PERKIN 2

GIAO-DFT study of ^{13}C NMR chemical shifts of highly pyramidalized alkenes

Santiago Vázquez *

Laboratori de Química Farmacèutica (Unitat Associada al CSIC), Facultat de Farmàcia,
Universitat de Barcelona, Av. Diagonal 643, Barcelona, E-08028, Spain.
E-mail: svazquez@farmacia.far.ub.es; Fax: +34 9340 35941; Tel: +34 9340 24542

Received (in Cambridge, UK) 18th July 2002, Accepted 1st October 2002
First published as an Advance Article on the web 1st November 2002

The ^{13}C NMR chemical shifts of several pyramidalized alkenes were calculated using the *ab initio* GIAO method at the B3LYP/6-31G(d) and MPW1PW91/6-31G(d) levels using the geometry optimized at the B3LYP/6-31G(d) level. Where comparison data were available, the experimental values were in good agreement with the calculated ones. From the data obtained, the olefinic ^{13}C chemical shifts are downfield shifted on increasing pyramidalization.

Introduction

Pyramidalized alkenes are molecules containing carbon–carbon double bonds in which one or both of the sp^2 carbon atoms do not lie in the same plane as the attached atoms.[1] These kind of alkenes are very interesting targets for both synthetically and theoretically oriented organic chemists due to their intriguing physical properties and their fascinating reactivity. In recent years considerable attention has been focused on the synthesis, chemical trapping and dimerization of highly pyramidalized alkenes. Some of the most recent examples of highly pyramidalized alkenes include cubene,[2] several unsaturated dodecahedranes,[3] tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene and related compounds,[4] tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene,[5] and others.[6] Due to the instability of these compounds, their physical and chemical properties have been studied only on the less pyramidalized ones.[7] *Ab initio* methods are a powerful tool for predicting properties of unstable compounds and many computational predictions carried out on pyramidalized alkenes have experimentally been confirmed.[8]

The calculation of NMR chemical shifts constitutes an important challenge for computational chemistry and during the last decade significant progress has been made in this field.[9] This work reports a DFT study of ^{13}C NMR chemical shifts of several pyramidalized alkenes using the GIAO method.[10]

Computational methods

Recent studies show that electron correlation contributions should be included to obtain the most accurate shielding tensor.[11] Density functional theory (DFT)[12] provides a lower cost alternative to the more traditional electron correlation techniques such as the Møller–Plesset (MP*n*) methods.[13] It has been found that, for the calculation of NMR chemical shifts, relatively simple and computationally inexpensive DFT approaches often give accurate and stable results, of a quality comparable or even better than MP2.[14] On the other hand, recent studies have shown that DFT calculations are probably the most reliable methods (excluding very expensive MCSCF calculations) for studying properties of highly pyramidalized alkenes.[15]

Therefore, geometry optimizations were carried out at Becke's three-parameter hybrid functional with the Lee, Yang and Parr correlation functional (B3LYP) level[16] using the 6-31G(d) basis set.[17] The minimum energy nature of the optimized structures was verified from vibrational frequency analysis. The ^{13}C NMR shielding (σ_c) calculations were carried out using the GIAO approach at different levels of the theory. The chemical shifts predictions (δ_c) with respect to tetramethylsilane were determined using the calculated shielding of tetramethylsilane (σ_{TMS}) at the same level ($\delta_c = \sigma_{TMS} - \sigma_c$). †

All quantum chemical calculations were carried out with the Gaussian 94[18] and Gaussian 98[19] programs on an IBM SP/2 computer.

Results and discussion

In order to examine the dependence of the ^{13}C NMR chemical shift of non-isolable, highly pyramidalized alkenes on the level of theory, calculations were performed for (i) two highly pyramidalized but isolable compounds: 1,16-dodecahedradiene (pyramidalization angle,[1a] $\Phi = 39.9°$), **1**,[3a] and hexacyclo-[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione ($\Phi = 46.5°$), **2**;[20] (ii) the less pyramidalized alkenes tricyclo[3.3.3.0^{3,7}]undec-3(7)-ene ($\Phi = 28.1°$), **3**,[8] and bicyclo[3.3.0]oct-1(5)-ene ($\Phi = 5.9°$), **4**,[21] and (iii) the non-pyramidalized but highly strained bicyclo[2.2.0]hex-1(4)-ene, **5**,[22] (Fig. 1).

