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Silicon−Hydrogen Bond Activation and Hydrosilylation of Alkenes Mediated by CpCo Complexes: A Theoretical Study

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Abstract: Using DFT techniques, we show that triplet cyclopentadienylcobalt activates Si−H bonds to generate singlet silylcobalt hydrides without the intervention of σ-silanes. The cobalt is configurationally unstable, as evidenced by the diastereoisomerization of derivatives bearing chiral silyl ligands. Inversion at the metal proceeds in the singlet state via a bridging hydride. We demonstrate that a two-state mechanism for the transformation of silyl hydride cobalt complexes into disilyl dihydride cobalt species is feasible. Our calculations predict that catalytic hydrosilylation of alkenes should be achievable in the coordination sphere of cyclopentadienylcobalt.

Introduction

Hydrosilylation of alkynes, ketones, and especially alkenes is a fundamental catalytic reaction for the formation of industrially important organosilicon compounds.[1] Oxidative addition of hydrosilanes to transition metal complexes is the key mechanistic step of these transformations. For instance, alkene hydrosilylation may follow the Chalk−Harrod mechanism (Fe, Co, Rh, Ir, Pd, Pt, etc.)[2,3] in which, initially, a silyl hydride complex is formed by Si−H activation (Scheme 1).[4] This entity then coordinates the alkene and subsequently inserts into the M−H (typical Chalk−Harrod mechanism) or M−Si bond (modified Chalk−Harrod mechanism).[3,5,6] The reaction product is finally obtained after reductive elimination. Alternatively, the oxidative addition of hydrosilanes to metals may lead to silene hydride complexes. These species also catalyze hydrosilylation

Scheme 1. Typical Mechanistic Rationale for Metal-Catalyzed Hydrosilylation of Alkenes
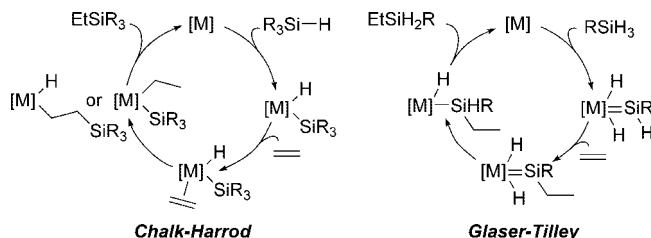
of alkenes according to the Glaser−Tilley mechanism (Ru).[7,8] Formally, the alkene undergoes direct addition to the Si−H bond of the silene moiety; reductive metal-to-silicon hydride transfer then occurs, followed by reductive elimination of a dialkylsilane.

An alternative mechanism has been proposed by Seitz and Wrighton for the hydrosilylation of alkenes catalyzed by silylcobalt carbonyls (Scheme 2).[9] The main features of the catalytic cycle are the oxidative addition of silane after the silylation of the alkene by the catalyst and C−H reductive elimination of the final product. This two-silicon cycle avoids the quite uncommon Si−C reductive elimination of the typical Chalk−Harrod mechanism. Duckett and Perutz described a similar mechanism for the hydrosilylation of alkenes catalyzed by (η^5-cyclopentadienyl)rhodium complexes.[10] A two-silicon cycle was also reported by Brookhart and co-workers for the palladium(II)-catalyzed hydrosilylation of alkenes.[11]

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(1) (a) Ojima, I. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds; John Wiley & Sons: Chichester, U.K., 1989; p 1479. (b) Ojima, I.; Zhu, Z. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds; John Wiley & Sons: Chichester, U.K., 1998; Vol. 2, p 1687. (c) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds; Elsevier: Oxford, U.K., 1991; Vol. 8, p 763. (d) Ball, Z. T. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M., Eds; Elsevier: Oxford, U.K., 2007; Vol. 10, p 789. (e) Hayashi, T. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M., Eds; Elsevier: Oxford, U.K., 2007; Vol. 10, p 815.
(2) (a) Chalk, A.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Magistrato, A.; Woo, T. K.; Togni, A.; Rothlisberger, U. *Organometallics* **2004**, *23*, 3218.
(3) Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510.
(4) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.
(5) Sakaki, S.; Sumimoto, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* **2002**, *21*, 3788.
(6) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128.

(7) (a) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640. (b) Brunner, U. *Angew. Chem., Int. Ed.* **2004**, *43*, 2749. (d) Beddie, C.; Hall, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 13564. (e) Beddie, C.; Hall, M. B. *J. Phys. Chem. A* **2006**, *110*, 1416.
(8) Böhme, U. *J. Organomet. Chem.* **2006**, *691*, 4400.
(9) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289.
(10) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90.

