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H_2XO and $(CH_3)_2XO$ Compounds (X = C, Si, Ge, Sn, Pb): Double Bonds vs Carbene-Like Structures—Can the Metal Compounds Exist at All?

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Abstract: The relative stabilities of the R_2XO, *trans*-RXOR, and *cis*-RXOR isomers (X = C, Si, Ge, Sn, Pb; R = H, CH_3) were investigated by ab initio and DFT pseudopotential calculations. Geometry optimizations and frequency computations were performed at the MP2 and Becke3LYP levels with DZ+P basis sets. MP4SDTQ/(DZ+P)//MP2/DZ+P and CCSD(T)/(DZ+P)//MP2/DZ+P single point calculations gave high level ab initio data. The CCSD(T)/(DZ+P)//MP2/(DZ+P) and the Becke3LYP/(DZ+P) relative energies both agree and show that the C_{2v} H_2XO isomers (with the exception of formaldehyde) are the least stable and that the *cis*- and *trans*-HXOH C_s isomers are very close in energy. Acetone and dimethylsilanone are the most stable isomers in the Me_2XO series. However, with the notable exception of HPbOH, the H_2XO compounds are not stable thermodynamically toward cyclotrimerization or to hydration. The NPA/NLMO charges, bond orders, and orbital hybridizations support the polar description $^-O{:}{:}{:}X^+R_2$ of all metal "double bond" species. The $^-O{:}{:}{:}X^+$ symbol implies the polarization of both π and σ bonds, which are stabilized electrostatically by methyl substitution. Only weak π interactions occur in the carbene-like RXOR metal isomers, and the σ bonds are mainly formed by p orbitals. In contrast, the X s orbitals participate strongly in the σ_{X-O} bonds of the $^-O{:}{:}{:}X^+$ systems; the oxygen hybridization is far from sp^2.

Introduction

The "nonexistence" of heavy element analogs of common organic functional groups are striking examples of the unique behavior of the Li−Ne row elements.[1] While a large variety of organic carbonyl derivatives are essential for synthetic chemistry,[2,3] silanone was first detected in the early 1980s by Eaborn et al.[4] Withnall and Andrews proved the existence of $H_2Ge{=}O$ only six years ago.[5]

In contrast, many theoretical studies on derivatives containing $Si{=}O$ groups have been reported.[6,7] The potential energy surfaces for CH_2O and SiH_2O are completely different. Formaldehyde is 54.0 kcal/mol more stable than *trans*-HCOH and 59.1 kcal/mol than the *cis*-HCOH carbene.[8] In contrast, *trans*-HSiOH was found to be the absolute minimum[9] but is only slightly more stable than the *cis* isomer (0.2 to 0.5 kcal/mol) as well as silanone $H_2Si{=}O$ (1.3 kcal/mol).[7b,9]

Germanone and its derivatives also have been considered theoretically.[10,11] Trinquier et al. found *cis*-HGeOH to be 1.0 kcal/mol lower in energy than *trans*-HGeOH and 18.0 kcal/mol more stable than $H_2Ge{=}O$.[10a,b] So computed *cis*-HGeOH is 0.6 kcal/mol more stable than *trans*-HGeOH at the SCF level, but electron correlation reversed the stability order.[11]

Although the group 14 metal $R_2X{=}O$ systems are often postulated as intermediates,[12] the experimental structures of stananone $H_2Sn{=}O$ and plumbanone $H_2Pb{=}O$ are not known. These compounds are prone to oligomerization and addition reactions.[13] For example, the polysiloxane chains and rings formally are built from $R_2Si{=}O$ subunits (poly**silic**oket**ones**). A thorough theoretical investigation should take these thermodynamic aspects into account.[14] However, such studies have not even been reported for the heavier element $R_2X{=}O$ monomers.

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(1) (a) Streitwieser, Jr., A.; Heathcock, C. H. *Introduction to Organic Chemistry*; Macmillan Publishing: New York, 1986. (b) Klapötke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, 1994.

(2) Falbe, J. *Methoden der Organische Chemie (Houben-Weil)*; G. Thieme Verlag: Stuttgart, 1983; Vol. E3.

(3) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

(4) (a) Aiube, Z. H.; Chojnowski, J.; Eaborn, C.; Stanczyk, W. A. *J. Chem. Soc., Chem. Commun.* **1983**, 493. (b) Eaborn, C.; Stanczyk, W. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2099.

(5) Withnall, R., Andrews, L. *J. Phys. Chem.* **1990**, *94*, 2351.

(6) (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Raabe, G.; Michl, *J. Chem. Rev.* **1985**, *85*, 419. (c) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270. (d) Srinivas, R.; Böhme, D. K.; Sülzle, D.; Schwarz, H. *J. Phys. Chem.* **1991**, *95*, 9836.

(7) (a) Jaquet, R.; Kutzelnigg, W.; Staemmler, V. *Theor. Chim. Acta* **1980**, *54*, 205. (b) Darling, C. L.; Schlegel, B. H. *J. Phys. Chem.* **1993**, *97*, 8207. (c) Hrusák, J.; Böhme, D. K.; Wlodek, S.; Schwarz, H. *J. Phys. Chem.* **1992**, *96*, 5355. (d) Remko, M.; Liedl, K. R.; Rode, B. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2375.

(8) (a) Lucchese, R. R.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 298. (b) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394.

(9) (a) Tachibana, A.; Fueno, H.; Yamabe, T. *J. Am. Chem. Soc.* **1986**, *108*, 4346. (b) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833. (c) Lucas, D. J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1993**, *99*, 6697, and references therein.

(10) (a) Trinquier, G.; Pelissier, M.; Saint-Roch, B.; Lavayssiere, H. *J. Organomet. Chem.* **1981**, *214*, 169. (b) Trinquier, G.; Barthelat, J. C.; Satgé, J. J. *Am. Chem. Soc.* **1982**, *104*, 5931. (c) Antoniotti, P.; Grandinetti, F. *Gazz. Chim. Ital.* **1990**, *120*, 701.

(11) So, S. P. *J. Phys. Chem.* **1991**, *95*, 10658.