The experimental ^{13}C NMR chemical shifts of these compounds have been previously described.[3a,8,20–22] The ^{13}C NMR shielding calculations were carried out using the GIAO

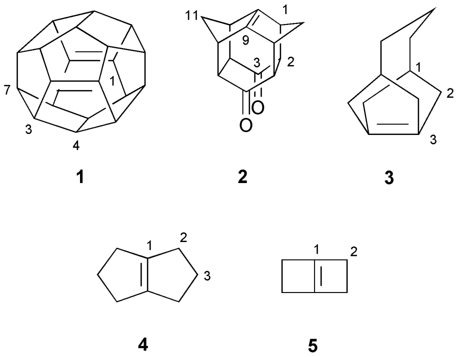

Fig. 1 Pyramidalized and strained alkenes.

---

† The absolute shielding values for the carbon atom of tetramethylsilane at HF/6-31G(d)//B3LYP/6-31G(d) is 200.0, at B3LYP/6-31G-(d)//B3LYP/6-31G(d) is 189.7 and at MPW1PW91/6-31G(d)//B3LYP/6-31G(d) is 193.8.

DOI: 10.1039/b207060j

Table 1 Calculated and experimental ^{13}C NMR chemical shifts (δ, ppm) and $\Delta E_{HOMO-LUMO}$ (eV) for **1**–**5**

		HF/6-31G(d)	B3LYP/6-31G(d)	MPW1PW91/6-31G(d)	Exp.	$\Delta E_{HOMO-LUMO}$ [a]
	C1	170.0	165.9	167.0	170.5	
	C3	54.5	62.4	62.6	61.4	
1	C4	65.7	74.6	74.6	73.3	5.48
	C7	51.4	59.4	58.9	57.4	
	C1	44.7	54.1	53.7	52.3	
	C2	47.1	58.1	57.1	56.6	
2	C3	206.1	200.4	202.1	211.7	5.68
	C9	157.9	152.0	152.6	154.9	
	C11	37.4	42.7	42.6	42.3	
3 [b]	C3	161.2	155.0	156.1	157.3	6.00
	C1	146.6	142.7	143.9	146.0	
4	C2	27.5	30.8	31.0	29.2	6.90
	C3	27.4	31.2	31.0	28.4	
5	C1	168.7	158.0	159.7	163.5	
	C2	40.3	43.8	44.6	43.7	7.40
rms		5.4	4.0 [c]	3.3 [c]		

[a] HOMO–LUMO gap calculated by B3LYP/6-31G(d). [b] Although compound **3** is known, only the chemical shift of the olefinic carbon atom was published by the author.[8] [c] If the carbonyl carbon C3 of compound **2** is not considered, the rms for B3LYP/6-31G(d) is 2.8 and for MPW1PW91/6-31G(d) is 2.1.

approach at different levels of the theory [HF/6-31G(d), B3LYP/6-31G(d) and MPW1PW91/6-31G(d)[23]] (see Table 1). Although the calculated values using GIAO-HF/6-31G(d) are in acceptable agreement with the experimental data, some of the differences are large (see for example C4 in **1**, C2 in **2** or C1 in **5**). GIAO-B3LYP/6-31G(d) ^{13}C NMR chemical shifts are in very good agreement with the experimental data and GIAO-MPW1PW91/6-31G(d) performs even better, in line with recent findings of Wiberg.[14c]

Worthy of note, using DFT, all the chemical shifts calculated for the olefinic carbon atoms are slightly underestimated (2–5 ppm) and for the non-olefinic carbons are slightly overestimated (1–3 ppm). It is remarkable the excellent agreement found in the highly pyramidalized dodecahedradiene, **1**. The better results found with DFT calculations are not unexpected taking into account that correlation energy plays an unusually important role in strained systems[24] and that for molecules containing significant electron correlation effects HF methods are generally unreliable and fail to accurately predict the nuclear shielding parameters.[11] Nevertheless, for compound **5**, all the methods used in this work give results that are in better agreement with the experimental values than the results previously calculated by Prakash *et al.* using the IGLO method at the DZ level.[25]