Scheme 2. Two-Silicon Cycles for Hydrosilylation of Alkenes with Silylcobalt Tetracarbonyls and (η^5-Cyclopentadienyl)rhodium Complexes, Respectively

Seitz-Wrighton   *Duckett-Perutz*
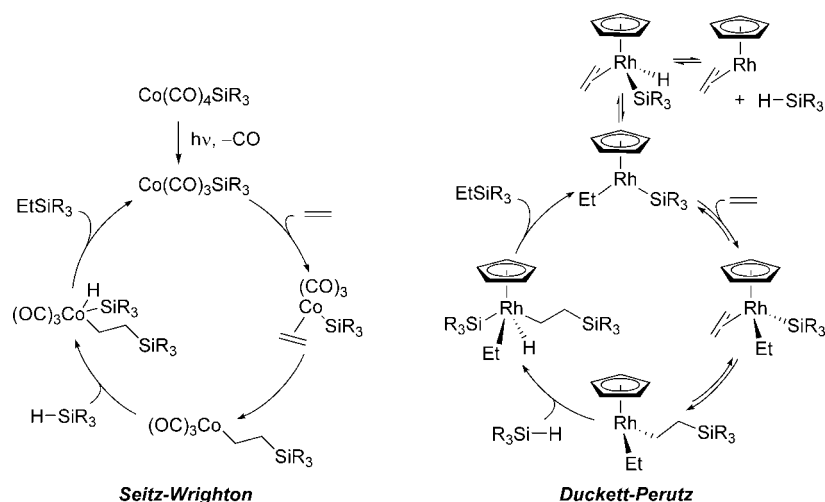
Scheme 3. Reaction of CpCo^I Complexes with Silanes (Selected Examples)
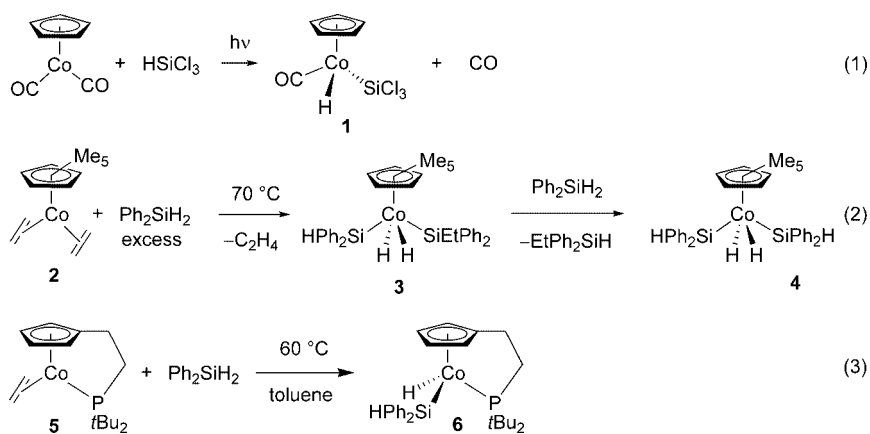
Turning to (η^5-cyclopentadienyl)cobalt complexes, silyl (but not silene) hydride species have been obtained in stoichiometric reactions of organosilanes with compounds of type CpCoL$_2$ (Cp = η^5-cyclopentadienyl), and they can be hydrosilylation catalysts (Scheme 3). To the best of our knowledge, the first transformation of this kind was reported by Jetz and Graham in 1969.[12] Stable **1** was formed upon irradiation of CpCo(CO)$_2$ in the presence of trichlorosilane (eq 1). In 1978, Wakatsuki and Yamazaki showed that the reaction of Cpcobaltacyclopentadiene(phosphine) complexes with triethylsilane at 70 °C led to dienylsilanes.[13] In 1997, Ko and co-workers achieved a double silylation of CpCo(C$_2$H$_4$)$_2$ with o-bis(dimethylsilyl)benzene at room temperature.[14] In 2000, Brookhart prepared disilylcobalt dihydrides (e.g., **3** and **4**) using, for instance, [(C$_5$Me$_5$)Co-

