Organometallics **1996,** *15,* 1218−1222

$[ML_n(SiR_3)(\eta^2\text{-}H{-}H)]$ or $[ML_n(H)(\eta^2\text{-}H{-}SiR_3)]$? An ab Initio MO Study on $[OsCl(CO)(PR_3)_2\text{“}H_2SiR_3\text{”}]$ Complexes

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Received August 7, 1995[⊗]

Ab initio MO calculations at the MP2 and MP4 levels on the $[OsCl(CO)(PH_3)_2\text{“}H_2SiH_3\text{”}]$ model system predict the possible existence of two different stable species, one of $[OsCl(CO)(PH_3)_2(SiH_3)(\eta^2\text{-}H{-}H)]$ nature and another of $[OsCl(CO)(PH_3)_2(H)(\eta^2\text{-}H{-}SiH_3)]$ nature, very close in energy. From data on this particular system, the importance of different energy contributions for the relative stability of $[ML_n(SiR_3)(\eta^2\text{-}H{-}H)]$ and $[ML_n(H)(\eta^2\text{-}H{-}SiR_3)]$ complexes is analyzed.

Introduction

There is an ever growing number of examples of nondestructive σ bond coordination to transition metals in the chemical literature.[1−6] Dihydrogen H−H complexes[2] are no longer a novelty, and their formal relationship with the intramolecular agostic C−H species[4] is nowadays well established. Bonding in σ complexes is well characterized, and a clear picture of donation from the σ_{H_2} orbital and back-donation to the $\sigma^*_{H_2}$ orbital has emerged from theoretical calculations[7] on dihydrogen H−H complexes, probably the best characterized[3] among all these species. However, intermolecular C−H complexes, of obvious catalytic and synthetic interest, keep being relatively elusive, in contrast with the ready availability of H−H and, especially, Si−H coordination.[5,6]

Comparison between the coordination features of different σ bonds (H−H, C−H, Si−H) to transition metals seems therefore a promising field for an improved understanding of bonding in these molecules. In this sense, recent developments on coordination of different types of σ bonds to the same $[Mo(CO)(R_2PC_2H_4PR_2)_2]$ fragments look exciting.[8] A complementary approach to this kind of comparison is the study of systems where more than one different σ complex is possible. The present paper is concerned with the study of one of such systems, in particular $[OsCl(CO)(PR_3)_2\text{“}H_2SiR_3\text{”}]$ complexes, where “H_2SiR_3” stands for $(SiR_3)(\eta^2\text{-}H{-}H)$ or $(H)(\eta^2\text{-}H{-}SiR_3)$.

Complex $[Os(SiEt_3)Cl(CO)(P^iPr_3)_2(H_2)]$ has been characterized as a dihydrogen complex from relaxation time T_1 measurements,[9] favoring therefore a $[ML_n(SiR_3)(\eta^2\text{-}H{-}H)]$ formulation. On the other hand, Luo and Crabtree[10] reported a $[ML_n(H)(\eta^2\text{-}H{-}SiR_3)]$ structure for the $[IrH_2(\eta^2\text{-}H{-}SiEt_3)_2(PPh_3)_2]^+$ complex. Although the two complexes are intrinsically different in metal and ligands, such a different behavior was not in principle to be expected. This paper tries to shed some light on the topic through theoretical ab initio MO calculations on the $[OsCl(CO)(PH_3)_2\text{“}H_2SiH_3\text{”}]$ system. The present theoretical calculations constitute, to our knowledge, the first ab initio attempt to the characterization of η^2-Si−H complexes. EHMO studies on η^2-Si−H complexes[11] and ab initio studies on Si−H activation by transition metal complexes[12,13] had been published before by other authors.

Computational Details

All calculations were performed with the Gaussian/92 program.[14] A molecular orbital ab initio method with introduction of correlation energy through the Møller−Plesset (MP) perturbational approach,[15] excluding excitations concerning the lowest energy electrons (frozen core approach) was applied. Effective core potentials (ECP) were used to represent the 60 innermost electrons (up to the 4d shell) of the osmium atom,[16]

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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as well as the 10-electron core of the phosphorus and chlorine atoms.[17] For these atoms, the basis set was that associated with the pseudopotential,[16,17] with a standard LANL2DZ contraction.[14] A 6-31G basis set was used for carbon, oxygen, and the hydrogen atoms of the PH$_3$ and SiH$_3$ groups,[18] while a more accurate 6-31G** description was used for silicon and for the hydrogen atoms directly attached to the metal.[18,19]

Geometry optimizations were carried out at the second level of the Møller–Plesset theory (MP2). All geometrical parameters were optimized except the dihedral angle of one of the hydrogen atoms of each phosphine ligand, which was fixed to be oriented toward the chlorine atom, in order to avoid chemically meaningless rotations around the M–P axis. Single-point energy-only calculation were made at a higher computational level with the MP2-optimized geometries. This was the fourth level of the same perturbational theory (MP4), with consideration of single, double, triple, and quadruple excitations.

