Spin−Orbit Coupling and Outer-Core Correlation Effects in Ir- and Pt-Catalyzed C−H Activation

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S *Supporting Information*

ABSTRACT: The transition metal-dependent spin−orbit coupling (SOC) and outer-core (5s5p) correlation effects in Ir- and Pt-catalyzed C−H activation processes are studied here using high level ab initio computations. The catalysts involve complexes with oxidation states: Ir(I), Ir(III), Pt(0), and Pt(II). It is demonstrated that for these heavy 5d transition metal-containing systems, the SOC effect and outer-core correlation effect on C−H activation are up to the order of ∼1 kcal/mol, and should be included if chemical accuracy is aimed. The interesting trends in our studied systems are: (1) the SOC effect consistently increases the C−H activation barriers and is apparently larger in higher oxidation states (Pt(II) and Ir(III)) than in low-oxidation states (Pt(0) and Ir(I)); and (2) the magnitude of outer-core (5s5p) correlation effects is larger in less coordinate-saturated system. The effect of basis set on the outer-core correlation correction is significant; larger basis sets tend to increase the C−H activation barriers.

I. INTRODUCTION

Relativistic effects play important roles in the chemistry of heavy transition metal containing molecules.[1−5] Nowadays, scalar relativistic effects are routinely taken into account in theoretical calculations of electronic structure, using either relativistic effective core potentials (ECPs) or all-electron approaches like Douglas−Kroll−Hess (DKH) transformation.[6] On the other hand, despite their potentially high impact on many transition metal containing systems,[7] nonscalar relativistic effects like spin−orbit coupling (SOC) are much less considered in theoretical studies. However, due to the dependence of SOC on nuclear charge,[6] it is natural to expect non-negligible SOC effects for heavy late transition metals. To explore this factor, we present here systematic ab initio wave function theory (WFT) computations, based on a combined CASSCF/CCSD(T)&CASPT2/SO approach, to explore SOC effects on well-known homogeneous Ir- and Pt-catalyzed C−H activation processes as shown in Scheme 1.[8−10] The catalytic systems under study cover a full set of oxidation states used in C−H activation by these two heavy late 5d transition metals,

that is, Ir(I), Ir(III), Pt(0), Pt(II), which are capable of activating strong C−H bonds as those in methane. Through these systematic comparisons, we aim to obtain general trends and insights for SOC effects on C−H activation by these two metals.

Because of the expected large relativistic effects of these heavy 5d transition metals, Ir and Pt, significant theoretical efforts have been invested to explore the SOC effects on their reactivity, especially for the naked metal atoms and ions.[11−13] However, for molecular catalysis beyond the naked transition metal systems, our knowledge on the potential SOC effect is still limited. One assumption employed in previous theoretical studies is that for ligand-coordinated molecular systems, the SOC effect is "quenched", due to the ligand field splitting that removes the near degeneracy of the various electronic states of naked transition metal on ligation.[13] However, this assumption was never examined by direct computations of the SOC effects of realistic large systems. Using a systematic study, we provide herein a quantitative assessment of the assumption that in practically usable molecular catalysts the SOC effect is "quenched". We additionally examine the impact of transition metal outer-core (5s5p) electron correlation on the C−H activation processes shown in Scheme 1. Trends from these quantitative results will be discussed.

Scheme 1. C−H Activation Processes Studied in This Work
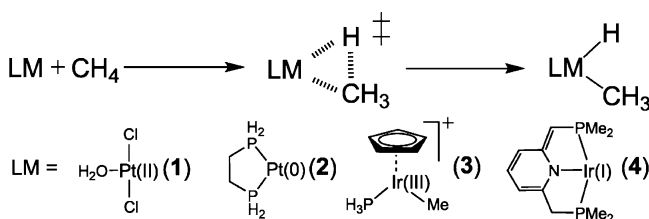
II. COMPUTATIONAL DETAILS