(C$_2$H$_4$)$_2$] (**2**) and diphenylsilane according to eq 2.[15] At 70 °C, 2 equiv of Ph$_2$SiH$_2$ displaced one of the ethene ligands, while the other emerged hydrosilylated, as in **3**, which was generated admixed with equimolar amounts of **4**. It was shown that **3** was a precursor to the symmetrical piano-stool array **4**, which was characterized by X-ray diffraction.[15] Complex **6**, the structure of which was also determined, was obtained by Butenschön by the addition of hydrosilanes to the pendant phosphane system **5** at 60 °C (eq 3).[16] Such silyl hydride CpCo^{III} derivatives have been used recently as catalysts for hydrosilylation of alkynes.[17]

For all of these transformations, it was postulated that the 18-electron starting material dissociates to give the corresponding 16-electron species after CO or ethene loss. Oxidative addition then occurs to furnish a saturated Co^{III} complex as in Scheme 3, eqs 1 and 3. The case of the dihydrodisilylation of **2** is more complicated (Scheme 4): After formation of the first silyl hydride **8**, insertion of ethene may occur into the Co−H bond, as in the Chalk−Harrod mechanism (vide supra), or into the Co−Si bond, as in the modified Chalk−Harrod mechanism. Brookhart suggested that the resulting species **9** or **10** might

(11) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

(12) Jetz, W.; Graham, A. G. *J. Am. Chem. Soc.* **1969**, *91*, 3375.

(13) (a) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *149*, 385. This paper also describes related S−H, N−H, and C−H activations. See: (b) Aubert, C.; Betschmann, P.; Eichberg, M. J.; Gandon, V.; Geny, A.; Heckrodt, T. J.; Lehmann, J.; Malacria, M.; Masjost, B.; Paredes, E.; Vollhardt, K. P. C.; Whitener, G. D. *Chem.−Eur. J.* **2007**, *13*, 7443. (c) Aubert, C.; Gandon, V.; Geny, A.; Heckrodt, T. J.; Malacria, M.; Paredes, E.; Vollhardt, K. P. C. *Chem.−Eur. J.* **2007**, *13*, 7466. (d) Gandon, V.; Aubert, C.; Malacria, M.; Vollhardt, K. P. C. *Chem. Commun.* **2008**, 1599.

(14) Kang, Y.; Kim, K.-i.; Kang, S.-O.; Ko, J.; Heaton, B. T.; Barkley, J. V. *J. Organomet. Chem.* **1997**, *532*, 79.

(15) Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676.

(16) Yong, L.; Hofer, E.; Wartchow, R.; Butenschön, H. *Organometallics* **2003**, *22*, 5463.

(17) Yong, L.; Kirleis, K.; Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833.

Scheme 4. Postulated Mechanism for the Formation of Disilyl Dihydride CpCo Complexes
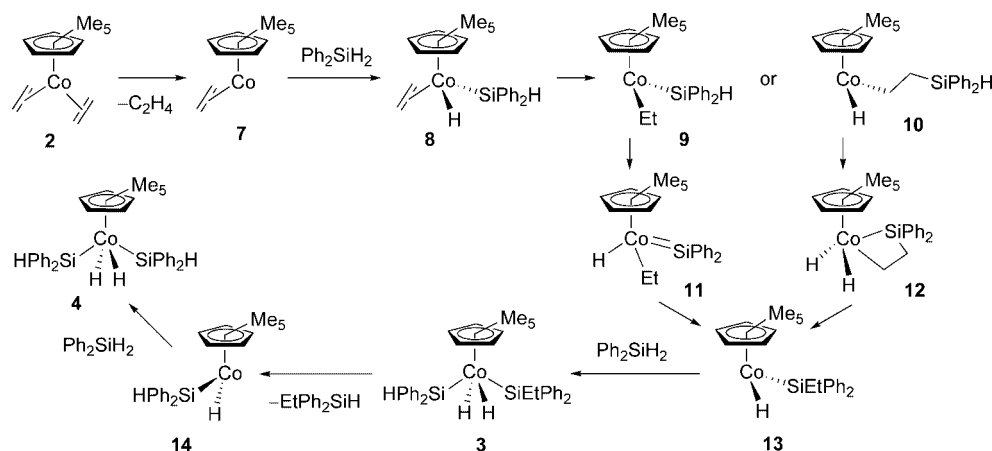
Scheme 5. Reaction of Silanes with CpCo(C₂H₄)₂