(12) (a) Riviere, P.; Castel, A.; Satge, J. *J. Am. Chem. Soc.* **1980**, *102*, 5413. (b) Kalinina, G. S.; Basalgina, T. A.; Vyazankin, N. S.; Razuaev, G. A., Yablokov, V. A.; Yablokova, N. V. *J. Organomet. Chem.* **1976**, *117*, 231. (c) Barrau, J.; Rima, G.; Satgé, J. *Phosphorus, Sulfur, Silicon* **1990**, *54*, 23. (d) Lazarq, M.; Couret, C.; Escudié, J.; Satgé, J. *Organometallics* **1991**, *10*, 1771. (e) Satgé, J. *J. Adv. Organomet. Chem.* **1982**, *21*, 241. (f) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

(13) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*; VCH: Weinheim, 1989; pp 95−146. For recent examples, see: (a) Glowacki, A.; Huber, F.; Preut, H. *J. Organomet. Chem.* **1986**, *306*, 9. (b) Blaschette, A.; Hamann, T.; Michalides, A.; Jones, P. G. *J. Organomet. Chem.* **1993**, *456*, 49. (c) Blaschette, A.; Wieland, E.; Jones, P. G.; Hippel, I. *J. Organomet. Chem.* **1993**, *445*, 55.

(14) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1995**, *99*, 2166.

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Nevertheless, double bonds of the third and lower periods are not weakened due to problems with π overlap.[15-17] The energy of a π bond tends to increase with increasing electronegativity of both of the participating elements,[16b] since their electron binding capability is larger (higher ionization potential). On the other hand, the relative energies of H_3Si-X and H_3C-X bonds are influenced differently by the group X electronegativity.[16a] X's with very high electronegativity (e.g., OH) form stronger σ bonds to silicon than to carbon, due to the larger ionic contributions in the $H_3Si^+-X^-$ systems. For example, the σ and π bond energies of formaldehyde have been deduced to be 86 and 93 kcal/mol at the MP4SDTQ/6-31G*//6-31G* level, while the silanone bond energies are 111 (σ) and 56 (π) kcal/mol.[16b] Only C=C, C=N, C=O, and C=S π bond energies are roughly similar to those of the corresponding single bonds.

However, the σ bonds formed by higher period elements differ from those of the first period. Since the relative radial extensions of the valence p vs s orbitals increases down the periodic table,[15] hybridization is less effective in heavy element compounds. Large "hybridization defects" can occur:[15] i.e., the hybridizations based on orbital occupancies are far from the idealized "sp^3", "sp^2", etc. values (e.g., the Pb−H bonds in tetrahedral PbH_4 adopt $sp^{1.80}$ hybridization[18]). More electronegative ligands as well as relativistic effects increase these deviations from the idealized values.[18]

In addition, the valence s and p orbital energy difference is larger for the group 14 metals than for carbon.[15,9] Thus, in the divalent state the metal s orbitals are too low in energy to participate effectively in bonding. Relativistic effects stabilize the divalent compounds of the heaviest group 14 metal even more[19,20] and dominate the inorganic chemistry of lead.[18,21] Furthermore, the divalent X atoms in the carbene-like structures investigated here are stabilized by a good π-donor group (OR). Hence, the divalent forms should be preferred increasingly down group 14.

We now compare the energies, geometries, and hybridizations of the double bonded $H_2X=O$ and the carbene-like $H-X-O-H$ isomers for all group 14 elements. The effects of methyl substitution on structures and stabilities also are considered as well as the magnitude of the relativistic effects in the lead compounds. The hydrogenation energies of the H_2XO species (to form H_3XOH) and the cyclotrimerization (as a model for polymerization) provide assessments of the relative thermodynamic stabilities of the double bonded and the carbene-like isomers.

Computational Details

All structures were optimized with the GAUSSIAN94 program[22] with the electron correlated Becke3LYP DFT functional.[23] Frequency calculations of the R_2XO isomers then gave the zero point vibrational energies and the number of imaginary frequencies.[24] To obtain results of the same quality for the complete set of compounds, we replaced the core electrons of all group 14 elements and oxygen by (quasi-) relativistic pseudopotentials (PSP) of Stoll et al.[25] The corresponding DZ+P basis sets were employed. Additional calculations were performed with a nonrelativistic Pb-pseudopotential (R = H) for comparison with the relativistic results.[26] The 6-31++G** (R = H) and 6-31+G** ($R = CH_3$) basis sets were employed for hydrogen.[27]

The relative Becke3LYP energies are often in excellent agreement with high level ab initio results.[28] This set of pseudopotential calculations was used to examine their quality for unusual heavy element compounds. Therefore, the R_2XO species also were optimized at the MP2 level of theory[29] with the same basis sets and pseudopotentials. Higher level electron correlated MP4SDTQ[30] and CCSD(T)[31] single-point calculations were performed at the MP2 optimized geometries.[32]

Reed and Weinhold's NBO analysis[33] of the different isomers gave atomic charges, bond orders, and orbital hybridizations. The NBO representation of ab initio wave functions in terms of localized Lewis structures provides a quantitative interpretation of MO interactions. The results of coupled cluster and density functional theory are very similar. Therefore, only the results of the Becke3LYP NBO-analysis are discussed.

Results and Discussion

The total energies, computed at the various levels, are listed in Table 1, together with zero point vibrational energies (ZPE). The relative energies of the different isomers are given in Table 2 (see also Figure 1). Only planar C_s (RXOR) and C_{2v} ($R_2X=O$) structures were considered, since these either are minima (NIMAG = 0) or have only a very small negative eigenvalue corresponding to the methyl group rotation in some

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(15) Kutzelnigg analyzed the σ and p bonding of main group element compounds in detail in a landmark review: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(16) (a) Luke, B. T.; Pople, J.A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260. Also see ref 6b. (b) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

(17) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

(18) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061.

(19) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

(20) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518.

(21) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; Wiley: New York, 1988. (b) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper: Cambridge, MA, 1983. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984. (e) For a recent syntheses of stable divalent Ge, Sn, and Pb compounds, see: Driess, M.; Janoschek, R.; Pritzkow, H.; Rell, S.; Winkler, U. *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 1614 and literature therein. (f) Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 1334.

(22) GAUSSIAN 94; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R., Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN, Inc.: Pittsburgh, PA, 1995.

(23) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley & Sons: New York, 1986.

(25) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431. d-Polarization Functions: *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: New York, 1984.

(26) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245.

(27) (a) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (b) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(28) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1992**, *197*, 499.