The scalar relativistic effect of the transition metals was treated by usage of the recently developed energy-consistent pseudopotentials (PP)[14] for 5d transition metals throughout this work. All of the geometries were fully optimized with the density functional theory (DFT) method at the TPSS/cc-pVTZ level (for transition metals, cc-pVTZ-PP basis set[14] developed for the adopted pseudopotentials was used).[15,16] All optimized C−H activation transition states were verified by vibrational analysis. The geometries of the corresponding transition metal σ-CH$_4$ complexes, which serve here as the reference states for the C−H activation barriers, were verified to have no imaginary frequencies. The thermal correction for the barriers at 298 K to the free energy was computed with the vibrational analysis. To assess solvent effects, we employed the CPCM continuum solvation model,[17] with the experimentally used solvent in the corresponding C−H activation reactions. All DFT calculations were performed with the Gaussian 09 program.[18]

The subsequent single-point ab initio WFT calculations employing CCSD(T),[19] CASSCF,[20] and CASPT2[21] methods with DFT-optimized structures were all performed with the MOLPRO2010 package.[22] In all ab initio calculations, the 1s electrons of C, O, N and the 1s2s2p electrons of P, Cl atoms were not correlated; that is, only valence electrons of these main group elements were correlated. The SOC effect was included using a state-interacting method[23] with two-component spin−orbit (SO) pseudopotentials[14] on transition metals. The SOC matrix was constructed on the basis of the CASSCF state-specific scalar relativistic states (also called unperturbed states). This matrix was then diagonalized to obtain the SO states and energies. For accurate determination of the state-specific scalar relativistic energies of all states, the diagonal elements of SOC matrix were replaced by the individual state energies calculated by CCSD(T) (for S$_0$ and T$_1$ states) and CASPT2 (for all triplet states) methods. All of the CCSD(T) and CASPT2 calculations were performed with the same CASSCF state-averaged orbitals. The CASPT2 calculations involved the standard IPEA shift of 0.25.[24] In addition, a level shift of 0.1 was used to avoid intruder state problems.[25] For SOC effects, we used the valence-only correlation consistent cc-pVDZ-PP[14] and cc-pVDZ[16] basis sets, for transition metals and the main group elements, respectively. Employing a larger basis set like triple-ζ correlation consistent bases for the relatively larger systems **3** and **4** is prohibitively costly. However, extension of the basis set to polarized triple-ζ quality (cc-pVTZ-PP and cc-pVTZ) was tested for **1** and **2** and found to have only very limited influence on the SOC results (see Table S2 in the Supporting Information). More computational details of our CASSCF/ CCSD(T)&CASPT2/SO calculations, such as active space and excited states involved in SOC effect calculations, can be found in the Supporting Information.

The 5s5p electron-correlation effect was investigated for the smaller systems **1** and **2** with the canonical coupled cluster method (CCSD(T)), while for **3** and **4** we used the local coupled cluster method (LCCSD(T0)[26]). The default distance criteria in MOLPRO program for pair classification in local correlation approximation were used (R_{close} = 1 bohr, R_{weak} = 3 bohr) for the LCCSD(T0) calculations. To guarantee a balanced treatment of reactant and transition state, and between different basis sets, the merged domains from all of them are used in the local coupled cluster calculations. All of

these 5s5p electron-correlation calculations were performed by use of the correlation consistent polarized weighted core− valence basis sets cc-pwCVDZ-PP and cc-pwCVTZ-PP[14] for transition metals, combined with the cc-pVDZ and cc-pVTZ for main group elements, correspondingly. To reduce the computational effort, density fitting approximations were employed in the LCCSD(T0) calculations,[27] using the corresponding auxiliary basis sets.[28]