Scheme 6. Mechanism of Diastereoisomerization of **16** and **17**
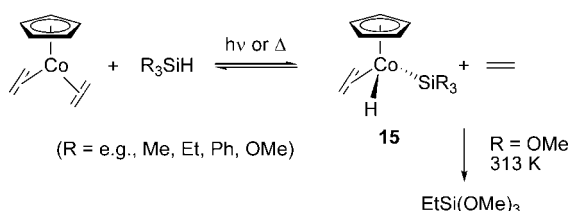
evolve via α-elimination to give the silene hydride **11** or via Si−H insertion and formation of the four-membered ring species **12**, respectively.[15] Reductive elimination through ethyl−silene coupling for **11**, or γ-H addition for **12**, would then lead to the same unsaturated silyl hydride **13**. Subsequent oxidative addition of diphenylsilane is expected to generate the unsymmetrical piano-stool Co^V complex **3**. Finally, reductive elimination of diphenylethylsilane and subsequent recombination with diphenylsilane would furnish **4**.

Important mechanistic investigations shedding light on both the activation of the Si−H bond by CpCo, as well as on the reactivity of the resulting silyl hydrides toward alkene hydrosilylation, have been published.[18−20] Perutz and co-workers studied the photochemical and thermal reactions of CpCo(C₂H₄)₂ with silanes by ^{1}H NMR (Scheme 5).[20] Disilyl dihydride complexes were not detected. Instead, monosilyl hydrides **15** were formed in equilibrium concentrations which depended on the substituents at the silicon atom. These species reacted very rapidly with ethene to regenerate the starting material. In the case of HSi(OMe)₃, heating the four-component mixture to 313 K furnished ethyltrimethoxylsilane, pointing to [CpCo(Si(OMe)₃)-(H)(C₂H₄)] **15** (R = OMe) as the likely catalyst for the hydrosilylation of ethene with trimethoxysilane.

The molecular dynamics of species **15** are intriguing, as the stereogenic Co center appears to be unstable configurationally. This is indicated by the facile diastereoisomerization of compounds of type **6** and **15** bearing chiral silyl groups.[16,20] For example, the silylcobalt hydrides obtained from CpCo(C₂H₄)₂ and ClMePhSiH (**16** and **17**, Scheme 6) interconvert with a free
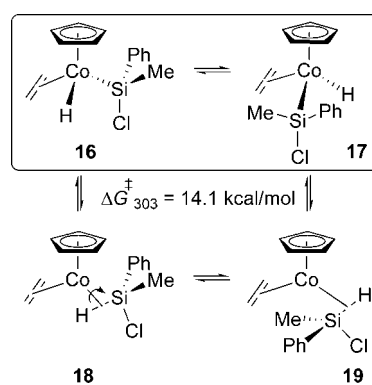
energy of activation of ∼14 kcal/mol.[20] As a mechanism of this inversion, Perutz suggested, as one of the possibilities, reductive elimination to the η^2-silane σ-complexes **18** and **19**, respectively, rotation around the coordinated Si−H bond, and oxidative addition to the other respective diastereomer.[20,21]

Using ultrafast UV pump/IR probe techniques and theoretical calculations, Harris and co-workers found interesting features of the reaction of CpCo(CO)₂ with triethylsilane (Scheme 7, eq 4).[19] On irradiation, 18-electron diamagnetic CpCo(CO)₂ loses CO to give rise to paramagnetic triplet [CpCo(CO)] (**20**). When generated in heptane, this molecule is stable and, as expected for a triplet cobalt species, does not coordinate to solvent. On the other hand, when generated in triethylsilane, it undergoes oxidative addition to the Si−H bond to give the corresponding diamagnetic silyl hydride **21** at a nearly diffusion-controlled rate. Although this transformation requires a spin change, it is even faster than the corresponding singlet-state reaction of CpRh(CO) (**22**) with Et₃SiH (Scheme 7, eq 5). Because **22** displays a singlet ground state, it forms stable solvates, such as **23**, with the alkyl chain of the silane. This association contributes to the diminution of the rate of addition to the Si−H bond, compared to the cobalt analogue. Thus, 16-electron d^8 CpCoL species have a certain advantage compared to CpRhL (and also CpIrL) fragments: due to their high-spin triplet ground state, they do not efficiently bind (and ultimately activate)[22] the C−H bond of alkanes[23] and thus can react selectively with Si−H bonds and rapidly so, despite the so-called spin forbidden nature of this transformation.

(18) (a) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (b) Doherty, M. D.; Grant, B.; White, P. S.; Brookhart, M. *Organometallics* **2007**, *26*, 5950.

(19) Snee, P. T.; Payne, C. K.; Kotz, K. T.; Yang, H.; Harris, C. B. *J. Am. Chem. Soc.* **2001**, *123*, 2255.

