Organometallics **2005,** *24,* 6283−6286

Stability of Heavier Group 14 Analogues of Vinylidene Complexes: A Theoretical Study

Alireza Ariafard and Zhenyang Lin*

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

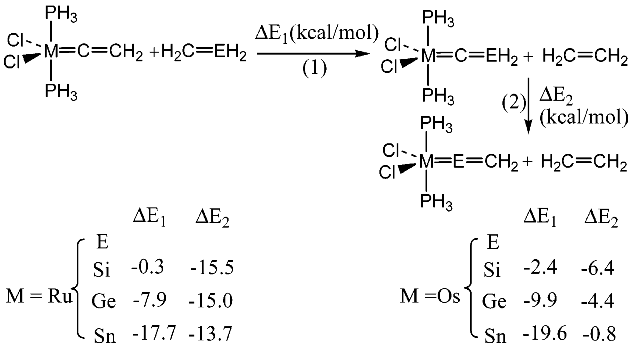
Received July 5, 2005

Summary: Density functional calculations were carried out to study the stability of the heavier group 14 analogues of vinylidene complexes $M(Cl)_2(=C=EH_2)(PH_3)_2$, $M(Cl)_2(=E=CH_2)(PH_3)_2$ (M = Ru, Os), $Cp_2M(=C=EH_2)(Cl)$, and $Cp_2M(=E=CH_2)(Cl)$ (M = Nb, Ta), where E = C, Si, Ge, Sn. The results of the calculations show that the d^6 osmium complexes $Os(Cl)_2(=C=EH_2)(PR_3)_2$ are the most promising targets for synthesis.

The concept of a double bond between a transition metal and the group 14 elements is interesting. In 1964, Fischer et al. isolated $(CO)_5W=C(Ph)(OMe)$.[1] Thereafter, Schrock synthesized a number of tantalum carbene complexes.[2] At the same time, Marks developed synthetic methods for preparing heavier homologous carbene complexes.[3] Up to now, a number of complexes with M=E (E = Si, Ge, Sn) double bonds have been synthesized and characterized.[4,5] In recent years, the nature of the chemical bonding in such complexes has also been the subject of several theoretical studies.[6]

The chemistry of compounds containing C=E (E = Si, Ge, Sn) double bonds has also been developed rapidly. Many compounds with C=Si, C=Ge, and C=Sn bonds have been characterized[7] and studied theoretically.[8] Recently, attempts have been made to synthesize group 14 allene analogues. However, such compounds are very limited. A few of them were prepared and identified by X-ray crystallography in the 1990s.[9] A recent theoretical study concluded that the compounds $R_2E=C=CR_2$ (1-metallaallenes) are more stable than $R_2C=E=CR_2$ (2-metallaallenes).[10]

Scheme 1



$$\mathrm{Cl_2M(PH_3)_2(=C=CH_2) + H_2C=EH_2 \xrightarrow[(1)]{\Delta E_1\,(kcal/mol)} Cl_2M(PH_3)_2(=C=EH_2) + H_2C=CH_2 \xrightarrow[(2)]{\Delta E_2\,(kcal/mol)} Cl_2M(PH_3)_2(=E=CH_2) + H_2C=CH_2}$$

M = Ru, E	ΔE1	ΔE2
Si	-0.3	-15.5
Ge	-7.9	-15.0
Sn	-17.7	-13.7

M =Os, E	ΔE1	ΔE2
Si	-2.4	-6.4
Ge	-9.9	-4.4
Sn	-19.6	-0.8

Transition-metal vinylidene complexes are similar to 1-metallallenes in which the main-group metal is replaced by a transition metal. Various types of vinylidene complexes have been synthesized.[11,12] However, complexes having M=C=E or M=E=C groups (E = heavier group 14 elements) have not yet been found. To study the stability of such transition-metal complexes, we carried out a theoretical study using the density functional theory method.[13] We hope to provide theoretical information to assist experimental efforts to synthesize heavier group 14 analogues of vinylidene complexes.

In the literature, many vinylidene complexes containing Os and Ru metals can be found.[11] Therefore, we first chose to study the stability of the model complexes $M(Cl)_2(=C=EH_2)(PH_3)_2$ and $M(Cl)_2(=E=CH_2)(PH_3)_2$ (M = Ru, Os; E = Si, Ge, Sn).

