

# Allyl complexes of chromium and zirconium: molecular structures from DFT and ab initio calculations

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## Abstract

The molecular structures of trisallylchromium, tris-2-methylallylchromium, allylchromium dibromide, tetrakisallylzirconium, tetrakis-2-methylallylzirconium and allylzirconium tribromide have been investigated by means of quantum chemical calculations. Restricted Hartree–Fock (HF) geometries show some  $\sigma$ -character in the allyl bonding to the metal centres, especially for the chromium systems, while the allyl groups coordinate in a purely trihapto fashion at the DFT level. For allylchromium dibromide, test calculations at the unrestricted HF level show problematic SCF convergence and severe spin contamination, indicating strong correlation effects; hence, we place higher confidence in the DFT results. All molecules under study are fluxional. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Chromium; Zirconium; Allyl compounds; Structural chemistry

## 1. Introduction

During the last two decades, a large number of olefin polymerisation catalysts based on cyclopentadienyl complexes of early transition metals have been developed [1]. These highly active catalysts have been subject of substantial research efforts, including quantum chemical investigations [2]. Although many allyl complexes of Group 4 and 6 transition elements are one-component polymerisation catalysts [3], these complexes have been studied to a much smaller extent. In fact, due to poor thermal stability, the molecular structures of the simplest allyl compounds, such as  $\text{Cr}(\text{allyl})_3$  and  $\text{Zr}(\text{allyl})_4$ , have not been determined experimentally [4].

Trisallyl complexes of chromium are paramagnetic, and for this reason their investigation by standard NMR techniques is not straightforward. The electronic structure of  $\text{Cr}(\text{allyl})_3$  has been investigated by photoelectron spectrometry together with ab initio calculations

[5]. Also, its IR spectrum in hydrocarbon solution has been reported [6], although strict structural conclusions could not be drawn from the spectrum due to the presence of unsaturated byproducts that are not easily removed. The use of  $\text{Cr}(\text{2-Me-allyl})_3$  and different halogenated allyl–chromium complexes as polymerisation catalysts have also been reported [3,6], but without any references to the characterisation of the complexes.

For Group 4 allyl complexes, the situation is somewhat better. Low temperature NMR results have been reported for the homoleptic allyl complexes of zirconium and hafnium. Although the barrier for the equilibration of the *syn* and *anti* hydrogens of the allyl ligand has been determined for the zirconium compound, the results are not conclusive concerning the ground state structures of these complexes [7]. A combined infrared and  $^1\text{H-NMR}$  study of  $\text{Zr}(\text{allyl})_4$  and  $\text{Hf}(\text{allyl})_4$  indicates that the former has all allyl ligands trihapto bonded to zirconium, while the latter also has at least one ligand  $\sigma$ -bonded to the metal [8]. Recently, Landis et al. [9] reviewed the experimental attempts to determine the structure of tetrakisallylzirconium, and, based

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on molecular mechanics calculations, they concluded that a ground state geometry of  $S_4$  symmetry is the most stable.

As part of a continuing study of these systems, we have undertaken a quantum chemical investigation of the molecular and electronic structure of some chromium and zirconium allyl complexes. In the present paper, the ground state structures of the homoleptic complexes  $\text{Cr}(\text{allyl})_3$ ,  $\text{Cr}(2\text{-Me-allyl})_3$ ,  $\text{Zr}(\text{allyl})_4$  and  $\text{Zr}(2\text{-Me-allyl})_4$  and of the simpler di- and tribromide complexes  $(\text{allyl})\text{CrBr}_2$  and  $(\text{allyl})\text{ZrBr}_3$ , as determined by Hartree–Fock (HF) and DFT calculations, are reported. For the bromine-containing complexes, computed vibrational spectra are reported as well.