Recently, Forsyth *et al.* demonstrated that accurate predictions of ^{13}C chemical shifts for a variety of organic molecules containing C, H, N and O could be achieved through empirical scaling of shieldings calculated from GIAO theory with a small basis set and with geometries obtained from a computationally inexpensive molecular mechanics methods.[26] However, for compounds **1**–**5**, Forsyth's relationship gave worse results than those obtained in Table 1 by just taking the difference between the calculated shieldings and that for TMS. Presumably, Forsyth's parameterization is not effective for highly strained compounds. In fact, it is known that molecular mechanics methods are not reliable for highly pyramidalized alkenes.[27]

Taking into account the good agreement between B3LYP/6-31G(d) and MPW1PW91/6-31G(d) calculations and the experimental data for compounds **1**–**5**, we next carried out GIAO-B3LYP/6-31G(d) and GIAO-MPW1PW91/6-31G(d) calculations on the highly pyramidalized alkenes shown in Fig. 2. Compounds **6**,[28] **7**,[29] **8**,[4c] **9**,[4a] **10**,[15a] **11**[30] and **12**[2b] had been previously synthesized but they were found too unstable and were isolated as Diels–Alder adducts or dimers.

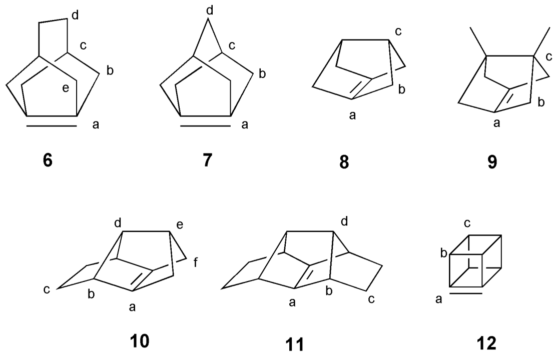

Fig. 2 Highly pyramidalized alkenes.

Table 2 shows the GIAO-B3LYP/6-31G(d) and GIAO-MPW1PW91/6-31G(d) calculated ^{13}C NMR chemical shifts for the highly pyramidalized alkenes **6**–**12**. The change in the ^{13}C NMR chemical shifts with increasing pyramidalization indicates that pyramidalization shifts the resonances for olefinic carbon atoms to lower fields. A similar effect had been previously observed in the acetylenic carbons of bent alkynes[31] and on fullerenes and fullerene-related hydrocarbons.[32]

In order to further check the relationship between pyramidalization and deshielding, MPW1PW91/6-31G(d) calculations were carried out on ethylene‡ at geometries in which both carbon atoms were pyramidalized in a *syn* fashion by freezing the HCH angle (α) and the carbon–carbon and the carbon–hydrogen bonds at the experimental values of $\alpha = 117.6°$, $r_{C-C} = 1.338$ Å and $r_{H-C} = 1.086$ Å, as previously described by Hrovat and Borden.[27] GIAO-MPW1PW91/6-31G(d) calculations were carried out at $\Phi = 0$, 18, 36, 54, 72 and 90°. An angle of $\Phi = 0°$ corresponds to planar ethylene, while $\Phi = 90°$ can be understood as a ethylene geometry created by joining two methylenes so that the σ bond is formed between the p orbitals rather than the sp^2 orbitals of the bent CH_2 fragments. Indeed, as shown in Table 3, as the pyramidalization increases, the HOMO–LUMO gap become smaller and the olefinic carbon atoms become increasingly deshielded.§

---

‡ The author thanks one of the referees for suggesting these calculations.

§ GIAO-B3LYP/6-31G(d) gave very similar results.