To investigate the stability of these unknown vinylidene analogues, we calculated reaction energies for reactions 1 and 2, shown in Scheme 1. Reaction 1 is an isodesmic reaction. Therefore, ΔE_1 is a good criterion for estimating the stability of the unknown $M(Cl)_2(=C=EH_2)(PH_3)_2$ complexes. ΔE_2 shows how stable the two isomers are relative to each other.

---

* To whom correspondence should be addressed. E-mail: chzlin@ust.hk.

(1) (a) Fischer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(2) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(3) Marks, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 7090.

(4) Lappert, M. S.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267.

(5) (a) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357. (b) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221.

(6) (a) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. (b) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775. (c) Lein, M.; Szabü, A.; Kovács, A.; Frenking, G. *Faraday Discuss.* **2003**, *124*, 365.

(7) (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (b) Escudie, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178*, 565. (c) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157. (d) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

(8) (a) Tsumuraya, T.; Batcheler, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *32*, 902. (b) Jacobson, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667. (c) Gordon, M. S.; Windus, T. L. *J. Am. Chem. Soc.* **1992**, *114*, 9559. (d) Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489.

(9) (a) Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598. (b) Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1999**, *18*, 540. (c) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *Chem. Lett.* **1998**, 811.

(10) Sigal, N.; Apeloig, Y. *Organometallics* **2002**, *21*, 5486.

(11) (a) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193-195*, 977. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Hill, A. F.; Hulkes, A. G.; White, A. J. P.; Williams, D. J. *Organometallics* **2000**, *19*, 371. (d) Coalter, J. N.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925. (e) Bustelo, E.; Carbo, J. J.; Lledos, A.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2003**, *125*, 3311.

(12) (a) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1988**, *7*, 1046. (b) Baker, P. K.; Baker, G. K.; Gree, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1321. (c) Mike, J.; Sunkel, K.; Beck, W. *J. Organomet. Chem.* **1997**, *543*, 39.

(13) See the Supporting Information for computational details.

10.1021/om050557t CCC: $30.25

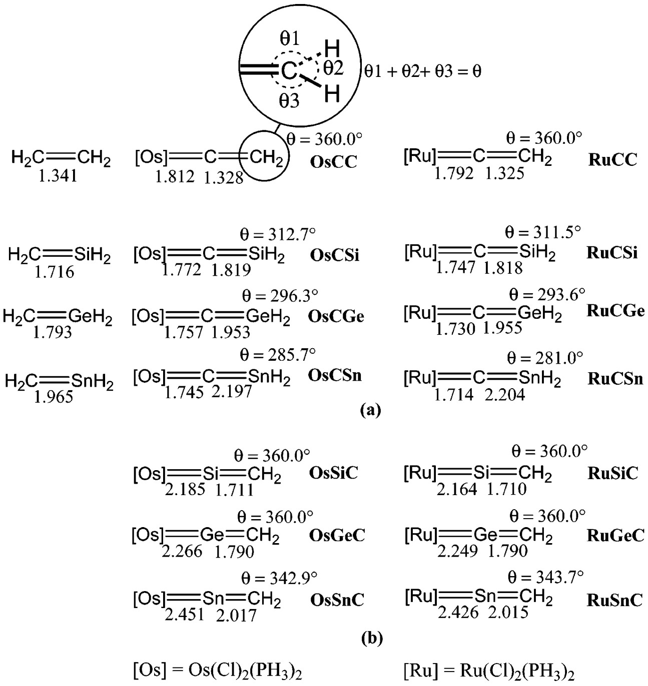
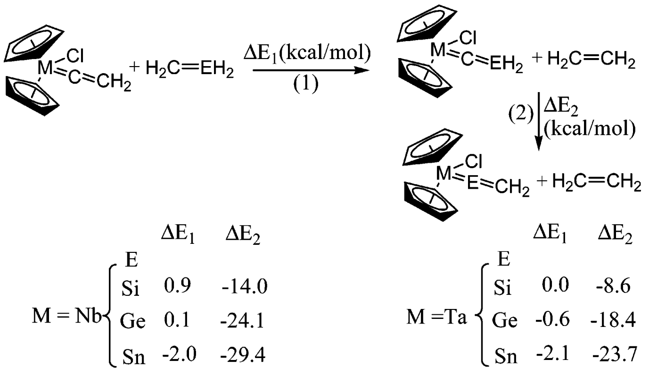


Figure 1. Selected calculated structural parameters (distances in Å and angles in deg) for the complexes $M(Cl)_2(=C=EH_2)(PH_3)_2$ and $M(Cl)_2(=E=CH_2)(PH_3)_2$ (M = Ru, Os).

