Siliranes

DOI: 10.1002/anie.201105097

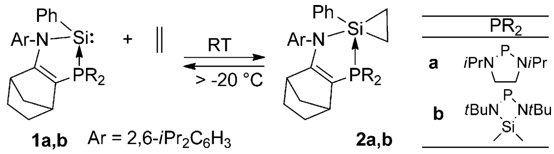
Reversible Binding of Ethylene to Silylene–Phosphine Complexes at Room Temperature**

Ricardo Rodriguez, David Gau, Tsuyoshi Kato, Nathalie Saffon-Merceron, Abel De Cózar, Fernando P. Cossío, and Antoine Baceiredo**

Since the discovery of Zeise's salt [$Cl_3Pt(\eta^2$-$CH_2{=}CH_2)$]K in 1825,[1] the binding in π-ethylene transition-metal complexes rationalized by Dewar–Chatt model[2] has been recognized as one of the most fundamental coordination modes;[3] its labile character allows the reversible process (dissociation–association)[4] and is essential for various catalytic reactions. The π backdonation ($d_{metal}\rightarrow\pi^*_{ethylene}$) associated with the Lewis acidic character ($\pi_{ethylene}\rightarrow d_{metal}$) is one of the key features of transition metals,[2b,c,5] which further distinguish their coordination properties and reactivity from those of non-metal Lewis acids.

A few types of main-group-element species, presenting small energy splitting of the valence orbitals, efficiently interact with nonpolarized poorly reactive molecules[6] such as ethylene. The bulky borane–phosphine combination known as a "frustrated Lewis pair"[7] irreversively forms a zwitterionic adduct with ethylene, in which the interaction of boron-centered Lewis acid is assisted by the Lewis base component.[8] The heavier Group 14 element analogues of alkynes with two nondegenerate π bonds, owing to their *trans* bent structure, also react with ethylene by means of a [2+1] cycloaddition reaction.[9] Remarkably, the stable distannyne reacts with two ethylene molecules, resulting in the formation of a bicyclic ethylene bis-adduct and the reactions are reversible.[10] The thermal lability of Sn–C σ bond, a major factor for the reversibility, was elegantly demonstrated by the much higher thermal stability of the germanium analogue. In addition to these new systems, the concerted [2+1] cycloaddition is a typical reaction for divalent species.[11] In the case of singlet species, the filled and unfilled orbitals, with σ and π symmetry respectively, interact with the valence orbitals of ethylene in the cycloaddition process. It is interesting to note that retro-cycloadditions, at room temperature, are extremely rare.[12] The only known example concerns a stannirane derivative which is in rapid equilibrium with its stannylene precursor.[13] Not surprisingly, in the case of siliranes the retro-cycloaddition requires a higher thermal activation.[12] Furthermore, in contrast to the extremely reactive transient silylenes,[14] only few examples of cycloaddition reactions involving a stable silylene, photochemically activated or non-activated, with an alkene have been reported.[15]

Recently we described the synthesis of the first stable phosphonium sila-ylides **1**[16] with an enhanced silylenoid character. In particular, they react with carbonyl compounds in a barrier-free concerted [2+1] cycloaddition reaction.[17] Extrapolating this result, we report herein on the interaction of **1a,b** with the much less reactive ethylene gas (Scheme 1).



Scheme 1. The reversible reactions of silylene–phosphine complexes **1a,b** with ethylene.

Phosphonium sila-ylides **1a,b** react with ethylene at room temperature to afford the corresponding pentacoordinate siliranes **2a,b**. The conversion of the reaction is strongly dependent on the ethylene pressure (80% conversion with 10 bar; Table 1a). The formation of silirane **2a** was clearly indicated, in its ^{29}Si NMR spectrum, by a high-field doublet ($\delta = -68.6$ ppm, $^1J_{PSi} = 24.0$ Hz), and inequivalent signals in ^{13}C and ^{1}H NMR spectra due to the adjacent chiral silicon center. Particularly, the two doublets in the ^{13}C NMR spectrum at −0.06 and −1.68 ppm ($^2J_{PC} = 14.3$ and 30.6 Hz) are in agreement with a silirane structure rather than a η^2-ethylene complex. The ^{31}P NMR signal at 75 ppm, which is in the region between the signals of the free phosphine ($\delta =$ 116 ppm) and the previously reported sila-oxirane analogue ($\delta = 40$ ppm), suggests a weaker Si–P interaction. More interestingly, the reaction is reversible. This was clearly

Table 1: a) Proportions of silylene–phosphine complex **1a** and silirane **2a** at different ethylene pressures. b) Equilibrium constants ($K_{2\text{-}1}$) at room temperature; NA = not available.

