Central metal dependence of the NO^+–NO^- isomerism in pentacoordinate $MX(CO)(NO)(PR_3)_2$ complexes

Alexandros L. Rizopoulos and Michael P. Sigalas*

Laboratory of Applied Quantum Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 540 06 Thessaloniki, Greece. E-mail: siglas@chem.auth.gr

Received (in Montpellier, France) 12th March 2001, Accepted 18th April 2001
First published as an Advance Article on the web 12th June 2001

A metal dependence of the structure adopted by $ML_4(NO)$ complexes has been found in the isoelectronic $OsCl(CO)(NO)(PR_3)_2$ and $[IrCl(CO)(NO)(PR_3)_2]^+$ complexes, in addition to the well-known effects of the nature of the co-ligands L. In the *ab initio* potential energy surfaces of the two complexes at the HF and MP2 levels two minima have been located, with their relative energies dependent on the nature of the central metal atom. In the case of the Os complex, a trigonal bipyramidal coordination sphere with a linear NO group is the global minimum, whereas the most stable structure for the Ir complex is square pyramidal with an apical bent NO. Finally, a trigonal bipyramidal structure with a linear NO was calculated as the optimum structure for the related complex $Os(CH_2)(CO)(NO)(PR_3)_2$.

Introduction

A considerable amount of experimental[1–3] and theoretical work[4–8] has been done on pentacoordinate nitrosyl complexes, $ML_4(NO)$, mainly focused on the effect of the spectator ligands L on the structure of the complexes and the bending of the NO ligand. It has been shown that if L are strong π-acceptor ligands, a trigonal bipyramid (TBP) with an equatorial linearly coordinated nitrosyl is preferred, whereas in the case of π-donor substituents L, a preference for a square pyramid (SP) with a strongly bent nitrosyl has been found.

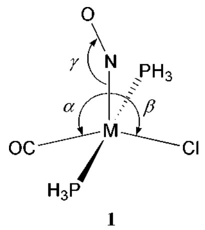
In the case of the coexistence of both π-donor and π-acceptor ligands L, the energy difference between the two structures should be small due to the opposing influences and a possible effect of the central transition metal atom on the structural preference should be considered.

In this work, we describe the results of *ab initio* calculations for the isoelectronic complexes $OsCl(CO)(NO)(PR_3)_2$ and $[IrCl(CO)(NO)(PR_3)_2]^+$, where a π-donor, Cl^-, and a π-acceptor, CO, ligand coexist in the coordination sphere. A search for the two types of structures on the potential energy surface of the two model complexes $OsCl(CO)(NO)(PH_3)_2$ and $[IrCl(CO)(NO)(PH_3)_2]^+$ was carried out. It appears that the relative energies of the two possible isomers depend on the central metal atom. The importance of the energies of the frontier orbitals of the central metal atom in stabilizing the TBP or SP structure was also investigated. Finally, the *ab initio* structure of the related model complex $Os(CH_2)(CO)(NO)(PH_3)_2$ was also calculated.

Results and discussion

An X-ray crystallographic study of the iridium complex $[IrCl(CO)(NO)(PPh_3)_2]^+$ revealed that the structure is a SP with a bent NO at the apical site.[9] The same structure is suggested from the spectroscopic data for the $RuCl(CO)(NO)(P^tBu_2Me)_2$ complex[8] and has also been found from *ab initio* calculations on the $RuCl(CO)(NO)(PH_3)_2$ model complex.[8] The formal oxidation state of the central atoms in all these complexes is regarded as Ir(III)/Ru(II), since the formal charge on the bent nitrosyl is treated as negative (NO^-). In the IR spectra of these complexes, the nitrosyl stretches are observed at low frequencies (1570–1680 cm^{-1}), also suggesting that the NO ligand is coordinated in a bent fashion.

