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Theoretical determination of δ in $18+\delta$ organometallic complexes

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Abstract

The 19-electron organometallic complexes $[Co(CO)_3(L_2)]$ ($L_2 = 2,3$-bis phosphino maleic anhydride), $[Co(CO)_2(PH_3)(L_2)]$, $[Fe(CO)_3(L_2)]^-$ and $[ReBr(CO)_3(L_2)]^-$ were studied theoretically at the B3LYP level. The SBKJC effective core potentials and their associated basis sets were used for metals and the 6-31G(d) basis set was used for all other elements. The theoretically calculated geometries are compared with experiment, where known. The results reveal that the 19th electron is predominantly distributed over the chelating ligand, although partially localized onto the metal fragment, showing $18+\delta$ character. Two different methods, calculated IR-frequencies and natural atomic charges, were used to determine the value of δ. The computed δ values are compared with the available experimental data.

Keywords: Organometallic complexes; IR-frequencies; Natural charges

1. Introduction

In general, 19-electron organometallic complexes are formed by the reaction of 2-electron donor ligands with 17-electron radicals [1–17]. These systems are unstable if the 19th electron occupies the high energy M–L antibonding orbital [2,13]. However, if the 19th electron occupies the MO resulting from the interaction of an additional metal orbital with the ligand's π* MO rather than the M–L antibonding MO, then these compounds are stable and have been denoted as $18+\delta$ complexes [1,2,13,16,18]. Though $18+\delta$ complexes are stable relative to 19e systems, they are reactive since they are radicals and only a few of them have been studied by X-ray crystallography [18–28]. The δ is defined as the fraction of the electron charge of the 19th electron on the metal. For complexes with no electron charge of the 19th electron on the metal, δ would be 0, and for those with the 19th electron delocalized between the metal and ligands, δ will lie between 0 and 1. There are some previous reports in the literature in which the value of δ has been estimated using spectrascopic methods [29–31]. The first value of δ (0.016) was determined for $[Co(CO)_3(bma)]$ (bma = 2,3-bis(diphenylphosphino)maleic anhydride) in frozen toluene using EPR [29]. Tyler and coworkers have devised an ingenious method to measure δ in $18+\delta$ complexes using the analysis of C=O vibrational frequencies (IR method) [31]. These measurements are restricted to experimentally known complexes. There has been only one theoretical study estimating the value of δ in these complexes (using the semi-empirical density functional theory (DFT), SCF-Xα-SW method) [32]. In the present study we determine δ using two different methodologies. The first method is analogus to the experimental IR method, but uses computed C=O frequencies. In the second method, δ is derived from the calculated atomic charges on the metal and ligand. These results are compared with the experimentally known values of δ. We have first selected $[Co(CO)_3L_2]^+$ (**1**, $L_2 = 2,3$-bis phosphino maleic anhydride) and $[Fe(CO)_3L_2]$ (**2**) to compute δ as their values are known experimentally. Then we have selected two experimentally known complexes $[Co(PH_3)(CO)_2L_2]^+$ (**3**) and $[ReBr(CO)_3L_2]$ (**4**) for which δ has not been measured. The experimentally known complexes have bma as L_2. However, for the feasibility of computations, all the phenyl groups were replaced by hydrogen on P,

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leading to 2,3-bis phosphino maleic anhydride (Hbma) as L_2 instead of bma and PH_3 instead of PPh_3.

2. Computational methods

All the 18 electron (**1**–**4**) and 19 electron complexes (**1a**–**4a**) were optimized using the hybrid B3LYP method [33]. This DFT method uses the combination of the three parameter Becke exchange functional with the Lee-Yang-Parr non-local correlation functionals. The relativistic effective core potentials (SBKJC) and their associated basis sets (Re: [4111/4111/311], Co and Fe: [4211/4211/411]) were used for the transition metals [34,35]. These effective core potentials replace all but the outermost electrons. For all other elements, the 6-31G(d) basis set was used [36]. The nature of the stationary points was determined by evaluating the second derivatives of the energy (Hessian matrix) [37]. All the computations were performed using the GAUSSIAN 98 program package [38]. Natural atomic charges were obtained from NBO analysis [39].