Table 2 Pyramidalization angle (Φ), HOMO–LUMO gap (in eV) and ^{13}C NMR chemical shifts (δ_c, ppm) calculated for the highly pyramidalized alkenes **6**–**12**[a]

	6	**7**	**8**	**9**	**10**	**11**	**12**
Φ[b]	42.0	53.7	61.9	61.7	62.3	62.4	85.4
$\Delta E_{\text{HOMO–LUMO}}$[c]	5.42	4.79	4.17	4.21	4.18	4.19	4.76
C_a	167.3/168.6	176.7/178.2	199.7/201.2	190.9/192.5	204.3/205.7	208.3/209.6	189.1/189.6
C_b	43.5/43.2	54.7/54.1	57.3/57.1	62.1/61.9	67.9/67.3	65.7/65.1	79.8/80.1
C_c	61.1/60.5	74.1/73.6	70.8/71.1	85.9/85.0	26.3/26.0	26.1/25.9	42.8/41.7
C_d	33.5/32.5	38.0/36.8	—	20.5/20.9	84.2/84.5	82.6/82.8	—
C_e	46.0/45.6	—	—	—	69.8/69.9	—	—
C_f	—	—	—	—	55.1/54.9	—	—

[a] For each carbon atom, the value on the left refers to B3LYP/6-31G(d) while the value on the right refers to MPW1PW91/6-31G(d). [b] Calculated on the B3LYP/6-31G(d) optimized geometry. [c] Calculated by B3LYP/6-31G(d).

Table 3 Pyramidalization energies (kcal mol^{-1}) relatives to planar ethylene (energy = −78.5612 E_h), HOMO–LUMO gap (in eV) and ^{13}C NMR chemical shifts (δ_c, ppm) calculated with MPW1PW91/6-31G(d)

Φ[a]	Energy	$\Delta E_{\text{HOMO–LUMO}}$	δ_c
0	0	8.19	120.5[b]
18	9.1	7.50	124.6
36	32.9	6.18	139.6
54	67.1	4.98	174.3
72	109.5	4.13	242.6
90	163.0	3.63	360.8

[a] Pyramidalization angle in degrees. [b] Experimental value is 123.3.

The magnetic shielding constant (σ) is described in terms of three contributions: the diamagnetic contribution, that depends only on the ground state electron density distribution, the paramagnetic contributions, that depend on both the ground state orbitals and the virtual orbitals, and the effect of neighbouring groups. It is well-known that ^{13}C chemical shifts are determined mainly by variation of the paramagnetic shielding term. This term, that is typically negative, increases with a decreasing of the value of the transition of lowest energy,[33] so the shielding is expected to decrease and the chemical shifts to increase¶ as the HOMO–LUMO gap is smaller. It is also known that pyramidalized alkenes, as a consequence of the rehybridization, show an important decrease of the LUMO and a small increase of the HOMO energies on increasing pyramidalization.[15a,27] This behaviour may explain the observed trend in ^{13}C chemical shifts for the studied pyramidalized alkenes. The aforementioned trend is more evident from the data of Table 3 and in the series of the tricyclo[3.3.*n*.0]alkenes, **3** (n = 3, Φ = 28.1°), **6** (n = 2, Φ = 42.0°), **7** (n = 1, Φ = 53.7°) and **8** (n = 0, Φ = 61.9°), the most pyramidalized olefin carbon atom being the most deshielded (δ = 199.7/201.2 ppm for the olefinic carbon atom of **8**).[34] The differences between **8**, **9**, **10** and **11**, that contain the bis-nor-adamantane skeleton and have very similar Φ, but different predicted ^{13}C NMR chemical shifts for the olefinic carbon atoms, can be easily explained taking into account the β and γ effects due to the different substituents.[35]

Conclusions

In summary, geometry optimization has been performed on several pyramidalized alkenes using DFT. Employing the GIAO method, the ^{13}C NMR chemical shifts were evaluated at several levels of theory. For the pyramidalized alkenes that have been characterized experimentally, the calculated values at the B3LYP/6-31G(d) or MPW1PW91/6-31G(d) levels of theory are in very good agreement with the experimental ones. From the calculated data obtained for pyramidalized ethylene and for the highly pyramidalized alkenes **6**–**12**, olefinic ^{13}C chemical shifts increase when the pyramidalization increases.

Acknowledgements

The author thanks Prof. P. Camps and Prof. F. J. Luque for helpful discussions. Financial support from *Ministerio de Ciencia y Tecnología* (*Programa Ramón y Cajal*) and *Comissionat per a Universitats i Recerca* of the *Generalitat de Catalunya* (project 1999-SGR-00080) is gratefully acknowledged. We thank the *Centre de Supercomputació de Catalunya* (CESCA) for computational facilities.

