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Electronic transitions of racemic ethylene-bridged bis(indenyl)-type siloxy substituted zirconocene dichlorides. A combined UV/VIS spectroscopic and theoretical study

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The ligand to metal charge transfer (LMCT) transitions of racemic siloxy substituted ethylene bridged bis(indenyl)-type zirconocenes were studied using UV/VIS spectroscopy in combination with *ab initio* Hartree–Fock and hybrid density functional B3LYP methods. Clear correlations between the experimental LMCT absorption energies and theoretical HOMO–LUMO energy gaps were observed. The LMCT absorption energies were analysed as a function of the ligand structure. Hydrogenation of the indenyl ring and position of the siloxy substituent have strong influences on HOMO–LUMO energy gaps, and consequently on the observed absorption energies.

Introduction

Ligand to Metal Charge Transfer (LMCT) transitions can experimentally be detected using UV/VIS spectroscopy.[1] The lowest energy absorption band in the UV/VIS spectrum of a d^0 metallocene arises from charge transfer between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO of a d^0 metallocene is mainly Cp′-ligand based (Cp′ = any η^5-Cp type ligand) while the LUMO is mostly of metal character.[2] The energy of this particular absorption is of great importance, since it can be used to estimate the electron donating character of the Cp′ ligand as well as the electron deficiency of the metal center.[3] Such variations in the electronic structures of metallocenes have a significant influence on their most important industrial application *i.e.* olefin polymerisation by Group IV zirconocene catalysts.[4]

In the present work UV/VIS spectroscopy is utilised to measure the lowest energy LMCT absorptions for five racemic ethylene-bridged bis(indenyl)-type siloxy substituted zirconocene dichlorides. The corresponding unsubstituted zirconocene is included as a reference (Fig. 1). The studied catalyst precursors represent a uniform group of molecules with high olefin polymerisation activities. The absorption energies are studied as a function of the ligand structure with the object of clarifying the correlations between the electronic and steric structure of the ligand, and the energy of the lowest energy absorption. As mentioned, the lowest energy absorption should correlate with the HOMO–LUMO energy gap. Therefore the experimental absorption energies are compared with theoretical HOMO–LUMO energy gaps.

Experimental

Siloxy substituted zirconocenes were synthesized and characterised by Leino *et al.*[5] and complex **6** was purchased from Witco. All measurements were performed in inert conditions. For the UV/VIS measurements the appropriate concentration of the

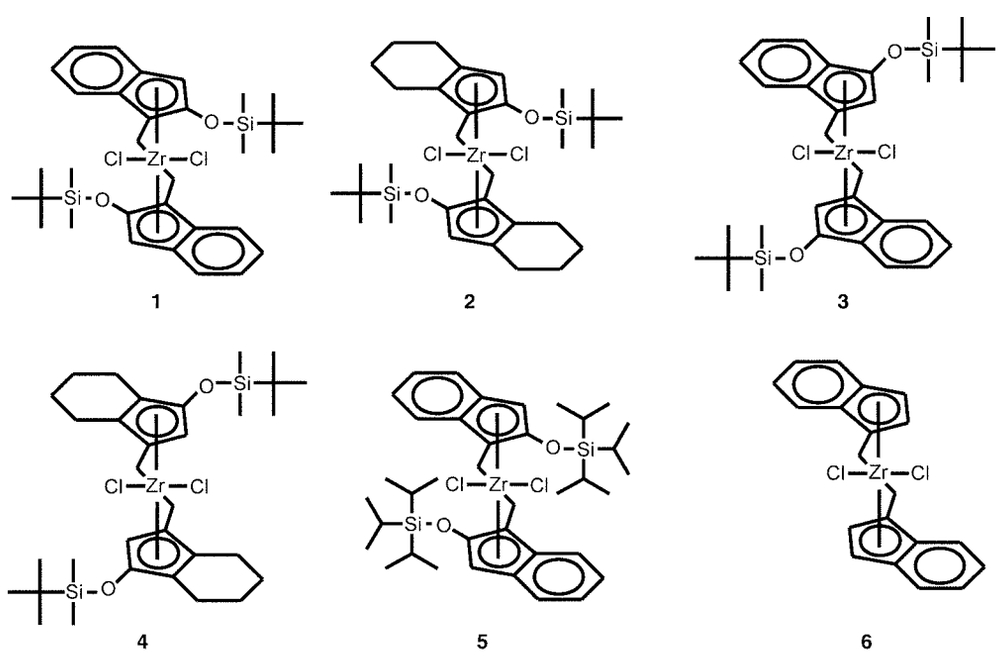

Fig. 1 Schematic structures of the studied zirconocenes.

