)_2$	2.09(1)	2.05(0)	1.71	1.66	0.0	0.1	180.0	172.1[c]
Fe	$(Me_5Cp)_2$	2.10(1)	2.05(0)	1.71	1.66	0.0	0.0	36.0	36.0[c]
Fe	$(Et_4Cp)_2$	2.10(1)	2.05(0)	1.71	1.66	1.8	2.8	76.8	54.0
Fe	$(Et_5Cp)_2$	2.10(0)	2.05(0)	1.71	1.67	1.0	0.1	23.2	23.0
Fe	$[1,2\text{-}(t\text{Bu})_2Cp]_2$	2.06(1)	2.06(1)	1.66	1.67	0.0	0.0	180.0	180.0
Fe	$[1,3\text{-}(t\text{Bu})_2Cp]_2$	2.06(1)	2.06(1)	1.67	1.68	8.9	11.1	88.2	89.6
Fe	$[1,2,4\text{-}(Cyh)_3Cp]_2$	2.06(0)	2.05(1)	1.66	1.67	2.0	1.9	177.9	177.4
Ru	$(Cp)_2$	2.19(0)	2.18(0)	1.81	1.82	0.7	3.5	0.4	30.8
Ru	$(1,3\text{-}Me_2Cp)_2$	2.18(0)	2.18(0)	1.82	1.82	1.6	0.5	2.9	0.5
Ru	$(Me_4Cp)_2$	2.18(0)	2.18(0)	1.81	1.82	1.9	1.0	2.6	34.2
Ru	$(Me_5Cp)_2$	2.18(0)	2.17(0)	1.81	1.82	0.2	0.1	0.8	22.3
Ru	$(Me_4EtCp)_2$	2.18(2)	2.18(0)	1.82	1.82	5.1	0.6	141.7	123.2
Os	$(Cp)_2$	2.19(0)	2.18(0)	1.80	1.82	1.8	0.3	0.6	28.1[c]
Os	$(Me_5Cp)_2$	2.04(2)	2.17(0)	1.69	1.81	0.0	0.0	36.0	36.0[c]
Fe	$\{Cp\text{-}[1,1,2,2\text{-}(Me)_4Et]\text{-}Cp\}$	2.04(2)	2.05(1)	1.64	1.67	23.6	28.3	10.4	11.9
Fe	$[(3\text{-}t\text{BuCp})_2\text{-}1,1,2,2\text{-}(Me)_4Et]$	2.08(3)	2.05(1)	1.69	1.67	29.4	27.3	10.2	12.1
Fe	(Cp−Prop−Cp)	2.03(0)	2.04(0)	1.63	1.66	7.9	12.6	2.2	0.0
Fe	$[(Cp\text{-}Me)_2\text{-}O]$	2.03(1)	2.04(1)	1.63	1.66	11.9	15.5	1.3	0.0
Fe	$[(Cp\text{-}Me)_2\text{-}S]$	2.03(1)	2.04(0)	1.63	1.66	6.0	7.3	2.4	0.1
Fe	(Cp−Pent−Cp)	2.08(4)	2.06(1)	1.74	1.67	13.3	15.9	3.6	21.6
Ru	(Cp−Et−Cp)	2.16(2)	2.20(1)	1.79	1.85	29.6	37.1	8.5	10.0
Ru	(Cp−Prop−Cp)	2.17(1)	2.18(0)	1.81	1.82	14.8	20.6	0.5	0.1
Ru	$(Me_4Cp\text{-}Prop\text{-}CpMe_4)$	2.17(2)	2.18(1)	1.79	1.82	11.2	16.8	0.5	1.2
Ru	[(Cyp)Cp−Prop−Cp]	2.17(1)	2.18(0)	1.80	1.82	15.6	20.5	1.0	0.2
Ru	(Cp−But−Cp)	2.18(0)	2.18(0)	1.82	1.82	1.7	0.2	3.0	14.1