3. Results and discussion

All the 18 and 19 electron complexes studied here are minima (Fig. 1) and $s^2 \approx 0.76$ for all the radical (19e) systems. The s^2 (squared spin angular momentum) should be 0.75 for a pure doublet, and the present value of 0.76 for the 19e systems indicate that there is no spin contamination. It is interesting to note that the single crystal X-ray diffraction studies of **1a** and **3a** differ stereochemically [18–20,29]. The structure of **3a** is close to trigonal bipyramidal (TBP), whereas the structure of **1a** is close to square pyramidal (SP). It has been suggested in the literature that **1a** and **3a** might have at least two local potential energy minima (TBP and SP) and may exhibit non-rigid stereochemical character [29]. Our present theoretical investigations have shown that **3** is indeed a minimum as TBP, and an SP initial conformation for **3** collapsed to TBP on optimization, in which the PH_3 is in the equatorial plane (this TBP structure is 1.7 kcal mol^{-1} less stable than **3**). Similar results were found for **1** and **2**, that is **1** and **2** are minimum in TBP geometry and an SP starting geometry collapsed to TBP on optimization (Fig. 1). Therefore, in the present study, a TBP geometry was used for both 18 and 19 electron systems of Co and Fe. The calculated geometrical parameters of **4a** agree quite well with the experimental values (to within 0–2.6% for computed bond distances) [21].

Similar to experimental observations, the present theoretical calculations have shown the following changes in geometrical parameters between 18 and 19 electron complexes [18–28]. The major change between 18e and 19e complexes occurs at the Hbma ligand. The C_6–C_7 bond distance (Fig. 1) is increased in 19e complexes by ~0.07–0.06 Å in **1a**–**4a**. Similarly, the C_2–O_4 and C_3–O_5 distances are increased in 19e complexes. However, the C_2–C_6 and C_3–C_7, C_6–P_8 and C_7–P_9 distances are shorter in the 19e complexes. Other than these major changes, the metal–P (in the Hbma ligand) distances are slightly lengthened and the metal–C distances are slightly shortened. These changes are in accord with the electronic structure of **1a**, **2a**, **3a** and **4a** where the SOMO is a π* orbital on the Hbma ligand, which has an antibonding character between C_2–O_4, C_3–O_5 and C_6–C_7, and bonding character between C_2–C_6, C_3–C_7, C_6–P_8 and C_7–P_9. A similar electronic structure has been reported for **1a** and **4a** using the SCF-Xα-SW and extended Huckel methods, respectively [21,30]. Therefore, the bonding in **1a**–**4a** clearly show $18+\delta$ character.

The carbonyl ligand (C≡O) is known to exhibit the π-acceptor properties in organometallic complexes. All the complexes (**1a**–**4a**) studied here contain carbonyl ligands. The differences in C≡O bond distances in carbonyl ligands are very small (~0.008 Å) in the 18e and 19e complexes (Fig. 1). Similarly, the change in the vibrational C≡O frequencies between 18e and 19e complexes is only ~45 cm^{-1}. These results clearly show that only a small fraction of the 19e in **1a**–**4a** is delocalized onto the carbonyl ligands.

The infrared spectroscopic method (IR method) for measuring δ in these complexes makes use of the linear relationship between C=O force constants and the charge on a ligand leading to [31]

$$\bar{\upsilon}_2^2 - \bar{\upsilon}_1^2 = b\Delta q \qquad (1)$$

$\bar{\upsilon}_2$and $\bar{\upsilon}_1$ corresponds to the C=O stretching frequencies of the $18+\delta$ and 18 electron complexes, respectively. Δq is the charge difference on the Hbma ligand between $18+\delta$ and 18 electron complexes, and b is the proportionality constant.