## 2. Computational details

The DFT calculations were carried out using the program system ADF developed by Baerends et al. [10]. The frozen-core approximation was used for all atoms except hydrogen, keeping the orbitals up to and including 3p, 2p, 3p, and 1s frozen in their atomic shapes for Zr, Cr, Br, and C, respectively. The orbitals were described by Slater type orbital (STO) basis sets. The number of unfrozen basis functions, in order of increasing angular momentum, is (5,4,3) for zirconium, (5,3,3) for chromium, (2,2,3) for bromine, (2,2,1) for chlorine and carbon, and (2,1) for hydrogen, yielding TZV quality for the metals and DZVP for the other atoms (note that the number of unfrozen orbitals is larger than the number of valence orbitals). Slater exchange and the VWN parametrisation of the LDA correlation energy [11], with the gradient corrections of Becke [12] for exchange and of Perdew [13] for correlation, were used for the exchange–correlation energies; the gradient corrections were added self-consistently. The accuracy of the numerical integration was set to  $10^{-5.0}$ , which may be assumed to give a numerical noise level of  $<0.1 \text{ kcal mol}^{-1}$  in the final energies [14]. It is a somewhat higher accuracy than necessary for most systems; its application here was necessitated by the fluxionality of the molecules under study. A precision of  $10^{-4.0}$  led to convergence of conformers that turned out not to be stationary points after increasing the precision. For the vibrational spectra, an accuracy of  $10^{-6.0}$  was employed. For  $(\text{allyl})\text{ZrBr}_3$ , the spectrum was also calculated with an accuracy of  $10^{-8.0}$ . This changed the frequencies by  $7 \text{ cm}^{-1}$  in the extreme case, with a typical discrepancy of  $1 \text{ cm}^{-1}$ .

The HF calculations were carried out using the GAMESS-US program package [15]. The MIDI basis sets reported by Huzinaga were applied [16], with the following extensions: for the metals, two  $p$ -type and one  $d$ -type exponents were added with the magnitudes

0.046, 0.017, 0.048 and 0.10, 0.04, 0.157 for Zr and Cr, respectively.  $d$ -Type polarisation exponents of magnitude 0.6 and 0.338 were added for carbon and bromine, respectively, and hydrogen was given a  $p$ -type exponent of 1.0.

The molecules under study are complex enough to have a large number of possible conformers. Conformational analysis was carried out through systematic searches with molecular mechanics calculations using the SPARTAN molecular modelling package [17].

All three chromium systems have uneven numbers of electrons. For each system, several electronic states were investigated. Quartet electronic states proved the most stable in all cases. The DFT calculations were run unrestrictedly, with separate sets of Kohn–Sham orbitals for each spin. The HF calculations were run restrictedly (ROHF), vide infra.

## 3. Results and discussion

All geometry optimisations were started from initial geometries without symmetry, in order to minimise the possibility of ‘false minima’. For the bromine compounds, the vibrational spectra have been computed, vide infra. For technical reasons, we have not performed calculations of the vibrational spectra for the homoleptic complexes. The technicalities of computing such spectra with the combination of numerical second derivatives and numerical integration have been discussed in the literature [18]. We infer that computing the vibrational spectrum of, for example,  $\text{Zr}(\text{allyl})_4$  would require 198 energy and gradient evaluations, with a finer integration grid than used in the geometry optimisations. Hence, several thousand CPU hours would be needed on the Cray T3E for a single spectrum.

For all systems, the vector between the metal and the central allyl carbon has an angle of ca.  $50^\circ$  to the plane spanned by the three allylic carbons on each ligand. Furthermore, we note that the substituent on the central atom of the allyl groups (H or  $\text{CH}_3$ ) does not lie in the plane of the three allylic carbon atoms; rather, it bends inwards towards the metal atom, the angle with the allyl plane being from six to  $16^\circ$  depending on the system. For transition metal cyclopentadienyls, this phenomenon has been explained in terms of maximisation of overlap between metal and carbon  $\pi$  orbitals [19].