The 5s5p electron-correlation correction was determined by the difference of two coupled cluster single point calculations with and without 5s5p electrons correlated, using the same basis sets cc-pwCVDZ-PP/cc-pVDZ and cc-pwCVTZ-PP/cc- pVTZ for transition metals/main group elements, then extrapolating to the complete basis set limit (CBS). The two-point CBS extrapolation was performed on the basis of eq 1 proposed by Truhlar.[29] The predetermined optimal parameter β (β = 2.46)[30] was used for the cardinal number n = 2, 3. Alternatively, the inverse square and Helgaker's inverse cubic scaling dependence[31] of the correlation energy on the basis set were also explored to have some indication of the possible error bars of the CBS extrapolation. Hartree−Fock (HF) orbitals were used as reference of these coupled-cluster calculations of 5s5p electron-correlation effect. The cc-pVnZ and cc-p(wC)- VnZ-PP bases are all abbreviated as (w)VnZ hereafter.

$$E_{corr,n} = E_{corr,CBS} + \frac{A}{n^\beta} \tag{1}$$

III. RESULTS AND DISCUSSION

The optimized C−H activation transition states of methane by catalysts **1−4** are shown in Figure 1. The bond distances of the
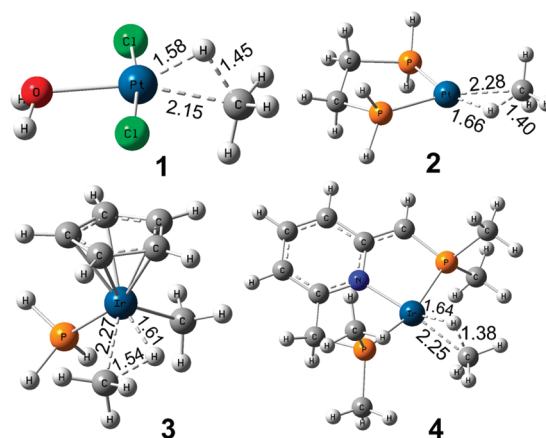

Figure 1. Selected bond lengths of C−H activation transition states for **1−4** (in angstroms).

C−H bond undergoing activation are seen to range from 1.38 to 1.54 Å, values that are close to recent calculations based on B3LYP functional with different basis set and PP.[33] Comparison of these C−H distances in the transition state for the Pt(0) catalyst **2** to that of the Pt(II) catalyst **1** reveals that the former has a much larger barrier despite the shorter activated C−H bond. Thus, an earlier transition state in C−H activation by Pt catalyst **2** than by Pt catalyst **1** does not correspond to lower barrier, in discord with the Hammond postulate.[32] According to a previous theoretical analysis, Pt(II)- mediated C−H activation was classified to be electrophilic,

Table 1. Calculated C−H Oxidative Addition Barriers ($\Delta E^{\ddagger}$), SOC Corrections ($\Delta\Delta E^{\ddagger}_{SOC}$), and 5s5p Correlation Corrections ($\Delta\Delta E^{\ddagger}_{5s5p}$) for 1−4 (in kcal/mol)[a]

	catalyst			
	1 Pt(II)	**2** Pt(0)	**3** Ir(III)	**4** Ir(I)
$\Delta E^{\ddagger}$[b]	1.11	8.35	9.35	0.70
$\Delta\Delta E^{\ddagger}_{SOC}$[c]	1.01	0.17	0.89	0.24
$\Delta\Delta E^{\ddagger}_{5s5p}$[d]	−0.10	−0.68	−0.23	0.10
	(−0.42)	(−1.20)	(−0.69)	(−0.26)
	{−0.22}	{−0.87}	{−0.40}	{−0.03}
	[−0.06/−0.13]	[−0.61/−0.73]	[−0.16/−0.27]	[0.15/0.06]
$\Delta\Delta E^{\ddagger}_{SOC} + \Delta\Delta E^{\ddagger}_{5s5p}$	0.91	−0.51	0.66	0.34

[a]The structures used in calculations are from TPSS/VTZ geometry optimization; positive correction corresponds to increasing barrier. [b]Values are from CCSD(T)/VDZ calculations. [c]Values are from combined CASSCF/CCSD(T)&CASPT2/SO approach with VDZ basis set. [d]Values outside parentheses are from CCSD(T)/CBS extrapolation according to eq 1 with $\beta = 2.46$; values in parentheses are from CCSD(T)/wVDZ/VDZ level; values in braces are from CCSD(T)/wVTZ/VTZ level; values inside brackets are from CCSD(T)/CBS extrapolation according to eq 1 with [$\beta = 2$/ $\beta = 3$]. All CBS extrapolations use wVDZ/VDZ and wVTZ/VTZ basis sets on transition metals/other elements.