Fe	$(Cp\text{-}1,2\text{-}Et_2\text{-}Cp)$	2.01(2)	2.07(2)	1.61	1.69	28.7	33.2	2.6	3.2
Fe	$(Cp\text{-}1,2\text{-}Prop_2\text{-}Cp)$	2.07(1)	2.04(0)	1.68	1.66	18.4	18.0	0.0	0.0
Fe	$(Cp\text{-}1,2\text{-}Prop_2\text{-}Cp)$	2.03(1)	2.04(0)	1.63	1.66	13.0	17.9	1.2	0.0
Fe	$(Cp\text{-}1,3\text{-}Prop_2\text{-}Cp)$	2.01(1)	2.03(1)	1.60	1.64	9.9	15.4	1.4	0.1
Fe	$[(Cyp)Cp\text{-}1,2\text{-}Prop_2\text{-}Cp(Cyp)]$	2.03(1)	2.04(0)	1.62	1.65	11.0	17.8	2.2	0.7
Fe	[Cp−1,2-(Prop)(Me−O−Me)−Cp]	2.03(1)	2.04(0)	1.62	1.66	15.0	20.0	0.6	0.0
Fe	[Cp−1,3-(Prop)(Me−O−Me)−Cp]	2.02(1)	2.03(2)	1.62	1.64	12.9	17.6	0.8	0.8
Fe	$(Cp\text{-}1,2\text{-}Bu_2\text{-}Cp)$	2.03(1)	2.04(0)	1.65	1.66	6.9	9.0	11.6	17.1
Fe	$(Cp\text{-}1,3\text{-}Bu_2\text{-}Cp)$	2.03(1)	2.02(1)	1.63	1.63	0.0	1.2	36.0	36.1
Fe	$(Cp\text{-}1,2,4\text{-}Prop_3\text{-}Cp)$	2.04(2)	1.99(2)	1.61	1.59	3.7	7.2	2.2	0.1
Fe	$[(Cyp)Cp\text{-}1,2,3\text{-}Prop_3\text{-}Cp(Cyp)]$	2.01(1)	2.03(1)	1.60	1.64	11.2	23.4	1.9	1.0
Fe	$(Cp\text{-}1,2,4\text{-}Bu_3\text{-}Cp)$	2.04(0)	2.03(0)	1.63	1.64	5.5	7.1	15.0	16.3
Fe	$(Cp\text{-}1,2,4\text{-}Pent_3\text{-}Cp)$	2.05(0)	2.05(0)	1.65	1.67	3.1	2.9	0.5	0.1
Fe	$(Cp\text{-}1,1'\text{-}Prop\text{-}2,4',4,2'\text{-}Bu_2\text{-}Cp)$	2.02(0)	2.03(1)	1.62	1.64	5.7	11.0	0.8	2.9
Fe	$(Cp\text{-}Pent_4\text{-}Cp)$	2.06(1)	2.07(1)	1.66	1.69	6.6	11.1	1.1	2.4
Fe	$(Cp\text{-}2\text{-}Prop\text{-}1,3,4\text{-}Bu_3\text{-}Cp)$	2.03(0)	2.03(1)	1.62	1.64	0.2	4.0	1.3	5.7
Fe	$(Cp\text{-}1,3\text{-}Prop_2\text{-}2,4\text{-}Bu_2\text{-}Cp)$	2.02(1)	2.01(2)	1.61	1.62	8.7	12.2	31.5	32.5
Fe	$(Cp\text{-}Bu_5\text{-}Cp)$	2.01(1)	2.00(2)	1.59	1.61	1.0	7.3	1.6	3.9
Fe	$(Cp\text{-}Prop\text{-}Bu_4\text{-}Cp)$	2.02(0)	2.03(0)	1.61	1.64	1.8	1.5	0.9	16.8