Another isoelectronic complex in this family is $OsCl(CO)(NO)(PPh_3)_2$,[10,11] whose molecular structure has not been solved by X-ray crystallography. In the IR spectra, with the exception of a band at 1560 cm^{-1}, the nitrosyl peaks appear at higher frequencies (1629 and 1769 cm^{-1}), as verified by isotopic substitution.[11] These high frequencies could be assigned[11,12] to a linearly coordinated nitrosyl, leading to the suggestion of a dynamic equilibrium in solution between the expected SP structure with a bent NO and a TBP structure with a linear NO.[11] In the last structure, the metal would be in the Os(0) formal oxidation state since linear nitrosyl is formally NO^+. There is precedent for this equilibrium in the case of the $CoCl_2(NO)(PPh_3Me)_2$ complex, where the two nitrosyl frequencies in the IR spectra have been explained by the coexistence of two structures, in solution and in the solid state.[13] This experimental evidence led us to carry out an *ab initio* investigation of the potential energy surface (PES) of the isoelectronic model complexes $OsCl(CO)(NO)(PH_3)_2$ and $[IrCl(CO)(NO)(PH_3)_2]^+$.



1

The general features of the *ab initio* PES of the Os complex at the RHF level, are shown in Fig. 1. The variables are the two angles α and β in the $[MCl(CO)(NO)]$ plane in **1**. All other geometrical parameters, including the M–N–O angle, γ, have been optimized at each point. In the low energy region of this PES, two minima were located; ($\alpha = 90$, $\beta = 110$, $\gamma = 125°$) and ($\alpha = 130$, $\beta = 140$, $\gamma = 165°$). Starting from the two minima located, full geometry optimizations were carried out at both RHF and MP2 levels. The MP2 optimized structures are shown in Fig. 2 and some selected calculated structural parameters for both isomers are listed in Table 1.

DOI: 10.1039/b102308j

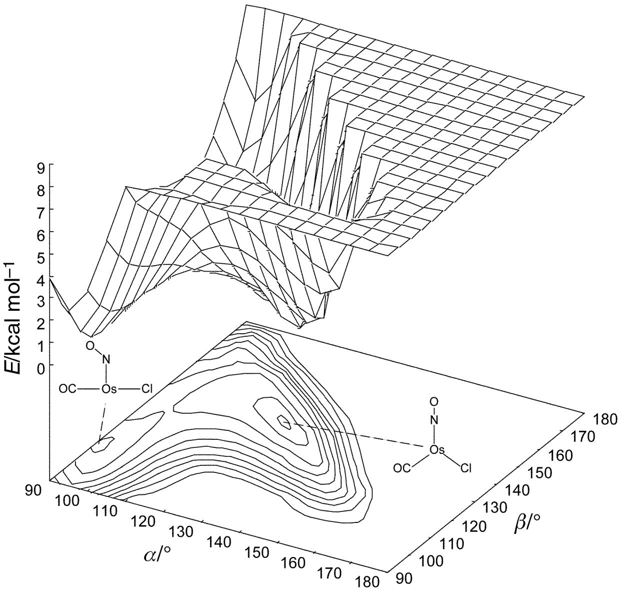


Fig. 1 Potential energy surface at the RHF level for $OsCl(CO)(NO)(PR_3)_2$. The variables are the angles α and β shown in **1**.

The symmetry of both optimized isomers of the Os complex is C_s. The most stable structure is a distorted TBP with an almost linear NO ($\gamma = 165.1°$ at MP2), corresponding to an 18-electron d^8 Os(0) complex. The other isomer, 5.6 kcal mol^{-1} above the previous structure at MP2 (2.1 kcal mol^{-1} at RHF), is a SP with an apical bent NO ($\gamma = 126.8°$ at MP2). As previously noted by Hoffmann *et al.*,[7] the NO bends in the D–M–A plane towards A, where D is the π-donor (Cl) and A the π-acceptor ligand (CO). Although there are no experimental structural data for such a complex, the calculated geometrical parameters agree with those of related nitrosyl complexes of osmium.[10,14–18] Calculation of the Hessians confirmed that the two isomers are real minima on the PES. The two calculated scaled harmonic ν(NO) frequencies agree well with the experimentally observed bands,[11] particularly at the MP2 level (1705 and 1550 cm^{-1} for the SP and TBP isomers, respectively). The relatively small energy difference between the two isomers (2–5 kcal mol^{-1}) explains the experimental prediction for their co-existence in the solid state and/or in a dynamic equilibrium in solution.[11]