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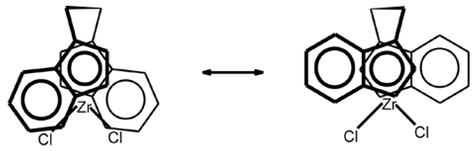

Π Y

Fig. 2 Top view of indenyl-forward (Π) and indenyl-backward (Y) conformations.

metallocene was found to be 8×10^{-4} mol L^{-1} and dry toluene was used as solvent. One cm path length Suprasil quartz cells with Teflon stoppers were filled with the sample in inert atmosphere. UV/VIS spectra of the complexes were measured with a Perkin-Elmer Lambda 11 spectrophotometer in the wavelength range 200–800 nm, scan speed 240 nm min^{-1} and data interval 1 nm.

Computational aspects

The treatment of transition metal complexes by *ab initio* molecular orbital methods is generally difficult mainly due to near-degeneracy and relativistic effects.[6,7] However, because of the location of zirconium at the beginning of the second transition row in the Periodic Table, resulting in small near-degeneracy and relativistic effects, the geometry optimisation of the zirconocenes is exceptionally feasible. This has been demonstrated with a set of 62 bridged zirconocenes using the Hartree–Fock method at the 3-21G* level.[8] Based on this finding, the HF/3-21G* method was selected for geometry optimisations in the present work. All reported calculations were carried out with the GAUSSIAN 94 program package.[9]

For studies concerning electronic transitions in molecules sophisticated methods are generally required. High level methods are, however, impractical for zirconocenes of this size, and unnecessary considering the purpose of this work. Instead of high quantitative accuracy at any cost, the capability of a lower level method in providing the right trends is often more beneficial. Succeeding in this would mean the capability of producing LMCT energies for non-existing zirconocenes of at least the same type. Orbital energy calculations were performed using HF/3-21G*, HF/6-31G*, and the hybrid density functional B3LYP/6-31G* method.[10,11] The GAUSSIAN 94 program includes standard basis sets up to 3-21G* for zirconium. Therefore, when a larger basis set than 3-21G* was utilised for the rest of the molecule zirconium was described by Huzinaga's extra basis (Zr,433321/433/421).[12]

The ethylene bridge, as well as any other two-atom interannular bridge, creates an element of fluxionality in metallocenes. The bridge combined with bis(indenyl) or bis(tetrahydroindenyl) based ligands, results in two limiting conformations, indenyl-forward (Π) and indenyl-backward (Y) (Fig. 2).[13] In siloxy substituted zirconocenes these conformations are separated by a small rotation barrier, and the conformational energy differences are relatively small.[14] Hence, the interconversion between the Π and Y conformations is rapid and both conformers exist in solution. The consequence of the facility of this interconversion is that the crystal structure alone is inadequate to describe the structures of the studied zirconocene dichlorides. Therefore, geometry optimisation as well as orbital energy calculations were performed for both Π and Y conformations. The geometry minima were confirmed by frequency calculations.

Results and discussion

Correlations between experimental and theoretical results

Frontier orbitals of complex **1** are shown in Fig. 3. As illustrated, the HOMOs of the studied zirconocenes are mainly of Cp′ ligand character whereas the LUMOs are zirconium based. These characteristics of the frontier orbitals make comparisons between the lowest energy LMCT absorptions and HOMO–LUMO energy gaps viable.

Comparisons between the lowest energy LMCT absorptions and the HOMO–LUMO energy gaps calculated at the Hartree–Fock level are presented in Fig. 4. Energies are given for both Π and Y conformations. Overall, the differences in orbital energies between the conformations are small. This is in contrast to the unbridged indenyl ligand for which Hückel calculations have demonstrated that the HOMO–LUMO energy gap is considerably changed if the orientation of the indenyl ligand is altered.[16] It should be noted, however, that the unbridged ligand has more freedom for movement than its ethylene bridged congener. Hence, the fluxionality of the indenyl ligand in ethylene-bridged metallocenes is restricted to a narrower area, and within this the frontier orbital energy differences are almost constant.

