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REGULAR ARTICLE

Geometry prediction of hafnocenes by quantum chemical methods

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Abstract The performance of quantum chemical methods for geometry prediction of hafnocenes was evaluated. HF, B3LYP and MP2 in combination with nonrelativistic (MHF) and relativistic (MWB and LANL2DZ) basis sets for hafnium together with standard basis sets 3-21G*, 6-31G* and 6-311G** for other elements were applied. Five basic structural parameters of the optimized structures of the hafnocenes were compared with experimental crystal structures obtained from the Cambridge structural database. Altogether 80 hafnocenes were included in the analysis. The results show that relativistic corrections are necessary for Hf atom. However, even the Hartree–Fock (HF) method, when combined with relativistic pseudopotentials, reproduces the experimental crystal structures with significant accuracy. The good performance of the HF method can be understood to originate from the absence of significant near-degeneracy correlations for hafnium. On average, the B3LYP and MP2 methods provide structural parameters somewhat closer to the experimental ones.

Keywords Ab initio calculations · Metallocenes · Hafnium · Geometry

1 Introduction

Group IV metallocene catalysts are applied in the polymerization of olefins, and in particular of ethylene and propylene. The single site nature of the metallocene catalysts strongly influences the properties of the polymer, such as polymer structure and molecular weight distribution. The single site catalyst center also makes it practical to study metallocene catalyzed polymerization processes by quantum chemical methods, for recent reviews see, e.g., [1,2]. In addition to enabling the control of polymer properties, the metallocenes can provide enhanced catalytic activities compared with the traditional Ziegler–Natta catalysts [3]. The catalytic activity is sensitive to several factors, such as reaction conditions and the nature of the cocatalyst [4] activating the catalyst precursor. Nevertheless, the mere geometry of the metallocene catalyst precursor has been shown to correlate with catalytic activity due to both steric and electronic effects [5–8]. Most theoretical studies of group IV metallocene complexes have focused on zirconocenes, for recent articles, see, e.g., [9–19], fewer on hafnocenes, see, e.g., [20–27]. The zirconocenes and the hafnocenes are isostructural due to the stronger relativistic contraction of the orbitals of Hf, resulting in practically the same atomic radii, [28]. In the polymerization process, however, the two behave differently: Whereas zirconocenes generally have higher activity, hafnocenes produce polyolefins with higher molecular weights [3].

Generally, the theoretical treatment of transition metal complexes is not straightforward, owing to the near-degeneracy and relativistic effects. In this respect, zirconocenes have been shown to be a special case, HF/3-21G* method producing geometries close to the experimental ones [29]. This is due to the location of Zr at the beginning of the second transition row, where both near-degeneracy correlation and relativistic effects are relatively weak [30,31]. Near-degeneracy effects become weaker when moving down in the periodic table, while the relativistic effects become stronger. Hence, one could suggest that relatively low level quantum chemical methods would also perform well for hafnocenes, if relativistic effects are taken into account.

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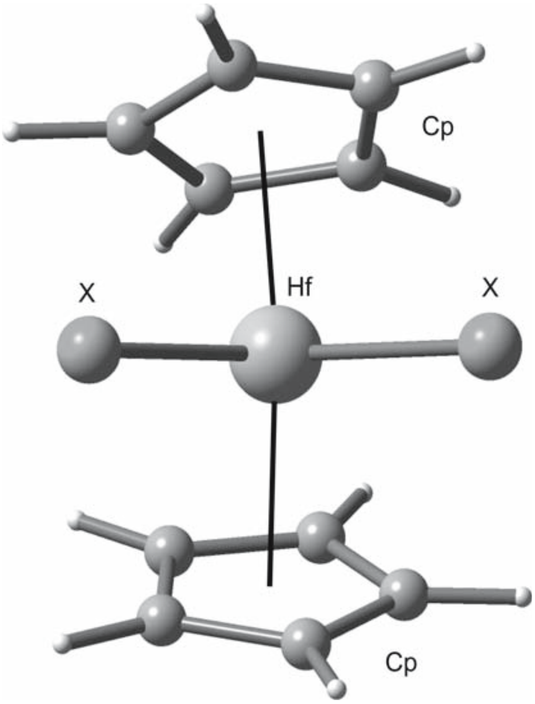

Fig. 1 Schematic structure of hafnocene with two cyclopentadienyl ligands and two additional ligands

The ligand structures of the metallocene catalysts have significant influences on the polymerization process. Proper clarification of the ligand structure – polymerization behavior relationships requires plenty of experimental and theoretical data. Hence, the level of theory selected for the calculations is critical, having to be both practical and sufficiently accurate to produce correct trends. In this paper, we evaluate the performance of various quantum chemical methods for geometry prediction of hafnocene polymerization catalysts. The molecular structures of 80 crystallographically characterized hafnocenes are optimized and compared with the experimental structures to draw conclusion on the optimal cost/performance ratio for hafnocene polymerization catalysts.