[a] For definition of the structural parameters, see Figure 1. − [b] Standard deviation (SD, in%) in brackets; $SD = \sqrt{\frac{n\sum x^2 - (\sum x)^2}{n^2}}$. − [c] Corresponds to a local minimum; see Table 5 for global minimum.

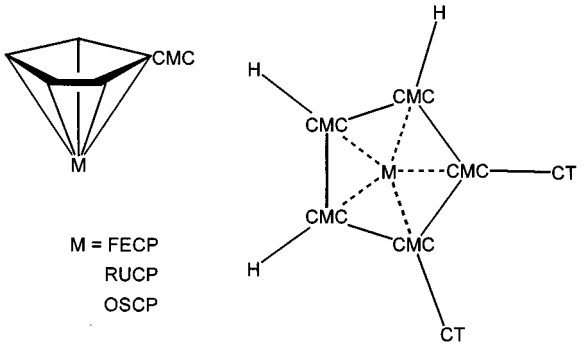

Figure 2. Definition of atom types used in Table 3

low) indicates that an arbitrary selection of test structures is acceptable.

The MOMEC program and force field were used for the calculations.[22] Parameters not previously published[23] are given in Table 3 (the atom-type labels are defined in Figure 2; starting values for the parameters were taken from vibrational spectroscopic data and/or from other force fields[6][12] and refined by fitting to the set of test structures). The conformational space was searched with a cartesian stochastic search routine ("random kick" Monte Carlo method), which has recently been implemented in MOMEC and validated for a series of (amine)cobalt(III) compounds.[29]

Table 3. New MOMEC force-field parameters[a−c]

Bond-stretch parameters				Valence-angle parameters				
Atom 1	Atom 2	k_b [mdyn Å^{-1}]	r_0 [Å]	Atom 1	Atom 2	Atom 3	k_θ [mdyn Å rad^{-2}]	θ_0 [rad]
FECP	CMC	0.750	2.020	FECP	CMC	CMC	0.010	1.222
RUCP	CMC	0.500	2.176	FECP	CMC	CT	0.100	2.217
OSCP	CMC	0.350	2.180	FECP	CMC	H	0.100	2.217
CMC	CMC	7.400	1.400	CMC	FECP	CMC	0.000	3.141
CMC	CT	5.000	1.500	RUCP	CMC	CMC	0.010	1.222
CMC	H	5.000	1.090	RUCP	CMC	CT	0.100	2.217
				RUCP	CMC	H	0.100	2.217
				CMC	RUCP	CMC	0.000	3.141
				OSCP	CMC	CMC	0.010	1.222
				OSCP	CMC	CT	0.100	2.217
				OSCP	CMC	H	0.100	2.217
				CMC	OSCP	CMC	0.000	3.141
				CMC	CMC	CT	0.350	2.199
				CMC	CMC	CMC	0.400	1.885
				CMC	CMC	H	0.350	2.199
				CMC	CT	CT	0.250	1.909
				CMC	CT	H	0.160	1.911

Torsional-angle parameters							Out-of-plane parameters				
Atom	Atom	Atom	Atom	k_ϕ [mdyn Å]	m	ϕ_{offset} [rad]	Atom 1	Atom 2	Atom 3	Atom 4	k_{oop} [mdyn Å rad^{-2}]
H	CMC	CMC	CT	0.015	2	1.571	CMC	CMC	CMC	CT	2
CMC	CMC	CMC	CT	0.015	2	1.571	CMC	CMC	CMC	H	2
H	CMC	CMC	CMC	0.015	2	1.571					
CT	CMC	CMC	CT	0.015	2	1.571					
H	CMC	CMC	H	0.015	2	1.571					

Non-bonded parameters		
Atom	r_{VdW} [Å]	ε
FECP	0.000	0.000
OSCP	0.000	0.000
RUCP	0.000	0.000
CMC	2.100	0.044

[a] All other parameters have been published previously.[23] − [b] For atom-type labels, see Figure 2. − [c] 1 dyn = 10 $^{-5}$ N.

