Theor Chim Acta (1995) 92: 361–367

Theoretica
Chimica Acta

Theoretical study of the protonation of square-planar palladium(II) complexes. Assessment of basis set and correlation effects

A. Milet, A. Dedieu

Laboratoire de Chimie Quantique, UPR 139 du CNRS Université Louis Pasteur,
4, rue Blaise Pascal, F-67070 Strasbourg, France

Received April 21, 1995/Accepted June 12, 1995

Abstract. The protonation of the $[Pd(H)_2(Cl)(NH_3)]^-$ and $[Pd(H)_2(NH_3)_2]$ taken as models of anionic and neutral square-planar d^8 palladium complexes is investigated through SCF, MP2, MP4, CASSCF and CASPT2 calculations, using various basis sets on the metal and the ligands. It is shown that correlation effects, mainly those associated with the covalent character of the metal hydrogen and metal ligand bonds, are important. The importance of diffuse functions on the ligands, especially for the anionic system, is stressed.

Key words: Protonation – Transition metal complexes – Basis set – Electron correlation

Introduction

Protonation of the transition metal and proton transfer reactions to or from the transition metal are prototypical reactions of organometallic chemistry, either in solution or in the gas phase. It is only recently, however, that attention has been paid to the obtention of comprehensive acidity scales for transition metal complexes in solution [1]. Gas-phase data are still quite scarce [2] and to our knowledge no systematic theoretical study has been devoted to this problem. This is in contrast with the situation found in inorganic or organic chemistry where numerous and thorough theoretical investigations have now been carried out [3] for water, ammonia, various amines and acids, including more and more solvent effects [4]. We have recently studied the nature of the bonding of the bridging hydrogen in zwitterionic hydrogen Pd(II) complexes of the form $L_4Pd(II)^- \ldots H{-}NH_3^+$ [5]. In particular we were led to compare the zwitterionic $[Pd(Cl)(Me)_2(NH_3)^- \ldots H{-}NH_3^+]$ system to its Pd(IV) hydride tautomer $[Pd(Cl)(H)(Me)_2(NH_3)_2]$ [5]. The calculations were carried out at the SCF and CASSCF levels using a split valence basis set and a rather limited active space for the CASSCF wave function. No systematic investigation of the basis set and correlation effects was attempted. In the course of a related study pertaining to the hydrogen transfer from water to square planar palladium(II) complexes [6], we thought that it might be worthwhile to investigate such effects and we report here the results of our investigations for the protonation of the $[Pd(H)_2(Cl)(NH_3)]^-$

model system taken as a model of bis alkyl anionic square-planar Pd(II) complexes [7]. We also compare the protonation of such anionic complexes to the protonation of neutral ones by looking at the protonation of $[Pd(H)_2(NH_3)_2]$.

Computational details

SCF, MP2, MP3 and MP4 calculations were carried out using the Gaussian 92 program system [8], optimizing the geometry by a gradient geometry optimization, either at the SCF or at the MP2 level (*vide infra*). CASSCF [9] and CASPT2 calculations [10] were performed using the MOLCAS code [11].

The basic sets were set as follows: Our smallest basis set, which was used for the geometry optimization, was a split valence type basis set without polarization functions, except for the active hydrogen atom. The 28 innermost core electrons (up to 3*d*) of the palladium atom were described by the relativistic pseudopotential of Hay and Wadt [12] and the remaining outer core and valence electrons by a (8,6,4) $\langle 3,3,2 \rangle$ basis set [12]. For nitrogen, chlorine and the hydrogen atoms of NH_3 the (9, 5), (11, 7) and (4) basis sets of Huzinaga [13, 14] contracted respectively into $\langle 3,2 \rangle$, $\langle 4,3 \rangle$ and $\langle 2 \rangle$ were used. The protonating hydrogen atom, which in the $[Pd(H)_3(Cl)(NH_3)]^-$ product becomes a hydride, was for this reason described by a somewhat more flexible (6, 1) contracted to $\langle 3,1 \rangle$ basis set [13]. This smallest basis set is hereafter denoted as BPS. The addition of polarization functions first on palladium only (with an exponent $\alpha_f = 1.472$ [15]) and then on Pd ($\alpha_f = 1.472$ [15]), N ($\alpha_d = 0.95$ [16]), Cl ($\alpha_d = 0.54$ [17]) and H ($\alpha_p = 0.8$) yielded two types of polarized basis sets which we denote, following the terminology of the Gaussian system of programs as BPS(*) and BPS* respectively. The addition of even tempered *s* and *p* diffuse function on the N ($\alpha_s = 0.0658$, $\alpha_p = 0.0529$) and Cl atoms ($\alpha_s = 0.0674$, $\alpha_p = 0.0527$) was also tested for these BPS and BPS* basis sets (the Pd and H atoms having already diffuse functions). The corresponding notation is BPS + and BPS* +. Finally, an all-electron (16, 11, 9) $\langle 7,5,5 \rangle$ basis set for palladium [18] eventually *f* polarized was investigated in conjunction with the above basis sets for N, Cl and H. The corresponding notations are BAE, BAE*, BAE + and BAE* +. In this case the relativistic effects were not taken into account.