In the present study we have used the above Eq. (1) to calculate the value of δ theoretically. To determine the proportionality constant, b, the free ligand (Hbma) was optimized in its neutral (**5**) and anionic (**5a**) configurations. The scaled C=O stretching frequencies (Table 1) were used to calculate the root-mean-square (r.m.s.) frequencies, from which one finds $b = 4.07 \times 10^5$. Similarly, the r.m.s. C=O frequencies (after scaling them) of 18 and 19 electron complexes (**1**–**4** and **1a**–**4a**) were used in Eq. (1) to compute the values of Δq and δ $(1-\Delta q)$ (Table 1). Though present theoretical predictions are in vacuum, the calculated δ value (Table 1) for **1a** (0.20) is very close to the experimentally known values in 2-MeTHF (0.25±0.03) and THF (0.19±0.03) solvents (with a bma ligand) [31]. However, for **2a** there is no experimental δ value known in 2-MeTHF and THF solvents, and the value in CH_2Cl_2 solvent (0.01±0.03) is

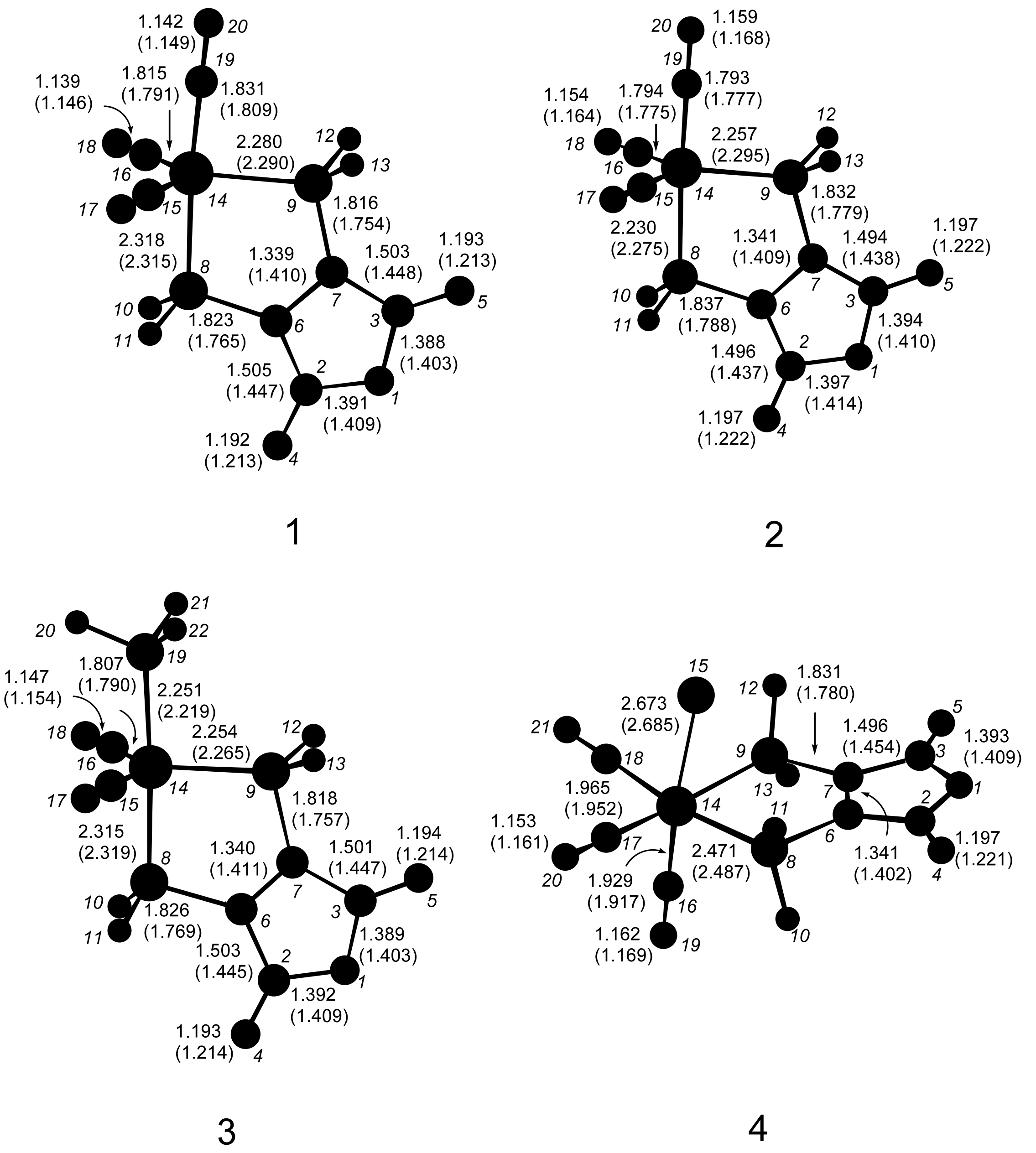

Fig. 1. Optimized structures and important geometrical parameters of the 18-electron complexes $[Co(CO)_3(Hbma)]^+$ (**1**), $[Fe(CO)_3(Hbma)]^+$ (**2**), $[Co(CO)_2(PH_3)(Hbma)]$ (**3**), $[ReBr(CO)_3(Hbma)]$ (**4**). The values in parenthesis are for the 19-electron systems **1a**–**4a**.

smaller than the present theoretical prediction [31]. It is known in the literature that δ is sensitive to the solvent, and changes by as much as a factor of four between THF and CH_2Cl_2 (δ is 0.19 and 0.05 in THF and CH_2Cl_2, respectively for $Co(CO)_3(bma)$) [31]. Further computational analysis by optimizing **2a** with CH_2Cl_2 solvent effects has given a δ value ($\delta \approx 0.0$; $\Delta q \approx 1.0$), which is very close to the experimental data [40].