while Ir(III)- and Ir(I)-mediated C−H bond activations were considered to be ambiphilic and nucleophilic, respectively.[33]

Table 1 summarized the SOC effects on C−H activation barriers of these oxidative addition processes shown in Scheme 1. The barriers ($\Delta E^{\ddagger}$) without including SOC effects are calculated at the CCSD(T)/VDZ level, for which the SOC corrections ($\Delta\Delta E^{\ddagger}_{SOC}$) are calculated from CASSCF/CCSD-(T)&CASPT2/SO approach with VDZ basis set. We note that VDZ may not be sufficiently large to produce very accurate CCSD(T) barriers (for effect of VTZ basis set on barriers, see our calculations in Table S1 for 1 and 2 where CCSD(T)/VTZ computation is affordable). However, the objective of this work concerns mainly the SOC effect on the barriers, and our test calculations for 1 and 2 (see Table S2 in the Supporting Information) show that VDZ is quantitatively sufficient. Although these C−H activations all proceed in the ground singlet state for which zero-order SOC is not present, nevertheless, the SOC effect is still considerable in some cases (∼1 kcal/mol) and has to be accounted for if quantitative accuracy is aimed. The magnitudes of the SOC effect on barriers are on par with that of solvent effect corrections or thermal free energy corrections (see Table S1 in the Supporting Information). Complexes 1 and 3, which are Pt(II) and Ir(III) catalysts, have a much larger SOC effect than 2 and 4, which are Pt(0) and Ir(I) catalysts. The trend from the magnitude of SOC effect is thus clear: higher oxidation states would have larger SOC effect. We note that the four complexes involve quite different ligands, and these may certainly affect the SOC through orbital delocalization, in addition to the oxidation state effects. Furthermore, as seen in the Supporting Information (Tables S5−S7), the SOC is dominated by the triplet states, which involve d−d type excitations. Another feature that is also interesting is that the SOC effect raises the C−H activation barrier in all four cases. This could be understood by the general trend that the degree of coordinative saturation for the transition metal always increases along C−H activation process from methane-transition metal σ-complexes to oxidative addition product. Thus, the coordinative saturation of the metal center for the transition state is larger than that in reactant complex, which leads to larger ligand field and hence larger separation of the triplet state from the ground singlet state. This increase of the singlet−triplet gap in transition state weakens the SOC due to the singlet−triplet mixing, and hence the inclusion of SOC raises the transition state relative to the reactant. Additionally, the transition metal orbitals, which

contribute the most to the SOC, become more delocalized in transition state than in reactant, which constitutes another factor to decrease the SOC effect in the transition state. Consequently, the transition state will be less stabilized by SOC as compared to the reactant complex, and the barrier will consistently increase. Because the calculated $\Delta\Delta E^{\ddagger}_{SOC}$ in Table 1 is very slightly dependent on the basis set (see Table S2 in the Supporting Information) and the correlation treatment used for the excited state energy levels (see Table S5 in the Supporting Information), we feel that the ab initio computed $\Delta\Delta E^{\ddagger}_{SOC}$ values may be safely transferrable to DFT calculations.

The transition metal outer-core (5s5p) electron correlation in Table 1 exhibits quite a different behavior. First, unlike the SOC effect, which is almost unaffected by enlargement of the basis set, the outer-core correlation effect is significantly affected by basis set incompleteness error (BSIE). CBS limit extrapolation, to alleviate the BSIE, increases the value of outer-core correlation correction ($\Delta\Delta E^{\ddagger}_{5s5p}$) significantly. Previous calibration calculations for naked transition metal atoms and transition metals containing very small molecules covering the whole transition metal series from 3d to 5d elements have shown that the dependence of outer-core electron correlation effect on basis set completeness may be case-dependent,[14,34] so it is hard to predict BSIE effect on outer-core electron correlation before actually doing the calculations. Here, in the four complexes of two 5d transition metals, consistently signed shifts of $\Delta\Delta E^{\ddagger}_{5s5p}$ are observed for CBS values, as compared to the values of polarized double-ζ quality basis set (wVDZ/VDZ). Similar results were reported in a recent study of Au-alkene/alkyne/allene interaction.[35]