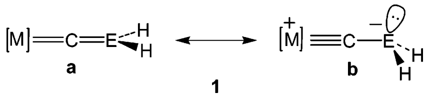
The results are shown in Scheme 1. The ΔE_1 values are negative and are even more negative on going from E = Si to E = Sn. The negative values suggest that $M(Cl)_2(=C=EH_2)(PH_3)_2$ can be reasonably stable. The trend observed in the ΔE_1 values from E = Si to E = Sn indicates that the stability of $M(Cl)_2(=C=EH_2)(PH_3)_2$ increases significantly as E becomes heavier. The ΔE_1 values presented here, which measure the stability of $L_nM=C=EH_2$, are significantly more negative than the ΔE_1 values reported in the literature, which measure the stability of $H_2C=C=EH_2$[10] (1.1, 1.4, and −3.3 kcal/mol for E = Si, Ge, Sn, respectively). These results are very encouraging, because they suggest that we have a greater chance to synthesize heavier group 14 analogues of vinylidene complexes versus $H_2C=C=EH_2$.

To understand what factors influence the trend observed in ΔE_1, we examined the structures of the complexes. Figure 1a shows the important structural parameters calculated for $M(Cl)_2(=C=EH_2)(PH_3)_2$. The $M=CEH_2$ bond distances decrease gradually while the C=E bond distances increase along the C → Sn series. In comparison with the C=E distances in $H_2C=EH_2$, the C=E distances in the $M(Cl)_2(=C=EH_2)(PH_3)_2$ complexes are also longer. These results indicate that the heavier group 14 elements in the complexes enhance the bonding interactions between the metal fragment $M(Cl)_2(PH_3)_2$ and the ligand $C=EH_2$ and weaken the C=E bonding interaction. The M=C bond distances in the complexes having a heavier E atom are quite short, in view of the M≡C triple-bond distances calculated for $[M(Cl)_2(\equiv CH)(PH_3)_2]^+$ (1.716 Å for M = Os and 1.688 Å for M = Ru). One structural feature that appears to be important is the degree of pyramidalization at E, measured by the sum of the bond angles around E (θ in Figure 1). The calculations indicate that no matter what the metal center is, Os or Ru, the degree of pyramidalization at E increases down the group 14. $H_2C=EH_2$ and $C=EH_2$ were calculated to be planar in their ground states. Thus, the presence of the d^6 metal fragment $M(Cl)_2(PH_3)_2$ (M = Os, Ru) should play a crucial role in the pyramidalization at E.

Scheme 2



To account for the short M=C distances and the pyramidalization at E of the $M(Cl)_2(=C=EH_2)(PH_3)_2$ complexes, we feel it necessary to invoke the concept of a resonance hybrid between Lewis structures **a** and **b** shown in **1**. Invoking the resonance hybrid, we can easily understand the increasing pyramidalization for $M(Cl)_2(=C=EH_2)(PH_3)_2$ as one goes down the group of E. As one goes down the group of E, the valence s orbital becomes progressively more contracted relative to the valence p orbitals and the C=E π bonding is disfavored.[14] As a result, the contribution of Lewis structure **b** becomes more and more significant. With greater and greater participation of the Lewis structure **b**, it is expected that the bonding interaction between the metal fragment and $:C=EH_2$ will increase. Therefore, we see the increasing negative values of ΔE_1 reported in Scheme 1.



1

The Lewis structure **b** has one more pair of electrons in comparison with the Lewis structure **a**. Therefore, we expect that the electron configuration of the metal center in the metal fragment for a given $L_nM=C=EH_2$ complex is very important in addition to the large s−p difference in their orbital contractedness of the heavier E and the poor C=E π bonding, which are the driving force in localizing a pair of electrons having large s character on E, shown in Lewis structure **b**.