Theoretical Characterization of Possible Isomeric Forms

Published NMR experimental data provide conclusive evidence on the nature of the [Os(SiEt$_3$)Cl(CO)(P^{i}Pr$_3$)$_2$(H$_2$)] species as a dihydrogen complex[9] but do not give information on the particular stereochemistry around the metal center. Ab initio MO calculations are used in this section to characterize the most stable isomer, as well as eventual competitive species. We restricted ourselves in principle to 6-coordinate octahedral d^6 [OsCl(CO)(PH$_3$)$_2$(SiH$_3$)(η^2-H–H)] and [OsCl(CO)(PH$_3$)$_2$H(η^2-H–SiH$_3$)] species. 7-coordinate [OsCl(CO)(PH$_3$)$_2$(SiH$_3$)] isomers, also possible in this kind of system, would show up in the course of geometry optimization should they be more stable. Complexes with a cis disposition of the phosphine ligands were not considered due to the bulk of the experimental P^{i}Pr$_3$ ligand, but there are still a number of available species.

The dihydrogen complexes that have been considered are shown in Chart 1. There are in the first place the three arrangements associated with the disposition of the ligands around the metal. They are **1**–**3**, with the dihydrogen being trans to the carbonyl, silyl, and chloride ligands, respectively. Furthermore, each of these three dispositions gives rise to two different isomers, **a** and **b**, depending on the orientation of the dihydrogen molecule, perpendicular or parallel to the P–Os–P direction. Geometry optimizations from these species cover all the possible dihydrogen complexes, and the dihydride species derived from them, for this system. Since no symmetry restrictions are imposed, a staggered disposition of the dihydrogen ligand[20] would also be accessible should it be a minimum instead of the eclipsed conformation used as starting geometry. In the case of the η^2-H–SiR$_3$ species, there are also three possible arrangements, **4**–**6**, with the H–SiR$_3$ ligand trans to carbonyl, silyl, or chloride, respectively. But in this case the number of possible isomers associated with each arrangement increases to 3, due to the asymmetry of the η^2 ligand. These three isomers, **a**–**c**, are presented in Chart 2 for the case of the arrangement **4**.

Chart 1

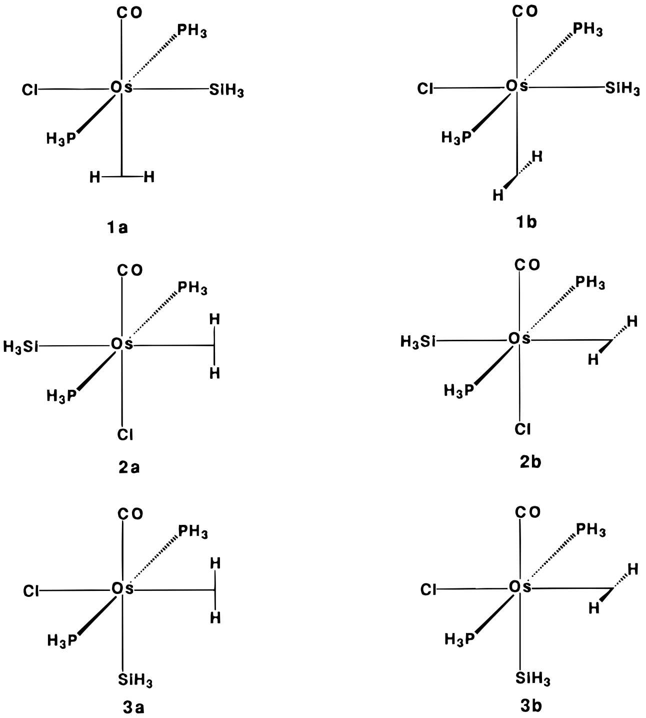
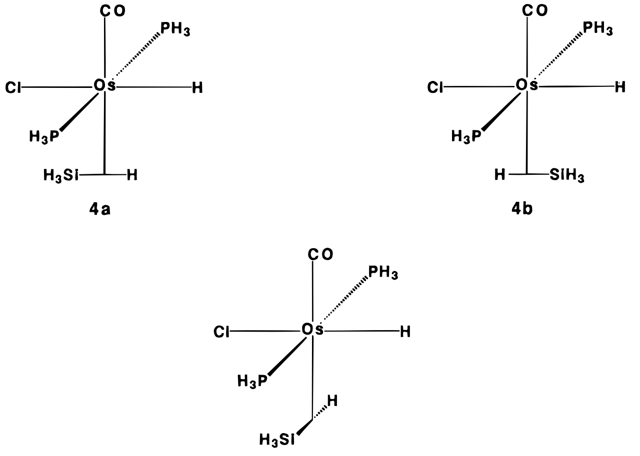