### 3.1. Chromium

The most important interatomic distances and angles for  $\text{Cr}(\text{allyl})_3$ ,  $\text{Cr}(2\text{-Me-allyl})_3$  and  $(\text{allyl})\text{CrBr}_2$  are given in Table 1, and the molecules (DFT structures) are depicted in Figs. 1–3, respectively. There is a

Table 1  
Selected interatomic distances (Å) and angles (°) for the chromium molecules

Method	HF			DFT		
	Allyl	2Me	Br	Allyl	2Me	Br
r(Cr–C1)	2.18	2.18	2.18	2.30	2.25	2.18
r(Cr–C2)	2.33	2.33	2.25	2.24	2.27	2.18
r(Cr–C3)	2.43	2.43	2.20	2.23	2.26	2.18
r(C1–C2)	1.43	1.43	1.40	1.41	1.41	1.41
r(C2–C3)	1.37	1.37	1.40	1.40	1.41	1.41
r(C2–Cm)	—	1.51	—	—	1.51	—
r(Cr–Br)	—	—	2.37	—	—	2.35
∠C1–C2–C3	123	123	120	122	119	120
∠Br–Cr–Br	—	—	139	—	—	135
∠Cr-plane	49	46	46	53	51	50
∠H/Me-plane	16	10	20	14	9	16

C<sub>n</sub> denotes allylic carbon atom *n* in the only symmetrically independent allyl group. The ∠Cr-plane is the angle between the Cr–C2 vector and the plane spanned by the allylic carbons, and the ∠H/Me-plane is the angle between the allyl plane and the C2–H or C2–Me bond as appropriate.

striking difference between the DFT and HF results, as the ROHF optimisations yield pseudo-monohapto geometries for both compounds. An UHF test calculation on (allyl)CrBr<sub>2</sub> shows great spin contamination, severe

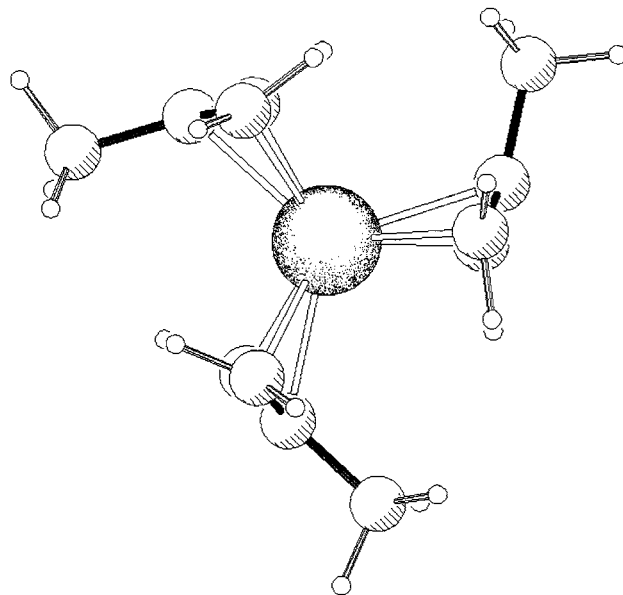


Fig. 2. The molecular structure of tris-2-methylallylchromium in the ground state.

SCF convergence difficulties, and a blunter Br–Cr–Br angle of 156°. This might indicate strong near-degeneracy effects, and it gives reason to place more confidence in the DFT results than the HF results. Calculated vibration frequencies and intensities for (allyl)CrBr<sub>2</sub> are listed in Table 3.

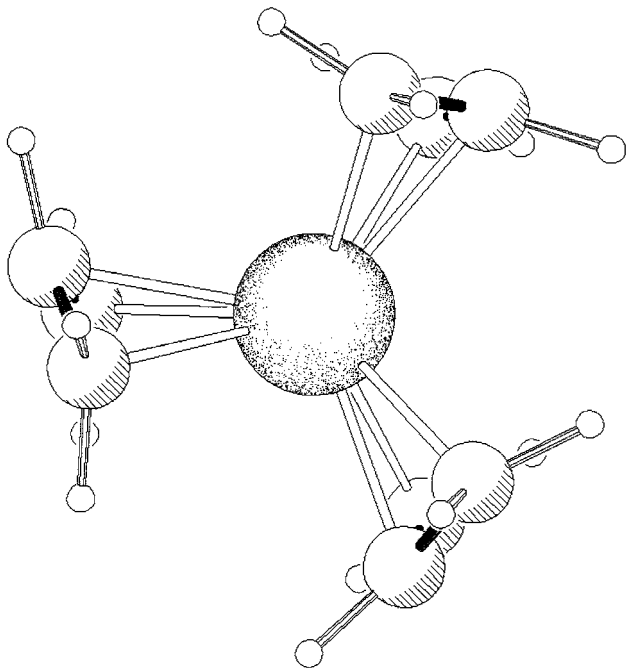


Fig. 1. The molecular structure of trisallylchromium in the ground state.