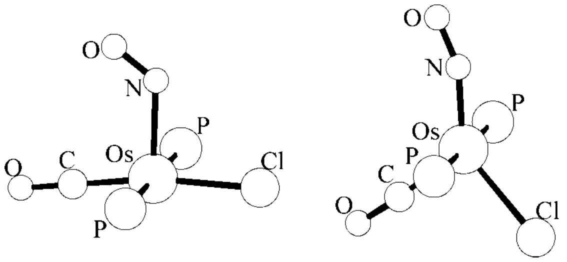


Fig. 2 MP2 optimized structures of $OsCl(CO)(NO)(PR_3)_2$, showing SP (left) and TBP forms.

Table 1 Selected calculated bond lengths (Å), angles (°) and ν(NO) frequencies (cm^{-1}) for the trigonal bipyramidal (TBP) and square pyramidal (SP) structures of the $OsCl(CO)(NO)(PH_3)_2$ complex optimized at the HF and MP2 levels

	TBP		SP	
	HF	MP2	HF	MP2
Os–P	2.48	2.44	2.48	2.45
Os–Cl	2.52	2.52	2.49	2.50
Os–C	1.89	1.87	1.90	1.87
Os–N	1.87	1.74	1.97	1.75
C–O	1.15	1.22	1.15	1.22
N–O	1.20	1.26	1.22	1.26
Os–N–O	160.2	165.1	125.6	126.8
N–Os–Cl	142.7	129.8	109.3	103.5
N–Os–C	125.2	120.7	92.8	94.4
C–Os–Cl	92.1	109.5	157.9	162.1
ν(NO)	1609	1705	1514	1550

A similar study was also carried out for the $[IrCl(CO)(NO)(PH_3)_2]^+$ model complex giving the PES shown in Fig. 3. The MP2 optimized structures calculated starting from the two minima found on the PES ($\alpha = 90$, $\beta = 100$, $\gamma = 120°$) and ($\alpha = 130$, $\beta = 140$, $\gamma = 176°$) have C_s symmetry and are depicted in Fig. 4. Some selected calculated structural parameters for the two isomers are given in Table 2.

In this case, the two minima have a reversed energy preference from the previous Os complex. The global minimum is a SP with an apical NO bending towards CO ($\gamma = 124.1°$ at MP2), corresponding to a 16-electron d^6 Ir(III) complex. The calculated structural parameters compare well with the experimental SP stucture found for $[IrCl(CO)(NO)(PPh_3)_2]^+$.[9] The second isomer, 7.3 kcal mol^{-1} higher in energy at MP2 (4.4 kcal mol^{-1} at RHF), has a distorted TBP structure with a linear NO ($\gamma = 176.4°$ at MP2). The calculated ν(NO) frequency for the SP structure (1632 cm^{-1} at MP2) is very close to that found experimentally (1680 cm^{-1}).[9] The higher energy difference between the two isomers of the Ir complex compared to those of the Os complex, should lead to a less favored isomer which is not experimentally detectable. Thus, although the calculated frequencies for the two isomers are

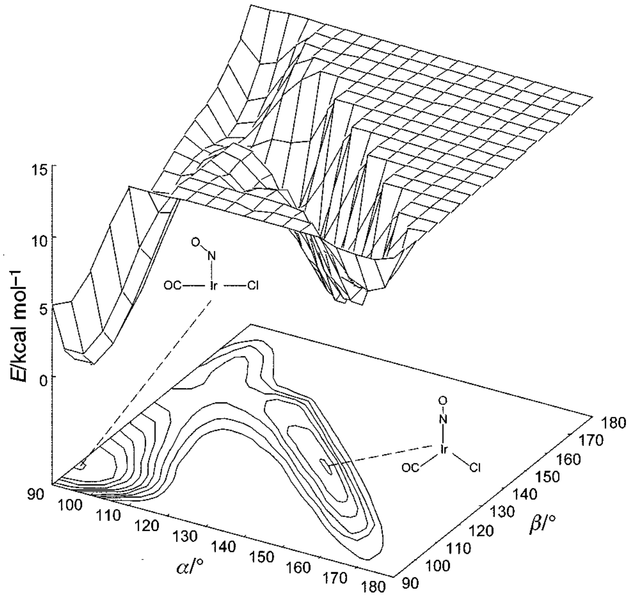


Fig. 3 Potential energy surface at the RHF level for $[IrCl(CO)(NO)(PR_3)_2]^+$. The variables are the angles α and β shown in **1**.