Chart 2



MP2 geometry optimizations are performed starting out from each of the 15 species just proposed. These geometry optimizations give rise to only seven different stationary points, labeled from **7** to **13**, presented in Figures 1 and 2. Figure 1 shows the three species obtained having an η^2 ligand. **7** and **8** are η^2-H–H species, corresponding respectively to **1a** and **2b** (Chart 1). They are clearly dihydrogen complexes, with H(7)–H(8) distances of 0.809 and 0.821 Å, respectively. **9** is the only η^2-H–SiH$_3$ complex that has been found to be stable, corresponding to **5c**. The H(7)–Si(8) distance is 1.737 Å, well within the range of what is considered to be acceptable η^2-H–SiR$_3$ species.[6] Figure 2 presents the four 7-coordinate [OsCl(CO)(PH$_3$)$_2$H$_2$(SiH$_3$)] complexes that are obtained from all the geometry optimizations: **10**–**13**. They were obtained from **3b**, **4a**, **4b**, and **6b**, respectively. The 7-coordinate nature of these species is apparent from the optimized values of the

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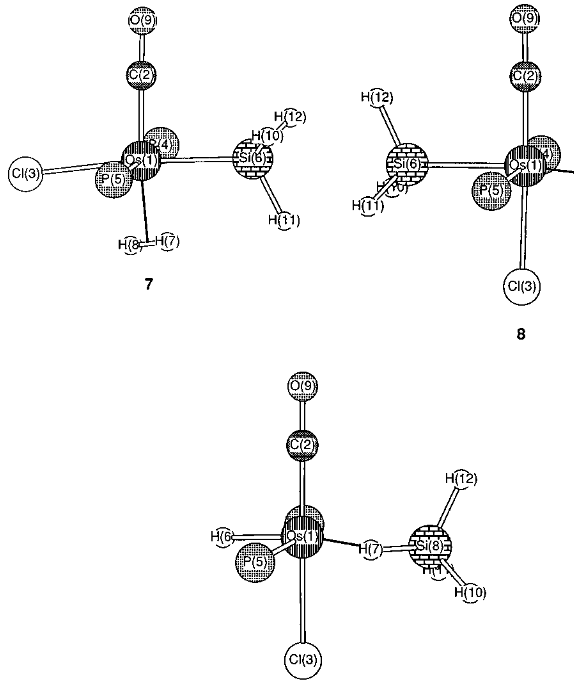
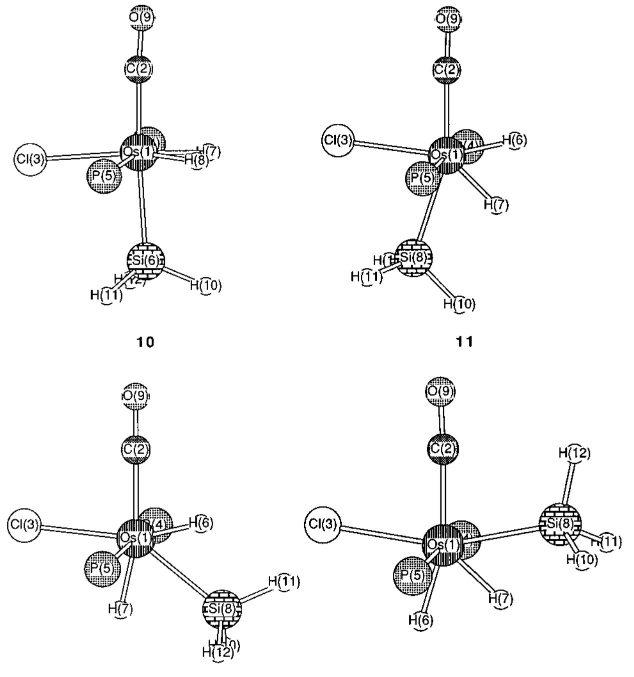