For complexes with a metal center that does not have an extra pair of electrons, the results should be very different, because the Lewis structure **b** is impossible. To investigate if this is the case, we calculated $Cp_2M(=C=EH_2)(Cl)$ (M = Nb, Ta; E = Si, Ge, Sn). The energetic results are given in Scheme 2. From Scheme 2, the ΔE_1 values are close to zero and their variations are negligible on going from E = Si to E = Sn. From the calculated structural parameters in Figure 2a, we can see that there is no pyramidalization at E of $Cp_2M(=C=EH_2)(Cl)$ (M = Nb, Ta) when E = C, Si, Ge and the pyramidalization for E = Sn is quite small. The M=C bond distances for the complexes having heavier

---

[14] Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

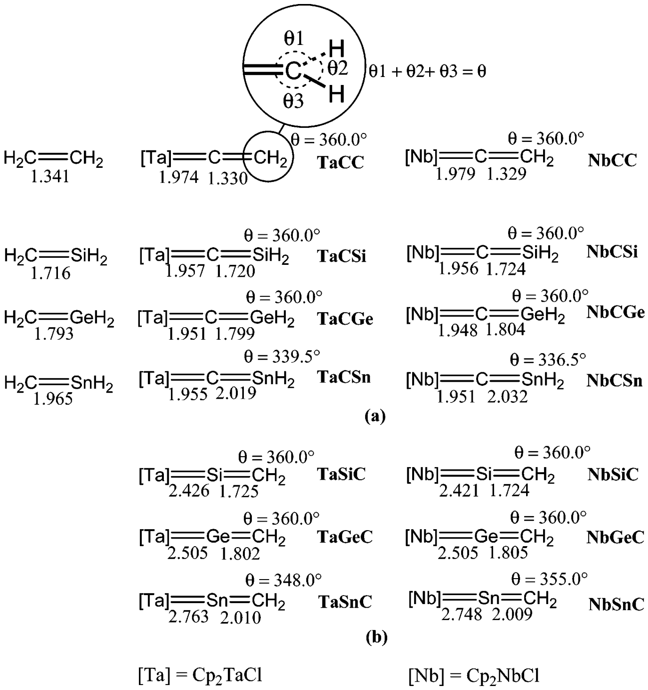


Figure 2. Selected calculated structural parameters (distances in Å and angles in deg) for the complexes $Cp_2M(=C=EH_2)(Cl)$ and $Cp_2M(=E=CH_2)(Cl)$ (M = Nb, Ta).

group 14 elements are only slightly shorter than the M═C bond distance for the vinylidene complex $Cp_2M=C=CH_2(Cl)$. Also, in comparison with those in $H_2C=EH_2$, the C═E distances in the $Cp_2M=C=EH_2(Cl)$ complexes are almost unchanged. These results indicate that Lewis structure **b** is absent in these complexes.

While the resonance hybrid is extremely helpful, a molecular orbital argument can be also used to explain the different stability behaviors of the two classes of $[M]=C=EH_2$ complexes. Vinylidene ligands are strong single-face π acceptors with the accepting orbital lying in the ligand plane. The C═E π bond, which is perpendicular to the ligand plane, acts as a π donor. For the $[M]=C=EH_2$ complexes of osmium and ruthenium, the C═E π bonding electrons are engaged in a four-electron repulsion with the metal electrons occupying a symmetry-adapted d orbital, giving rise to an antibonding combination as the highest occupied molecular orbital (HOMO) (see **2**). When one goes down the group of E, the four-electron repulsive interaction becomes severe, because the more electron positive E makes the C═E π bond a stronger donor. To minimize the four-electron repulsive interaction, a second-order Jahn–Teller distortion, i.e., pyramidalization at E, occurs, leading to localization of a lone pair of electrons on E (see the Lewis structure **b** in **1**). For the $[M]=C=EH_2$ complexes of tantalum and niobium, the antibonding combination shown in **2** is not occupied and, therefore, pyramidalization at E is not necessary.