(29) (a) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503. (b) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275. (c) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

(30) Krishnan, R.; Pople, J. A. *Int. J. Quant. Chem.* **1978**, *14*, 91.

(31) (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1978**, *14*, 545. (b) Purvis III, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (c) Scuseria, G. E.; Jansen, C. L.; Schaefer III, H. F. *J. Chem. Phys.* **1988**, *89*, 7382. (d) Scuseria, G. E.; Schaefer III, H. F. *J. Chem. Phys.* **1989**, *90*, 3700. (d) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(32) For systems of this size the MP2 optimizations are about 1.5 times slower than the corresponding Becke3LYP computations (HP735 workstation). However, the MP4SDTQ and CCSD(T) single point calculations are 20 to 75 times more expensive than similar DFT computations with the same basis sets.

(33) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (d) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

Table 1. Absolute MP4SDTQ//MP2, CCSD(T)//MP2, and Becke3LYP Energies, Becke3LYP Zero Point Vibrational Energy (ZPE) [au and kcal/mol][e]

	C	Si	Ge	Sn	n-Pb[a]	Pb
			$H_2X{=}O$			
MP4SDTQ	−22.771 34	−20.988 66	−20.868 96	−20.413 17	−20.164 51	−20.409 47
CCSD(T)	−22.770 01	−20.984 66	−20.861 30	−20.401 41	−20.150 04	−20.397 23
Becke3LYP	−22.907 17	−21.129 43	−21.016 52	−20.563 51	−20.311 39	−20.575 05
ZPE	16.73	11.59	10.11	8.74	8.18	8.03
			cis-HXOH			
MP4SDTQ	−22.675 00	−20.989 44	−20.913 60	−20.484 02	−20.236 20	−20.516 93
CCSD(T)	−22.676 43	−20.990 57	−20.913 36	−20.483 46	−20.235 93	−20.515 20
Becke3LYP	−22.814 54	−21.134 42	−21.068 91	−20.646 57	−20.397 26	−20.692 24
ZPE	16.10	12.69	11.91	11.23	10.98	10.92
			trans-HXOH			
MP4SDTQ	−22.685 30	−20.989 97	−20.913 82	−20.483 44	−20.235 72	−20.515 47
CCSD(T)	−22.686 39	−20.990 95	−20.913 39	−20.482 68	−20.235 25	−20.513 52
Becke3LYP	−22.824 05	−21.134 39	−21.068 60	−20.645 56	−20.396 53	−20.690 44
ZPE	16.76	12.93	12.12	11.34	11.09	10.98
			cyclo-$(H_2XO)_3$			
Becke3LYP	−68.768 23	−63.708 23	−63.306 45	−61.981 55	−61.254 03	−61.949 40
			H_3XOH[b]			
Becke3LYP	−24.127 28	−22.383 08	−22.277 43	−21.835 13	−21.589 03	−21.843 42
			$Me_2X{=}O$			
MP4SDTQ	−36.473 17	−34.706 79	−34.576 35	−34.115 93		−34.106 33
CCSD(T)	−36.471 92	−34.703 62	−34.569 39	−34.104 65		−34.093 15
Becke3LYP	−36.699 10	−34.936 71	−34.812 38	−34.353 77		−34.356 30
ZPE	52.26	47.82	47.01	46.10		45.70
			cis-MeXOMe			
MP4SDTQ	−36.351 22	−34.667 83	−34.585 50	−34.153 92		−34.183 31
CCSD(T)	−36.352 68	−34.668 91	−34.585 15	−34.153 33		−34.181 51
Becke3LYP	−36.582 83	−34.901 32	−34.830 01	−34.405 15		−34.446 65
ZPE	51.48[c]	48.67	47.94	47.39		47.11
			trans-MeXOMe			
MP4SDTQ	−36.365 89	−34.670 64	−34.588 36	−34.155 07		−34.183 39
CCSD(T)	−36.366 92	−34.671 56	−34.587 87	−34.154 33		−34.181 50
Becke3LYP	−36.596 92	−34.903 32	−34.832 19	−34.405 95		−34.446 63
ZPE	51.79	48.62	47.97	47.42		47.13
NIMAG[d]		55.8*i*	39.8*i*	27.5*i*		

[a] Nonrelativistic Pb pseudopotential. [b] Absolute dihydrogen energy at Becke3LYP/6-31++G**: −1.178 97 au (reaction 1). [c] C_1 symmetry. [d] Magnitude of the imaginary frequency in cm^{-1} for nonminimum structures. [e] See Figure 1.

of the CH_3XOCH_3 species. The only exception is cis-CH_3XOCH_3 with C_1 symmetry. However, the planarization barrier is almost zero.

Relative Energies. The relative energies of Becke3LYP, MP4SDTQ//MP2, and CCSD(T)//MP2 calculations are compared in Table 2. Indeed, for both $R = H$ and $R = CH_3$ the coupled cluster and the density functional relative energies agree remarkably well (within ±0.4 kcal/mol for the H_2XO isomers and ±1.0 kcal/mol for the Me_2XO compounds). The deviations of the MP4SDTQ relative energies are several kcal/mol; the double bond isomers are favored more. These $R_2X{=}O$ forms become increasingly less stable vs the carbene-like structures down group 14. Accordingly, the difference between the MP4SDTQ and the CCSD(T)/Becke3LYP relative stabilities increase with increasing atomic number of X. Thus, the CCSD(T) and Becke3LYP relative energies are discussed below.

Stabilities. Even for silicon, the carbene-like structures, *cis*- and *trans*-HSiOH, are favored over $H_2Si{=}O$, although the energy differences are small (∼2 kcal/mol, see Table 3). These results agree well with older computations.[7,9] However, this difference increases rapidly from germanium (∼30 kcal/mol) to tin and to nonrelativistic lead compounds (for both ∼50 kcal/mol). The relative stability of the divalent state is increased strongly by relativistic effects:[18−20] the Pb(II) species are 70 kcal/mol more stable than a hypothetical plumbanone, $H_2Pb{=}O$.