2 Computational methods

The hafnocenes were fully optimized without any constraints and five basic geometry parameters (see Fig. 1), Hf–X distance (X = first atom connected to Hf in the leaving group), Hf–Cp distance (Cp = centroid of the five-ring for any cyclopentadienyl-based ligand), X–Hf–X angle, Cp–Hf–Cp angle and Cp–Cp plane angle were measured and compared with the experimental crystal structures. Geometry optimizations were carried out with the Gaussian03 program package [32]. Hartree–Fock, hybrid density functional B3LYP [33,34] and MP2 methods in conjunction with standard 3-21G*, 6-31G* and 6-311G** basis sets were applied for all elements except Hf and Sn. For Hf, the Stuttgart/Dresden small core nonrelativistic MHF, relativistic MWB ECPs [35] and Los Alamos ECP [36,37] (LANL2DZ) were employed. The LANL2DZ basis set was used for Sn.

3 Results and discussion

3.1 Choice of the hafnocenes

The evaluation includes all successfully characterized hafnocenes found in a search from Cambridge Structural database.[1] The criteria for selection were the following: (1) exactly one Hf atom, (2) at least two cyclopentadienyl rings attached to Hf and (3) altogether four ligands bound to Hf. Furthermore, the structures containing other transition metals than Hf were omitted. These criteria were fulfilled for a total of 80 hafnocenes, which were all taken under consideration. The R1 factor was below 5% for 63, between 5 and 7% for 12, and between 7 and 10% for five structures. Five structures in the present of solvent were included. Each of those had R1 factors below 5%.

The ancillary ligands of the hafnocenes consisted of cyclopentadienyls, indenyls and fluorenyls in their different combinations, combined with various ligand substituents and bridging units. The most common bridging atoms were carbon and silicon, and a few other elements were represented: N, O, P and Ge. Most ligand substituents were alkyl groups, but several elements were present in addition to carbon: B, N, O, F, Si, P, S, Ca, As, Se and Sn. The leaving groups consisted mostly of halogens and alkyl groups. Schematic pictures of the whole data set are given in the Appendix 1.

3.2 Evaluation of the methods

The calculations were initiated by optimizing three typical hafnocene dichlorides (Table 1) by each combination of methods and basis sets, excluding MP2/3-21G*. This resulted in 24 method/basis set combinations. Comparisons of the geometry parameters of the experimental structures and the optimized structures are given in Table 1. The Hf–Cl bond distances are overestimated with all method/basis set combinations, except B3LYP/LANL2DZ 3-21G* and MP2/LANL2DZ 6-311G**. The deviations range from –0.01 to 0.08 Å. Inclusion of relativistic pseudopotentials (MWB and LANL2DZ) clearly improves the structure prediction by shortening the Hf–Cl bond distances by approximately 0.04 Å, LANL2DZ generally providing structures closest to the experimental ones. Within the Hartree–Fock method, the HF/LANL2DZ 3-21G* combination produces the best Hf–Cl bond distances, deviations from the experimental structures being just 0.02–0.03 Å. The B3LYP method improves the structure prediction over HF, and is at its best

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[1] The search was done in February 2004.

Table 1 Deviations of optimized structures from experimental structures for three typical hafnocene dichlorides