7 **8** **9**

Figure 1. MP2-optimized geometries of [OsCl(CO)-$(PH_3)_2$“H_2SiH_3”] complexes **7**−**9** containing a coordinated σ bond to the metallic center. Hydrogen atoms of the phosphine ligands are omitted for clarity. σ bond coordination is graphically represented by a solid line connecting the center of the bond to the metal atom.



10 **11** **12** **13**

Figure 2. MP2-optimized geometries of [OsCl(CO)$(PH_3)_2H_2$-(SiH_3)] complexes **10**−**13**. Hydrogen atoms of the phosphine ligands are omitted for clarity.

distances that should correspond to coordinate σ bonds. These values are 1.296 Å for H(7)−H(8) in **10**, 1.577 Å for H(6)−H(7) and 2.309 Å for H(7)−Si(8) in **11**, 2.075 Å for H(6)−Si(8) and 2.264 Å for H(7)−Si(8) in **12**, and 1.736 Å for H(6)−H(7) and 2.015 Å for H(7)−Si(8) in **13**. As for the rest of their geometrical features, the four species **10**−**13** have a pentagonal bipyramidal structure, not rare in 7-coordinate species.[21] The axial positions are occupied by the carbonyl and silyl ligands in **10**, being occupied by the two phosphine ligands in **11**−**13**.

Table 1. MP2 and MP4 Relative Energies (kcal/mol) of the MP2-Optimized Structures of the Different [OsCl(CO)$(PH_3)_2$“H_2SiH_3”] Complexes

	7	8	9	10	11	12	13
MP2	+7.8	0.0	−0.4	+8.7	+8.4	+4.9	+5.1
MP4	+9.2	0.0	+0.4	+10.6	+12.6	+8.4	+9.1

Table 2. Selected Geometrical Parameters (Å and deg) for the [OsCl(CO)$(PH_3)_2(SiH_3)(\eta^2$-H−H)] Complex 8 Optimized at the MP2 Level[a]

Os(1)−X	1.809	Os(1)−Si(6)	2.457
H(7)−H(8)	0.821	Os(1)−C(2)	1.857
Os(1)−H(7)	1.855	Os(1)−Cl(3)	2.517
Os(1)−P(4)	2.422	Si(6)−H(10)	1.496
C(2)−Os(1)−X	95.4	C(2)−Os(1)−Cl(3)	178.5
C(2)−Os(1)−P(4)	93.7	H(7)−Os(1)−H(8)	25.6
C(2)−Os(1)−Si(6)	91.3	Os(1)−Si(6)−H(10)	112.9

[a] X corresponds to a dummy atom in the midpoint of the H(7)−H(8) bond.

The relative energies of the MP2-optimized geometries at the MP2 and MP4 computational levels are presented in Table 1. Although all the species have quite low energies, being therefore likely actors in the chemistry of the system, two of them are way ahead of the others as candidates to be the absolute minimum. These are complexes **8** and **9**. The difference of 0.4 kcal/mol between them is too small for the precision of the method to give a clear answer on which is the most stable. At any rate, we notice that the most stable isomer at the best computational level MP4 is **8**, a dihydrogen complex. This is in agreement with experimental NMR results for the [Os$(SiEt_3)$Cl(CO)$(P^iPr_3)_2$-(H_2)] complex.[9]

Theoretical Analysis of the Most Stable Isomeric Forms

Species **8** and **9**, which have been found to be the most stable isomeric forms, are precisely an η^2-H−H complex (**8**) and an η^2-Si−H complex (**9**). They constitute therefore examples of the two different classes of species that can be in principle considered as possible for complexes of this stoichiometry. Their structures and the relationship between them are analyzed in some deeper detail in this section.