The calculated HOMO–LUMO energy gaps are practically independent of the basis set used. They are approximately three times higher than the experimental LMCT absorption energies, but the overestimation is very systematic. As a consequence, the correlations between the HF calculations and the experimental absorption energies are highly accurate with correlation coefficients of 0.99 for both conformations with both basis sets. Apparently, the Hartree–Fock method even with small basis sets can reliably be utilised in qualitative studies at least concerning the electronic transitions in the siloxy substituted zirconocenes.

The corresponding comparison between experimental lowest energy LMCT absorptions and HOMO–LUMO energy gaps calculated at the B3LYP/6-31G* level is presented in Fig. 5. As with the Hartree–Fock method, the energy gaps between the Π and Y conformations are small, and the trends in calculated energy gaps correlate with the experimental absorption energies. The correlation is slightly worse than at the Hartree–Fock level, with coefficients of 0.98 and 0.94 for Π and Y conformations, respectively. However, the quantitative prediction is far more accurate. Experimental lowest energy LMCT absorptions and theoretical HOMO–LUMO energy gaps are summarised in Table 1.

The influence of molecular structure on the LMCT absorptions

The basic geometry parameters of d^0 zirconocenes are shown in Fig. 6 and presented for the studied zirconocene complexes together with the lowest energy LMCT absorptions and calculated energies of HOMOs and LUMOs in Table 2. In the following the influence of molecular structure on LMCT absorption energies will be analysed.

The siloxy group. In order to avoid multiple simultaneous effects that would complicate the interpretation, the general influence of a siloxy group should be studied by comparing the unsubstituted bis(indenyl) zirconocene **6** to the siloxy substituted bis(indenyl)-type complexes **1**, **3** and **5**. While the LMCT absorption energies are influenced only slightly, the changes in orbital energies are significant. Both HOMO and LUMO become destabilised by the introduction of siloxy substituent (Fig. 7a). The destabilisation of the frontier orbitals is dependent on the type of the siloxy substituent, resulting in different changes in LMCT absorption energies.

The destabilisation of the Cp′-ligand based HOMO is directly proportional to a decrease in LMCT absorption energy because of the lowered LUMO–HOMO energy gap. Hence, the energy of the HOMO is related to the facility of electron transfer from the ligand (HOMO) to the metal (LUMO). A siloxy group destabilises the HOMO by donating electrons to the Cp′ ligand, which facilitates donation of electrons from it to the metal. Consequently, the siloxy groups are electron donors like the similar methoxy group.[17]