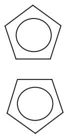
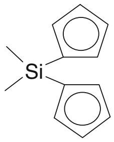
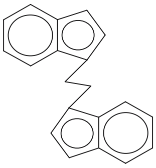
Ligand structure	Method	ΔHf–Cl (Å)	ΔHf–Cp (Å)	ΔCl–Hf–Cl (°)	ΔCp–Hf–Cp (°)	ΔCp–Cp (°)	CPU[a]
	Experimental [38]	2.4235	2.181	96.17	129.14	52.37	
	HF/MHF 3-21G*	0.07	0.12	4.47	0.47	0.66	2
	HF/MHF 6-31G*	0.08	0.11	3.73	0.41	0.14	6
	HF/MHF 6-311G**	0.08	0.10	3.62	0.41	0.06	17
	HF/MWB 3-21G*	0.04	0.10	2.69	−0.33	0.54	1
	HF/MWB 6-31G*	0.05	0.09	2.17	0.16	0.15	7
	HF/MWB 6-311G**	0.05	0.09	1.89	0.09	0.10	15
	HF/LANL2DZ 3-21G*	0.02	0.07	2.19	0.05	0.27	1
	HF/LANL2DZ 6-31G*	0.04	0.07	2.11	0.55	−0.12	5
	HF/LANL2DZ 6-311G**	0.04	0.06	1.77	0.65	−0.58	12
	B3LYP/MHF 3-21G*	0.03	0.10	4.91	−0.29	1.12	2
	B3LYP/MHF 6-31G*	0.05	0.10	4.26	0.15	0.71	15
	B3LYP/MHF 6-311G**	0.05	0.10	4.13	0.13	0.00	10
	B3LYP/MWB 3-21G*	0.01	0.08	3.24	−0.40	0.88	1
	B3LYP/MWB 6-31G*	0.02	0.09	2.64	−0.06	0.63	4
	B3LYP/MWB 6-311G**	0.02	0.08	2.43	0.11	0.00	14
	B3LYP/LANL2DZ 3-21G*	−0.01	0.05	2.27	−0.18	0.51	2
	B3LYP/LANL2DZ 6-31G*	0.00	0.06	2.29	0.31	0.30	3
	B3LYP/LANL2DZ 6-311G**	0.01	0.05	2.03	0.55	0.00	6
	MP2/MHF 6-31G*	0.04	0.05	3.51	−0.43	1.02	14
	MP2/MHF 6-311G**	0.03	0.04	4.55	−1.11	1.49	43
	MP2/MWB 6-31G*	0.01	0.02	1.41	−0.49	0.71	14
	MP2/MWB 6-311G**	0.00	0.02	1.79	−1.09	0.93	78
	MP2/LANL2DZ 6-31G*	0.01	0.02	1.91	−0.38	0.63	11
	MP2/LANL2DZ 6-311G**	0.00	0.00	2.06	−0.76	0.25	61
	Experimental [39]	2.421	2.182	97.64	127.63	57.74	
	HF/MHF 3-21G*	0.07	0.11	7.35	−4.43	5.66	2
	HF/MHF 6-31G*	0.08	0.11	4.11	−3.96	4.68	6
	HF/MHF 6-311G**	0.08	0.10	4.41	−3.90	4.71	16
	HF/MWB 3-21G*	0.04	0.10	5.06	−4.19	4.99	2
	HF/MWB 6-31G*	0.05	0.09	2.16	−3.60	3.96	7
	HF/MWB 6-311G**	0.05	0.09	2.21	−3.57	4.03	16
	HF/LANL2DZ 3-21G*	0.02	0.07	4.24	−3.58	4.09	2
	HF/LANL2DZ 6-31G*	0.04	0.07	2.04	−2.85	3.35	5
	HF/LANL2DZ 6-311G**	0.04	0.06	2.19	−2.56	3.19	11
	B3LYP/MHF 3-21G*	0.03	0.10	8.61	−3.25	4.21	6
	B3LYP/MHF 6-31G*	0.05	0.10	4.61	−3.37	3.93	9
	B3LYP/MHF 6-311G**	0.05	0.10	4.80	−3.52	4.19	20
	B3LYP/MWB 3-21G*	0.01	0.08	6.23	−2.93	3.36	4
	B3LYP/MWB 6-31G*	0.02	0.08	2.59	−2.98	3.02	8
	B3LYP/MWB 6-311G**	0.02	0.08	2.58	−3.14	3.30	19
	B3LYP/LANL2DZ 3-21G*	−0.01	0.05	4.83	−2.54	2.52	3
	B3LYP/LANL2DZ 6-31G*	0.00	0.06	2.06	−2.41	2.60	6
	B3LYP/LANL2DZ 6-311G**	0.01	0.05	2.24	−2.16	2.47	16
	MP2/MHF 6-31G*	0.04	0.05	3.45	−2.14	1.51	34
	MP2/MHF 6-311G**	0.03	0.04	4.73	−2.35	0.91	89
	MP2/MWB 6-31G*	0.01	0.03	0.84	−1.64	0.73	28
	MP2/MWB 6-311G**	0.00	0.02	1.35	−1.84	0.06	91

Table 1 continued

Ligand structure	Method	ΔHf–Cl (Å)	ΔHf–Cp (Å)	ΔCl–Hf–Cl (°)	ΔCp–Hf–Cp (°)	ΔCp–Cp (°)	CPU[a]
	MP2/LANL2DZ 6-31G*	0.01	0.02	1.10	−1.28	0.85	26
	MP2/LANL2DZ 6-311G**	−0.01	0.00	1.25	−0.85	−0.33	65
	Experimental [40]	2.396	2.217	96.4	125.71	60.18	
	HF/MHF 3-21G*	0.08	0.09	4.66	−1.98	2.92	2
	HF/MHF 6-31G*	0.10	0.10	2.68	−1.80	3.13	9
	HF/MHF 6-311G**	0.09	0.09	3.05	−1.83	2.95	23
	HF/MWB 3-21G*	0.05	0.08	3.11	−1.82	2.37	2
	HF/MWB 6-31G*	0.06	0.09	1.34	−1.57	2.60	10
	HF/MWB 6-311G**	0.06	0.08	1.47	−1.61	2.46	20
	HF/LANL2DZ 3-21G*	0.03	0.05	2.39	−1.06	1.80	2
	HF/LANL2DZ 6-31G*	0.05	0.06	1.26	−0.06	2.23	6
	HF/LANL2DZ 6-311G**	0.05	0.05	1.23	−0.53	1.73	14
	B3LYP/MHF 3-21G*	0.04	0.08	6.48	−1.14	2.13	3
	B3LYP/MHF 6-31G*	0.06	0.10	4.12	−1.23	3.03	12
	B3LYP/MHF 6-311G**	0.06	0.10	4.46	−1.39	3.03	28
	B3LYP/MWB 3-21G*	0.02	0.06	4.72	−1.00	1.56	4
	B3LYP/MWB 6-31G*	0.03	0.08	2.65	−0.85	2.37	11
	B3LYP/MWB 6-311G**	0.03	0.08	2.80	−1.07	2.40	26
	B3LYP/LANL2DZ 3-21G*	−0.01	0.04	3.69	−0.36	1.06	3
	B3LYP/LANL2DZ 6-31G*	0.01	0.06	2.33	−0.09	2.22	8
	B3LYP/LANL2DZ 6-311G**	0.02	0.05	2.26	−0.02	1.74	16
	MP2/MHF 6-31G*	0.06	0.02	1.22	−0.95	0.24	69
	MP2/MHF 6-311G**	0.04	0.00	2.59	−1.36	−0.44	315
	MP2/MWB 6-31G*	0.03	0.00	−0.65	−0.62	−0.53	58
	MP2/MWB 6-311G**	0.01	−0.02	0.19	−0.96	−1.27	232
	MP2/LANL2DZ 6-31G*	0.02	−0.01	−0.52	−0.04	−0.42	45
	MP2/LANL2DZ 6-311G**	0.01	−0.03	−0.39	−0.07	−2.01	272

[a] Relative CPU times for the calculations

in the B3LYP/LANDL2DZ 6-31G* combination, where the deviations range from 0.00 to 0.01 Å. The MP2/MWB 6-311G** and MP2/LANL2DZ 6-311G** methods provide accuracy comparable with that of B3LYP/LANDL2DZ 6-31G*, the deviations ranging from –0.01 to 0.01 Å.