The above method requires reference molecules (i.e. free ligand) to calculate the value of δ. However, we feel that an alternative and more general method to calculate δ is by using atomic charges. Let us say q_{18} is the sum of all the atomic charges on the chelating ligand Hbma of the 18-electron complex. Similarly, q_{19} will be the sum of all the atomic charges on the chelating ligand Hbma of the 19-electron complex. The difference between q_{19} and q_{18} should be Δq, from which one may again determine δ as $1-\Delta q$. Natural atomic charges obtained by the NBO analysis have been used to calculate δ and the values are given in Table 1. The calculated values of δ by this method are consistently higher for **1a**–**4a** than the values obtained from IR frequencies. The difference in δ values between the two methods (IR frequencies and atomic charges) is much larger in **2a**. It is also interesting to note that the change in the ligand sphere at the metal from CO to PH_3 (between **1a** and **3a**) results a

Table 1
Calculated C=O frequencies and the δ values

Molecule	C=O frequencies		R.m.s. frequency [a]	Exptl. δ	Calculated δ (IR method)	Calculated δ (atomic charges method)
1	1931	1874	1829.3	0.19	0.20	0.24
1a	1834	1781	1737.9			
2	1920	1864	1819.2	0.01	0.06	0.18
2a	1809	1749	1710.6			
3	1930	1873	1828.3		0.18	0.23
3a	1831	1777	1734.5			
4	1921	1864	1819.6		0.09	0.16
4a	1812	1754	1714.4			
5	1913	1849	1808.6			
5a	1791	1729	1692.3			

[a] The r.m.s. frequencies were calculated after scaling the absolute frequencies by 0.9614 [42].

small change in the value of δ. Similarly, **1a** has a higher δ than **2a** due to the difference in the electronegativities of Co (1.88) and Fe (1.83) [31]. However, a similar comparison may not be appropriate between **1a** and **4a** or between **2a** and **4a** due to the changes in the ligand sphere (presence of Br in **4a**) at Re compared to Co and Fe.