The coordination in both complexes is clearly octahedral. The general shape shown in Figure 1 is quite clear, and the L−M−L angles shown in Tables 2 and 3 confirm this impression, their values being close to the ideal values of 90 and 180°. As for the bond lengths, apart from the short H−H (complex **8**) and Si−H (complex **9**) distances commented above, other values can also be mentioned. For instance, the Os(1)−H(7) distance in complex **8** (1.855 Å) is much larger than a typical osmium−hydride bond, like that of Os(1)−H(7) in complex **9** (1.694 Å). A similar reasoning can be applied to the Os−Si distances (2.457 Å in **8**, 2.600 Å in **9**). A last piece of data reinforcing the assignment of an η^2 character to the silane coordination in **9** is the

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Table 3. Selected Geometrical Parameters (Å and deg) for the [$OsCl(CO)(PH_3)_2H(\eta^2$-$H{-}SiH_3)$] Complex 9 Optimized at the MP2 Level[a]

Os(1)−X	2.015	Os(1)−P(5)	2.426
H(7)−Si(8)	1.737	Os(1)−H(6)	1.644
Os(1)−H(7)	1.694	Os(1)−C(2)	1.858
Os(1)−Si(8)	2.600	Os(1)−Cl(3)	2.522
Os(1)−P(4)	2.414	Si(8)−H(10)	1.487
C(2)−Os(1)−X	95.0	C(2)−Os(1)−Cl(3)	179.5
C(2)−Os(1)−P(4)	93.3	H(7)−Os(1)−Si(8)	41.3
C(2)−Os(1)−P(5)	94.0	Os(1)−Si(8)−H(10)	86.9
C(2)−Os(1)−H(6)	92.6		

[a] X corresponds to a dummy atom in the midpoint of the H(7)−Si(8) bond.

Os(1)−Si(8)−H(10) angle of 86.9°, far from the expected tetrahedral value for an η^1-silyl ligand.

Another topic of interest that can be addressed in a quite simple way from a theoretical point of view is the energetics. We have computed bond energies for the dissociation of the η^2 ligand in both complexes **8** (eq 1)

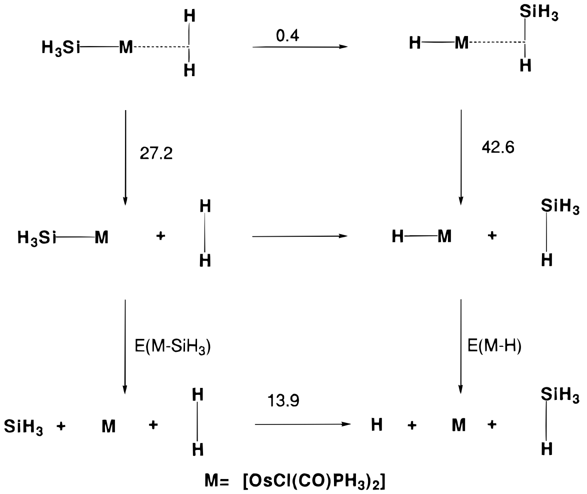
$$[OsCl(CO)(PH_3)_2(SiH_3)(\eta^2\text{-}H{-}H)] \rightarrow [OsCl(CO)(PH_3)_2(SiH_3)] + H_2 \quad (1)$$

$$[OsCl(CO)(PH_3)_2(H)(\eta^2\text{-}H{-}SiH_3)] \rightarrow [OsCl(CO)(PH_3)_2(H)] + SiH_4 \quad (2)$$

and **9** (eq 2). Using optimized MP2 geometries for **8**, **9**, H_2, and SiH_4, and geometries frozen at the corresponding ML_6 geometry for the ML_5 fragments, we obtained MP4 bonding energies of 27.2 kcal/mol for **8** and 42.6 kcal/mol for **9**. Absolute values for binding of the dihydrogen ligand are somehow larger than previously reported theoretical values of 19.8 [22] and 12.0 kcal/mol,[23] but discrepancies can be easily attributed to differences in the nature of the complex[22] or to the poor quality of the RHF computational method applied before.[23] The binding value for $H{-}SiH_3$ is certainly quite high and would even make it competitive with other more traditional ligands. Caution is adviced however in the extrapolation of the numbers obtained for this particular complex to different cases.