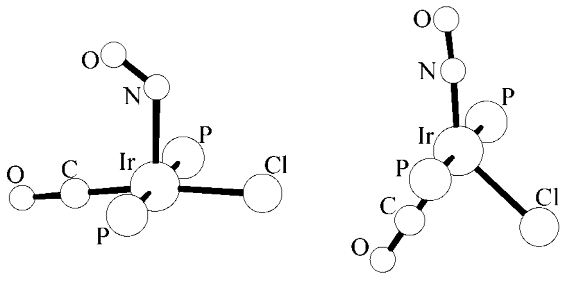


Fig. 4 MP2 optimized structures of $[IrCl(CO)(NO)(PR_3)_2]^+$, showing SP (left) and TBP forms.

Table 2 Selected calculated bond lengths (Å), angles (°) and ν(NO) frequencies (cm^{-1}) for the trigonal bipyramidal (TBP) and square pyramidal (SP) structures of the $[IrCl(CO)(NO)(PH_3)_2]^+$ complex optimized at the HF and MP2 levels compared to the experimental data[a]

	TBP		SP		
	HF	MP2	HF	MP2	Exp.
Ir–P	2.48	2.45	2.47	2.44	2.408
Ir–Cl	2.46	2.49	2.40	2.44	2.343
Ir–C	1.99	1.90	1.99	1.85	1.86
Ir–N	1.83	1.82	1.98	1.98	1.97
C–O	1.13	1.20	1.13	1.18	1.16
N–O	1.17	1.21	1.18	1.19	1.16
Ir–N–O	176.8	176.4	119.5	124.6	124.1
N–Ir–Cl	135.3	121.8	96.6	89.1	101.3
N–Ir–C	142.6	140.6	93.0	99.7	97.4
C–Ir–Cl	82.1	97.6	170.4	171.2	161.3
ν(NO)	1753	1816	1579	1632	1680

[a] Experimental values for $[IrCl(CO)(NO)(PPh_3)_2]^+$.[9]

well separated, there are no experimental data for a second NO stretching frequency in the IR spectra.

The third model complex studied is $Os(CH_2)(CO)(NO)(PH_3)_2$. The optimization of the structure (Fig. 5) gives a TBP with a linear NO ($\gamma = 159.3°$ at MP2) and with the CH_2 ligand perpendicular to the basal plane. The structural data, listed in Table 3, and the ν(NO) frequency calculated are in good agreement with the experimental findings (1598 at MP2 *vs.* 1628 cm^{-1}).[16] No SP structure with an apical NO has been found as a minimum on the PES and any hypothetical structures converged to the previously found TBP minimum. However, in an attempt to optimize a TBP structure with the CH_2 in the basal plane, the minimum located was a SP structure of high energy (17.9 kcal mol^{-1} at RHF and 45.8 kcal mol^{-1} at MP2) with a linear NO ($\gamma = 156.1°$ at MP2) *trans* to Cl ligand and with the apical CH_2 ligand perpendicular to the P–Os–P axis (Fig. 5). Although this structure is of high energy and has not been experimentally observed, in the two known structures with the NO in the base of a SP, $RuCl(NO)_2(PPh_3)_2$[12,19] and $[Os(OH)(NO)_2(PPh_3)_2]^+$,[18,20] the nitrosyl is indeed linearly coordinated.