Results and discussion

The results for the protonation reaction $[Pd(H)_2(Cl)(NH_3)]^- + H^+ \rightarrow [Pd(H)_3(Cl)(NH_3)]$ are summarized in Table 1. We use the usual Gaussian notation to denote the level of the calculation. Several conclusions can be drawn from this table.

(i) The proton affinity is strongly sensitive to the inclusion of correlation effects, compare for instance the entries (1)–(7) with the entries (8)–(14). There is an increase in the proton affinity of about 40 kcal/mol on going from the SCF to the MP2 level. This increase is not an artifact of the MP2 method since it hardly changes at the MP4SDTQ level, as seen from the comparison between the entries (15), (17), (19) and (20) and the entries (24), (26), (28) and (30) respectively.
(ii) On the other hand it does not seem to depend very much on whether the geometry optimization has been carried out at a correlated level or not. This is best seen from the one-to-one comparison of the entries (8)–(11), (13), (14) with the

Table 1. Total SCF, MP2, MP3 and MP4 energies (in a.u.) for the $[Pd(H)_2(Cl)(NH_3)]^-$ system and its conjugate acid, and corresponding proton affinities (in kcal/mol)

Entry	Calculation	$[Pd(H)_2(Cl)(NH_3)]^-$	$[Pd(H)_3(Cl)(NH_3)]$	Proton affinity
HF optimization (Pd–H = 1.44 Å)				
(1)	HF/BPS//HF/BPS	– 642.0686	– 642.5091	276.4
(2)	HF/BPS(*)//HF/BPS	– 642.0724	– 642.5149	277.7
(3)	HF/BPS*//HF/BPS	– 642.1122	– 642.5613	281.8
(4)	HF/BPS +//HF/BPS	– 642.0854	– 642.5193	272.3
(5)	HF/BAE//HF/BPS	– 5443.6955	– 5444.1367	276.9
(6)	HF/BAE*//HF/BPS	– 5443.7549	– 5444.2010	279.9
(7)	HF/BAE* +//HF/BPS	– 5443.7755	– 5444.2122	274.0
(8)	MP2/BPS//HF/BPS	– 642.3761	– 642.8802	316.3
(9)	MP2/BPS(*)//HF/BPS	– 642.6038	– 643.1135	319.8
(10)	MP2/BPS*//HF/BPS	– 642.8389	– 643.3521	322.0
(11)	MP2/BPS +//HF/BPS	– 642.4035	– 642.8982	310.4
(12)	MP2/BAE//HF/BPS	– 5444.0333	– 5444.5405	318.3
(13)	MP2/BAE*//HF/BPS	– 5444.4202	– 5444.9295	319.6
(14)	MP2/BAE* +//HF/BPS	– 5444.4458	– 5444.9438	312.5
MP2 optimization (Pd–H = 1.46 Å)				
(15)	MP2/BPS//MP2/BPS	– 642.3791	– 642.8826	315.9
(16)	MP2/BPS(*)//MP2/BPS	– 642.6059	– 643.1150	319.5
(17)	MP2/BPS*//MP2/BPS	– 642.8405	– 643.3487	318.9
(18)	MP2/BPS +//MP2/BPS	– 642.4052	– 642.9004	310.7
(19)	MP2/BAE*//MP2/BPS	– 5444.4212	– 5444.9253	316.3
(20)	MP2/BAE* +//MP2/BPS	– 5444.4468	– 5444.9397	309.3
(21)	MP2/BAE +//MP2/BPS	– 5444.0645	– 5444.5593	310.5
(22)[a]	MP2/BAE* +//MP2/BAE* +	– 5444.4538	– 5444.9482	310.2
(23)	MP3/BPS//MP2/BPS	– 642.3858	– 642.8829	311.9
(24)	MP4SDTQ/BPS//MP2/BPS	– 642.4187	– 642.9240	317.1
(25)	MP3/BPS*//MP2/BPS	– 642.8475	– 643.3437	311.4
(26)	MP4SDTQ/BPS*//MP2/BPS	– 642.8853	– 643.3918	317.8
(27)	MP3/BAE*//MP2/BPS	– 5444.4234	– 5444.9110	306.0
(28)	MP4SDTQ/BAE*//MP2/BPS	– 5444.4659	– 5444.9676	314.8
(29)	MP3/BAE* +//MP2/BPS	– 5444.4484	– 5444.9252	299.2
(30)	MP4SDTQ/BAE* +//MP2/BPS	– 5444.4919	– 5444.9824	307.8