(20) Ampt, K. A. M.; Duckett, S. B.; Perutz, R. N. *Dalton Trans.* **2007**, 2993.

(21) Ampt, K. A. M.; Duckett, S. B.; Perutz, R. N. *Dalton Trans.* **2004**, 3331.

Scheme 7. Reaction of Silanes with CpCo(CO)$_2$ and CpRh(CO)$_2$
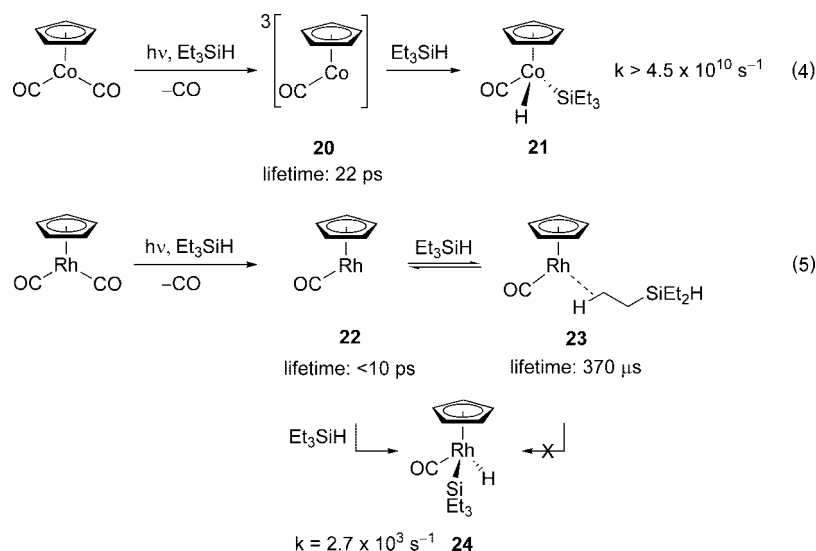
Harris located a geometry at which triplet/singlet crossover for the reaction of triplet [CpCo(CO)] with methylsilane to give singlet [CpCo(SiH$_2$Me)(H)(CO)] might occur at an energy that was only 0.73 kcal/mol above that of the reactants. This case is not isolated, and other fast reactions of triplet cobalt species that end in singlet products have been described[24] and studied computationally.[23]

Reactions that require a spin change are likely to occur when the singlet and triplet surfaces are close to each other or cross (two-state mechanism).[25] Semiquantitative information can be gleaned by determination of the enthalpy of a crossing point at which the two spin states differ minimally in structure and energy (MECP).[23,26,27] While finding such a point is not sufficient for the evaluation of the probability of surface hopping,[28] it presents enthalpic data that can be used to explain the outcome of kinetic studies.[23] This technique has proven useful in the rationalization of the mechanism of important cobalt-catalyzed or -mediated reactions, such as the cyclotrimerization of alkynes,[29] the cocyclization of alkynes with alkenes,[30] and the cycloaddition of alkynes and alkenes to benzosilacyclobutenes.[31]

The aim of this study is to shed further light on how high spin [CpCo(C$_2$H$_4$)] species[30,32] can activate hydrosilanes to generate silylcobalt hydrides and how such complexes behave in the presence of alkenes to produce eventually hydrosilylation products. We will focus on the results described by Perutz and Brookhart, first for the calibration of the chosen computational methods.[15,20] We will then address the specifics of the reported complexes: Possible structures, in particular silyl hydride Co^{III} versus Co^I η^2-silane σ-complexes, and the mechanism of their stereomutation. We will also study the reactivity of these compounds and try to find a pathway for the formation of the piano-stool disilyl dihydrides described in Scheme 3, eq 2.[15] Finally, we will show that a catalytic cycle of hydrosilylation of ethene can be completed obviating the formation of disilyl dihydride cobalt complexes and that such a cycle is also feasible for trialkylsilanes.

Computational Methods

Except for the calibration of the computing methodology used herein (vide infra), to save computer time, the C$_5$Me$_5$ ligand was replaced by η^5-C$_5$H$_5$. However, some of the results were reproduced with C$_5$Me$_5$ to verify that the replacement of the methyl groups by hydrogen atoms did not affect the conclusions reached. Similarly, diphenylsilane was replaced by dimethylsilane, and again, occasional checks proved this change to be qualitatively inconsequential. All geometries of intermediates and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.[33] The DFT computations were carried out using the B3LYP or the BP86 functional as implemented in Gaussian and using the LACVP(d,p) basis set: The cobalt atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),[34] and the 6−31G(d,p) basis set[35] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate computations (IRC). The minimum energy crossing points (MECPs) were optimized using the code developed by Harvey and co-workers.[36] The vibrational

(22) For exeptions, see: Bolig, A. D.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 14544.