a)	C_2H_4 [bar]	1	3	8	10	b)	Cmpd.	**1a**	**1b**	**1c**
	1a/2a	25:1	4:1	1:1	1:4		$K_{2\text{-}1}$	1.147	0.142	NA

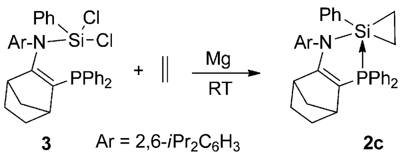
---

[*] Dr. R. Rodriguez, Dr. D. Gau, Dr. T. Kato, Dr. A. Baceiredo
Université de Toulouse, UPS, and CNRS, LHFA UMR5069
31062 Toulouse Cedex 9 (France)
E-mail: baceired@chimie.ups-tlse.fr
Homepage: http://hfa.ups-tlse.fr
Dr. N. Saffon-Merceron
Université de Toulouse (France)
Dr. A. De Cózar, Prof. F. P. Cossío
Universidad del País Vasco/Euskal Herriko Unibertsitatea
San Sebastian–Donostia (Spain)

[**] We are grateful to the CNRS, the ANR (NOPROBLEM), and Ingenio-Consolider (CSD2007-00006) for financial support of this work. We also thank the SGI/IZO-SGIker UPV/EHU for allocation of computational resources.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105097.

demonstrated by the regeneration of the phosphonium sila-ylide **1a** after a decrease in ethylene pressure. The ethylene adduct **2a** is stable up to −30 °C in solution, and in the solid state at room temperature for weeks. Silirane **2c** (R = Ph) was obtained by generating the unstable phosphonium sila-ylide **1c** in the presence of ethylene gas (Scheme 2). In contrast to **2a,b**, the ethylene adduct **2c** is perfectly stable at room temperature and no back reaction was observed even at elevated temperatures (in toluene at 100 °C).



Scheme 2. The synthesis of silirane **2c**.

Colorless crystals of silirane **2a** were obtained from a cold pentane solution (−60 °C), and the structure was unambiguously confirmed by X-ray analysis (Figure 1 a).[18] The molecule shows a strongly distorted trigonal–bipyramidal (TBP) geometry around the pentacoordinate silicon center with the phosphorus atom and one methylene group at the apical positions (P-Si-C5 = 147.0°). The sum of the equatorial bond angles around the silicon atom (358.5°) is close to the ideal value for the TBP geometry. The apical and equatorial Si−C ring bonds are almost identical with values typical for σ bonds in a three-membered ring.[12b,19] This is probably a result of the weak phosphorus–silicon interaction and the steric congestion, which is consistent with a substantially long P−Si distance (3.273 Å). This P−Si bond is much longer than that observed in the related pentacoordinate sila-oxirane (2.58 Å).[17]

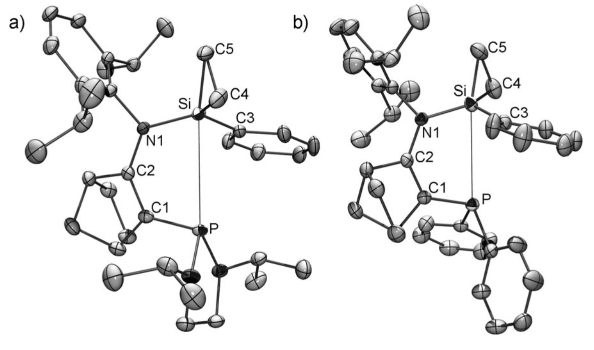


Figure 1. Molecular structures of a) **2a** and b) **2c**. Thermal ellipsoids represent 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2a**: P–Si 3.2733(11), Si–C4 1.8341(19), Si–C5 1.8354(18), C4–C5 1.570(3), Si–C3 1.8595(18), Si–N1 1.7475(13), N1–C2 1.4075(19), C1–C2 1.364(2), C1–P 1.8336(17); N1-Si-C4 121.85(9), N1-Si-C5 113.61(8), C4-Si-C5 50.66(9), N1-Si-C3 115.83(7), C4-Si-C3 119.48(9), C5-Si-C3 118.44(9); **2c**: P–Si 3.3234(8), Si–C4 1.825(2), C4–C5 1.576(3), Si–C5 1.828(2), Si–C3 1.8559(19), N1–Si 1.7400(15), P–C1 1.8031(19), C1–C2 1.348(2), C2–N1 1.407(2); N1-Si-C3 116.36(8), C4-Si-C5 51.13(11), N1-Si-C4 122.85(9), C4-C5-Si 64.34(12), N1-Si-C5 114.68(10), C4-Si-C3 117.89(10), C5-Si-C3 116.80(10).