However, any of the H_2XO isomers might not be stable except in isolation. Note, for example, the formation of trioxane $(H_2CO)_3$. Comparisons with tetracoordinated systems are instructive. The hydrogenated forms, H_3XOH (reaction 1), and the cyclo-$(H_2XO)_3$ trimers serve as models for polymers (reaction 2), e.g., silicones, or other tetravalent compounds. Considering the expected quality of the DFT relative energies, only Becke3LYP calculations were performed (H_3XOH in staggered C_s, trimers in C_{3v} symmetries, see Figure 1).[34]

$$H_2XO + H_2 \rightarrow H_3XOH \qquad (1)$$

$$3H_2XO \rightarrow \text{cyclo-}(H_2XO)_3 \qquad (2)$$

Most of the computed energies for both reactions (Table 2) are highly exothermic. This is true even for the formaldehyde trimerization, since the formation of trioxane is favored by 10 kcal/mol per $H_2C{=}O$. These reaction energies are confirmed by other theoretical and experimental values.[35] For almost all group 14 metal compounds both tetracoordinated species are preferred strongly over the carbene-like structures (and, of course, over the less stable double bonded species). However, the relative energies of the H−X−O−H isomers vs H_3XOH and cyclo-$(H_2XO)_3$ decrease down group 14 (Si: 45−65 kcal/

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(34) Although the ZPE correction is necessary to obtain the exact reaction energies, the results differ only by some kcal/mol when the correction is omitted. For example, the relative stabilities of the R_2XO isomers change by 0−3 kcal/mol (Tables 1 and 2); this has no influence on the trends or the interpretation. Therefore, the ZPE was not included in the calculation of the reaction energies 1 and 2.

(35) (a) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280. (b) Gordon, M. S.; Pederson, L. A. *J. Phys. Chem.* **1990**, *94*, 5527.

Table 2. Relative Energies at Various Levels [kcal/mol]

	$H_2X{=}O$	*cis*-HXOH	*trans*-HXOH	*cyclo*-$(H_2XO)_3$[a]	H_3XOH[b]	$Me_2X{=}O$	*cis*-MeXOMe	*trans*-MeXOMe
				C				
MP4	0.0	59.84	53.99			0.0	75.77	66.87
CCSD(T)	0.0	58.11	52.47			0.0	74.07	65.43
B3LYP	0.0	57.52	52.16	−9.73	−25.82	0.0	72.21	63.67
				Si				
MP4	0.0	0.58	0.48			0.0	24.59	22.82
CCSD(T)	0.0	−2.64	−2.65			0.0	21.92	20.26
B3LYP	0.0	−2.06	−1.81	−66.92	−46.86	0.0	22.35	21.09
				Ge				
MP4	0.0	−26.26	−26.20			0.0	−4.84	−6.61
CCSD(T)	0.0	−30.92	−30.74			0.0	−9.10	−10.67
B3LYP	0.0	−31.12	−30.73	−53.73	−51.42	0.0	−10.17	−11.50
				Sn				
MP4	0.0	−42.04	−41.57			0.0	−22.60	−23.29
CCSD(T)	0.0	−49.07	−48.48			0.0	−29.31	−29.90
B3LYP	0.0	−49.70	−48.97	−61.70	−58.14	0.0	−31.00	−31.47
				n-Pb[c]				
MP4	0.0	−42.27	−41.86					
CCSD(T)	0.0	−51.18	−50.65					
B3LYP	0.0	−51.16	−50.65	−66.90	−61.92			
				Pb				
MP4	0.0	−64.63	−63.66			0.0	−46.65	−46.99
CCSD(T)	0.0	−71.23	−70.11			0.0	−54.10	−54.07
B3LYP	0.0	−70.74	−69.55	−46.90	−56.10	0.0	−55.34	−55.31

[a] Trimerization energy (reaction 2) per $H_2X{=}O$ molecule (no ZPE correction). [b] Hydration energy (reaction 1, no ZPE correction). [c] Nonrelativistic Pb pseudopotential.

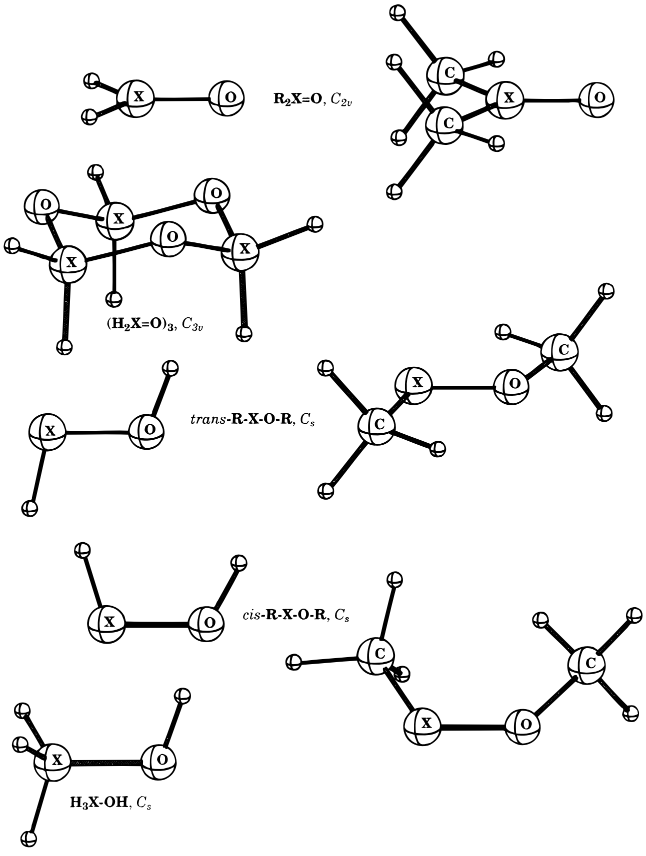

Figure 1. Schematic representations of the structures considered.

mol, Ge: 20−23 kcal/mol, Sn and nonrelativistic Pb: 9−16 kcal/mol, see data given in Table 2).

Lead behaves unlike the other group 14 metals; the stability order is HPbOH > H_3PbOH > cyclo-$(H_2PbO)_3$. This is due to the extra relativistic stabilization of Pb(II) (∼20 kcal/mol, see above) and the relativistic destabilization of Pb(IV) compounds with two electronegative ligands (i.e., O−Pb−O groups in the trimer).[18] In contrast, the hydrogenation energies are similar (47−62 kcal/mol) for all group 14 $H_2X{=}O$ metal systems.