Since the 19th electron is delocalized between the metal and the chelating ligand (Hbma), the value of δ predicted by the NBO method might be dependent on the quality of basis sets that are used on metal. To test the basis set dependency, we have estimated the δ value using different combination of basis sets on the metal and the ligands on a selected complexes (**1** and **3**). The estimated δ values (0.24 and 0.23 on **1a** and **3a**, respectively) using all-electron triple-ξ and one f polarization basis set [34,41] on metals (and 6-31G(d) on ligands) are very close to those estimated using SBKJC effective core potentials (Table 1). Similarly, a triple-ξ basis set on ligands (6-311g(d)) with SBKJC potentials on metal also did not change the calculated δ values (0.23 on **1a** and 0.23 on **3a**). Therefore, the δ values estimated by the NBO method have shown negligibly small differences between different basis sets.

Though the experimental measurement of atomic charges in a molecule is very difficult (determined by X-ray diffraction methods), the theoretical calculation of atomic charges is straight forward. The difficulty in experimental determination of δ is that the chelating ligand L_2 must be stable both in its neutral and anionic form. Therefore, the atomic charge method can be used as an attractive alternative way to predict the value of δ in $18+\delta$ organometallic complexes when the value cannot be determined by experiment. Indeed, it offers a method of predicting the extent of charge delocalization in a complex even prior to its synthesis. However, caution needs to be exercised since the value of δ depends on solvent [31].

4. Conclusion

The 19e complexes $[Co(CO)_3(Hbma)]$, $[Co(CO)_2(PH_3)(Hbma)]$, $[Fe(CO)(Hbma)]^-$ and $[ReBr(CO)_3(Hbma)]^-$ were studied at the B3LYP level. All these 19-electron systems can actually be classified as $18+\delta$ systems. The computed geometrical parameters agree well with experiment, where available. The value of δ was measured by two different methods, from computed IR frequencies and from atomic charges. Values of δ determined by the two methods are in reasonably close agreement. It has been found that δ is sensitive to the ligand sphere at the metal and the electronegativity of the metal. The suggested natural atomic charge method can be used as a promising model to predict the δ value in systems where the experimental determination is difficult.

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References

[1] D.R. Tyler, in: W.C. Trogler (Ed.), Organometallic Radical Processes (and references therein), Elsevier, New York, 1990, p. 338.
[2] A.E. Stiegman, D.R. Tyler, Comments Inorg. Chem. 5 (1986) 215.
[3] D. Astruc, New J. Chem. 16 (1992) 305.
[4] W.C. Watkins, D.H. Macartney, M.C. Baird, J. Organomet. Chem. 377 (1989) C52.
[5] M.C. Baird, Chem. Rev. 88 (1988) 1217.
[6] A.S. Goldman, D.R. Tyler, J. Am. Chem. Soc. 106 (1984) 4066.
[7] N.D. Silavwe, A.S. Goldman, R. Rittler, D.R. Tyler, Inorg. Chem. 28 (1989) 1231.

[8] M.W. Kokkes, W.G.J. deLange, D.J. Stufkens, A. Oskam, J. Organomet. Chem. 294 (1985) 59.

[9] J.W. Herschberger, R.J. Klingler, J.K. Kochi, J. Am. Chem. Soc. 105 (1983) 61.

[10] J.W. Herschberger, R.J. Klinger, J.K. Kochi, J. Am. Chem. Soc. 104 (1982) 3034.

[11] D.P. Summers, J.C. Luong, M.S. Wrighton, J. Am. Chem. Soc. 103 (1981) 5238.

[12] A. Avey, T.J.R. Weakley, D.R. Tyler, J. Am. Chem. Soc. 115 (1993) 7706.

[13] F. Mao, C.E. Philbin, T.J.R. Weakley, D.R. Tyler, Organometallics 9 (1990) 1510.

[14] A.S. Goldman, D.R. Tyler, Inorg. Chem. 26 (1987) 253.