The average observed and computed metal−carbon distances *b* are 2.10 Å and 2.10 Å for iron, 2.18 Å and 2.18 Å for ruthenium, and 2.11 Å and 2.18 Å for osmium (for osmium only two data sets were available, one of which related to a low-temperature structure). A similar degree of accuracy in the computations of the distances *d* of the metal center from the Cp planes is found, and the observed error in the tilt angle α is generally less than 3° and at most 7°. This is especially remarkable for the asymmetrically bridged compounds. The torsional angles δ are, in general, also predicted accurately (to within less than ±10°). Structures with larger differences between the computed and observed torsional angles have freely rotating Cp ligands (non-strapped) and crystal structures with staggered Cp rings. Plots of strain energy along the rotational coordinate indicate that structures similar to that observed are local minima (see below). Details concerning the quality of the computed structures are given in Table 4; full details are available as Supporting Information.

Cp Ring Rotation

Scanning of the strain energy along the rotational mode of the Cp rings is simple in models that use dummy atoms at the centroids of the Cp rings. We use constraints on plane-twist functions (angle between two planes; one of the planes is defined by three carbon atoms of a Cp ring, the other by the metal center and one carbon atom of each of the two Cp rings; from each of the constrained plane-twist angles the corresponding torsional angle δ is calculated). It is possible to apply a force on this rotation to increase the barrier for the Cp ring rotation. However, there does not seem to be an electronic reason for such a potential. The difference between the observed and computed energy barriers might be due to a reorganization of the solvent sheath, which is not considered explicitly in our calculations.[6] The computed energy barriers are mainly due to changes in van der Waals contacts, and it has been suggested previously that this is probably the most important effect.[6][12] It should be borne in mind, however, that our aim was to derive a structural force field for ferrocene, ruthenocene, osmocene and derivatives. Thus, the computation along the ring rotation mode is used here to evaluate local minima and not for the accurate determination of rotational barriers.

As expected, the computed energy barriers (Table 5) are generally underestimated, but the increasing barrier height upon substitution [cf. $Fe(Cp)_2$, $Fe(Me_5Cp)_2$] is of the expected order. A plot of the strain energy along the Me_5Cp rotation for the latter structure indicates that there is a concerted rotation of the methyl groups, which is shown in Figure 3. Here, the structural plots help to visualize the con-

Table 4. Comparison of observed and computed structures of ferrocene, ruthenocene, osmocene and their derivatives