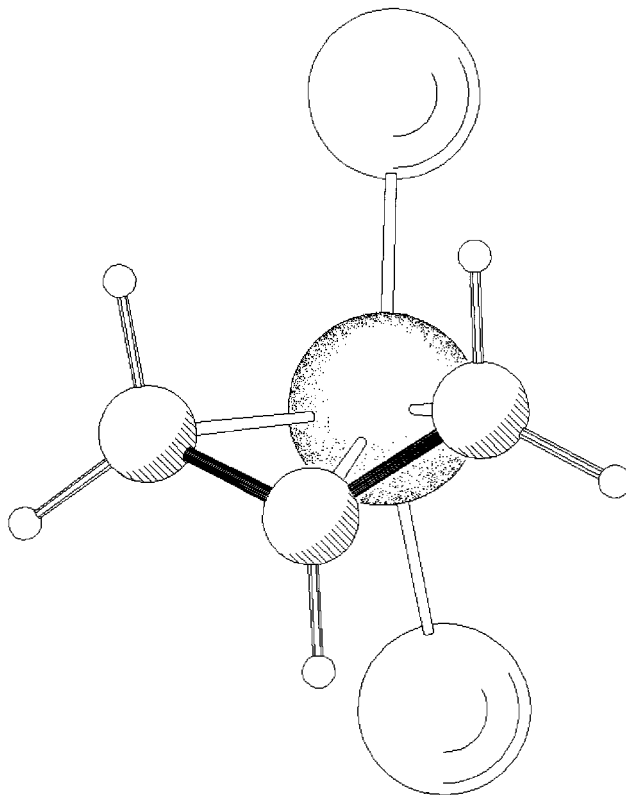


Fig. 3. The molecular structure of allylchromiumdibromide in the ground state.

Both  $\text{Cr}(\text{allyl})_3$  and  $\text{Cr}(2\text{-Me-allyl})_3$  show  $C_3$  symmetry; there is only one symmetrically independent allyl group, but all carbon atoms of each allyl group are symmetrically independent. Addition of a methyl group in the 2 position on the allyl ligands does not change the metal moiety much; the Cr–C distances are essentially the same, and the angle between the Cr–central C vector and the plane spanned by the three allylic carbons of a ligand changes only by  $2^\circ$  upon introducing methyl groups. The closest interligand C–C distance is 3.28 Å both for  $\text{Cr}(\text{allyl})_3$  and for  $\text{Cr}(2\text{-Me-allyl})_3$ . The single crystal XRD structure of  $\text{CpCr}(\text{allyl})_2$  show a piano-chair structure in which the  $\text{Cr}(\text{allyl})_2$  fragment has close to  $C_{2v}$  symmetry [20]. The chromium–allyl centroid distances of 1.908 Å is significantly shorter than the distance in  $\text{Cr}(\text{allyl})_3$  and  $\text{Cr}(2\text{-Me-allyl})_3$  of 2.00 Å, but similar to the distance in  $(\text{allyl})\text{CrBr}_2$  of 1.92 Å. When considering the higher co-ordination number of chromium in  $\text{CpCr}(\text{allyl})_3$  compared to the other complexes (CN = VII), the results are surprising. Also for Cr(II) bis(allyl) complexes in which chromium has a co-ordination number of VI, equal to that of the tris(allyl) complexes, the chromium–allyl distances are short, typically in the range 1.877–1.926 Å [21]. Due to the flat potential of the chromium–allyl bond and the general flexibility of the allyl ligand, the short chromium–allyl distances observed in complexes in the crystalline phase are attributed to crystal packing effects.