[a] See Ref. [19]

entries (15)–(20). This is also true whatever the basis set is, compare for instance the entries (14) and (20) with (22). We note however that the corresponding variation of the bond length can be larger: for instance the optimized apical Pd–H bond length amounts to 1.44 Å at the HF/BPS level, to 1.46 Å at the MP2/BPS level and to 1.47 Å at the MP2/BAE* + level [19]. This indicates that the potential energy surface around the minimum is quite flat. A similar feature has been observed on the $Pd(H)(CH_3)$ system by Siegbahn [20].

(iii) As far as the basis sets are concerned, the replacement of the inner core electron by a pseudopotential does not bring a significant change: at both the MP2 and MP4SDTQ levels the proton affinity is lowered by 2–3 kcal/mol only, see the comparison of (17) with (19), or of (26) with (28). Polarization functions increase

Table 2. Total SCF and MP2 energies (in a.u.) for the $[Pd(H)_2(Cl)(NH_3)]^-$ system using ghost orbitals (see the text) and corresponding proton affinities (in kcal/mol)

Entry	Calculation	$[Pd(H)_2(Cl)(NH_3)]^-$	Proton affinity
(1)	HF/BAEghost//HF/BPS	– 5443.7061	270.2
(2)	HF/BAE*ghost//HF/BPS	– 5443.7661	272.9
(3)	HF/BAE* +ghost//HF/BPS	– 5443.7847	268.3
(4)	MP2/BAEghost//HF/BPS	– 5444.0498	307.9
(5)	MP2/BAE*ghost//HF/BPS	– 5444.4385	308.1
(6)	MP2/BAE* +ghost//HF/BPS	– 5444.4620	302.3

the proton affinity, the effect being more sensitive at the HF and MP2 levels than at the MP4 level. But this increase is more than counterbalanced by the inclusion of diffuse functions on the ancillary ligands; the lowering of the proton affinity on going from the BAE* to the BAE* + basis set is 7 kcal/mol at both the MP2//MP2 (entries (19) and (20)) and MP4//MP2 levels (entries (28) and (30)). This was not unexpected owing to the anionic nature of the $[Pd(H)_2(Cl)(NH_3)]^-$ system. In fact it appears that for such anionic transition metal complexes the inclusion of diffuse functions is sufficient to get a reasonable estimate of the protonation energy (compare for instance the entries (21) and (20)).

One may of course worry about the effect of the basis set superposition error [21]. The basis set superposition error was obtained through the counterpoise method [22] by adding in the non-protonated system ghost functions corresponding to the apical hydride. One then gets, see Table 2, a decrease of the proton affinity between 6.7 and 5.7 kcal/mol at the SCF level and between 10.4 and 10.2 kcal/mol at the MP2 level for the BAE and BAE* + basis sets respectively.