The Hf–Cp bond distances are mostly overestimated, with the deviations of –0.03 to 0.12 Å from the experimental values. The relativistic pseudopotentials shorten the distances, by ca. 0.02 Å with MWB and ca. 0.04 Å with LANL2DZ, the latter thus producing Hf–Cp bond distances closer to the experimental ones. The bond distances are relatively insensitive to the standard basis sets, the deviations within HF/LANL2DZ varying between 0.05 and 0.07 Å. The B3LYP method provides slight improvements over HF, the respective deviations being 0.04–0.06 Å. Here the computationally expensive MP2/LANL2DZ 6-311G** reproduces the crystal structure most accurately, with deviations for the three hafnocenes being 0.00, 0.00 and –0.03 Å. Overall, the LANL2DZ basis set produces 0.03–0.05 Å shorter metal–ligand bond distances than the nonrelativistic MHF basis set. This is in good agreement with the previous studies, suggesting relativistic bond-length contraction of 0.04–0.05 Å for Hf [28].

The deviations in the angular parameter vary between –4.43° and 8.61°. The Cl–Hf–Cl angles and the Cp–Cp plane angles are generally overestimated, whereas the Cp–Hf–Cp angles are mostly underestimated. The relativistic pseudopotentials provide systematic improvements, by approximately 1° on average, LANL2DZ generally producing angles in better agreement with the crystal structures than MWB. The B3LYP method does not improve the accuracy over the HF method. MP2/LANL2DZ 6-31G* gives angles in best agreement with the experimental data, the average deviation being 0.8°. By way of comparison, the respective average deviation for B3LYP/LANL2DZ 6-311G* is 1.5°.

It should be noted that crystal packing effects and the uncertainties in the determination of the crystal structures introduce slight errors to the comparisons of the crystal

Table 2 Statistics of geometry optimizations of hafnocenes with the HF/LANL2DZ 3-21G*, the B3LYP/LANL2DZ 6-31G* and the MP2/LANL2DZ 6-31G* methods

Deviation	Hf–X (Å)	Hf–Cp (Å)	X–Hf–X (°)	Cp–Hf–Cp (°)	Cp–Cp (°)
HF/LANL2DZ 3-21G*					
Maximum	0.078	0.099	5.71	0.81	4.17
Minimum	−0.080	0.018	−2.00	−3.96	−2.95
Average	0.023	0.064	1.01	−1.39	0.77
Standard	0.026	0.017	1.64	1.02	1.49
Absolute average	0.031	0.064	1.54	1.47	1.34
Absolute average (corrected)	0.015	0.016	1.30	0.73	0.90
B3LYP/LANL2DZ 6-31G*					
Maximum	0.077	0.109	4.64	1.06	4.97
Minimum	−0.089	0.023	−2.74	−2.72	−2.51
Average	0.014	0.056	1.13	−0.39	0.71
Standard	0.019	0.013	1.29	0.74	1.62
Absolute average	0.019	0.056	1.42	0.70	1.39
Absolute average (corrected)	0.012	0.009	1.01	0.55	0.87
MP2/LANL2DZ 6-31G*					
Maximum	0.026	0.026	3.56	0.66	2.29
Minimum	−0.088	−0.033	−1.50	−3.47	−2.46
Average	0.003	0.005	1.00	−0.74	−0.05
Standard	0.024	0.005	1.60	1.10	1.31
Absolute average	0.018	0.010	1.48	0.94	1.01

structures and the gas-phase geometry optimizations. However, the errors due to crystal structure determinations are generally smaller than those obtained from the optimizations, the R1-factors mostly being <5%.

The evaluated combinations of methods and basis sets perform relatively well with no major failures in any particular case. Overall, taking into consideration both accuracy and cost of calculations, the HF/LANL2DZ 3-21G*, B3LYP/LANL2DZ 6-31G* and MP2/LANL2DZ 6-31G* methods are the most promising candidates for the geometry prediction of hafnocenes. These three levels of methods were accordingly selected for the more extensive evaluation carried out for the whole data set of 80 hafnocenes. The statistics of the comparison are summarized in Table 2. As an example, graphical comparison of the structural parameters is presented in Fig. 2 for the B3LYP/LANL2DZ 6-31G* method.

With the B3LYP/LANL2DZ 6-31G* method, the deviations range from –0.089 to 0.077 Å for the Hf–X bond distances and from 0.023 to 0.109 Å for the Hf–Cp bond distances. The Hf–Cp distances are thus systematically overestimated with an average deviation of 0.056 Å. The X–Hf–X angles and Cp–Cp plane angles are, on average, overestimated, the deviations ranging from –2.74° to 4.64° and from –2.51° to 4.97°, respectively. The deviations in Cp–Hf–Cp angles range from –2.72° to 1.06° being, on average, slightly underestimated the absolute average deviations for X–Hf–X angles, Cp–Hf–Cp angles and Cp–Cp plane angles are 1.42°, 0.70° and 1.39°, respectively.