To our knowledge, no NMR results have been reported for  $\text{Cr}(\text{allyl})_3$  or  $\text{Cr}(2\text{-Me-allyl})_3$ , a fact which, most probably, is due to the paramagnetism of the complexes in question. Ballard et al. [6] have reported IR spectra of  $\text{Cr}(\text{allyl})_3$  and  $\text{Cr}(2\text{-Me-allyl})_3$  in hexane and decaline, respectively. For both complexes, a strong peak was observed at ca.  $1520\text{ cm}^{-1}$ , indicating tri-hapto bonded allyl ligands. Also peaks at about  $1640\text{ cm}^{-1}$  were observed indicating uncoordinated double bonds. The presence of these were attributed to the coupling products of the ligands, namely 1,5-hexadiene and 2,5-dimethylhexa-1,5-diene. Our results support their interpretation of the IR spectra, as our search for a stable conformer with a monohapto ligand proved fruitless. Furthermore, our calculated C–C stretch frequencies for  $(\text{allyl})\text{CrBr}_2$  are  $1455$  and  $1495\text{ cm}^{-1}$ .

Allylchromiumdibromide,  $(\text{allyl})\text{CrBr}_2$ , exhibits  $C_s$  symmetry. As seen from Table 1, the M–C distances of this complex are significantly shorter compared to the homoleptic allyl complexes. Also, there are only two symmetrically independent carbon atoms in the allyl group, in contrast to the homoleptic case. The lowest vibration frequency,  $31\text{ cm}^{-1}$ , corresponds to rotation of the allyl group about an axis close to the Cr–central C axis. Hence, the molecule will be highly fluxional even at low temperatures.

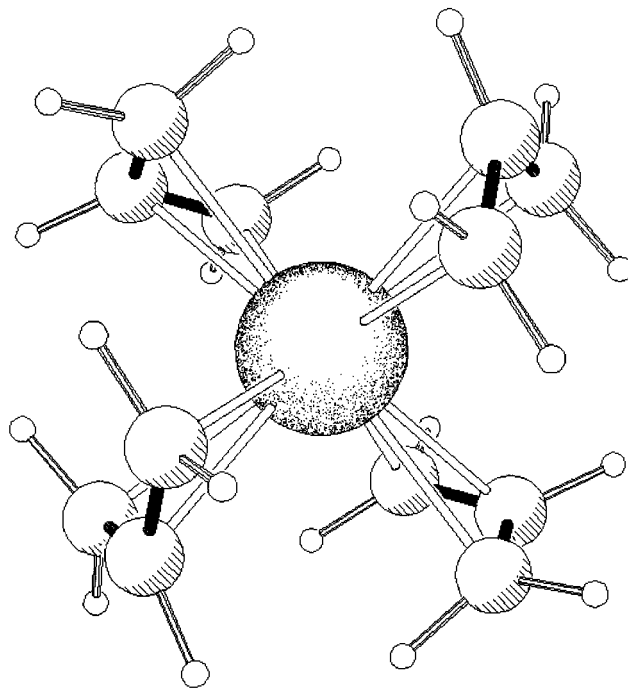


Fig. 4. The molecular structure of tetrakisallylzirconium in the ground state.

### 3.2. Zirconium

The ground-state DFT geometries for  $\text{Zr}(\text{allyl})_4$ ,  $\text{Zr}(2\text{-Me-allyl})_4$ , and  $(\text{allyl})\text{ZrBr}_3$  are shown in Figs. 4–6, respectively, and selected geometrical parameters from HF and DFT calculations are listed in Table 2. For these compounds, there is a somewhat better qualitative agreement between HF and DFT geometries. Calculated vibrational frequencies and intensities for  $(\text{allyl})\text{ZrBr}_3$  are listed in Table 3.