A van't Hoff analysis of the results of variable-temperature ^{31}P NMR spectroscopy affords a small value of Gibbs free energy for the addition reaction of **1a** to ethylene ($\Delta G_{20\,^{\circ}\mathrm{C}} = (-0.717 \pm 0.452)\ \mathrm{kcal\,mol^{-1}}$) showing the thermoneutrality of the reaction; this is in strong contrast to the generally highly exothermic cycloaddition reactions of silylenes with an olefin. This result is consistent with the reversible nature of the reaction. The value is also in good agreement with that theoretically predicted ($\Delta G = -2.04\ \mathrm{kcal\,mol^{-1}}$). The equilibrium constant for the reversible addition of ethylene to sila-ylides (**1a–c**) is strongly dependent on the type of phosphine ligand (Table 1 b). Particularly in the case of phosphonium sila-ylide **1c**, which has a weaker nucleophilic diphenylphosphine ligand, the reaction results in the formation of a perfectly stable silirane **2c**. Indeed, the fact that Si−P bond in **2c** (3.323 Å) is slightly longer than that in **2a** suggests a weaker P−Si interaction (Figure 1 b).[18] The calculations for the formation of **2c** reveal a more exothermic reaction ($\Delta G = -6.63\ \mathrm{kcal\,mol^{-1}}$). These results are consistent with the previously reported ligand-dependent thermal stability of the neutral pentacoordinated silicon species, in their ligand coupling reactions.[20]

We have calculated the transition structures (**TSa**, **TSc**) associated with the formation of adducts **2a,c**. Both saddle points were fully optimized and characterized at the M06-(PCM)/6-31G*//BHandH(PCM)/6-31G* level of theory in THF solution[21–23] (see the Supporting Information for additional details). The main features of these structures are summarized in Figure 2. In the case of **TSa**, the P−Si bond index is found to be 0.54, whereas in the case of **TSc** the corresponding value is 0.36. This is probably due to the lower nucleophilicity of the diphenylphosphino moiety, leaving the silylene moiety of **1c** more reactive toward the [2+1] process. Indeed, the activation energy associated with the **1c**→**2c** process is roughly 5.0 kcal mol^{-1} lower than that associated with the formation of **2a** from **1a**. In addition, the large negative volumes of activation ($-180.3\ \mathrm{bohr^3\,mol^{-1}}$ and $-229.4\ \mathrm{bohr^3\,mol^{-1}}$ for **TSa** and **TSc**, respectively) as well as the relatively high computed activation energies are in qualitative agreement with the requirement of high ethylene

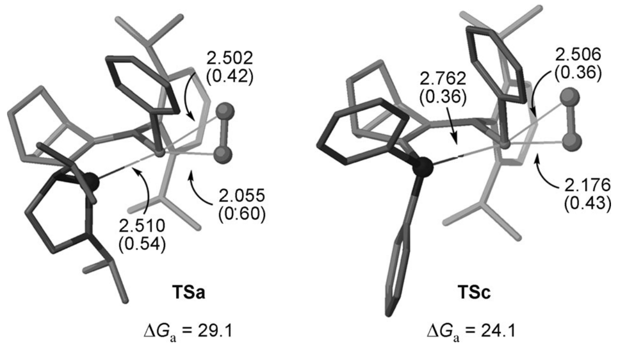


Figure 2. Fully optimized (M06(PCM)/6-31G*//BHandH(PCM)/6-31G* level of theory, THF solution) transition structures **TSa** and **TSc** leading to adducts **2a** and **2c**, respectively. Hydrogen atoms have been omitted for clarity. Activation Gibbs energies have been computed at 298 K and are given in kcal mol^{-1}. Bond lengths are given in Å. Numbers in parentheses correspond to the NBO bond indices.

pressures for the reaction to proceed according to a second-order rate law. An analysis of the f^-[24] values for the ethylene adducts **2a** and **2c** reveals the same trend for the respective phosphorus atoms (0.18 and 0.08e, respectively), indicating much less P→Si electron transfer in the case of **2c**. This is in turn connected with the observed irreversibility of the **1c**→**2c** process (vide supra).

In conclusion, we successfully demonstrated the reversible reaction of the stable phosphonium sila-ylides with ethylene at room temperature. Indeed, phosphine–silylene complexes **1**, featuring nucleophilic silylenoid character, react with ethylene under mild conditions to give the corresponding pentacoordinate siliranes **2**. The stability of the resulting pentacoordinate sila-cyclopropanes was found to be strongly related to the nucleophilic character of the phosphine ligand. Further studies on the application of this unique reversible reaction are underway.