2

Table 1. Gross Orbital Populations of the d_{xz}, d_{yz}, and d_{xy} Orbitals on the Metal Center in the Complexes $MCl_2(=C=EH_2)(PH_3)_2$ (M = Ru, Os)[a]

	d_{xz}		d_{yz}		d_{xy}	
complex	planar geom at E[b]	pyramidal geom at E[c]	planar geom at E[b]	pyramidal geom at E[c]	planar geom at E[b]	pyramidal geom at E[c]
OsCSi	1.767	1.665	1.350	1.390	1.931	1.936
OsCGe	1.758	1.620	1.359	1.405	1.931	1.936
OsCSn	1.737	1.588	1.364	1.415	1.932	1.938
RuCSi	1.815	1.712	1.415	1.458	1.962	1.960
RuCGe	1.803	1.688	1.428	1.475	1.958	1.961
RuCSn	1.785	1.631	1.432	1.482	1.958	1.962

[a] The Cartesian coordinate system is shown in **2**. [b] Geometry optimized with constraint. [c] Geometry optimized without constraint.

Table 2. Gross Orbital Populations of the d_{xz}, d_{yz}, and d_{xy} Orbitals on the Metal Center in the Complexes $Cp_2M(=C=EH_2)(Cl)$ (M = Nb, Ta)[a]

complex	d_{xz}	d_{yz}	d_{xy}
TaCSi	0.681	0.965	0.655
TaCGe	0.687	0.977	0.654
TaCSn	0.695	0.996	0.653
NbCSi	0.755	1.047	0.722
NbCGe	0.763	1.061	0.719
NbCSn	0.767	1.079	0.715

[a] The Cartesian coordinate system is shown in **2**.

Natural bond orbital (NBO) analyses[13] provide quantitative support to the resonance argument. Table 1 lists the gross orbital populations of the two d_π orbitals and one d_δ metal orbital for the $M(Cl)_2(=C=EH_2)(PH_3)_2$ (M = Ru, Os) complexes having a planar geometry at E, which were obtained with constraint geometry optimizations, and having a pyramidal geometry at E, which were obtained with full geometry optimizations. Here, the π and δ types are defined by viewing the orbitals along the M═C═E axis. When the Cartesian coordinate system shown in **2** is used, d_{xz} and d_{yz} are the d_π orbitals and d_{xy} is the d_δ orbital. For the Ru and Os complexes, the changes in the gross orbital populations of d_{xz} decrease significantly (Table 1) from the planar geometry to the pyramidal geometry. The changes in the populations of d_{xy} are very small while the changes in the populations of d_{yz} are not significant. As mentioned above, metal d electrons occupying the d_{xz} orbital are engaged in a repulsion with the C═E π bonding electrons. The significant decrease in the d_{xz} orbital populations from the planar geometry to the pyramidal geometry suggests that pyramidalization at E promotes transfer of electrons from the metal d_{xz} orbital to the C═E unit, giving rise to the importance of the Lewis structure **b**. From Table 1, we can see that the decrease in the population of d_{xz} for the **OsCSn** complex is the most significant. For the Nb and Ta complexes in which pyramidalization at E does not occur, the orbital populations of the three d orbitals do not differ much among the three complexes (Table 2).

We also examined the changes in the partial charges of the EH_2 groups from the planar geometry to the pyramidal geometry. We found that the partial charges of the EH_2 groups decrease significantly, indicating that the EH_2 groups gain electrons upon pyramidalization. The SiH_2 groups in the **RuCSi** and **OsCSi** complexes gain 0.18e and 0.19e, respectively. The GeH_2 groups in both the **RuCGe** and **OsCGe** complexes gain 0.25e. The SnH_2 groups in the **RuCSn** and **OsCSn** complexes gain 0.29e and 0.30e, respectively. These results further support the resonance argument that the pyramidalization causes localization of the electron pair at E.