Compound		RMS[a] [Å]	Plane[b] [Å]	
Fe	$(Cp)_2$	0.022	0.00	0.00
Fe	$(MeCp)_2$	0.303 (0.090)	0.00	0.00
Fe	$(Me_4Cp)_2$	0.095	0.01	0.00
Fe	$(Me_5Cp)_2$	0.056	0.00	0.00
Fe	$(Et_4Cp)_2$	0.235 (0.059)	0.00	0.00
Fe	$(Et_5Cp)_2$	0.045	0.00	0.00
Fe	$[1,2\text{-}(t\text{Bu})_2Cp]_2$	0.029	0.01	0.01
Fe	$[1,3\text{-}(t\text{Bu})_2Cp]_2$	0.040	0.02	0.02
Fe	$[1,2,4\text{-}(Cyh)_3Cp]_2$	0.041	0.01	0.01
Ru	$(Cp)_2$	0.312 (0.060)	0.00	0.00
Ru	$(1,3\text{-}Me_2Cp)_2$	0.041	0.00	0.00
Ru	$(Me_4Cp)_2$	0.236 (0.039)	0.00	0.00
Ru	$(Me_5Cp)_2$	0.201 (0.039)	0.00	0.00
Ru	$(Me_4EtCp)_2$	0.191 (0.095)	0.00	0.00
Os	$(Cp)_2$	0.288 (0.087)	0.00	0.00
Os	$(Me_5Cp)_2$	0.162	0.00	0.00
Fe	$(Cp)_2$–[1,1,2,2-$(Me)_4$Et]	0.068	0.04	0.04
Fe	$(3\text{-}t\text{BuCp})_2$–1,1,2,2-$(Me)_4$Et	0.067	0.04	0.04
Fe	(Cp–Prop–Cp)	0.061	0.01	0.01
Fe	[$(Cp–Me)_2$–O]	0.053	0.02	0.02
Fe	[$(Cp–Me)_2$–S]	0.038	0.01	0.01
Fe	(Cp–Pent–Cp)	0.247 (0.131)	0.04	0.00
Ru	(Cp–Et–Cp)	0.091	0.03	0.03
Ru	(Cp–Prop–Cp)	0.069	0.01	0.01
Ru	(Me_4Cp–Prop–$CpMe_4$)	0.113	0.02	0.02
Ru	[(Cyp)Cp–Prop–Cp]	0.070	0.01	0.01
Ru	(Cp–But–Cp)	0.114	0.00	0.00
Fe	(Cp–1,2-Et_2–Cp)	0.106	0.02	0.04
Fe	(Cp–1,2-$Prop_2$–Cp)	0.043	0.01	0.01
Fe	(Cp–1,2-$Prop_2$–Cp)	0.054	0.01	0.01
Fe	(Cp–1,3-$Prop_2$–Cp)	0.067	0.04	0.04
Fe	[(Cyp)Cp–1,2-$Prop_2$–Cp(Cyp)]	0.071	0.01	0.01
Fe	[Cp–1,2-(Prop)(Me–O–Me)–Cp]	0.060	0.01	0.01
Fe	[Cp–1,3-(Prop)(Me–O–Me)–Cp]	0.066	0.05	0.05
Fe	(Cp–1,2-Bu_2–Cp)	0.065	0.01	0.01
Fe	(Cp–1,3-Bu_2–Cp)	0.028	0.02	0.02
Fe	(Cp–1,2,4-$Prop_3$–Cp)	0.105	0.06	0.07
Fe	[(Cyp)Cp–1,2,3-$Prop_3$–Cp(Cyp)]	0.094	0.03	0.04
Fe	(Cp–1,2,4-Bu_3–Cp)	0.034	0.01	0.01
Fe	(Cp–1,2,4-$Pent_3$–Cp)	0.030	0.01	0.01
Fe	(Cp–1,1′-Prop–2,4′,4,2′-Bu_2–Cp)	0.072	0.03	0.02
Fe	(Cp–$Pent_4$–Cp)	0.061	0.01	0.01
Fe	(Cp–2-Prop–1,3,4-Bu_3–Cp)	0.087	0.04	0.01
Fe	(Cp–1,3-$Prop_2$–2,4-Bu_2–Cp)	0.063	0.06	0.05
Fe	(Cp–Bu_5–Cp)	0.082	0.06	0.06
Fe	(Cp–Prop–Bu_4–Cp)	0.170 (0.060)	0.01	0.01

[a] RMS overlay of the computed and the observed (CCDC) structures (metal center and 10 Cp carbon atoms only; values in brackets are the sums of individual RMS values for both M–CP fragments). – [b] RMS deviation of the best plane of the two computed Cp rings; $RMS = \sqrt{\frac{\sum_N (x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2}{N}}$.