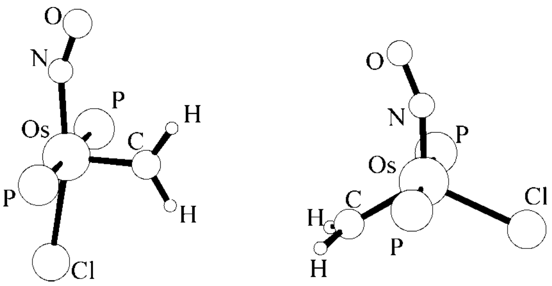


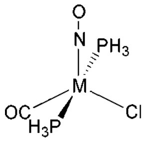
Fig. 5 MP2 optimized structures of $Os(CH_2)(CO)(NO)(PR_3)_2$, showing SP (left) and TBP forms.

Table 3 Selected calculated bond lengths (Å) and angles (°) and ν(NO) frequencies (cm^{-1}) for the trigonal bipyramidal (TBP) and square pyramidal (SP) structures of the $OsCl(CH_2)(NO)(PH_3)_2$ complex optimized at the HF and MP2 levels compared to the experimental data[a]

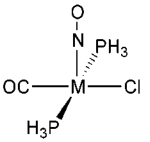
	TBP		SP		
	HF	MP2	HF	MP2	Exp.
Os–P	2.48	2.44	2.49	2.46	2.380
Os–Cl	2.49	2.51	2.54	2.55	2.409
Os–C	1.87	1.94	1.87	1.89	1.92
Os–N	1.88	1.74	2.01	1.78	1.93
C–H	1.08	1.11	1.08	1.11	
N–O	1.21	1.27	1.23	1.29	
Os–N–O	157.3	159.3	155.7	156.1	155.4
N–Os–Cl	130.6	115.7	167.8	154.6	114.6
N–Os–C	114.7	120.1	95.5	119.0	118.8
C–Os–Cl	114.7	124.2	96.7	86.4	126.6
ν(NO)	1546	1598	1534	1592	1628

[a] Experimental values for $OsCl(CH_2)(NO)(PPh_3)_2$.[16]

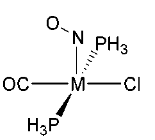
The above results show the existence of two isomers in which the coordination geometry of the metal (TBP, SP) is linked to the geometry of the nitrosyl (linear, bent). The main factor favoring one of the two minima calculated in a related study of the $RuX(CO)(NO)(PH_3)_2$ complexes (X = RCN, no ligand, H^- and CO) is the nature of ligand X.[8] In our case, the structure adopted depends on the central metal atom, with osmium preferring a TBP structure and iridium a SP structure. An accurate description of this difference and general predictions are difficult, but in an attempt to rationalize this dependence we rely on a simple MO picture.



2

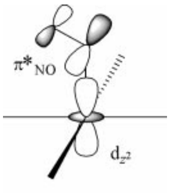


3



4

According to previous MO analyses the SP structure with a linear apical NO, **3**, is an unfavorable high energy structure.[7] The two geometric perturbations in **3** stabilizing the system are either the distortion towards a TBP leaving the NO linear, **2**, or the bending of NO in the SP structure, **4**, by turning on a d_{z^2}/π^*_{NO} interaction, **5**. The relative stabilization gained by each distortion depends mainly on the energy difference between d_{z^2} and p^*_{NO}. According to single point calculations on a model of the unfavorable structure **3** the d_{z^2} orbital is above the π^*_{NO} orbital and the d_{z^2}/π^*_{NO} energy difference is diminished in going from the Os to the Ir model.



5

In the case of the osmium model **3**, the high d_{z^2}/π^*_{NO} energy difference diminishes the stabilization gained by the d_{z^2}/π^*_{NO} interaction, the NO does not bend and the system is stabilized by distorting to a TBP, **2**. By moving to the right in the periodic table and replacing the osmium with iridium, the d block is lowered. The positive charge on iridium also lowers the d block. Thus, the d_{z^2}/π^*_{NO} energy separation in the iridium model **3** is small and one can reasonably expect the system to remain SP and undergo NO bending for stabilization. The nitrosyl bending also results in a change in the occupation of the two orbitals. In the iridium complex **4** the π^*_{NO} is occupied, whereas the d_{z^2} is empty. This should lead to an elongation of the NO bond in the SP structure, which is reproduced only at the HF level for both the osmium and iridium complexes.