Overall, atypical for transition metal complexes, the HF/LANL2DZ 3-21G* method produces structural parameters nearly as close to the experimental ones as does the B3LYP/LANL2DZ 6-31G* method. The good performance of the HF method is due to the absence of near-degeneracy correlations in hafnocenes. The accuracy of the HF method is clearly worse in Hf–X distances and Cp–Hf–Cp angles, the respective absolute average deviations being 0.031 Å (0.019 Å with B3LYP) and 1.47° (0.70° with B3LYP). The performance of the HF method is the worst for complexes with sterically crowded X ligands, when X = C, Si. In those cases the bond distances become overestimated by 0.06–0.07 Å. The performance of the B3LYP method remains unaffected by the bulk ligands.

In the case of the MP2/LANL2DZ 6-31G* method, the data set was limited to 20 randomly selected hafnocenes (see the Appendix). The statistics given in Table 2 must therefore be considered indicative only. It appears that the MP2 method significantly improves the prediction of the Hf–Cp distances, while elsewhere providing about the same accuracy as the B3LYP/LANL2DZ 6-31G* method. It should be noted that the MP2 method would likely perform better in combination with larger basis sets. Such calculations would not be practical, however.

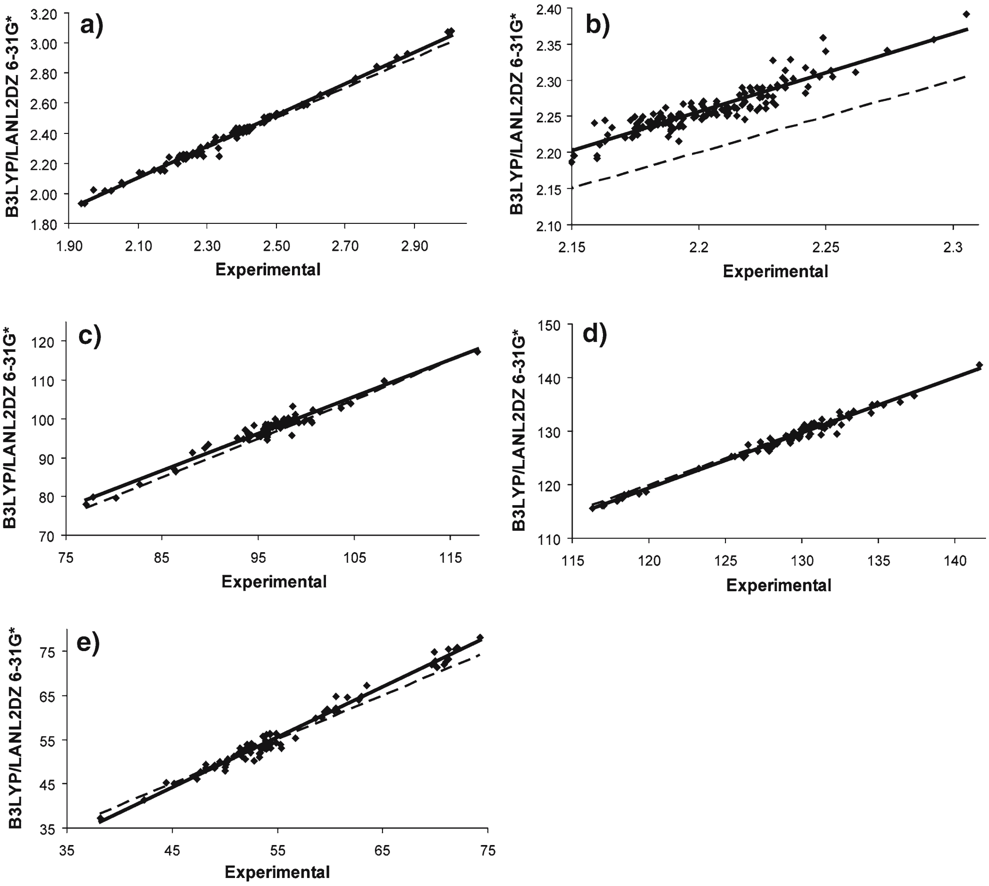


Fig. 2 Comparison of experimental and B3LYP/LANL2DZ 6-31G* optimized structural parameters. **a** Hf–X distance (Å), **b** Hf–Cp distance (Å), **c** X–Hf–X angle (°), **d** Cp–Hf–Cp angle (°), **e** Cp–Cp plane angle (°). *Dashed line* represents experimental structural parameters and *solid line* linear regression of optimized parameters

The accuracy of the geometry prediction can be improved by removal of systematic errors. Although the improvement is greatest for the systematically overestimated Hf–Cp distances, corrections were performed for each parameter and for both HF/LANL2DZ 3-21G* and B3LYP/LANL2DZ 6-31G* using a linear regression scheme. By way of example, equations for obtaining structural parameters free of systematic errors are given for the B3LYP/LANL2DZ 6-31G* method as Eqs. (1)–(5). The removal of systematic errors clearly decreases the absolute average error for all five parameters, and in particular for the systematically overestimated Hf–Cp distances (Table 2). In the case of the B3LYP/LANL2DZ 6-31G* method, the absolute average deviation in Hf–Cp distances is decreased from 0.056 to 0.009 Å.