Table 5. Comparison of some observed and computed rotational energy barriers for ferrocene, ruthenocene, osmocene and derivatives

Structure		Energy barrier[a] [kJ/mol]		Global minimum[b] [°]	
		Observed	Computed	Observed	Computed
Fe	$(Cp)_2$	3.7[c]	0.2	0.0[c] (e)	35.9
Ru	$(Cp)_2$	33.9[38]	0.5	0.0 (e)	30.8
Os	$(Cp)_2$	–	0.1	–	10.3
Fe	$(Me_4Cp)_2$	–	4.7	–	107.1
Ru	$(Me_4Cp)_2$	–	2.0	–	34.2
Fe	$(Me_5Cp)_2$	4.0[65]	6.4	23.7	22.2
Ru	$(Me_5Cp)_2$	–	3.1	–	22.3
Os	$(Me_5Cp)_2$	–	3.3	–	23.2
Fe	$(MeCp)_2$	–	1.1	–	30.6
Fe	$(Et_4Cp)_2$	–	5.4	–	24.6
Fe	$(Et_5Cp)_2$	–	7.9	–	22.7

[a] Conformational arrangement is indicated in brackets, where *e* = eclipsed, *s* = staggered. – [b] Minima determined by rotating one Cp ring in one direction using a plane-twist function (no force, i.e. $k_\delta = 0.0$); energy scan increment: 1°. – [c] Values obtained by electron diffraction in the gas phase. At low temperature, X-ray and neutron diffraction data indicate that the rings are staggered by about 10°.[66]

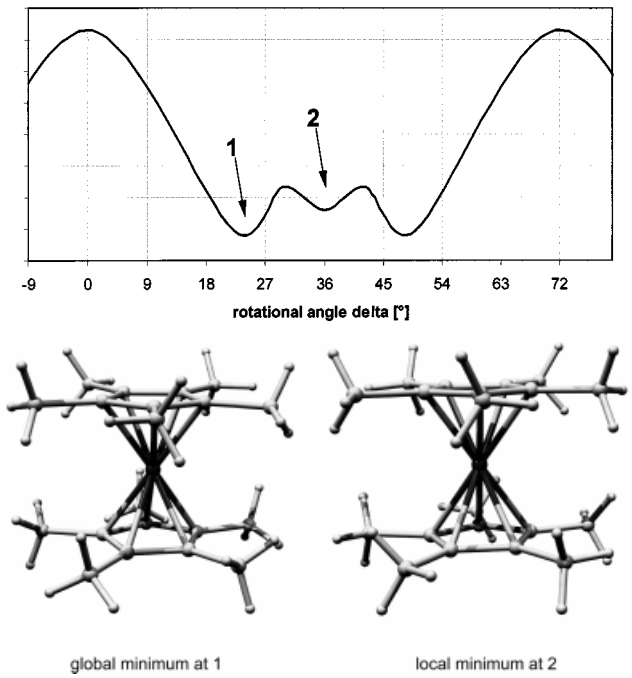

Figure 3. Rotational energy plot of $Fe(Me_5Cp_2)$ (grid: 1 kJ/mol)

certed rotations. The global energy minimum of $Fe(Me_5Cp)_2$ ($\delta = 22.2°$) is in excellent agreement with that computed using an alternative approach ($\delta = 23.7°$).[12] Thus, structural features, including those of the ring rotation, are well reproduced by our new force field, while dynamic properties are not. The approach used here allows the application of a force on the ring rotation; published data relating to other force fields suggest that this might lead to realistic energy barriers when the corresponding force constant is metal-ion-dependent.[12]

In conclusion, we have been able to demonstrate that the simple points-on-a-sphere model leads to an accurate structural force field for linear metallocenes, and that this approach may be extended to a range of other organometallic systems.

Supporting Information

Detailed structural data (comparison of experimentally observed and computed structural parameters) are available: Table S1 (supplementary to Table 2) gives the complete set of carbon-to-metal bond lengths *b* [see Figure 1; the metal center is atom number 1, C(2)–C(6) are carbon atoms of ring 1, and C(7)–C(11) are carbon atoms of ring 2] and rotational angles δ (the values given in parentheses after the rotational angles are RMS deviations of the carbon atoms from the best plane of each Cp ring). Table S2 (sup-

plementary to Table 5) lists the rotational energy barriers for all metallocene compounds discussed in Table 5.

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