To what extent do the OH groups stabilize the carbenic H−X−O−H isomers? The differences in the $H_2X{=}CH_2 \rightarrow HX{-}CH_3$ energies provides a comparison: ethene is favored over $HCCH_3$ by 73.6 kcal/mol, while the energy difference between formaldehyde and *trans*-H−C−O−H is 52.0 kcal/mol.[36] Hence, the relative stabilizing effect of a OH substituent on the carbene is +21.6 kcal/mol (evaluated in this manner); this stabilization decreases to +3.7 kcal/mol ($H_2Si{=}CH_2 \rightarrow HSi{-}CH_3$: 0.6 kcal/mol vs $H_2Si{=}O \rightarrow$ H−Si−O−H: −3.1 kcal/mol) and then increases again (+12.2 to +18.0 kcal/mol, X = Ge−Pb). Therefore, the silicon compounds seem to be exceptional. However, the very strongly negatively charged carbon atoms of the $HX{-}CH_3$ isomers (X = Si−Pb) are stabilized by polarization of the adjacent metal, X. The polarization effect is largest for the elements of the third period.[37] Thus, $HSi{-}CH_3$ is only 0.6 kcal/mol less stable than $H_2Si{=}CH_2$. Since the $H_2Si{=}O \rightarrow$ H−Si−O−H rearrangement energy is −3.1 kcal/mol, the stabilizing effect of the OH group on the silylene (+3.7 kcal/mol, see above) is very small.

The cis and trans isomers of the R−X−O−R metal compounds are very close in energy (see data given in Table 2). For R = H, the cis conformations are favored, but for R = CH_3 the reverse is true. However, H−C−O−H and CH_3−C−O−CH_3 are exceptions, since both prefer the trans conformations

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[36] Total energies of the $H_2X{=}CH_2$ species (in au): X = C −13.730 76, Si −11.911 90, Ge −11.828 43, Sn −11.378 85, nonrelativistic Pb −11.126 23, Pb −11.401 47. Total energies of the $HX{-}CH_3$ species (in au): X = C −13.613 46, Si −11.910 95, Ge −11.859 39, Sn −11.437 52, nonrelativistic Pb −11.187 58, Pb −11.487 62. Energy difference (in kcal/mol): C 73.61, Si 0.60, Ge −19.43, Sn −36.82, nonrelativistic Pb −38.50, Pb −54.44. The according $H_2X{=}O$/*trans*-HXOH energy differences are (in kcal/mol, no ZPE correction, Table 1): C 52.60, Si −3.11, Ge −31.59, Sn −51.49, nonrelativistic Pb −53.43, Pb −72.41. See also: Grev, R. S.; Schaefer III, H. F. *Organometallics* **1992**, *11*, 3489.

[37] (a) El-Nahas, A. M.; Schleyer, P. v. R. *J. Comp. Chem.* **1994**, *15*, 596. (b) Wiberg, K.; Castejon, H. *J. Am. Chem. Soc.* **1994**, *116*, 10489.

Table 3. Selected Becke3LYP Geometry Parameters (MP2 X−O Distances in Italics) [Å and deg][d]

$H_2X{=}O$	d_{XO}		d_{XH}	cyclo-$(H_2XO)_3$[b]	d_{XO}	d_{XH}	∠XOX	∠HXH
C	1.202	*1.216*	1.109	C	1.411	1.105	111.2°	110.0°
Si	1.529	*1.542*	1.482	Si	1.659	1.476	135.5°	111.7°
Ge	1.657	*1.675*	1.546	Ge	1.808	1.540	129.9°	114.9°
Sn	1.854	*1.864*	1.718	Sn	1.984	1.708	134.3°	115.3°
n-Pb[a]	1.943	*1.956*	1.813	n-Pb[a]	2.056	1.807	137.5°	114.7°
Pb	1.927	*1.912*	1.755	Pb	2.077	1.737	133.0°	119.7°

ϕ∠HXO: 121.5°−124.5°

cis-HXOH	d_{XO}		d_{XH}	∠XOH	∠HXO	*trans*-HXOH	d_{XO}		d_{XH}	∠XOH	∠HXO
C	1.310	*1.314*	1.124	117.0°	106.9°	C	1.314	*1.316*	1.116	109.2°	102.0°
Si	1.674	*1.678*	1.551	123.4°	97.6°	Si	1.681	*1.683*	1.531	117.0°	94.3°
Ge	1.842	*1.848*	1.633	115.9°	95.4°	Ge	1.846	*1.852*	1.610	112.4°	92.1°
Sn	2.026	*2.033*	1.804	117.2°	94.3°	Sn	2.032	*2.037*	1.783	115.3°	91.2°
n-Pb[a]	2.096	*2.105*	1.890	120.7°	93.9°	n-Pb[a]	2.100	*2.109*	1.869	119.5°	90.8°
Pb	2.119	*2.131*	1.861	116.0°	94.4°	Pb	2.126	*2.138*	1.836	114.3°	91.3°

ϕd_{OH}: 0.962−0.972

H_3XOH	d_{XO}	d_{XH}	∠XOH	$Me_2X{=}O$	d_{XO}		d_{XC}
C	1.423	1.097	109.2°	C	1.212	*1.222*	1.518
Si	1.665	1.480	121.3°	Si	1.533	*1.545*	1.869
Ge	1.831	1.540	113.3°	Ge	1.664	*1.679*	1.977
Sn	2.013	1.710	115.5°	Sn	1.861	*1.872*	2.177
n-Pb[a]	2.087	1.806	120.0°				
Pb	2.114	1.736	112.7°	Pb	1.937	*1.928*	2.168

ϕd_{OH}: 0.962−0.964 ∠HXO: 106.9°−110.2°

d_{CH}: 1.090−1.09 ∠OXC: 121.2°−124.2°
∠XCH: 108.5°−110.0°

cis-MeXOMe	d_{XO}		d_{XC}	∠XOC	∠CXO	*trans*-MeXOMe	d_{XO}		d_{XC}	∠XOC	∠CXO
C[c]	1.304	*1.309*	1.508	125.9°	115.2°	C	1.307	*1.309*	1.499	117.2°	108.0°
Si	1.668	*1.672*	1.931	136.3°	102.6°	Si	1.678	*1.680*	1.909	125.4°	97.8°
Ge	1.837	*1.842*	2.046	131.7°	100.7°	Ge	1.844	*1.848*	2.019	122.8°	94.4°
Sn	2.023	*2.027*	2.236	131.9°	97.6°	Sn	2.032	*2.033*	2.212	126.1°	92.1°
Pb	2.116	*2.125*	2.331	130.1°	96.9°	Pb	2.124	*2.131*	2.304	125.9°	91.0°