Received: July 20, 2011

Keywords: cycloaddition · phosphorus · silicon · silylenes · ylides

---

[1] a) W. C. Zeise, *Overs. K. Dan. Vidensk. Selsk. Forh.* **1825**, 13; b) W. C. Zeise, *Poggendorff's Ann. Phys.* **1827**, *9*, 632; c) W. C. Zeise, *Poggendorff's Ann. Phys.* **1831**, *21*, 497; d) W. C. Zeise, *Poggendorff's Ann. Phys.* **1837**, *40*, 234.

[2] a) M. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *1*, 8; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939; c) J. Chatt, L. A. Duncanson, L. M. Venanzi, *J. Chem. Soc.* **1955**, 4456.

[3] Review: a) G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717; b) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410.

[4] a) S. D. Ittel, *Inorg. Chem.* **1977**, *16*, 2589; b) C. A. Tolman, *J. Am. Chem. Soc.* **1974**, *96*, 2780; c) T. Yamamoto, A. Yamamoto, S. Ikeda, *J. Am. Chem. Soc.* **1971**, *93*, 3360.

[5] M. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *1*, 8.

[6] P. P. Power, *Nature* **2010**, *463*, 171.

[7] a) D. W. Stephan, *Dalton Trans.* **2009**, 3129; b) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535.

[8] J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968.

[9] a) R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto, S. Nagase, *J. Am. Chem. Soc.* **2007**, *129*, 7766; b) J. S. Han, T. Sasamori, Y. Mizuhata, N. Tokitoh, *J. Am. Chem. Soc.* **2010**, *132*, 2546.

[10] Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science* **2009**, *325*, 1668.

[11] *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones, Jr.), Wiley, New York, **2004**.

[12] Thermal decomposition of siliranes: a) D. Seyferth, D. C. Annarelli, *J. Am. Chem. Soc.* **1975**, *97*, 7162; b) D. H. Pae, M. Xiao, M. Y. Chiang, P. P. Gaspard, *J. Am. Chem. Soc.* **1991**, *113*, 1281.

[13] R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1988**, *110*, 5208.

[14] a) J. Vignolle, X. Cattoën, D. Bourissou, *Chem. Rev.* **2009**, *109*, 3333; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

[15] a) M. Kira, S. Ishida, T. Iwamoto, A. de Meijere, M. Fujitsuka, O. Ito, *Angew. Chem.* **2004**, *116*, 4610; *Angew. Chem. Int. Ed.* **2004**, *43*, 4510; b) S. Ishida, T. Iwamoto, M. Kira, *Heteroat. Chem.* **2011**, *22*, 2011.

[16] D. Gau, T. Kato, N. Saffon-Merceron, F. P. Cossío, A. Baceiredo, *J. Am. Chem. Soc.* **2009**, *131*, 8762.

[17] D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, F. P. Cossío, A. Baceiredo, *Chem. Eur. J.* **2010**, *16*, 8255.

[18] For crystal data for **2a** and **2c** see the Supporting Information. CCDC 833279 (**2a**), 833280 (**2c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] a) G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas, D. Seyferth, *J. Am. Chem. Soc.* **1976**, *98*, 1779; b) M. Ishikawa, S. Matsuzawa, H. Sugisawa, F. Yano, S. Kamitori, T. Higuchi, *J. Am. Chem. Soc.* **1985**, *107*, 7706; c) W. Ando, M. Fujita, H. Yoshida, A. Sekiguchi, *J. Am. Chem. Soc.* **1988**, *110*, 3310; d) H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11572; e) E. Kroke, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Organometallics* **1995**, *14*, 5695; f) W. Ando, T. Shiba, T. Hidaka, K. Morihashi, O. Kikuchi, *J. Am. Chem. Soc.* **1997**, *119*, 3629; g) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830.

[20] a) K. Tamao, K. Nagata, M. Asahara, A. Kawachi, Y. Ito, M. Shiros, *J. Am. Chem. Soc.* **1995**, *117*, 11592; b) A. Toshimitsu, T. Saeki, K. Tamao, *J. Am. Chem. Soc.* **1991**, *113*, 9210; c) A. Toshimitsu, S. Hirao, T. Saeki, M. Asahara, K. Tamao, *Heteroat. Chem.* **2001**, *12*, 392.

[21] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.

[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372.

[23] R. Cammi, B. Mennucci, J. Tomasi, *J. Phys. Chem. A* **2000**, *104*, 5631.

[24] This function is associated with a nucleophilic attack and has been computed using NBO charges and taking orbital relaxation into account: “The Fukui Function”: P. W. Ayers, W. Yang, L. J. Bartolotti in *Chemical Reactivity Theory: A Density Functional View* (Ed.: Chattaraj), P. Taylor & Francis, Boca Raton, **2009**, pp. 255–267, and references therein.