(23) Carreón-Macedo, J.-L.; Harvey, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 5789.

(24) (a) Wasserman, E. P.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1988**, *110*, 6076. (b) Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745.

(25) For selected reviews of the theoretical treatment of spin-forbidden reactions, see: (a) Harvey, J. N. *Phys. Chem. Chem. Phys.* **2007**, *9*, 331. (b) Carpenter, B. K. *Chem. Soc. Rev.* **2006**, *35*, 736. (c) Poli, R.; Harvey, J. N. *Chem. Soc. Rev.* **2003**, *32*, 1. (d) Schwarz, H. *Int. J. Mass. Spectrom.* **2004**, *237*, 75.

(26) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487.

(27) (a) Su, M.-D.; Chu, S.-Y. *Chem.—Eur. J.* **1999**, *5*, 198. (b) Smith, K. M.; Poli, R.; Harvey, J. N. *Chem.—Eur. J.* **2001**, *7*, 1679. (c) Petit, A.; Richard, P.; Cacelli, I.; Poli, R. *Chem.—Eur. J.* **2006**, *12*, 813. (d) Yarkony, D. R. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 642. (e) Yarkony, D. R. *J. Phys. Chem.* **1996**, *100*, 18612.

(28) Mercero, J. M.; Matxain, J. M.; Lopez, X.; York, D. M.; Largo, A.; Eriksson, L. A.; Ugalde, J. M. *Int. J. Mass. Spectrom.* **2005**, *240*, 37.

(29) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860.

(30) Gandon, V.; Agenet, N.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2006**, *128*, 8509.

(31) Agenet, N.; Mirebeau, J.-H.; Petit, M.; Thouvenot, R.; Gandon, V.; Malacria, M.; Aubert, C. *Organometallics* **2007**, *26*, 819.

(32) Poli, R.; Smith, K. M. *Eur. J. Inorg. Chem.* **1999**, 877.

(33) Frisch, R. B. et al. *Gaussian 03*, v D02; Gaussian, Inc.: Wallingford, CT, 2004.

(34) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

analyses at these points were executed within the $(3N-7)$-dimensional hypersurface of the seam of crossing.[37] The spin−spin coupling constants $J(^1H-^{29}Si)$ for the complexes under study were calculated by the gauge-including atomic orbitals (GIAO) approach.[38] The completely decontracted IGLO-III basis set[39] was used according to the method described recently for silylrhodium hydride complexes.[40] Owing to the known discrepancy between calculated and experimental dissociation energies of cobalt complexes at the B3LYP/LACVP level,[23,32] single-point calculations were carried out using the 6−311+G(2d,2p) basis set,[32] and solvent effects (single points with benzene as solvent) were taken into account using the PCM approach. Despite these precautions, some results still proved unreliable (vide infra). Therefore, we also used the BP86 functional, which had been shown to be more accurate than B3LYP in one case related to our study.[23] Very good agreement with experimental data were obtained at the BP86/LACVP(d,p) level (including zero-point correction), without more sophistication.[41] The calculated structures were drawn with the Chemcraft program.[42]

Results and Discussion

Calibration of the Computing Methods. In a previous study, the LACVP(d,p) level of theory had given very good geometrical agreement with the X-ray structure of a cobaltasilacyclopentene;[31] hence this method was chosen for the present work. Indeed, we obtained a reasonable accordance between the computed geometry and the reported structural data of the disilyl dihydride **4** (Table 1),[15] even better than that obtained with LACVP(d).[15]

The energy required for the dissociation of $CpCo(C_2H_4)_2$ to $[CpCo(C_2H_4)]$ (**25**) and C_2H_4 can be estimated by comparing the energy difference between these components, **25** being optimized in its triplet ground state (Scheme 8).[30,32] A value of 5.5 kcal/mol was obtained with the B3LYP methodology (including single points at the 6−311G+(2d,2p) level and PCM corrections).[43] This number appears excessively small considering that $CpCo(C_2H_4)_2$ can be sublimed at ∼300 K under vacuum, suggesting a value of 20 kcal/mol or more.[44] Indeed, at the BP86 level, it computes to 21.7 kcal/mol after zero-point correction (24.9 kcal/mol without zero-point correction).[45] To further validate this approach, we calculated the dissociation energy of $CpCo(CO)_2 \rightarrow {}^3[CpCo(CO)] + CO$ for which an experimental value of 44 ± 1 kcal/mol is available.[46] Whereas the B3LYP methodology gave a corresponding value of 27.5 kcal/mol, BP86 revealed 44.2 kcal/mol (47.3 kcal/mol without zero-