ϕd_{CH}: 1.088−1.100 d_{CO}: 1.420−1.470 ∠HCH: 109.0°−112.0°

d_{CH}: 1.088−1.098 d_{CO}: 1.420−1.450 ∠HCH: 108.0°−112.0°

[a] Nonrelativistic Pb pseudopotential. [b] The calculated geometry parameters of the Si−Sn rings are in very good agreement with the experimental values: Puff, H.; Franken, S.; Schuh, W.; Schwab, W. *J. Organomet. Chem.* **1983**, *254*, 33. [c] C_1 symmetry. HCCO-dihedral: 32.4°, COCH-dihedral: 173.6°. [d] See Figure 1.

by 5−8 kcal/mol. The hydrogen atoms of HCOH and of the methyl groups in CH_3COCH_3 are positively polarized, and the electrostatic as well as steric repulsions disfavor the cis isomers.

The change of the *cis*/*trans* preference is not the only effect of methyl substitution: the double bond isomers are stabilized preferably. Not only acetone but also dimethylsilanone $Me_2Si{=}O$ is the most stable minimum. Germanone is only 10 kcal/mol less stable than its divalent isomers. Indeed, both $Me_2Si{=}O$ and $Me_2Ge{=}O$ have been detected experimentally.[38]

However, the stabilizing effect of methyl groups on double bonds decrease down group 14 from Si (∼23 kcal/mol) to Pb (∼15 kcal/mol). Methyl substituted divalent tin and lead compounds are 30 and 45 kcal/mol more stable than the $R_2X{=}O$ forms. It will be very difficult to observe molecules with Sn═O or Pb═O double bonds, since both intramolecular rearrangement toward the carbene-like isomers and intermolecular reactions are more likely alternatives.

Geometries. All the structures are depicted in Figure 1. Important Becke3LYP/DZ++PP optimized geometry parameters are given in Table 3 (MP2 X−O bond lengths in italics are shown for comparison).

Some trends are apparent: (i) The X−O single bonds are 11−17 pm longer than the X═O double bonds. (ii) The changes in the X═O and X−O bond lengths upon methyl substitution are small (1 pm or less). (iii) The metal $H_3X{-}OH$ bond length are close (Δ ∼1 pm) to the X−O distances of the HXOH carbene-like structures, while the trimer X−O distances are shorter (∼4 pm). (iv) In contrast, the cyclo-$(H_2C{-}O)_3$ and the $H_3C{-}OH$ bond lengths exceed those in *cis*- and *trans*-HCOH by ∼10 pm.

Electronic Structures. The decrease of the electronegativity between carbon (2.50) and the other group 14 elements (2.02−1.55)[39] is of primary importance, since the X−R (R = H, CH_3) bond polarity is reversed and a reduction of the π bond energies results. The XO, XC, and XH bonds (X = Si−Pb) are partially ionic (i.e., the covalent contributions are decreased). In addition, the hybridization of the other group 14 atoms differs from the carbon hybridization (see the discussion in the introduction).[15] Therefore, the behavior of carbon systems is unusual compared with the metal compounds; e.g., the H_2CO isomer relationships are exceptional.

Unlike the NPA bond order of 2.0 for ethene,[33d] the formaldehyde C−O bond order is only 1.4 (Table 4). This reflects the polar character of the double bond. The natural atomic charges (C: +0.3, O: −0.5) and the polarization of both the σ and π bonds confirm this description (Table 5).

The C−O NPA bond orders of the H-C-O-H carbene systems are only 0.83 and 0.84. Nevertheless, they are still higher than the methanol C−O bond order (0.67), indicating some π interactions. Indeed, the out-of-plane oxygen lone pair is polarized toward carbon (Table 5). The electron densities are increased at carbon (+0.09 to +0.14, no electron withdrawing π bond) and at oxygen (−0.68, polar O−H bond) compared with formaldehyde (Table 4).

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(38) $Me_2Si{=}O$: Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1986**, *108*, 8118. $Me_2Ge{=}O$: Khabashesku, V. N.; Kerzina, Z. A.; Boganov, S. E.; Nefedov, O. M. In *IX International Symposium on Organosilicon Chemistry*, Edinburgh, 1990; Abst. P. 8.25.

(39) Allred, A. L.; Rochow, E. J. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

Table 4. Natural Atomic Charges (NAC) and Bond Orders (NPA) from the Becke3LYP-NBO Analysis[b]