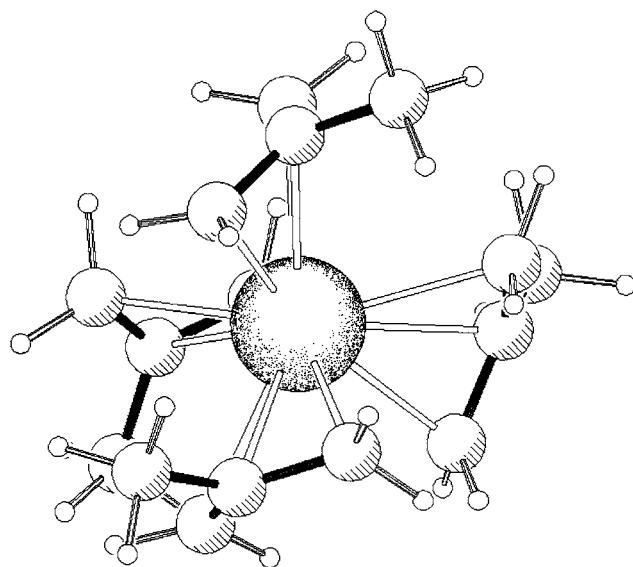


Fig. 5. The molecular structure of tetrakis-2-methylallylzirconium in the ground state.

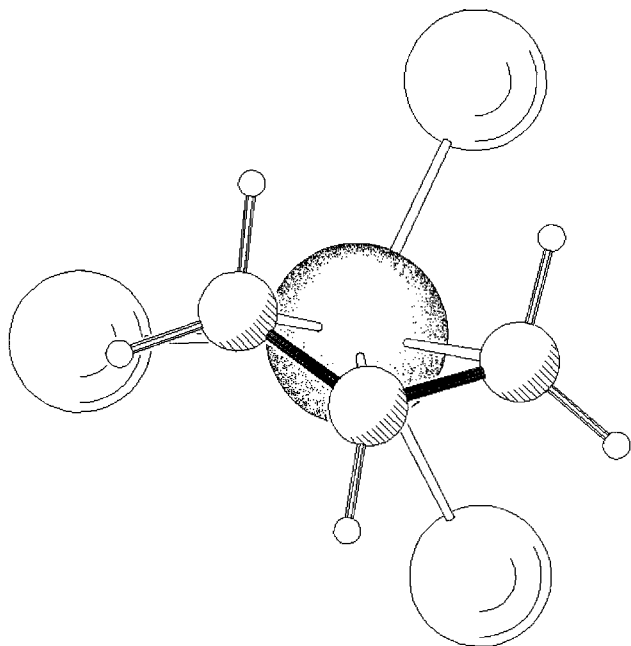


Fig. 6. The molecular structure of allylzirconiumtribromide in the ground state.

Tetrakisallylzirconium has a ground state geometry with  $S_4$  symmetry both according to the HF and DFT calculations, consistent with the results of Landis et al.

Table 2  
Selected interatomic distances (in Å) and angles (in degrees) for the zirconium compounds

Method	HF			DFT		
	Allyl	2Me	Br	Allyl	2Me	Br
r(Zr–C1)	2.46	2.16	2.21	2.56	2.52	2.40
r(Zr–C2)	2.61	2.38	2.55	2.59	2.62	2.50
r(Zr–C3)	2.69	2.44	2.85	2.56	2.60	2.52
r(C1–C2)	1.36	1.37	1.46	1.39	1.39	1.39
r(C2–C3)	1.43	1.45	1.35	1.40	1.42	1.41
r(C2–Cm)	—	1.51	—	—	1.51	—
r(Zr–Br)	—	—	2.49	—	—	2.53
$\angle$ C1–C2–C3	124	120	123	125	121	123
$\angle$ Br1–Zr–Br2	—	—	105	—	—	102
$\angle$ Br1–Zr–Br3	—	—	105	—	—	111
$\angle$ Br2–Zr–Br3	—	—	120	—	—	111
$\angle$ Zr-plane	51	50	52	51	51	50
$\angle$ H/Me-plane	14	6	13	13	6	16

C<sub>n</sub> denotes allylic carbon atom *n* in the only symmetrically independent allyl group. The  $\angle$  Zr-plane is the angle between the Zr–C2 vector and the plane spanned by the allylic carbons, and the  $\angle$  H/Me-plane is the angle between the allyl plane and the C2–H or C2–Me bond as appropriate.