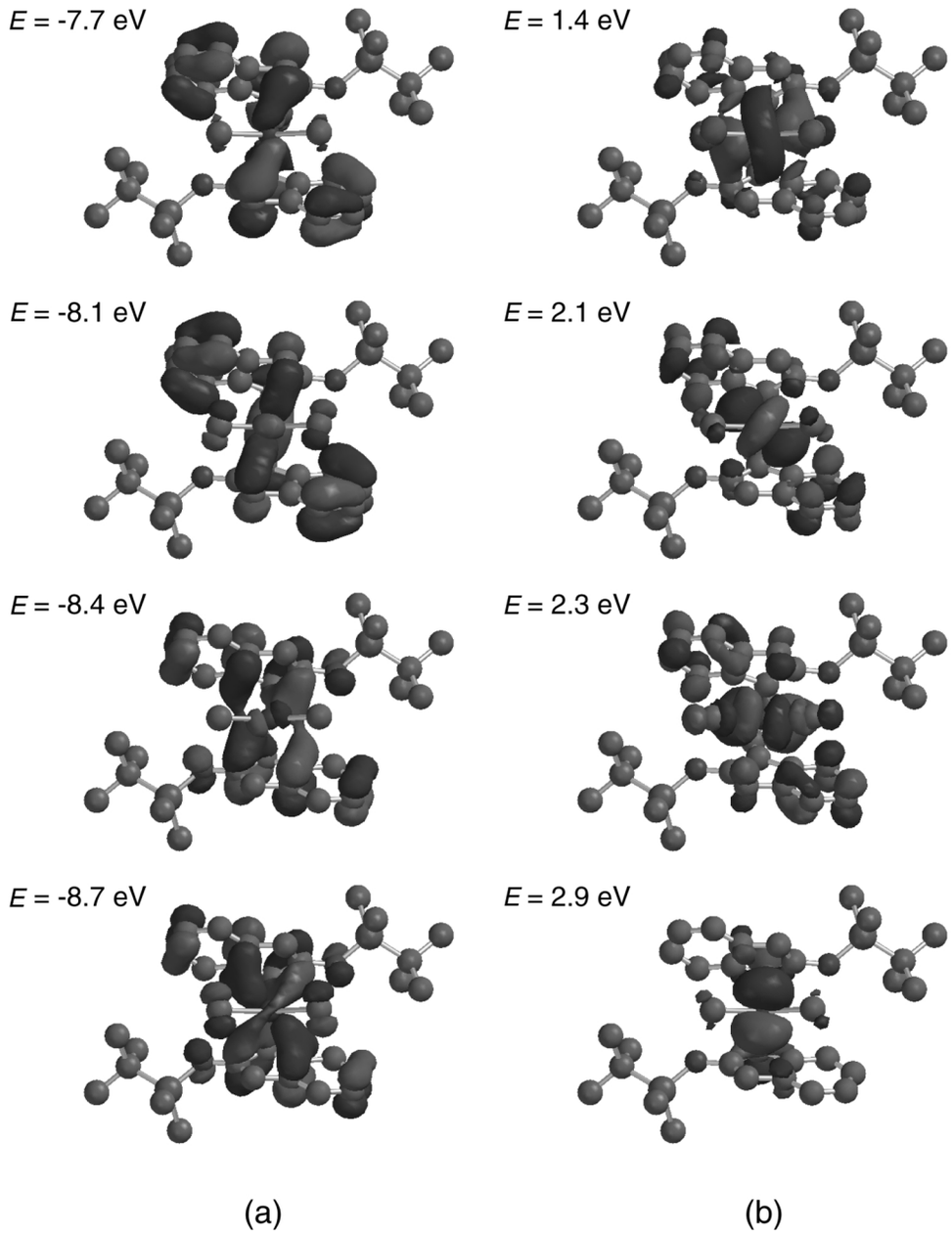

Fig. 3 HF/3-21G* calculated frontier orbitals for the crystal structure conformation (Y) of complex **1**. (a) Four highest occupied molecular orbitals and (b) four lowest unoccupied molecular orbitals. Hydrogens are omitted for clarity.[15]

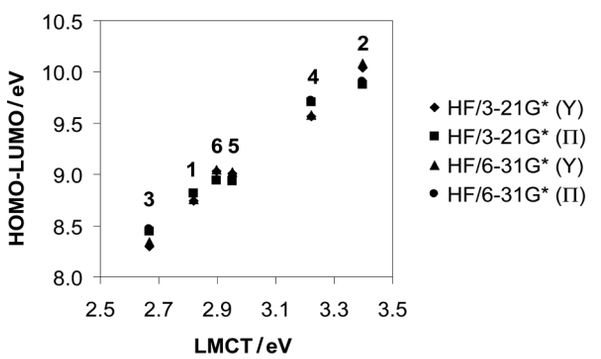

Fig. 4 Comparison of the experimental lowest energy LMCT absorptions and the HOMO–LUMO energy gaps calculated at the Hartree–Fock level.

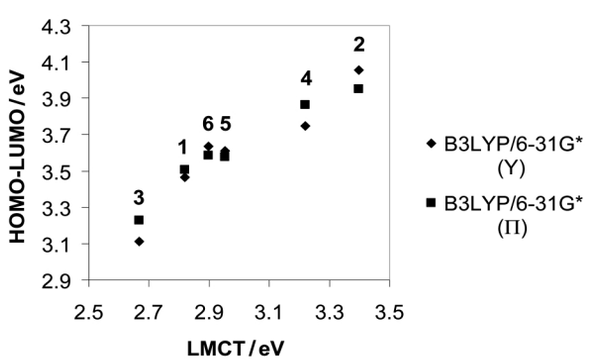

Fig. 5 Comparison of the experimental lowest energy LMCT absorptions and the HOMO–LUMO energy gaps at the B3LYP/6-31G* level.