NAC	C	Si	Ge	Sn	n-Pb[a]	Pb	NPA	C	Si	Ge	Sn	n-Pb[a]	Pb
$H_2X{=}O$													
H	0.12	−0.26	−0.22	−0.27	−0.35	−0.25	HX	0.81	0.73	0.76	0.69	0.64	0.72
X	0.29	1.64	1.49	1.71	1.86	1.54	XO	1.40	0.84	0.90	0.85	0.80	0.91
O	−0.53	−1.12	−1.05	−1.12	−1.17	−1.04							
cis-HXOH													
H	0.06	−0.39	−0.38	−0.45	−0.48	−0.44	HX	0.93	0.61	0.62	0.55	0.52	0.56
X	0.14	1.02	0.99	1.13	1.20	1.11	XO	0.84	0.38	0.39	0.32	0.29	0.32
O	−0.68	−1.14	−1.11	−1.17	−1.20	−1.15							
ϕ*NAC* OH: 0.49−0.52							NPA OH: 0.47−0.51						
trans-HXOH													
H	0.09	−0.36	−0.35	−0.42	−0.46	−0.41	HX	0.90	0.64	0.65	0.58	0.54	0.59
X	0.09	0.97	0.95	1.09	1.16	1.07	XO	0.83	0.39	0.40	0.33	0.29	0.34
O	−0.69	−1.13	−1.09	−1.16	−1.19	−1.13							
ϕ*NAC* OH: 0.47−0.51							NPA OH: 0.46−0.52						
H_3XOH													
H	0.19	−0.24	−0.19	−0.27	−0.32	−0.21	HX	0.78	0.75	0.80	0.72	0.67	0.78
X	−0.29	1.32	1.14	1.44	1.64	1.22	XO	0.68	0.37	0.40	0.35	0.31	0.34
O	−0.79	−1.13	−1.08	−1.13	−1.17	−1.09							
ϕ*NAC* OH: 0.48−0.52							NPA OH: 0.47−0.51						
$Me_2X{=}O$													
C	−0.75	−1.26	−1.18	−1.20		−1.11	CX	0.99	0.54	0.59	0.55		0.60
X	0.58	2.07	1.89	2.04		1.82	CO	1.35	0.79	0.85	0.79		0.85
O	−0.57	−1.16	−1.10	−1.17		−1.09							
ϕ*NAC* H: 0.25−0.26							NPA CH: 0.73−0.75						
cis-MeXOMe													
C	−0.83	−1.32	−1.27	−1.30		−1.26	CX	0.94	0.45	0.48	0.42		0.45
X	0.31	1.20	1.16	1.27		1.23	XO	0.85	0.36	0.37	0.31		0.32
O	−0.55	−0.97	−0.93	−0.97		−0.94							
ϕ*NAC* OC: −0.27 HCX: 0.23−0.25 HCO: 0.18−0.22							NPA OC: 0.59−0.70 HCX: 0.74−0.76 HCX: 0.77−0.79						
trans-MeXOMe													
C	−0.81	−1.30	−1.25	−1.29		−1.24	CX	0.96	0.47	0.50	0.44		0.47
X	0.25	1.16	1.13	1.24		1.20	XO	0.81	0.37	0.37	0.31		0.32
O	−0.56	−0.95	−0.91	−0.95		−0.92							
ϕ*NAC* OC: −0.28 HCX: 0.24−0.25 HCO: 0.18−0.22							NPA OC: 0.59−0.70 HCX: 0.74−0.75 HCX: 0.77−0.79						

[a] Nonrelativistic Pb pseudopotential. [b] See Figure 1.

The metal "$H_2X{=}O$" NPA bond orders are less than one (0.8−0.9, Table 4), the oxygens are single negative, and the metals are very positively charged (+1.5 to +1.9). Most of the π electron density is located at oxygen (80−85%, Table 5). However, the σ bonds are strongly polarized toward oxygen as well (70−80%). Hence, the traditional "semipolar" ${}^{-}O{-}X^{+}$ representation is misleading. It is often misinterpreted: not only the π bond but also the σ bond is polarized. Thus, we propose to describe these significantly ionic "double bonds" with the ${}^{-}O{:::}X^{+}$ symbol to emphasize the semipolar character of **both** the σ and π bonds.[40]

The bond orders of the carbene-like Si−Pb isomers and the alcohol analogs are very similar and are quite small (0.3−0.4). Furthermore, in the carbene-homologs over 90% of the lone pair electron density is located at oxygen (Table 5); consequently, the O−X π interactions are weak. Interestingly, the natural oxygen charges are similar in all metal compounds (−1.08 to −1.19), while the positive charge of the metals decreases from the ${}^{-}O{:::}X^{+}H_2$ systems (+1.5 to +1.85) to the alcohol analogs H_3XOH (+1.2 to +1.6, no π withdrawal) and to the carbene-like isomers HXOH (+0.95 to +1.20, less hydrogen atoms bound to the metals).

The effect of methyl substitution is primarily electrostatic (Table 4);[3,41] hyperconjugation contributions are small. The positive NPA charges of X increase, especially in the ${}^{-}O{:::}X^{+}(CH_3)_2$ metal compounds by 0.3−0.4. The additional intramolecular Coulomb stabilization which results is small in acetone, but it is large in dimethylsilanone and then decreases due to the larger X−C distances down group 14 (Tables 2 and 4).

Natural localized molecular orbital (NLMO) hybridization analysis gives some unexpected results (Table 5). In the *cis*- and *trans*-HXOH structures, the X lone pairs (lp_X) are almost pure s orbitals (note the trend down group 14), while the X p orbital contributions to the σ_{XO} bond dominate (Table 5). Therefore, the X bonding orbitals become less electronegative.[42] However, the oxygen 2p contributions to the σ_{XO} bonds increase down the group, even though the oxygen orbitals involved in bonding to electropositive ligands are expected to possess strong 2s contributions.[43] However, such assumptions are based on experience with compounds of first, second, and third row elements.[44] Heavy main group elements have larger orbital extensions (compared to oxygen).[15] Stronger oxygen 2p

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(40) A referee suggested that the X=O π bond energies might be evaluated from the trimerization energies. Although this is an interesting suggestion, the energies obtained by this procedure (C=O: 72 kcal/mol, Si=O: 44 kcal/mol) strongly deviate from π bond estimates obtained from other, more general procedures (C=O: 98 kcal/mol, Si=O: 55 kcal/mol), see ref 16b. Obviously, the involvement of the σ system (Table 3) is not negligible.

(41) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831.

(42) (a) Mullay, J. *J. Am. Chem. Soc.* **1986**, *108*, 1770. (b) *Electronegativity*. In *Structure and Bonding*; Sen, K. D., Ed.; Springer Verlag: Berlin, 1987; Vol. 66. (c) Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.

(43) Glidewell, C. *Inorg. Chim. Acta* **1978**, *29*, L283.

(44) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

Table 5. NLMO Hybridizations and Polarization from the Becke3LYP-NBO Analysis[e]