$$\text{Hf–X}: \text{B3LYP(corr)} = \frac{\text{B3LYP} + 0.09}{1.04} \tag{1}$$

$$\text{Hf–Cp}: \text{B3LYP(corr)} = \frac{\text{B3LYP} + 0.13}{1.09} \tag{2}$$

$$\text{X–Hf–X}: \text{B3LYP(corr)} = \frac{\text{B3LYP} + 4.53}{1.03} \tag{3}$$

$$\text{Cp–Hf–Cp: B3LYP(corr)} = \frac{\text{B3LYP} - 5.53}{0.95} \tag{4}$$

$$\text{Cp–Cp: B3LYP(corr)} = \frac{\text{B3LYP} + 6.92}{1.14} \tag{5}$$

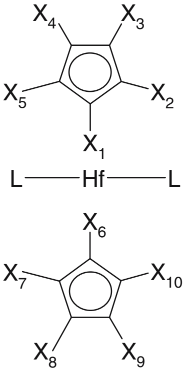
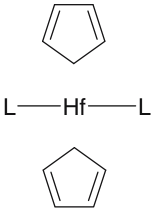
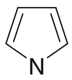
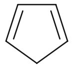
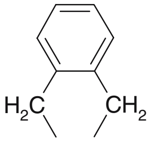
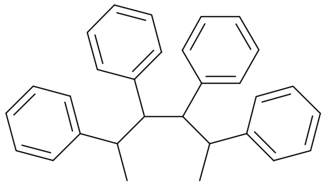
Statistically, the deviations are similar to those calculated previously for zirconocenes [29]. The comparable performance of the methods for zirconocenes and hafnocenes is understandable, both having d orbitals of the same size and insignificant near-degeneracy effects. The main difference comes from the relativistic effects, which are insignificant for the zirconocenes but must be taken into account in the case of hafnocenes.

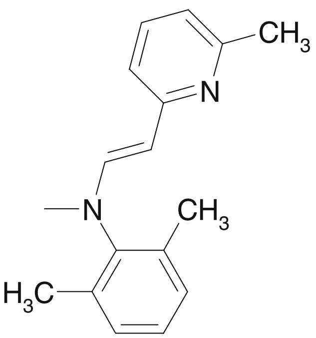
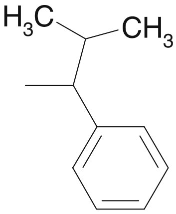
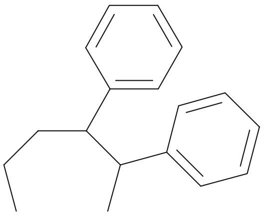
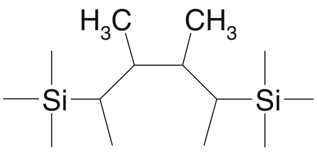
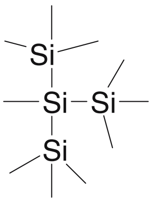
4 Conclusions

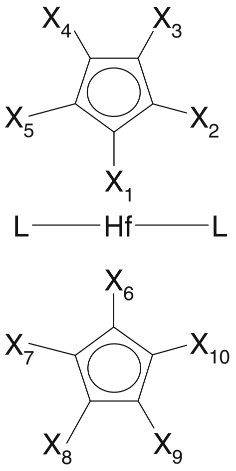
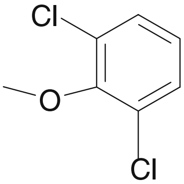
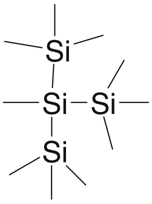
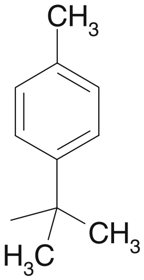
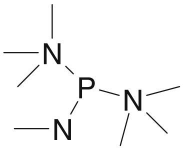
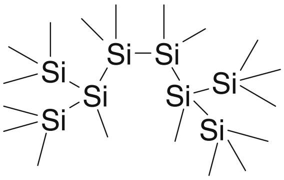
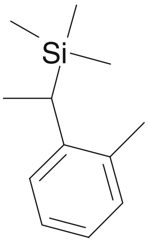
The applicability of various quantum chemical methods for geometry prediction of hafnocenes was evaluated. Generally, the theoretical treatment of hafnocenes is straightforward. Comparison of the nonrelativistic MHF and the relativistic MWB and LANL2DZ basis sets showed that the relativistic effects cannot be ignored in the case of Hf atom. On the other hand, owing to the absence of the near-degeneracy correlation, relatively low-level methods, even Hartree–Fock, in combination with relativistic pseudopotentials for Hf, are capable of producing realistic structures for hafnocenes. Overall, the LANL2DZ basis set provided geometries closer to the experimental ones than did MWB. B3LYP method improved the accuracy over the HF method with slightly increased computational resources. The MP2 method provided only marginal improvements over B3LYP. Taking its expensiveness into consideration, it appears less reasonable choice for the hafnocenes.