The destabilisation of the metal-based LUMO orbital is directly proportional to an increase in LMCT absorption energy because of a widened LUMO–HOMO energy gap. Therefore, the energy of the LUMO is naturally dependent on the electron deficiency of the metal. Also destabilisation of it occurs because of the presence of the electron donating siloxy group. The oxygen donor atom of the substituent approaches the metal center, and the calculated Zr–O distance varies between 3.45 and 3.62 Å. The closeness of oxygen decreases the

Table 1 Summary of experimental lowest energy LMCT absorptions (eV) and theoretical HOMO–LUMO energy gaps (eV)

		Indenyl-forward (Π)			Indenyl-backward (Y)		
Complex	LMCT	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*	HF/3-21G*	HF/6-31G*	B3LYP/6-31G*
1	2.90	8.94	8.94	3.59	9.03	9.04	3.64
2	3.40	9.88	9.90	3.95	10.04	10.08	4.05
3	2.67	8.45	8.47	3.23	8.30	8.34	3.11
4	3.22	9.71	9.72	3.86	9.57	9.58	3.75
5	2.95	8.93	8.93	3.58	9.01	9.03	3.61
6	2.82	8.81	8.82	3.51	8.74	8.76	3.46

Table 2 LMCT absorptions (eV), HF/3-21G* optimised geometry parameters (Å and °), and B3LYP/6-31G* calculated HOMO and LUMO energies (eV) for the studied zirconocene dichlorides. Experimental geometry parameters, when available, are given in parentheses

		Indenyl-forward (Π)						Indenyl-backward (Y)					
Complex	LMCT	*a*	*α*	*β*	*θ*	HOMO	LUMO	*a*	*α*	*β*	*θ*	HOMO	LUMO
1	2.90	2.27	60	126	3	−5.43	−1.84	2.27 (2.25)	60 (61)	127 (126)	3 (3)[a]	−5.57	−1.94
2	3.40	2.25	58	124	1	−5.76	−1.81	2.25 (2.23)	58 (58)	125 (125)	1 (2)[b]	−5.84	−1.79
3	2.67	2.28	66	127	7	−5.15	−1.93	2.28	65	128	7	−5.16	−2.04
4	3.22	2.26 (2.24)	64 (64)	126 (126)	5 (5)[c]	−5.71	−1.84	2.26	63	126	5	−5.63	−1.88
5	2.95	2.27 (2.24)	60 (58)	126 (126)	3 (2)[d]	−5.44	−1.86	2.27	61	126	4	−5.58	−1.97
6	2.82	2.27 (2.24)	62 (60)	125 (125)	3 (3)[e]	−5.64	−2.14	2.27	60	126	3	−5.75	−2.28

[a] Ref. 5(*a*). [b] Ref. 5(*b*). [c] Ref. 5(*e*). [d] Ref. 5(*c*). [e] Ref. 6.

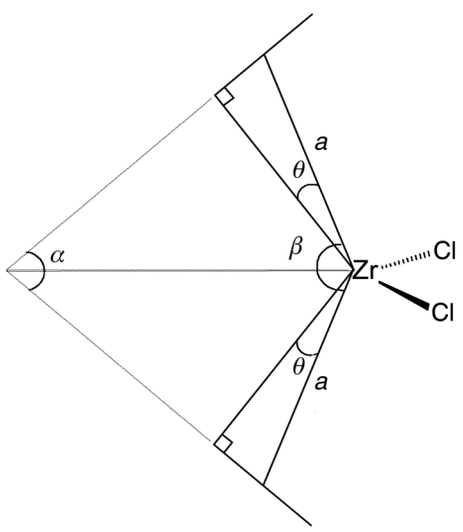

Fig. 6 Cross section of a zirconocene dichloride. a = Zr–Cp′ distance, α = Cp′–Cp′ plane angle, β = Cp′–Zr′–Cp′ angle, θ = displacement of the ring centroid from the normal to the ring plane = $\frac{1}{2}(\alpha + \beta - 180)$.

partial positive charge of zirconium which leads to stabilisation of the LUMO.

Indenyl ring hydrogenation. The bis(indenyl)-based complexes **1** and **3** have the LMCT absorptions at 2.90 eV and 2.67 eV, respectively. The absorption energies are clearly higher for the corresponding bis(tetrahydroindenyl)-based complexes **2** (3.40) and **4** (3.22 eV). Hydrogenation of the indenyl ring leads to increased LMCT absorption energies, due to considerable stabilisation of the HOMO combined with destabilisation of the LUMO (Fig. 7b). The influences on the structure parameters of the complexes, which apparently contribute to the energies of the frontier orbitals, are systematic. Cp′–Zr–Cp′ angles, Cp′–Cp′ plane angles and ring slippage angles somewhat decrease, while Zr–Cp′ distances shorten by 0.02 Å.