In order to shed more light on these results, and in particular to check whether the strong increase in the proton affinity on going from SCF to either the MP2 or MP4 level was the result of pure dynamical correlation effects or whether some imbalance in the treatment of the formation of the covalent Pd–H bond was also involved, we carried out CASSCF calculations followed by CASPT2 calculations. Two different active spaces were used. In the first one (which we denote by CAS4*a*4*e*) four electrons in four active orbitals were correlated. The active orbitals were chosen so as to correspond to the bonding and antibonding metal–ligand interactions involving d_{z^2} and $d_{x^2-y^2}$. The $d_{z^2}+s_H$ and $d_{z^2}-s_H$ orbitals account for the description of the covalent character of the axial Pd–H bond. The other two orbitals had to be added to ensure the stability of the CAS wavefunction for the unprotonated system. Thus the 4*a*4*e* active space yields not only the non-dynamical electron correlation associated with the axial Pd–H bond but also a fraction of the non-dynamical electron correlation associated with the equatorial metal–ligand bonds (especially the Pd–H equatorial bonds). Thus we chose to assess the non-dynamical electron correlation associated with all metal–ligand σ covalent bonds (axial and equatorial). This was done by correlating 10 electrons in 11 orbitals. These orbitals correspond to the five bonding and five antibonding metal–ligand σ interactions and to the $5p_z$ orbital. It is clear from the results of Table 3 that most of the correlation effects are of non-dynamical nature. The difference between the results of the CAS11*a*10*e*/BAE* +ghost//HF/BPS and the CASPT211*a*10*e*/BAE* +ghost//HF/BPS calculations is 6.3 kcal/mol only, to be

Table 3. Total CASSCF and CASPT2 energies (in a.u.) for the $[Pd(H)_2(Cl)(NH_3)]^-$ system and its conjugate acid, and corresponding proton affinities (in kcal/mol)

Entry	Calculation	$[Pd(H)_2(Cl)(NH_3)]^-$	$[Pd(H)_3(Cl)(NH_3)]$	Proton affinity
HF optimization				
(1)	CAS4*a*4*e*/BAEghost//HF/BPS	− 5443.7379	− 5444.1974	288.3
(2)	CASPT24*a*4*e*/BAEghost//HF/BPS	− 5444.1705	− 5444.6531	302.8
(3)	CAS4*a*4*e*/BAE* +ghost//HF/BPS	− 5443.8162	− 5444.2725	286.3
(4)	CASPT24*a*4*e*/BAE* +ghost//HF/BPS	− 5444.7020	− 5445.1784	298.9
(5)	CAS11*a*10*e*/BAE* +ghost//HF/BPS	− 5443.8690	− 5444.3380	294.3
(6)	CASPT211*a*10*e*/BAE* +ghost//HF/BPS	− 5444.7109	− 5445.1900	300.6

Table 4. Total SCF and MP2 energies (in a.u.) for the $[Pd(H)_2(NH_3)_2]$ system and its conjugate acid, and corresponding proton affinities (in kcal/mol)

Entry	Calculation	$[Pd(H)_2(NH_3)_2]$	$[Pd(H)_3(NH_3)_2]^+$	Proton affinity
HF optimization				
(1)	HF/BPS//HF/BPS	− 239.2617	− 239.5412	175.4
(2)	HF/BPS*//HF/BPS	− 239.3507	− 239.6337	177.6
(3)	HF/BPS +//HF/BPS	− 239.2690	− 239.5474	174.7
(4)	HF/BPS* +//HF/BPS	− 239.3523	− 239.6356	177.8
(5)	MP2/BPS//HF/BPS	− 239.6436	− 239.9769	209.1
(6)	MP2/BPS*//HF/BPS	− 240.1361	− 240.4732	211.5
(7)	MP2/BPS +//HF/BPS	− 239.6634	− 239.9945	207.8
(8)	MP2/BPS* +//HF/BPS	− 240.1511	− 240.4875	211.1

compared with the 26.0 kcal/mol increase from HF/BAE* +ghost//HF/BPS to CAS11*e*10*a*/BAE* +ghost//HF/BPS. But these non-dynamical electron correlation effects are *not* restricted to the Pd–H bond that is formed upon protonation. Only 18.0 kcal/mol of correlation energy is recovered in the CAS4*a*4*e* (which in addition also recovers a fraction of the non-dynamical electron correlation associated with the equatorial ligands).

It is finally worthwhile to compare some of the above results to the results obtained for the protonation of the neutral $[Pd(H)_2(NH_3)_2]$ system, see Table 4. In both cases the increase in the proton affinity on going from SCF to MP2 is large. It amounts to about 40 kcal/mol for the anionic system and to about 33 kcal/mol for the neutral system. As expected, the influence of diffuse functions and polarization functions on the ligands is much less important in the neutral system than in the anionic $[Pd(H)_2(Cl)(NH_3)]^-$ system, at least at both the SCF and MP2 levels.