[9]. For Zr(2-Me-allyl)<sub>4</sub>, the ground state geometry has  $S_4$  symmetry but is still qualitatively different from that of Zr(allyl)<sub>4</sub>, assuming a more oblate-like overall shape. Also, the Zr–C distances are somewhat more elongated upon introduction of a methyl group compared to the chromium case, indicating a larger steric strain. However, the shortest C–C contact distance decreases only by 0.01 Å, from 3.20 to 3.19 Å.

(Allyl)ZrBr<sub>3</sub> has no symmetry. We note that the M–C distances are significantly shorter than that of the two homoleptic allyl complexes, just as in the analogous chromium molecule. The reason might be partially electronic: The comparatively electron-withdrawing bromine ligands enhance the metal–allyl bonding, the latter being dependent on donation of electron density from the allyl ligand to the metal atom. The population analyses support this hypothesis: the combined Hirshfeld charge [22] on the allyl fragment decreases from –0.57 to –0.48 upon substituting bromine for three of the allyl ligands in Zr(allyl)<sub>4</sub>, indicating a greater electron donation to the metal centre in the latter case.

As for (allyl)CrBr<sub>2</sub>, the potential energy curve for rotation of the allyl group around the Zr–central C axis is very flat, the vibration frequency of the corresponding mode being only 8 cm<sup>–1</sup>. Further evidence for fluxionality of zirconium allyl compounds is offered by the XRD study of Erker et al. [23] on CpZr(allyl)<sub>3</sub>, which is the only published experimental geometry of a zirconium allyl compound we are aware of. This molecule shows two allyl groups in ‘almost-trihapto’ coordinations to the central atom, and one  $\sigma$ -bonded propenyl group, with a conspicuous lack of even local symmetry in the crystal at liquid nitrogen temperature. This, and the authors’ comparison to spectroscopic results, indicates that the molecule is highly fluxional in solution. As for the chromium case, the average Zr–C bond distance for the two trihapto-bonded allyl ligands in CpZr(allyl)<sub>3</sub> of 2.51 Å is shorter than the average distances in Zr(allyl)<sub>4</sub> and Zr(2-Me-allyl)<sub>4</sub> of 2.57 and 2.58 Å, respectively. In a similar manner the shortening can be rationalised as a consequence of the softness of the metal–allyl bonds in conjunction with crystal packing effects.

Zr(allyl)<sub>4</sub> shows a stationary point on the potential energy surface in which one of the allyl groups is  $\sigma$ -bonded. Only 3.4 kcal mol<sup>–1</sup> is necessary to promote Zr(allyl)<sub>4</sub> into this conformation, and the barrier for flipping back to the all- $\pi$  conformation is very small, possibly zero. We have not succeeded in locating a transition state (TS) for this process, probably because of the very flat potential energy curve combined with numerical noise from the integration algorithm, and the fact that TS optimisations are less numerically robust than minimisations. Hence, we cannot exclude the possibility that the  $\sigma$  conformer is a TS.

Table 3  
Computed (DFT) vibration spectra for (allyl)CrBr<sub>2</sub> and (allyl)ZrBr<sub>3</sub> (frequencies in cm<sup>-1</sup>, intensities in km mol<sup>-1</sup>)