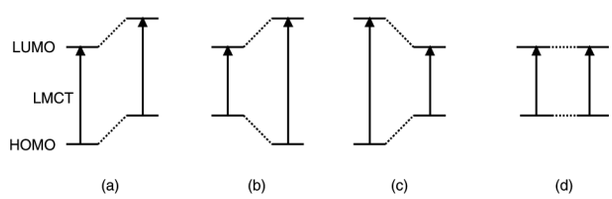

Fig. 7 Schematic presentation of the relationships between molecular structure, frontier orbital energies and LMCT absorption energies. The influences of (a) a siloxy group, (b) indenyl ring hydrogenation, (c) replacing a 2- with a 1-siloxy substituent and (d) increasing the size of a siloxy substituent.

The HOMOs of the genuine bis(indenyl)-based complexes are higher than those of the bis(tetrahydroindenyl)-based complexes. Destabilisation of the LUMO increases the Cp′→Zr charge transfer energy, therefore suggesting decreased electron deficiency of the metal for the hydrogenated complexes.

Position of the siloxy group. Moving the 2-siloxy group to position 1 decreases the LMCT absorption energy of complex **1** from 2.90 to 2.67 eV (complex **3**). Correspondingly, the LMCT absorption of bis(tetrahydroindenyl)-based **2** decreases from 3.40 to 3.22 eV (complex **4**). Decreased absorption energies are due to both destabilisation of the HOMO and stabilisation of the LUMO (Fig. 7c). The position of the siloxy substituent has a strong influence on the complex geometry. Zr–Cp′ distances and Cp-Zr–Cp′ angles are slightly enlargened, whereas in Cp′–Cp′ angles and in ring slippage angles the increase is considerable.

Destabilisation of the HOMO, resulting in facilitation of electron transfer, possibly occurs due to distortion of the geometry from the optimal bonding orientation between the metal and Cp′-ligand orbitals. The stabilisation of LUMO suggests increased electron deficiency of the metal for 1-siloxy substituted complexes, and can be explained by an interaction between zirconium and the substituent. The position of the substituent affects the distance between the metal and the

oxygen donor atom of the siloxy group. The calculated distances are shorter for 2-siloxy substituted **1** (3.45) and **2** (3.45 Å), than for 1-siloxy substituted **3** (3.62) and **4** (3.59 Å). Owing to longer Zr–O distances in 1-siloxy substituted complexes, the decrease in the charge of Zr is less significant. Consequently, the LUMO becomes stabilised and the LMCT absorption energy decreases.

Size of the siloxy group. The influence of the size of the siloxy group can be studied by comparing 2-*tert*-butyldimethylsiloxy substituted **1** with triisopropylsiloxy substituted **5**. The changes in LMCT absorptions, geometry parameters and orbital energies are only marginal (Fig. 7d). Therefore it can be concluded that small variations in the size of the 2-siloxy substituents result in neither steric nor electronic changes in the molecule.

Conclusions

Theoretical methods can be used to estimate the LMCT absorption energies of siloxy substituted zirconocenes. The lowest energy LMCT absorptions correlate very well with the HOMO–LUMO energy gaps calculated with Hartree–Fock and B3LYP methods. The numerical agreement is better for B3LYP, while qualitative trends are more accurately produced by the less expensive Hartree–Fock method.

The introduction of a siloxy group has no or marginal effects on LMCT absorptions as long as the structure of the complex is not significantly changed. This is due to equal destabilisation of both HOMO and LUMO. Hydrogenation of the indenyl ring stabilises the HOMO and destabilises the LUMO, hence increasing the HOMO–LUMO energy gap as well as LMCT absorption energies. Furthermore, the energies of the frontier orbitals are dependent on the position of the siloxy substituent, whereas the size of the substituent has no significant influence.

References

1 R. Denney, *Visible and Ultraviolet Spectroscopy*, John Wiley & Sons, New York, 1987; H. H. Jaffé and M. Orchin, *Theory and Applications of Ultravolet Spectroscopy*, John Wiley and Sons, Inc., New York, 1962, pp. 508–513; C. N. R. Rao, *Ultra-Violet and Visible Spectroscopy*, *Chemical Applications*, Butterworths, London, 1961, p. 111.