Conclusion

It is therefore clear from this study that electron correlation should be included to obtain, even at a qualitative level, a reliable picture of protonation and proton transfer reactions on transition metal complexes. The electron correlation effects are mostly of non-dynamical nature, being associated with the description of the formation of the covalent metal–hydrogen bond and with the changes, upon protonation, of the σ bonds between the metal and the spectator ligands. Yet the MP2 level of theory seems to be sufficient, the MP4 or CASPT2 levels bringing no substantial improvement to the energetics of the process. An SCF geometry optimization is also probably sufficient, at least when the energies are computed at the MP2 level. In line with these results, the energy difference between the $[Pd(Cl)(H)_2(NH_3)^- \ldots H\text{–}NH_3^+]$ zwitterionic system and the Pd(IV) hydride tautomer $[Pd(H)_3(Cl)(NH_3)_2]$ has been found [6] to be 18.7 kcal/mol in favour of the zwitterionic system at the HF/BPS//HF/BPS level and 11.1 and 10.3 kcal/mol in favor of the Pd(IV) system at the MP2/BPS//HF/BPS and MP2/BPS//MP2/BPS levels respectively. In this case the basis set superposition error should be minimal owing to the fact that in the zwitterionic system the proton lies already in the vicinity of the palladium complex. We have also seen that, as expected, diffuse functions are more important for anions than for neutral systems. But the zwitterionic system, with the cation close to the anion, should behave more like a neutral system and the above energy difference should not be greatly affected by further improvements of the basis set. One indeed gets moderate changes when diffuse and polarization functions are subsequently added: the MP2/BPS+//MP2/BPS and the MP2/BPS*+//MP2/BPS values amount to 8.4 and 13.6 kcal/mol respectively.

Acknowledgments. SCF, MP2, CASSCF and CASPT2 calculations were carried out on the IBM RS 6000 workstations of our laboratory and of the Institut du Developpement et de Ressources en Informatique Scientifique (IDRIS, Orsay). The MP4 calculations were carried out on the DEC 3000/600S workstations of the Centre Universitaire Regional de Ressources Informatiques (CURRI, Strasbourg). We thank the staffs of these two centers for their cooperation. We are also grateful to Dr. L. Padel and Mrs. Fersing for their help and technical assistance.

References and Notes

1. (a) For a review see Kristjandottir S, Norton JR (1992) In: Dedieu A (ed) transition metal hydrides. VCH, New York, p 309. (b) See also Rottink MK, Angelici RJ (1993) Inorg Chem 115:7267 and references therein
2. (a) Schilling JB, Beauchamp JL (1990) Chem Rev 90:629. (b) Miller AES, Kawamura AR, Miller TM (1990) J Am Chem Soc 112:457
3. See for instance: (a) Scheiner S (1985) Acc Chem Res 18:174. (b) De Frees DJ, Mc Lean AD (1986) J Comput Chem 7:32. (c) Mó O, de Paz JLG, Yáñez M (1986) J Phys Chem 90:5597. (d) Cylbulski SM, Scheiner S (1987) J Am Chem Soc 109:4199. (e) Cylbulski SM, Scheiner S (1989) J Am Chem Soc 111:23. (f) Del Bene JE, Shavitt I (1990) J Phys Chem 94:5514. (g) Luth K, Scheiner S (1992) Int J Quant Chem Quant Chem Symp 26:817. (h) Luth K, Scheiner S (1992) J Chem Phys 97:7507, 7519. (i) Isaacson AD, Wang L, Scheiner S (1992) J Phys Chem 97:1765. (j) Del Bene JE (1993) J Phys Chem 97:107. (k) Gronert S (1993) J Am Chem Soc 115:10258. (l) Bernasconi CF (1994) J Am Chem Soc 116:5405. (m) Eckert-Maksic M, Klessinger M, Maksic ZB (1995) Chem Phys Lett 232:472. (n) Kar T, Scheiner S (1995) J Am Chem Soc 117:1344
4. See for instance: (a) Sanchez Marcos E, Terryn B, Rivail JL (1985) J Phys Chem 89:4695. (b) Karlström G (1988) J Phys Chem 92:1318. (c) Ford GP, Wang B (1992) J Am Chem Soc 114:10563. (d) Tuñon I, Silla E, Tomasi J (1992) J Chem Phys 96:9043. (e) Tuñon I, Silla E, Pascual-Ahuir JL (1993) J Am Chem Soc 115:2226. (f) Tortonda E, Pascual-Ahuir JL, Silla E, Tuñon E (1993) J Phys Chem 97:11087. (g) Orozco M, Luque F (1995) J Am Chem Soc 117:1378