	$H_2X{=}O$		
	σ_{HX}[a]	σ_{XO} X O	lp_O
C	$sp^{1.80}$	$sp^{2.13}{-}sp^{1.34}$	$sp^{0.73}$
Si	$sp^{1.09}$	$sp^{1.08}{-}sp^{1.67}$	$sp^{0.59}$
Ge	$sp^{1.02}$	$sp^{0.87}{-}sp^{3.25}$	$sp^{0.30}$
Sn	$sp^{0.93}$	$sp^{0.69}{-}sp^{5.23}$	$sp^{0.19}$
n-Pb[b]	$sp^{0.70}$	$sp^{0.70}{-}sp^{5.36}$	$sp^{0.18}$
Pb	$sp^{0.87}$	$sp^{0.56}{-}sp^{8.43}$	$sp^{0.11}$

	cis-HXOH				*trans*-HXOH			
	σHX[a] X	lp_x	σXO X O	lp_O	σ_{HX}[a] X	lp_x	σ_{XO} X O	lp_O
C	$sp^{3.19}$	$sp^{0.70}$	$sp^{3.38}{-}sp^{1.49}$	$sp^{1.61}$	$sp^{3.30}$	$sp^{0.67}$	$sp^{3.64}{-}sp^{1.70}$	$sp^{1.40}$
Si	$sp^{7.03}$	$sp^{0.24}$	$sp^{5.72}{-}sp^{1.47}$	$sp^{2.05}$	$sp^{6.86}$	$sp^{0.24}$	$sp^{6.31}{-}sp^{1.73}$	$sp^{1.60}$
Ge	$sp^{9.52}$	$sp^{0.17}$	$sp^{7.83}{-}sp^{2.59}$	$sp^{1.14}$	$sp^{9.02}$	$sp^{0.18}$	$sp^{8.73}{-}sp^{2.91}$	$sp^{0.99}$
Sn	$sp^{10.40}$	$sp^{0.15}$	$sp^{8.69}{-}sp^{2.94}$	$sp^{1.04}$	$sp^{9.92}$	$sp^{0.16}$	$sp^{10.07}{-}sp^{3.26}$	$sp^{0.93}$
n-Pb[b]	$sp^{9.29}$	$sp^{0.17}$	$sp^{7.95}{-}sp^{2.58}$	$sp^{1.18}$	$sp^{8.97}$	$sp^{0.17}$	$sp^{9.55}{-}sp^{2.89}$	$sp^{1.05}$
Pb	$sp^{14.66}$	$sp^{0.11}$	$sp^{13.10}{-}sp^{3.73}$	$sp^{0.86}$	$sp^{13.78}$	$sp^{0.11}$	$sp^{15.34}{-}sp^{4.04}$	$sp^{0.79}$

	$H_2X{=}O$[c]		*cis*/*trans*-HXOH[d]	
	σ_{XO} X O	π_{XO} X O	σ_{XO} X O	$\pi_{O\rightarrow X}$ X O
C	33:67	34:66	27:73	85:15
Si	19:81	19:81	12:88	93:7
Ge	25:75	19:81	13:87	94:6
Sn	25:75	16:84	11:89	95:5
n-Pb[b]	23:77	16:84	10:90	95:5
Pb	30:70	15:85	12:88	95:5

[a] H-AOs: 100% 1s. [b] Nonrelativistic Pb pseudopotential. [c] Electron density distribution in percent (polarization). [d] The *cis* and *trans* values are identically. [e] See Figure 1.

contributions are necessary to maintain good orbital overlap with the large and diffuse X p orbitals.

We emphasize that no significant group 14 element d orbital valence participation was found for any of the compounds.

The X s orbitals participate in bonding in the $^{-}$O:::X^{+} isomers. Surprisingly, they contribute strongly to the σ_{XO} bonds down group 14 (Table 5). Hence, the heavy element s orbitals are **not** inert![20] Except for $H_2C{=}O$, the $^{-}$O:::X^{+}H$_2$ hybridizations deviate grossly from sp^2. Although poor spatial orbital overlap results from these "hybridization defects",[15,18] the Xs contributions stabilize the σ_{XO} orbitals.[45]

However, the X valence s orbitals prefer bonding with less electronegative ligands.[18] The oxygen 2s contributions to the σ_{XO} bond decrease down group 14 and reduce the electron demand of oxygen (Table 5),[42] while the oxygen lone pair (lp_O) 2s character increases (the second lone pair and the oxygen AO forming the π bond are 2p orbitals). Both trends are strengthened by relativistic effects (lead vs nonrelativistic lead). The oxygen in $^{-}$O:::Pb^{+}H$_2$ is almost completely unhybridized: there is one 2s ($sp^{0.11}$) and one 2p lone pair, and the two remaining 2p orbitals form the σ_{PbO} ($sp^{8.43}$) and the π_{PbO} bonds (Table 5).[46]

Conclusions

Only formaldehyde is the global minimum in the set of group 14 H_2XO molecules. Instead, silicon and all the metals prefer the divalent HXOH *cis*- and *trans*-isomers, which are close in energy. Methyl substitution stabilizes the double bond isomers; $Me_2C{=}O$ especially so (the oxygen-substituted RCOR carbenes are only implicated as highly reactive intermediates[47]). Dimethylsilanone also is the Me_2SiO minimum and suitable substitution can stabilize the $^{-}$O:::Ge^{+} group toward intramolecular rearrangement.[38b] However, dimethylstananone and dimethylplumbanone are quite unfavorable, and unsaturated species with double bonds between oxygen and tin or lead are not likely to exist, whatever the substituents or conditions might be.

Moreover, the $^{-}$O:::X^{+} double bonds are strongly polarized and will undergo polymerization or other addition reactions, unless bulky or stabilizing substituents are present (for X = C, even methyl groups fulfill this purpose). These tetracoordinated group 14 metal polymers and other addition products are more stable than the carbene-like structures and dominate the $(R_2XO)_n$ and R_3XOR chemistry.[13] The exception is RPbOR, where relativistic effects result in the Pb(II) state being most favorable. However, the divalent RXOR compounds of the other group 14 metals (Si−Sn) also may be stabilized kinetically by appropriate substituents.[19e]

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(45) As Kutzelnigg pointed out in ref 15, π bonds formed by pure heavy element p orbitals are far less favorable than σ bonds with s contributions. However, an s lone pair (as in the divalent isomers) is even more favorable, since the electrons are not shared with other atoms.

(46) The 6s contributions also are enhanced in the Pb−H and Pb−C bonds of the tetravalent lead compounds (e.g., $HXCH_3$: $\sigma'_{n\text{-}Pb'-H}$: $sp^{1.40}$, σ_{Pb-H}: $sp^{1.30}$). The NPA Pb−R bond orders increase (Table 4), while the Pb−R distances decrease (R = H: 3−7 pm Table 3), see: Schwerdtfeger, P.; Silberbach, M.; Miehlich, B. *J. Chem. Phys.* **1989**, *90*, 762.

(47) (a) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563. (b) Evansek, J. D.; Houk, K. N. *J. Phys. Chem.* **1990**, *94*, 5518.