References

1 (*a*) W. T. Borden, *Chem. Rev.*, 1989, **89**, 1095–1109; (*b*) W. Luef and R. Keese, *Top. Stereochem.*, 1991, **20**, 231–318; (*c*) W. T. Borden, *Synlett*, 1996, 711–719.

2 (*a*) P. E. Eaton, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1421–1436; (*b*) K. Lukin and P. E. Eaton, *J. Am. Chem. Soc.*, 1995, **117**, 7652–7656.

3 (*a*) J. P. Melder, K. Weber, A. Weiler, E. Sackers, H. Fritz, D. Hunkler and H. Prinzbach, *Res. Chem. Intermed.*, 1996, **22**, 667–702; (*b*) T. Oβwald, M. Keller, C. Janiak, M. Kolm and H. Prinzbach, *Tetrahedron Lett.*, 2000, **41**, 1631–1635; (*c*) J. Reinbold, M. Bertau, T. Voss, D. Hunkler, L. Knothe, H. Prinzbach, D. Neschchadin, G. Gescheidt, B. Mayer, H.-D. Martin, J. Heinze, G. K. S. Prakash and G. A. Olah, *Helv. Chim. Acta*, 2001, **84**, 1518–1560; (*d*) J. Reinbold, E. Sackers, T. Oβwald, K. Weber, A. Weiler, T. Voss, D. Hunkler, J. Wörth, L. Knothe, F. Sommer, N. Morgner, B. von Issendorff and H. Prinzbach, *Chem. Eur. J.*, 2002, **8**, 509–524.

4 (*a*) P. Camps, M. Font-Bardia, F. Pérez, X. Solans and S. Vázquez, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 912–914; (*b*) P. Camps, M. Font-Bardia, F. Pérez, Ll. Solà, X. Solans and S. Vázquez, *Tetrahedron Lett.*, 1996, **37**, 8601–8604; (*c*) P. Camps, F. J. Luque, M. Orozco, F. Pérez and S. Vázquez, *Tetrahedron Lett.*, 1996, **37**, 8605–8608; (*d*) P. Camps, X. Pujol and S. Vázquez, *Org. Lett.*, 2000, **2**, 4225–4228.

5 S. Graf and G. Szeimies, *Tetrahedron*, 1993, **49**, 3101–3108.

6 See for example: (*a*) R. Haag, F.-M. Schüngel, B. Ohlhorst, T. Lendvai, H. Butenschön, T. Clark, M. Noltemeyer, T. Haumann, R. Boese and A. de Meijere, *Chem. Eur. J.*, 1998, **4**, 1192–1200; (*b*) A. P. Marchand, I. N. N. Namboothiri, B. Ganguly, W. H. Watson and S. G. Bodige, *Tetrahedron Lett.*, 1999, **40**, 5105–5109; (*c*) N. Saraçoglu, A. Menzek, S. Sayan, U. Salzner and M. Balci, *J. Org. Chem.*, 1999, **64**, 6670–6676; (*d*) H. Irngartinger, A. Altreuther, T. Sommerfeld and T. Stojanik, *Eur. J. Org. Chem.*, 2000, 4059–4070; (*e*) N. Saraçoglu and M. Balci, *Helv. Chim. Acta*, 2001, **84**, 707–714; (*f*) T. Fischer, U. Kunz, S. E. Lackie, C. Cohrs, D. D. Palmer and M. Christl, *Angew. Chem. Int. Ed.*, 2002, **41**, 2969–2971.

7 (*a*) J. G. Radziszewski, T. K. Yin, G. E. Renzoni, D. A. Hrovat, W. T. Borden and J. Michl, *J. Am. Chem. Soc.*, 1993, **115**, 1454–1456; (*b*) J. M. Smith, D. A. Hrovat and W. T. Borden, *Tetrahedron Lett.*, 1993, **34**, 5991–5994; (*c*) P. O. Staneke, S. Ingemann, P. E. Eaton, N. M. M. Nibbering and S. R. Kass, *J. Am. Chem. Soc.*, 1994, **116**, 6445–6446; (*d*) C. D. Cleven, S. H. Hoke II, R. G. Cooks, D. A. Hrovat, J. M. Smith, M. S. Lee and W. T. Borden, *J. Am. Chem. Soc.*, 1996, **118**, 10872–10878.