In addition, the CBS values shown in Table 1 demonstrate that except for 4, which is Ir(I) catalyst, all of the other 5s5p corrections $\Delta\Delta E^{\ddagger}_{5s5p}$ are negative, which means that they decrease the barriers. The absolute magnitude of $\Delta\Delta E^{\ddagger}_{5s5p}$ for 4 is also very small. The magnitude of $\Delta\Delta E^{\ddagger}_{5s5p}$, however, does not follow the same trend of dependence of the SOC effect on oxidation state as shown above. The largest value appears for 2, which is the least coordinatively saturated one. Both the significant magnitude and the negative sign of $\Delta\Delta E^{\ddagger}_{5s5p}$ for 2 are in line with previous theoretical results of outer-core (4s4p) correlation on oxidative addition of small alkanes (including CH_4) and H_2 to naked Pd(0).[36] In total, the $\Delta\Delta E^{\ddagger}_{SOC} + \Delta\Delta E^{\ddagger}_{5s5p}$ increases the C−H activation barrier for all cases except for 2, and the absolute magnitude decreases in the order

$1 > 3 > 2 > 4$. So the largest total effects are found in the Pt(II) system and amount to about 1 kcal/mol.

IV. CONCLUSIONS

Using high level ab initio approach, we have determined that in four realistic Pt and Ir containing catalysts that have closed shell singlet ground states, the SOC and outer-core correlation effects on the C−H activation reactions by these complexes amount to up to ~1 kcal/mol. The four systems we studied show interesting trends that: (1) SOC effect consistently increases the C−H activation barriers and is apparently larger in high oxidation state (Pt(II) and Ir(III)) than in low oxidation state (Pt(0) and Ir(I)); and (2) the outer-core (5s5p) correlation correction is larger in less coordinatively saturated complexes. These interesting findings pose intriguing open questions regarding the generality of the effects.

The outer-core correlation effect is sensitive to the basis set utilized, and the larger basis sets tend to increase the C−H activation barriers. These features indicate that SOC and/or outer-core correlations effects can be pertinent not only to open-shell or naked transition metal containing systems but also for ligated 5d transition metal systems. As such, systematic studies of both SOC and outer-core correlations effects in more such transition metal containing systems are certainly in order.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates, computational details, and seven tables of computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Schwarz, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4442−4454. (b) Schwarz, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 10096−10115.

(2) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395−403.

(3) (a) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412−4456. (b) Pyykkö, P. *Inorg. Chim. Acta* **2005**, *358*, 4113−4130. (c) Pyykkö, P. *Chem. Soc. Rev.* **2008**, *37*, 1967−1997. (d) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276−281. (e) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563−594.

(4) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271−276.

(5) Dedieu, A. *Chem. Rev.* **2000**, *100*, 543−600.

(6) Reiher, M.; Wolf, A. *Relativistic Quantum Chemistry, the Fundamental Theory of Molecular Science*; Wiley-VCH: Weinheim, 2009.

(7) (a) Neese, F.; Petrenko, T.; Ganyushin, D.; Olbrich, G. *Coord. Chem. Rev.* **2007**, *251*, 288−327. (b) Wang, X. Y.; Avendano, C.; Dunbar, K. R. *Chem. Soc. Rev.* **2011**, *40*, 3213−3238. (c) Baková, R.; Chergui, M.; Daniel, C.; Vlček, A., Jr.; Záliš, S. *Coord. Chem. Rev.* **2011**, *255*, 975−989. (d) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. *Coord. Chem. Rev.* **2011**, *255*, 2622−2652. (e) Schwarz, H. *Int. J. Mass Spectrom.* **2004**, *237*, 75−105. (f) Bühl, M.;

Kaupp, M.; Malkina, O. L.; Malkin, V. G. *J. Comput. Chem.* **1999**, *20*, 91−105. (g) Danovich, D.; Shaik, S. *J. Am. Chem. Soc.* **1997**, *119*, 1773−1786.