Localization of the electron pair at E becomes more significant when E becomes heavier, consistent with the inert pair effect observed for compounds of group 13 and 14 elements.[15]

From the theoretically predicted reaction energies in Schemes 1 and 2, we see that for the two classes of complexes the ΔE_2 values are always negative. The results imply that complexes having the M=E=CH$_2$ structural moiety are calculated to be more stable when compared with those having the M=C=EH$_2$ moiety. The higher stability of the [M]=E=CH$_2$ complexes versus the [M]=C=EH$_2$ complexes is a result of greater bond strengths of M=E + 2C−H versus M=C + 2E−H. The M=C bond is stronger than the M=E bond. Therefore, the much stronger C−H bonds as compared with the E−H bonds are responsible for the higher stability of the L$_n$M=E=CH$_2$ versus L$_n$M=C=EH$_2$ complexes.

The ΔE_2 values for the Os and Ru complexes become less negative on going from Si to Sn. In contrast, the ΔE_2 values for the Ta and Nb complexes with heavier E atoms are more negative. The different trends found in the two classes of complexes are the results of different relative stabilities of [M]=C=EH$_2$ versus [M]=E=CH$_2$ with the heavier E atoms. For the complexes of group 8, the stability of [M]=C=EH$_2$ increases (ΔE_1 values) when one goes down the group of E due to the extra stabilization energy gained from the contribution of the Lewis structure **b**. For the complexes of group 5, the stability of [M]=C=EH$_2$ does not change significantly (ΔE_1 values) when one goes down the group of E. The ΔE_2 values for the second-row transition-metal complexes are generally more negative than those for their third-row transition-metal analogues. The same holds true for the $\Delta E_1 + \Delta E_2$ values. The less diffuse d orbitals of the second row transition metals give relatively weaker M=C bonds, and therefore, the difference between the stabilities of the [M]=C=EH$_2$ and [M]=E=CH$_2$ complexes is significant. On the basis of the $\Delta E_1 + \Delta E_2$ values in Schemes 1 and 2, we see that formation of the complexes having an M=E=CH$_2$ moiety is much more favorable for second-row transition metals than for third-row transition metals.

One of the reviewers was concerned that complexes other than the metallocene complexes studied may not give results supporting the resonance argument. Therefore, different model complexes having the metal fragments M(Cl)$_2$ (M = Zr, Hf) were suggested by the reviewer. We optimized the structures, shown in Figure 3, for M(Cl)$_2$(=C=SnH$_2$) and M(Cl)$_2$(=C=SnH$_2$)(PH$_3$)$_2$ (M = Zr, Hf). As expected, no pyramidalization at E can be seen for any of the four structures. These additional calculations further support that the electronic structure of the metal center, instead of the ligand environment, determines whether the Lewis structure **b**, shown in **1**, is involved.

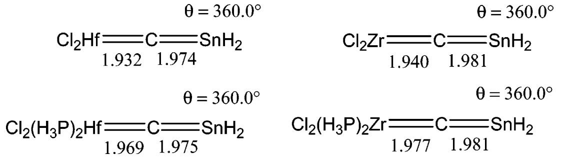


Figure 3. Selected calculated structural parameters (distances in Å and angles in deg) for the complexes M(Cl)$_2$(=C=SnH$_2$) and M(Cl)$_2$(=C=EH$_2$)(PH$_3$)$_2$ (M = Zr, Hf). See Figure 1 or 2 for the definition of θ.

In summary, the heavier group 14 analogues of vinylidene complexes containing M=E=CH$_2$ are relatively stable, regardless of the type of metal center. For analogues containing M=C=EH$_2$, the d^6 osmium complexes, Os(Cl)$_2$(=C=EH$_2$)(PR$_3$)$_2$, are the most promising targets for synthesis. For these osmium complexes, the ΔE_1 values, which measure the overall stability of the targeted complexes, are negative and the ΔE_2 values, which measure their stability relative to the more stable isomers Os(Cl)$_2$(=E=CH$_2$)(PR$_3$)$_2$, are relatively small. It should be pointed out that the real challenge, which cannot be theoretically dealt with, is to design a proper synthetic route to obtain these interesting species.

Acknowledgment. We acknowledge financial support from the Hong Kong Research Grants Council (Grant Nos. HKUST 6023/04P and DAG03/04.SC15) and the University Grants Committee of Hong Kong through the Area of Excellence Scheme (Grant No. Aoe/P-10/01).

Supporting Information Available: Tables giving Cartesian coordinates for all the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050557T

---

[15] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 878.