(Allyl)CrBr <sub>2</sub>				(Allyl)ZrBr <sub>3</sub>		
Freq.	Irrep.	Int.	Assignment	Freq.	Int.	Assignment
30.7	A''	0.0	τ(Cr–allyl)	8.23	0.0	τ(Zr–allyl)
44.9	A'	0.9	δ(BrCrBr)	57.09	0.40	δ(BrZrBr)
86.6	A''	2.8	Allyl rocking	68.78	0.0	δ(BrZrBr)
95.6	A'	0.4	Allyl rocking	75.02	0.4	δ(BrZrBr)
211.3	A'	6.9	ν <sub>s</sub> (Cr–Br)	83.30	0.7	δ(ZrBr <sub>3</sub> ) umbrella
279.9	A''	5.3	Allyl rocking	95.27	0.0	Allyl rocking
322.6	A'	57.9	ν <sub>a</sub> (Cr–Br)	218.4	0.2	Allyl rocking
365.7	A'	16.0	ν(Cr–allyl)	231.1	8.8	ν <sub>s</sub> (Zr–Br)
410.6	A'	14.1	ν(Cr–allyl)	263.1	46.9	ν <sub>a</sub> (Zr–Br)
490.6	A'	9.0	δ(CCC)	284.8	51.1	ν <sub>a</sub> (Zr–Br)
630.9	A''	7.5	τ(CH <sub>2</sub> )	326.9	29.8	ν(Zr–allyl)
719.6	A'	2.6	τ(CH <sub>2</sub> )	370.0	5.8	ν(Zr–allyl)
821.4	A''	22.3	ρ(CH <sub>2</sub> )	435.2	10.6	δ(CCC)
867.8	A'	35.5	ρ(CH <sub>2</sub> ) out of plane	601.0	9.7	τ(CH <sub>2</sub> )
901.0	A''	0.0	ρ(CH <sub>2</sub> ) in plane	739.0	1.7	τ(CH <sub>2</sub> )
965.4	A'	8.0	ρ(CH) out of plane	778.0	14.3	ρ(CH <sub>2</sub> )
1012.6	A'	4.6	ν <sub>s</sub> (CCC)	845.8	88.4	ρ(CH <sub>2</sub> ) out of plane
1213.7	A''	13.0	ν <sub>a</sub> (CCC)	900.5	0.3	ρ(CH <sub>2</sub> ) in plane
1219.2	A'	1.0	ν <sub>s</sub> (CCC)	1007.1	24.8	ρ(CH) out of plane
1377.7	A''	3.1	δ <sub>a</sub> (CH <sub>2</sub> )	1023.0	0.9	ν <sub>s</sub> (CCC)
1455.5	A'	10.9	δ <sub>s</sub> (CH <sub>2</sub> )	1220.8	4.0	ν <sub>s</sub> (C–C)
1495.3	A''	26.7	ν <sub>a</sub> (CCC)	1240.7	8.7	ν <sub>a</sub> (C–C)
3036.8	A''	3.0	ν <sub>a</sub> (CH <sub>2</sub> )	1381.0	4.2	δ <sub>a</sub> (CH <sub>2</sub> )
3041.5	A'	0.9	ν <sub>s</sub> (CH <sub>2</sub> )	1454.5	11.2	δ <sub>s</sub> (CH <sub>2</sub> )
3084.9	A'	0.0	ν(CH)	1531.5	34.3	ν <sub>a</sub> (CCC)
3148.9	A''	0.1	ν <sub>a</sub> (CH <sub>2</sub> )	2995.6	7.1	ν(CH <sub>2</sub> )
3151.1	A'	1.8	ν <sub>s</sub> (CH <sub>2</sub> )	3027.3	6.3	ν(CH <sub>2</sub> )
				3053.9	0.9	ν(CH)
				3158.6	0.9	ν <sub>a</sub> (CH <sub>2</sub> )
				3160.5	0.8	ν <sub>s</sub> (CH <sub>2</sub> )

#### 4. Conclusions

All molecules investigated in the present study have ground state geometries with all allyl groups in trihapto coordination. HF calculations yield results in discrepancy with this for the homoleptic chromium systems. Based on the observation that UHF wavefunctions are heavily spin contaminated, we ascribe the discrepancy to near-degeneracy effects; hence the DFT results are more reliable. Attempts were made to find conformers with one of the allyl groups in monohapto coordination. Such a conformer was found for Zr(allyl)<sub>4</sub>. In all other cases the attempts were unsuccessful as the optimisations invariably converged to the ground state conformers regardless of the starting geometry. For the 2-methylallyl molecules, the steric strain appears to be somewhat greater for zirconium than for chromium. All systems seem to be easily deformed.

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