In any case, the main result we extract from these energy calculations is that binding of the η^2-Si−H ligand to the [$OsCl(CO)(PH_3)_2(H)$] fragment is 15.4 kcal/mol stronger than that of the η^2-H−H ligand to the [$OsCl(CO)(PH_3)_2(SiH_3)$] fragment. Putting this value together with the experimental fact that the H−H bond is 13.9 kcal/mol stronger than the $H{-}SiH_3$ bond,[24] and with the relative stabilities we have computed for **8** and **9** (see above), it is possible to compare the strength of the metal−silyl and metal−hydride bonds in both complexes. Certainly, through a trivial thermodynamical cycle (Scheme 1), we get a difference between the $L_nM{-}SiH_3$ bond in **8** and the $L_nM{-}H$ bond in **9** of 1.9 kcal/mol in favor of the metal−silyl bond. This slightly superior strength of the metal−silyl bond is in agreement with previous theoretical calculations for other transition metal complexes.[12,13]

Scheme 1



From the energetics for this particular species we can attempt a general discussion on the relative stability of [$ML_n(SiR_3)(\eta^2$-$H{-}H)$] and [$ML_n(H)(\eta^2$-$H{-}SiR_3)$] complexes. In a simplified analysis, the difference between the two coordination modes can be reduced to the difference in strength of three bonds. These are as follows: (i) the η^2 binding of the X−H (X = SiH_3, H) ligand to the metal fragment; (ii) the X−H bond in the isolated X−H fragment; (iii) the Os−X bond. The calculations presented here allow a quantification of these three terms. We find that term i, the η^2 coordination, favors strongly the η^2-$H{-}SiR_3$ complex, term ii, X−H bond strength, favors strongly the η^2-H−H complex, and term iii, Os−X bond strength, favors slightly the η^2-H−H complex. In other words, there are two large, nearly compensating, contradictory contributions, with a third minor term, nevertheless able to decide the coordination mode in certain conditions. This simple analysis, despite neglecting possible significant contributions (differential trans effects, changes in the electron density at the metal center, etc.), has the virtue of showing how subtle can be the balance between the two different coordination modes. Therefore, they must exist in the appropriate transition metal species, as certainly happens.[9,10] Further proof of the near degeneracy of the two isomeric forms is provided by recent experimental results on the [$OsCl(CO)(P^iPr_3)_2$“H_2SiPh_3”] complex that indeed suggest the existence of a stable η^2-$H{-}SiPh_3$ species.[25]

One may wonder if it would not be possible to isolate the two isomeric forms for a certain complex under proper experimental conditions. Although this would be compatible with the calculations presented here, and it can even be suggested from them, it is not a necessary conclusion. Certainly, we have only considered structural aspects, the determination of the most stable species (local minima in the potential hypersurface), and have not studied the reactivity aspects, the chemical paths connecting the stable species (transition states in the potential hypersurface). Such a reactivity study, which is beyond the scope of this work, would be the only theoretical method to study the eventual interconversion between the different isomeric forms.

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Conclusions

The theoretical study of [OsCl(CO)$(PH_3)_2$"H_2SiH_3"] complexes predicts the existence of two stable octahedral 6-coordinate species of very close energy: a dihydrogen complex [OsCl(CO)$(PH_3)_2(SiH_3)(\eta^2$-H−H)] and an η^2-H−SiH_3 complex [OsCl(CO)$(PH_3)_2$H(η^2-H−SiH_3)]. A more detailed analysis of our results leads to an evaluation of the relative weight of the different terms contributing to the general stability of [$ML_n(SiR_3)(\eta^2$-H−H)] and [ML_n(H)(η^2-H−SiR_3)] complexes. In particular, we find that the η^2 coordination of the H−SiR_3 ligand to the [OsCl(CO)$(PH_3)_2$(H)] fragment is stronger than that of the H−H ligand to the [OsCl(CO)$(PH_3)_2$-(SiH_3)] fragment by *ca.* 15 kcal/mol, a value that compensates almost exactly the superior strength of the H−H bond with respect to the H−SiR_3 bond. Hence, the decision on the relative stability of the two possible isomeric forms depends essentially on the subtle balance between the magnitude of these two terms. It is therefore not a surprise that both coordination modes are found in nature.

Acknowledgment. We thank Profs. M. A. Esteruelas and L. A. Oro (Zaragoza, Spain) for helpful discussions and for communication of results prior to publication. Financial support is acknowledged from the Spanish "Dirección General de Investigación Científica y Técnica" (DGICYT) under Project No. PB92-0621.

Supporting Information Available: Listings of the absolute energies and MP2-optimized Cartesian coordinates of complexes **7**−**13** (8 pages). This material is contained in many libraries in microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM9506072