Finally, although the above arguments interpret the relative energies of the two minima found in the *ab initio* PESs of the complexes studied, it should be noted that the small energy differences encountered could easily be affected by small changes in the spectator ligands. An excellent example is the case of the $OsCl(CO)(NO)(P^iPr_3)_2$ and $OsCl(CO)(NO)(P^iPr_2Ph)_2$ complexes, whose ν(NO) frequencies (1755 and 1560 cm^{-1}, respectively) reveal that even a small alteration in the phosphine ligands results in different stereochemistry (TBP and SP, respectively).[10] The P^iPr_3 phospine ligand, being a better σ-donor, destabilizes the d_{z^2} orbital more, hence the d_{z^2}/π^*_{NO} energy difference increases and the system deforms to the TBP with a linear NO.

Computational details

Ab initio calculations were carried out at the HF and MP2 computational levels. The effective core potential (ECP) approximation of Hay and Wadt was used for Os, Ir and P and Cl atoms.[21–23] For Os and Ir atoms, the *n*s and *n*p electrons were explicitly described. The basis set used was of valence double-ζ quality.[24] The phosphine ligands were modeled by PH_3. For the PES calculation, a partial geometry optimization at the HF level was carried out for each point, under the symmetry constraints of the C_s point group, with the values of the variables kept constant at each point, as described in the text. Full geometry optimizations were carried out for the minima located on each PES at both HF without symmetry constraints. The two minima were also fully reoptimized at the MP2 level in order to take into account the electron correlation effects. Frequency calculations at both levels of theory ensure that the optimized structures are real minima on the potential energy surface of the studied complexes. The values of the ν(NO) frequency reported are scaled using the scaling factors 0.8929 (HF)[25] and 0.9434 (MP2).[26] All of the calculations were performed using the GAUSSIAN 94 package.[27]

References

1 F. Basolo, *Polyhedron*, 1990, **9**, 1503.
2 G. B. Richter-Addo and P. Legzdins, *Metal Nitrosyls*, Oxford University Press, New York, 1992.
3 B. F. G. Johnson, B. L. Haymore and J. R. Dilworth, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, 1987, vol. 2, p. 99.
4 R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 1972, **11**, 437.
5 D. M. P. Mingos, *Inorg. Chem.*, 1973, **12**, 1209.
6 J. H. Enemark and R. C. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
7 R. Hoffmann, M. M. L. Chien, M. Elian, A. R. Rossi and D. M. P. Mingos, *Inorg. Chem.*, 1974, **13**, 2666.
8 M. Ogasawara, D. Huang, W. E. Streib, J. C. Huffmann, N. Gallego-Planas, F. Maseras, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1997, **119**, 8642.
9 D. J. Hodgon and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.
10 H. Werner, R. Flügel, B. Windmüller, A. Michenfelder and J. Wolf, *Organometallics*, 1995, **14**, 612.
11 R. D. Wilson and J. A. Ibers, *Inorg. Chem.*, 1979, **18**, 336.
12 C. G. Pierpont, D. G. Van Derveer, W. Durland and R. Eisenberg, *J. Am. Chem. Soc.*, 1970, **92**, 4760.
13 C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.
14 C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 199.
15 G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 1972, 119.
16 A. F. Hill, W. R. Roper, J. M. Waters and A. H. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 5939.
17 W. R. Roper, *J. Organomet. Chem.*, 1986, **300**, 167.
18 J. M. Waters and K. R. Whittle, *Chem. Commun.*, 1971, 518.
19 C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1088.
20 K. R. Grundy, K. R. Laing and W. R. Roper, *Chem. Commun.*, 1970, 1500.
21 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
22 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.
23 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
24 T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, ed. H. F. Schaefer III, Plenum, New York, 1976.
25 M. W. Wong, K. B. Wiberg and M. J. Frisch, *J. Chem. Phys.*, 1991, **95**, 8991.
26 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502.
27 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, 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. Gonzalez and J. A. Pople, GAUSSIAN 94, Gaussian, Inc., Pittsburgh, PA, 1995.