[15] A.E. Stiegman, D.R. Tyler, Coord. Chem. Rev. 63 (1985) 217.

[16] D.R. Tyler, F. Mao, Coord. Chem. Rev. 97 (1990) 119.

[17] A. Fox, J. Malito, A. Poë, J. Chem. Soc. Chem. Commun. (1981) 1052.

[18] F. Mao, D.R. Tyler, D. Kerzler, J. Am. Chem. Soc. 111 (1989) 130.

[19] D. Fenske, Chem. Ber. 112 (1979) 363.

[20] D. Fenske, Angew. Chem. Int. Ed. Engl. 15 (1976) 381.

[21] K. Yang, S.G. Bott, M.G. Richmond, Organometallics 14 (1995) 2387.

[22] K. Yang, S.G. Bott, M.G. Richmond, Organometallics 13 (1994) 3788.

[23] K. Yang, J.M. Smith, S.G. Bott, M.G. Richmond, Organometallics 12 (1993) 4779.

[24] K. Yang, S.G. Bott, M.G. Richmond, Organometallics 13 (1994) 3767.

[25] R. Meyer, D.M. Schut, K.J. Keana, D.R. Tyler, Inorg. Chim. Acta 240 (1995) 405.

[26] W. Bensmann, D. Fenske, Angew. Chem. Int. Ed. Engl. 18 (1979) 677.

[27] D. Fenske, A. Christidis, Angew. Chem. Int. Ed. Engl. 20 (1981) 129.

[28] A. Klein, C. Vogler, W. Kaim, Organometallics 15 (1996) 236.

[29] F. Mao, D.R. Tyler, A.L. Rieger, P.H. Rieger, J. Chem. Soc. Faraday Trans. 87 (1991) 3113.

[30] F. Mao, D.R. Tyler, M.R.M. Bruce, A.E. Bruce, A.L. Riegee, P.H. Rieger, J. Am. Chem. Soc. 114 (1992) 6418.

[31] D.M. Schut, K.J. Keana, D.R. Tyler, P.H. Rieger, J. Am. Chem. Soc. 117 (1995) 8939.

[32] D.A. Braden, D.R. Tyler, Organometallics 19 (2000) 3762.

[33] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(c) S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.

[34] Basis sets were obtained from the extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland WA 99352, USA, and funded by the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for additional information.

[35] (a) W.J. Stevens, H. Basch, M. Krauss, J. Chem. Phys. 81 (1984) 6026;
(b) W.J. Stevens, M. Krauss, H. Basch, P.G. Jasien, Can. J. Chem. 70 (1982) 612;
(c) T.R. Cundari, W.J. Stevens, J. Chem. Phys. 98 (1993) 5555.

[36] (a) W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986;
(b) W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.

[37] J.A. Pople, K. Raghavachari, H.B. Schlegel, J.S. Binkley, Int. J. Quantum Chem. Symp. 13 (1979) 255.

[38] Gaussian 98, Revision A.9, 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, A.G. Baboul, 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, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[39] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

[40] Solvent effects were calculated using the Onsager model as implemented in G98; (a) L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486; (b) M.W. Wong, M.J. Frisch, K.B. Wiberg, J. Am. Chem. Soc. 113 (1991) 4776; (c) M.W. Wong, K.B. Wiberg, M.J. Frisch, J. Chem. Phys. 95 (1991) 8991; (d) M.W. Wong, K.B. Wiberg, M.J. Frisch, J. Am. Chem. Soc. 114 (1992) 523; (e) M.W. Wong, K.B. Wiberg, M.J. Frisch, J. Am. Chem. Soc. 114 (1992) 1645.

[41] (a) A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033;
(b) A.J.H. Wachters, IBM Technol. Rept. RJ584, 1969.;
(c) C.W. Bauschlicher, Jr., S.R. Langhoff, L.A. Barnes, J. Chem. Phys. 91 (1989) 2399.

[42] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.