(8) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526. (b) Shilov, A. E.; Shil'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932. (c) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987−1007.

(9) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (b) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463. (c) Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 1400−1410.

(10) (a) Ben-Ari, E.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 15390−15391. (b) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588−602.

(11) (a) Heinemann, C.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *245*, 509−518. (b) Pavlov, M.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Wesendrup, R.; Heinemann, C.; Schwarz, H. *J. Phys. Chem. A* **1997**, *101*, 1567−1579. (c) Heinemann, C.; Schwarz, H.; Koch, W.; Dyall, K. G. *J. Chem. Phys.* **1996**, *104*, 4642−4651.

(12) (a) Rakowitz, F.; Casarrubios, M.; Seijo, L. *J. Chem. Phys.* **1998**, *108*, 7980−7987. (b) Rakowitz, F.; Marian, C. M.; Schimmelpfennig, B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2481−2488.

(13) Carroll, J. J.; Weisshaar, J. C.; Siegbahn, P. E. M.; Wittborn, C. A. M.; Blomberg, M. R. A. *J. Phys. Chem. A* **1995**, *99*, 14388−14396.

(14) Figgen, D.; Peterson, K. A.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2009**, *130*, 164108.

(15) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(16) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(17) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995−2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669−681.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloini, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Comperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

(19) (a) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219−5227. (b) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718−8733. (c) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(20) (a) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053−5063. (b) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1985**, *115*, 259−267. (c) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399−445.

(21) Celani, P.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 5546−5557.

(22) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO*, version 2010.1, a package of ab initio programs, see: http://www.molpro.net.

(23) Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. *Mol. Phys.* **2000**, *98*, 1823−1833.

(24) Ghigo, G.; Roos, B. O.; Malmqvist, P. Å. *Chem. Phys. Lett.* **2004**, *396*, 142−149.

(25) Roos, B. O.; Andersson, K. *Chem. Phys. Lett.* **1995**, *245*, 215−223.

(26) (a) Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1996**, *104*, 6286−6297. (b) Schütz, M.; Werner, H.-J. *Chem. Phys. Lett.* **2000**, *318*, 370−378. (c) Schütz, M.; Werner, H.-J. *J. Chem. Phys.* **2001**, *114*, 661−681. (d) Werner, H.-J.; Pflüger, K. *Annu. Rep. Comput. Chem.* **2006**, *2*, 53−80.

(27) (a) Schütz, M.; Manby, F. R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3349−3358. (b) Werner, H.-J.; Schütz, M. *J. Chem. Phys.* **2011**, *135*, 144116.

(28) (a) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175−3183. (b) Hill, J. G. *J. Chem. Phys.* **2011**, *135*, 044105.

(29) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45−48.

(30) Neese, F.; Valeev, E. F. *J. Chem. Theory Comput.* **2011**, *7*, 33−43.

(31) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639−9646.

(32) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334−338.

(33) (a) Ess, D. H.; Nielsen, R. J.; Goddard, W. A., III; Periana, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 11686−11688. (b) Ess, D. H.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2010**, *29*, 6459−6472.

(34) (a) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107. (b) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2006**, *125*, 074110. (c) Peterson, K. A.; Figgen, D.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2007**, *126*, 124101. (d) Figgen, D.; Peterson, K. A.; Stoll, H. *J. Chem. Phys.* **2008**, *128*, 034110. (e) Peterson, K. A.; Puzzarini, C. *Theor. Chem. Acc.* **2005**, *114*, 283−296.

(35) Kang, R. H.; Chen, H.; Shaik, S.; Yao, J. N. *J. Chem. Theory Comput.* **2011**, *7*, 4002−4011.

(36) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 709−716.