¶ It should be noted that the shielding and chemical shift scales go in opposite directions.

8 J. M. Smith, D. A. Hrovat, W. T. Borden, M. Allan, K. R. Asmis, C. Bulliard, E. Haselbach and U. C. Meier, *J. Am. Chem. Soc.*, 1993, **115**, 3816–3817 . See also ref. 7.

9 (*a*) T. Helgaker, M. Jaszunski and K. Ruud, *Chem. Rev.*, 1999, **99**, 293–352; (*b*) D. B. Chesnut, in *The Ab Initio Computation of Nuclear Magnetic Resonance Chemical Shielding*, ed. K. B. Lipkowitz and D. B. Boyd, Reviews in Computational Chemistry, VCH Publ., Inc., New York, 1996, vol. 8, pp. 245–297. For some recent approaches see: (*c*) J. Gauss and H.-J. Werner, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2083–2090; (*d*) P. J. Wilson and D. J. Tozer, *J. Chem. Phys.*, 2002, **116**, 10139–10147; (*e*) T. Helgaker, P. J. Wilson, R. D. Amos and N. C. Handy, *J. Chem. Phys.*, 2000, **113**, 2983–2989; (*f*) P. J. Wilson, R. D. Amosa and N. C. Handy, *Chem. Phys. Lett.*, 1999, **312**, 475–484.

10 (*a*) R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789–807; (*b*) K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260; (*c*) J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem Phys.*, 1996, **104**, 5497–5509.

11 (*a*) J. Gauss, *Chem. Phys. Lett.*, 1992, **191**, 614–620; (*b*) J. Gauss, *J. Chem. Phys.*, 1993, **99**, 3629–3643; (*c*) J. Gauss, *Chem. Phys. Lett.*, 1994, **229**, 198–203; (*d*) C. van Wüllen, *J. Chem. Phys.*, 1995, **102**, 2806–2811; (*e*) T. Ziegler and G. Schreckenbach, *J. Phys. Chem.*, 1995, **99**, 606–611.

12 (*a*) R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989; (*b*) L. J. Bartolotti and K. Flurchick, in *An Introduction to Density Functional Theory*, ed. K. B. Lipkowitz and D. B. Boyd, Reviews in Computational Chemistry, VCH Publ., Inc., New York, 1996, vol. 7, pp. 187–216; (*c*) W. Koch M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, 2000.

13 (*a*) D. Cremer, in *Møller–Plesset Perturbation Theory*, ed. P. v. R. Schleyer, Encyclopedia of Computational Chemistry, John Wiley & Sons, Chichester, UK, 1998, vol. 3, pp. 1706–1735; (*b*) W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986; (*c*) C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618–622.

14 See for example:. (*a*) M. Bühl, M. Kaupp, O. L. Malkina and V. G. Malkin, *J. Comput. Chem.*, 1999, **20**, 91–105; (*b*) A. M. Orendt, J. C. Facelli, J. G. Radziszewski, W. J. Horton, D. M. Grant and J. Michl, *J. Am. Chem. Soc.*, 1996, **118**, 846–852; (*c*) K. B. Wiberg, *J. Comput. Chem.*, 1999, **20**, 1299–1303; (*d*) J. B. Foresman and A. E. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, 2nd edn., 1996, pp. 21, 53, 104.

15 (*a*) P. Camps, M. Font-Bardia, N. Méndez, F. Pérez, X. Pujol, X. Solans, S. Vázquez and M. Vilalta, *Tetrahedron*, 1998, **54**, 4679–4696; (*b*) I. Antol, M. Eckert-Maksic, D. Margetic, Z. B. Maksic, K. Kowski and P. Rademacher, *Eur. J. Org. Chem.*, 1998, 1403–1408; (*c*) R. V. Williams, M. E. Colvin, N. Tran, R. N. Warrener and D. Margetic, *J. Org. Chem.*, 2000, **65**, 562–567.