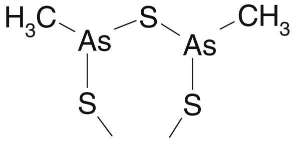
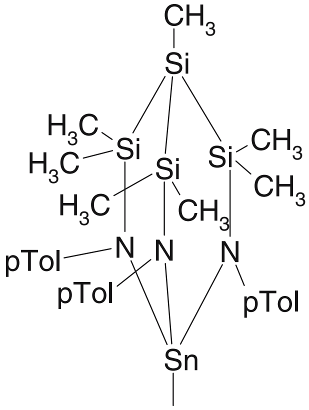
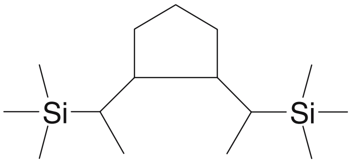
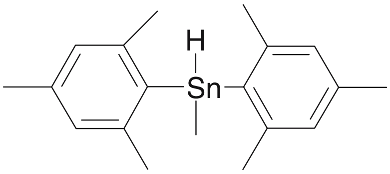
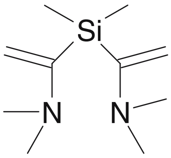
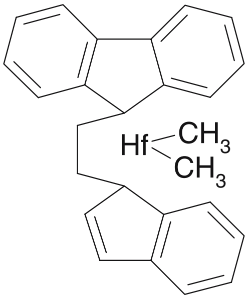
The combination of low cost and significant accuracy of the B3LYP/LANL2DZ 6-31G* geometry optimizations for hafnocenes is expected to assist in the development of new high-performance catalysts via rationalization of the influence of the ligand structure for the polymerization process. The capability of predicting the polymerization behavior of the catalyst before their synthesis would reduce the experimental workload. Prior to drawing the correlations between the ligand structure and the polymerization behavior, the catalytic steps—activation, chain propagation and chain termination—have to be carefully studied for a large set of hafnocene polymerization catalysts.

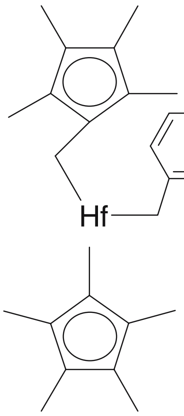
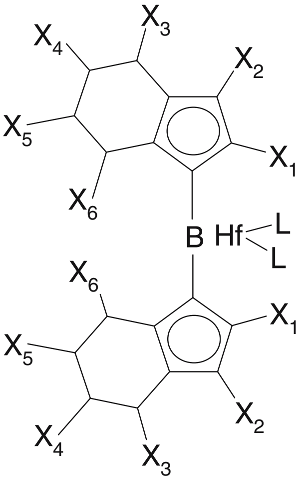
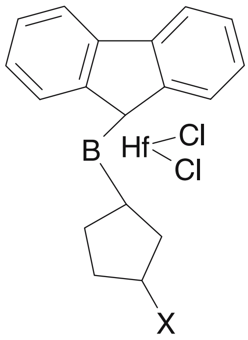
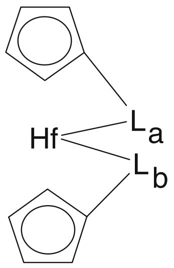
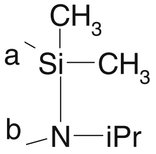
Appendix: Hafnocene structures

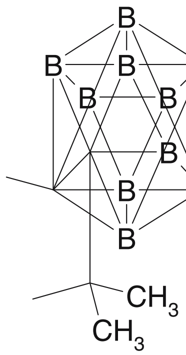
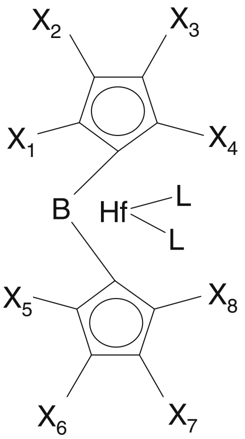
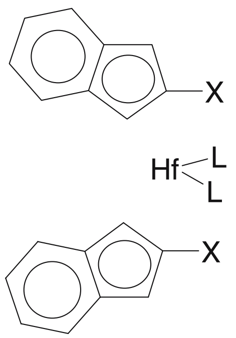
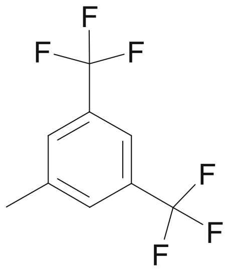
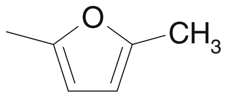
Structure	Bridge/ligand/substituent	Reference
	L = Cl, X_1 = CH_2–CH_3, X_6 = CH_2–CH_3	[41a]
	L = Cl, X_7 = C(Me)$_2$–C(Me)$_2$, X_2 = C(Me)$_2$–C(Me)$_2$	[42a]
	L = CH_3	[43]
	L = Cl, $X_{1–5}$ = CH_3	[44a]
	L = CH_2–CH_3, L = O–O–tButyl, $X_{1–10}$ = CH_3	[45]
	L–L = S–S–S–S–S	[46a]
	L = Cl, X_2 = Si(CH_3)$_2$Cl, X_7 = Si(CH_3)$_2$Cl	[47]
	L = CH_2–CH_3, $X_{1,4,6,9}$ = tButyl	[48]
	L = S–(CH_2)$_3$–CH_3, $X_{1–10}$ = CH_3	[49]
	L = S–Ph, $X_{1–10}$ = CH_3	
	L = S–Ph–O–CH_3, $X_{1–10}$ = CH_3	[49]
	L = Cl, $X_{1–5}$ = CH_3	[49]
	L = Si–Ph	[50]
	L = Cl, X_1–X_5 = –(CH_2)$_{10}$–, X_6–X_7 = –(CH_2)$_{10}$–	[51]
	L–L = Se–Se–Se–Se–Se	[52a]
	L = –CC–Ph, $X_{1,6}$ = Si(Me)$_3$	[53]
	L = Br, $X_{1–5}$ = CH_3	[54a]
	L = Br, $X_{1,2,4}$ = CH_3	[54a]
	L = Br	[54a]
	L = Cl, L = –Cl–Ca(Cp*)$_2$, $X_{1–10}$ = CH_3	[55]
	L = F, X_1 = Si(Me)$_3$ $X_{6–10}$ = CH_3	[56]
	L = Cl, $X_{2,7}$ = Si((–Ph)$_2$ –(Flu))	[57]
	L = Cl, L = As(Si(Me)$_3$)$_2$, $X_{2,10}$ = CH_3	[58]
	L = 	[59a]
	L = 	[60a]
	L–L = 	[61a]
	L–L = 	[62]
	L = CH_2–CH_3, L = 	[63]