5. Wehman-Ooyevaar ICM, Grove DM, de Vaal P, Dedieu A, van Koten G (1992) Inorg Chem 31:5484
6. Milet A, Dedieu A (to be published)
7. (a) Canty AJ, Honeyman RT, Roberts AS, Traill PR, Colton R, Skelton BW, White AH (1994) J Organomet Chem 471:C8. (b) Canty AJ, Fritsche SD, Jin H, Skelton BW, White AH, J Organomet Chem (in press)
8. (a) Gaussian 92, Revision E.2. Frisch MJ, Trucks GW, Head-Gordon M, Gill PMW, Wong MW, Foresman JB, Johnson BG, Schlegel HB, Robb MA, Reploge ES, Gomperts R, Andres JL, Raghavachari K, Binkley JS, Gonzales C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA (1992) Gaussian, Inc., Pittsburgh, PA. (b) The MP2, MP3 and MP4 calculations were carried out with a frozen core. (c) The zero point energy was not taken into account, our most interest being here the comparison of various basis sets and levels of calculation
9. Roos BO, Taylor PR, Siegbahn PEM (1980) Chem Phys 48:157. (b) Siegbahn PEM, Almlöf J, Heiberg A, Roos BO (1981) J Chem Phys 74:2384. (c) Roos BO (1980) Int J Quant Chem Symp 14:175
10. (a) Andersson K, Malmqvist PÅ, Roos BO, Sadlej A, Wolinski K (1990) J Phys Chem 94:5483. (b) Andersson K, Malmqvist PÅ, Roos BO (1992) J Chem Phys 96:1218
11. MOLCAS Version 3. Andersson K, Blomberg MRA, Fülscher MP, Kellö V, Lindh R, Malmqvist PA, Noga J, Roos BO, Sadlej AJ, Siegbahn PEM, Urban M, Widmark PO (1994) University of Lund, Sweden
12. Hay PJ, Wadt WR (1985) J Chem Phys 82:270
13. Huzinaga S (1971) Technical Report, University of Alberta, Edmonton
14. Huzinaga S (1965) J Chem Phys 42:1293
15. Ehlers AW, Böhme M, Dapprich S, Gobbi A, Höllwarth A, Jonas V, Köhler KF, Stegmann R, Veldkamp A, Frenking G (1993) Chem Phys Lett 208:111
16. Blomberg MRA, Siegbahn PEM, Svensson M (1993) Inorg Chem 32:4218
17. Pettersson LGM, Siegbahn PEM (1985) J Chem Phys 83:3538
18. (a) Veillard A, Dedieu A (1984) Theor Chim Acta 65:215. (b) The original (14, 9, 8) basis set was modified by the addition of an *s* function of exponent 0.30560 to suppress the gap between the functions needed to describe the widely separated 4*s* and 5*s* shells, two *p* functions of exponent 0.23560 and 0.08386, and one *d* function of exponent 0.07890
19. Due to program limitations the MP2/BAE* + optimization of the apical Pd–H bond in $Pd(H_3)(Cl)(NH_3)$ was carried out numerically, the $Pd(H_2)(Cl)(NH_3)$ equatorial plane being optimized through an analytical gradient evaluation but without *f* functions on the Pd atom. The corresponding optimized equatorial values are Pd–Cl = 2.28 Å, Pd–H = 1.63 Å, Pd–N = 2.12 Å. They are smaller than the values optimized at the MP2/BPS level: Pd–Cl = 2.35 Å, Pd–H = 1.68 Å, Pd–N = 2.15 Å. A similar feature is observed for $[Pd(H_2)(Cl)(NH_3)]^-$. There the values are: Pd–Cl = 2.39 Å, Pd–H = 1.63 Å, Pd–N = 2.11 Å to be compared with 2.43 Å, 170 Å, 2.16 Å at the MP2/BPS level
20. Siegbahn PE, Svensson M (1993) Chem Phys Lett 216:147
21. For reviews, see (a) Kolos W (1979) Theor Chim Acta 51:219. (b) van Lenthe JH, van Duijneveldt-van de Rijdt JGCM, van Duijneveldt FB (1987) Adv Chem Phys 69:521. (c) van Duijneveldt FB, van Duijneveldt-van de Rijdt JGCM, van Lenthe JH (1994) Chem Rev 94:1873
22. (a) Boys SF, Bernardi F (1970) Mol Phys 19:553. (b) Ostlund NS, Merrifield DL (1976) Chem Phys Lett 39:612