16 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

17 P. A. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.

18 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-Laham, 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. Andrés, 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. González and J. A. Pople, GAUSSIAN 94, Rev. E.1, Gaussian, Inc., Pittsburgh PA, 1996.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. González, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andrés, C. González, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Rev. A.5, Gaussian, Inc., Pittsburgh PA, 1998.

20 A. G. Griesbeck, T. Deufel, G. Hohlneicher, R. Rebentisch and J. Steinwascher, *Eur. J. Org. Chem.*, 1998, 1759–1762.

21 K. B. Becker, *Helv. Chim. Acta*, 1977, **60**, 68–80.

22 J. Casanova, J. Bragin and F. D. Cottrell, *J. Am. Chem. Soc.*, 1978, **100**, 2264–2265.

23 (*a*) C. Adamo and V. Barone, *J. Chem. Phys.*, 1998, **108**, 664–675; (*b*) J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev.*, 1996, **B54**, 16533; (*c*) See also ref. 14*c*.

24 (*a*) R. R. Sauers and J. S. Harris, *J. Org. Chem.*, 2001, **66**, 7951–7954; (*b*) W. Koch, B. Liu and D. J. DeFrees, *J. Am. Chem. Soc.*, 1988, **110**, 7325–7328; (*c*) M. Saunders, K. E. Laidig, K. B. Wiberg and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1988, **110**, 7652–7659.

25 G. K. S. Prakash, G. Rasul, V. P. Reddy and J. Casanova, *J. Am. Chem. Soc.*, 1992, **114**, 6484–6486 . The predicted chemical shifts using IGLO method at the DZ level for C1 and C2 for compound **5** are 172.3 and 35.6 ppm, respectively.

26 (*a*) D. A. Forsyth and A. B. Sebag, *J. Am. Chem. Soc.*, 1997, **119**, 9483–9494; (*b*) A. B. Sebag, D. A. Forsyth and M. A. Plante, *J. Org. Chem.*, 2001, **66**, 7967–7973.

27 D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, 1988, **110**, 4710–4718 . See also ref. 8.

28 G. E. Renzoni, T.-K. Yin, F. Miyake and W. T. Borden, *Tetrahedron*, 1986, **42**, 1581–1584.

29 G. E. Renzoni, T.-K. Yin and W. T. Borden, *J. Am. Chem. Soc.*, 1986, **108**, 7121–7122.

30 B. M. Branan, L. A. Paquette, D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 774–776.

31 A. Krebs and H. Kimling, *Justus Liebigs Ann. Chem.*, 1974, 2074.

32 (*a*) J. M. Schulman and R. L. Disch, *J. Comput. Chem.*, 1998, **19**, 189–194; (*b*) T. Heine, G. Seifert, P. W. Fowler and F. Zerbetto, *J. Phys. Chem. A*, 1999, **103**, 8738–8746; (*c*) G. Sun and M. Kertesz, *Chem. Phys. Lett.*, 2000, **328**, 387–395; (*d*) G. Sun and M. Kertesz, *J. Phys. Chem. A*, 2000, **104**, 7398–7403.

33 (*a*) H.-O. Kalinowski, S. Berger and S. Braun, in *Carbon-13 NMR Spectroscopy*, John Wiley & Sons, Chichester, 1988, pp. 92–99; (*b*) E. Breitmaier and W. Voelter, in *Carbon-13 NMR Spectroscopy*, VCH, Weinheim, 3rd edn., 1990, pp. 110–111.

34 Worthy of note, Borden *et al.* have observed that the ^{13}C NMR of the $(Ph_3P)_2Pt$ complexes of pyramidalized alkenes **3**, **6** and **7** show the opposite trend, the olefinic ^{13}C chemical shifts move towards higher field on increasing pyramidalization as a consequence of the increased back-donation of electron density from the Pt HOMO into the π^* LUMO of the olefin. (*a*) A. Nicolaides, J. M. Smith, A. Kumar, D. M. Barnhart and W. T. Borden, *Organometallics*, 1995, **14**, 3475–3485; (*b*) J. Uddin, S. Dapprich, G. Frenking and B. F. Yates, *Organometallics*, 1999, **18**, 457–465; (*c*) B. F. Yates, *J. Organomet. Chem.*, 2001, **635**, 142–152.

35 See ref. 33*b*, pp. 192–196.