Table 1. Comparison of Interatomic Distances (Å) and Bond Angles (deg) in **4**
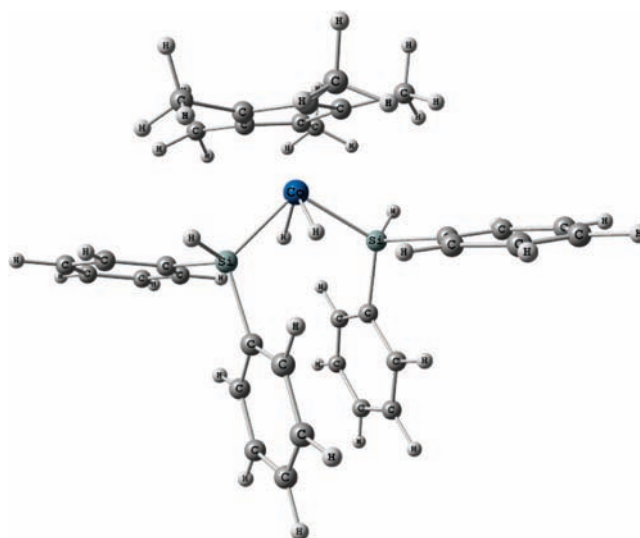
|	X-ray[a]	B3LYP/ LACVP(d)[a]	B3LYP/ LACVP(d,p)	BP86/ LACVP(d,p)
Co−Si	2.256−2.261[b]	2.29	2.28	2.28
	2.243−2.247[b]	2.28	2.28	2.28
Co−H	−[c]	1.49	1.47	1.48
Si−C	1.880−1.922[b]	1.90	1.90	1.91
H1−Co−H2	−[c]	100	97.2	100.0
Si1−Co−Si2	107.2[b]	109	107.9	108.0

[a] Reference 15. [b] Averaged over four molecules in the unit cell. [c] The positions of the hydride atoms were not determined in the X-ray analysis.

point correction). Therefore, the following discussion of geometries and energies rests on results obtained with BP86. Nevertheless, B3LYP values will be reported for comparison (see Supporting Information).

Formation of the Silylcobalt Hydrides. Structural and Conformational Analysis. The optimization of the triplet species **25** in the presence of dimethylsilane gave rise to the adduct **26** (Scheme 8), displaying a Co⋯H distance of 2.24 Å (normal Co−H bonds occur in the range 1.46−1.51 Å; see also Figure 2 in the Supporting Information).[47] The geometrical parameters of this species were found virtually unchanged compared to the component fragments. On the other hand, the Si−H bond of the Co⋯H−Si fragment is only slightly elongated compared to the computed Si−H bond distance in dimethylsilane (1.52 vs 1.50 Å). The energy of this adduct was found to lie 0.9 kcal/mol above the reactants.[48] Interestingly, its optimization in the singlet state led to the silyl hydride **27a**. We found a point of the two surfaces (**CP₁**) at an energy 3.8 kcal/mol above that of **26**, whose vibrational analysis proved fully consistent with a minimum energy crossing for the reaction of **25** with dimethylsilane to give **27a**. In **CP₁**, the Co−H distance is 1.78 Å, compared to 1.47 Å in **27a**. The Si−H and Co−Si bond lengths of 1.55 and 2.99 Å, respectively, in **CP₁** become 1.94 and 2.30 Å, respectively, in **27a**. Overall, this transformation is exothermic by 14.5 kcal/mol.[49] Several rotamers around the Co−Si

(35) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (e) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.
(36) Harvey, J. N.; Aschi, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5555.
(37) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95.
(38) Ditchfield, R. *J. Chem. Phys.* **1976**, *65*, 3123.
(39) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principle and Progress*; Dielh, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer: Berlin, 1990; Vol. 23, p 165.
(40) Vyboishchikov, S. F.; Nikonov, G. I. *Organometallics* **2007**, *26*, 4160.
(41) We thank a referee for this useful suggestion.
(42) http://www.chemcraftprog.com.
(43) A value of 3.6 kcal/mol was reported previously; see ref 32.
(44) We thank the referees for emphasizing the importance of this discrepancy.
(45) Energy differences between spin states are critically dependent on the nature of the functional used. For a discussion of the effect of exact exchange on spin-state splittings, see: (a) Harvey, J. N. *Struct. Bonding (Berlin)* **2004**, *112*, 151. (b) Salomon, O.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2002**, *117*, 4729.
(46) Sztaray, B.; Szepes, L.; Baer, T. *J. Phys. Chem. A* **2003**, *107*, 9486.