2 M. R. M. Bruce, A. Kenter and D. R. Tyler, *J. Am. Chem. Soc.*, 1984, **106**, 639; J. W. Kenney, III, D. R. Boone, D. R. Striplin, Y. Chen and K. B. Hamar, *Organometallics*, 1993, **12**, 3671.

3 R. W. Harrigan, G. S. Hammond and H. B. Gray, *J. Organomet. Chem.*, 1974, **81**, 79; D. Coevoet, H. Cramail and A. Deffieux, *Macromol. Chem. Phys.*, 1998, **199**, 1451; D. Coevoet, H. Cramail and A. Deffieux, *Macromol. Chem. Phys.*, 1998, **199**, 1459; J. Pédeutour, D. Coevoet, H. Cramail and A. Deffieux, *Macromol. Chem. Phys.*, 1999, **200**, 1215; P. J. J. Pieters, J. A. M. van Beek and M. F. H. van Tol, *Macromol. Rapid Commun.*, 1995 **16**, 463; J. A. M. van Beek, P. J. J. Pieters and M. F. H. van Tol, *Metallocenes '95*, Brussels, April 26–27, 1995.

4 For recent reviews, see for example: H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1143; W. Kaminsky, *Macromol. Chem. Phys.*, 1996, **197**, 3907; W. Kaminsky and M. Arndt, *Adv. Polym. Sci.*, 1997, **127**, 143; O. Olabisi, M. Atiqullah and W. Kaminsky, *J. Macromol. Sci.*, *Rev. Macromol. Chem. Phys.*, 1997, **C37**, 519; K. Soga and T. Shiono, *Prog. Polym. Sci.*, 1997, **22**, 1503; A. Togni and R. L. Halterman, (Editors), *Metallocenes: Synthesis*, *Reactivity*, *Applications*, Wiley-VCH, Weinheim, 1998.

5 (*a*) R. Leino, H. Luttikhedde, C.-E. Wilén, R. Sillanpää and J. H. Näsman, *Organometallics*, 1996, **15**, 2450; (*b*) R. Leino, H. J. G. Luttikhedde, P. Lehmus, C.-E. Wilén, R. Sjöholm, A. Lehtonen, J. V. Seppälä and J. H. Näsman, *Macromolecules*, 1997, **30**, 3477; (*c*) H. J. G. Luttikhedde, R. Leino, A. Lehtonen and J. H. Näsman, *J. Organomet. Chem.*, 1998, **555**, 127; (*d*) R. Leino, H. J. G. Luttikhedde, P. Lehmus, C. E. Wilen, R. Sjöholm, A. Lehtonen, J. V. Seppälä and J. H. Näsman, *J. Organomet. Chem.*, 1998, **559**, 65; (*e*) R. Leino, H. J. G. Luttikhedde, A. Lehtonen, P. Ekholm and J. H. Näsman, *J. Organomet. Chem.*, 1998, **558**, 181; (*f*) O. Härkki, P. Lehmus, R. Leino, H. J. G. Luttikhedde, J. H. Näsman and J. V. Seppälä, *Macromol. Chem. Phys.*, 1999, **200**, 1561; (*g*) P. Lehmus, O. Härkki, R. Leino, H. J. G. Luttikhedde, J. H. Näsman and J. V. Seppälä, *Macromolecules*, 1999, **32**, 3547.

6 P. E. M. Siegbahn, *Adv. Chem. Phys.*, 1996, **93**, 333.

7 P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563.

8 M. Linnolahti, P. Hirva and T. A. Pakkanen, *J. Comput. Chem.*, in press.

9 GAUSSIAN 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Lahman, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

10 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

11 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

12 S. Huzinaga, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, 1984.

13 F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, A. Sironi, M. Moret, R. Zeigler and N. Piccolrovazzi, *Organometallics*, 1995, **14**, 1256.

14 M. Linnolahti, T. A. Pakkanen, R. Leino, H. J. G. Luttikhedde, E.-C. Wilén and J. H. Näsman, *Eur. J. Inorg. Chem.*, submitted.

15 PC Spartan Pro 1.0., B. J. Deppmeier, A. J. Driessen, W. J. Hehre, P. E. Klunzinger, L. Lou and J. Yu, Wavefunction, Inc., Irvine, CA, 1999.

16 H. H. Brintzinger, personal communication.

17 N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi and M. Moret, *Organometallics*, 1990, **9**, 3098.