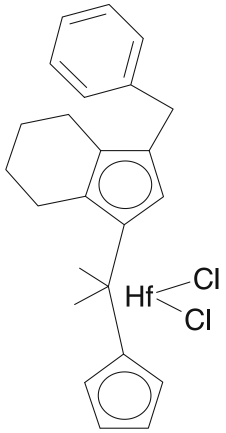
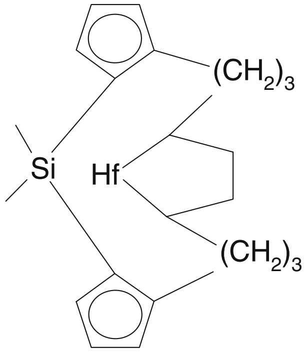
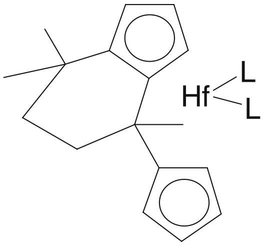
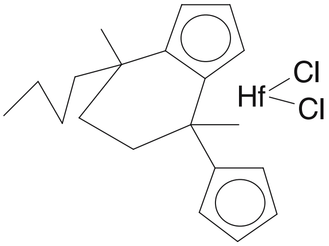
	L = 	[64]
	L = Cl, L = 	[65]
	L–L = 	[66]
	L–L = 	[67]
	L = 	[68]

	$X_3 = CH_3$, $X_8 = CH_3$ L = 	[69]
	L = Cl, $X_{1-5} = CH_3$ L = 	[70]
	L = Cl, $X_{2,7}$ = 	[71]
	L = Cl, L = 	[72]
	L–L = 	[73]
	L = Cl, L = 	[74]

	L–L =	[75]
	L–L = 	[76]
	L = Cl, L = 	[77]
	L–L = 	[78]
	L = Cl, L = 	[79]
	X_{1-5}= CH_3 L–L = 	[80]
		[81a]

		[82]
	B=CH_2–CH_2, L = Cl, $X_{3–6}$=H_2	[83a]
	B=Si–$(Me)_2$, L =$N(Me)_2$	[84]
	B=CH_2, L = Cl, X_2= tButyl	[85]
	B=CH_2, L = Cl	[86a]
	B=C–$(Me)_2$	[87a]
	B=C–$(Ph)_2$	[88]
	B=C–$(Me)_2$, X = $Si(Me)_3$	[89]
	B=C–$(Me)_2$, X = Me	[90]
	L = 	[91]

	L =  	[92]
 	B= Si(Me)$_2$–Si(Me)$_2$, L = Cl B= C(Me)$_2$, L = Cl B= P–Ph, L = CH$_3$, X$_{1-8}$ = CH$_3$ B= P–Ph, L = Cl, X$_{1-8}$ = CH$_3$ B = Si(Me)$_2$–[N–(CH$_2$)$_3$–CH$_3$]–Si(Me)$_2$, L = Cl B= Ge(Me)$_2$, L = Cl, X$_{1-4}$ = CH$_3$ B= C(=CH$_2$)–CH=C(–N(Me)$_2$), L = Cl B= Si(Me)$_2$, L = Cl, X$_{1-8}$ = CH$_3$ B= Si(CH–CH$_2$)$_2$, L = Cl, X$_{1-8}$ = CH$_3$ B= Si(Et)$_2$, L = Cl, X$_{1-8}$ = CH$_3$ B= Ge(Me)$_2$, L = Cl, X$_{1-8}$ = CH$_3$ B= (CH$_2$)$_3$, L = Cl B= Si(Me)$_2$, L = Cl, X$_{1-4}$ = CH$_3$	[93a] [94a] [95] [95] [96] [97] [98] [99] [99] [99] [99] [100a] [101]
 	L = CH$_3$ L = Cl, X = Ph L = Cl, X = Ph L = Cl, X = Ph L = Cl, X =  L = Cl, X =  	[102a] [103] [104] [104] [104] [105]

		[106]
		[107]
	L = Cl L = CH_3	[108] [108a]
		[109]

[a] Structures calculated with MP2 method

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