(47) For an example of an η^1-silane iridium complex, see: (a) Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141.
(48) The computed slightly higher enrgy of **26** relative to the the respective fragments may due to the difference in the basis sets used [6−31G(d,p) vs LANL2DZ].

Scheme 8. Two-State Formation of the Silyl Hydride **27a**[a]
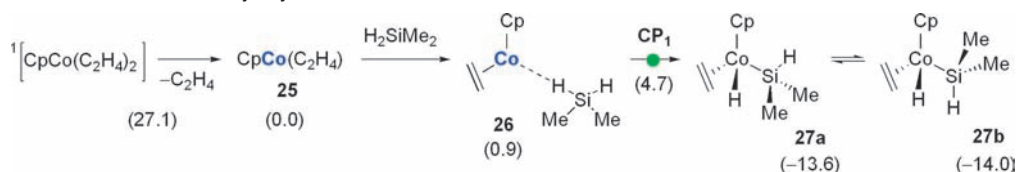
[a] Energies in kcal/mol relative to **25** and dimethylsilane; the triplet Co is depicted in blue, and the crossing point in green.

Scheme 9. Inversion of Configuration at Co in Complexes **16** and **17**[a]
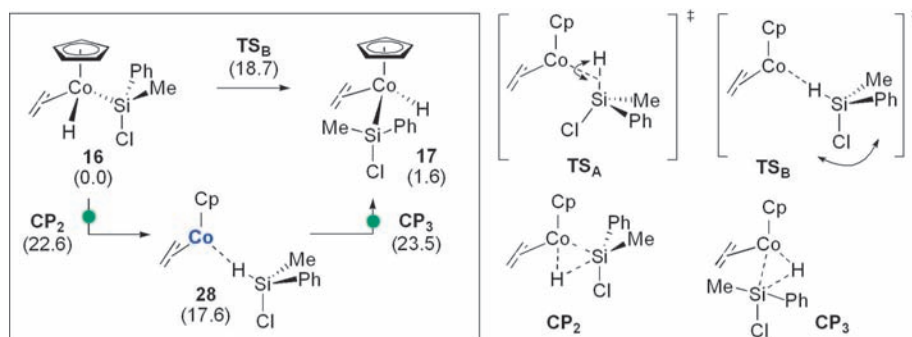
[a] Energies in kcal/mol relative to **16**.

bond can be modeled for **27**. The most stable one, **27b**, is staggered and has the Si–H bond pointing in the opposite direction as the Cp ligand [ΔE (relative to **27a**) = −0.4 kcal/mol]. While its computed relative stabilization is modest, it is in accord with the observation of NOE effects in [CpCo(SiHEt$_2$)(H)(C$_2$H$_4$)] pointing to the presence of a conformer analogous to **27b** in solution.[20,50]

We next studied the inversion of configuration in complexes **16** and **17** (Scheme 9). In principle, this inversion could occur in the singlet manifold via an η^2-silane transition state (**TS$_A$**), corresponding to a Si⋯H compression of the type discussed above, with concomitant rotation that aligns the Si–H vector perpendicular to the ethene bond, thus rendering the Co center achiral. Further rotation and Si⋯H decompression would then provide the other diastereomer (inversion at Co). All attempts to find such a TS failed. On the other hand, we could locate an alternative, namely a solvate-like **TS$_B$**, in which the only link to the silyl ligand is via a Co⋯H interaction. This species again features an achiral Co environment and leads to the other diastereomer. In **TS$_B$**, the Co⋯H distance (1.60 Å) and the Si–H separation (1.54 Å) are relatively large. The free energy associated with this transformation ($\Delta G^{\ddagger}$) was calculated to be 17.6 kcal/mol at 298 K and 17.4 kcal/mol at 303 K ($\Delta E^{\ddagger} =$ 18.7 kcal/mol). The latter value is in reasonable agreement with experiment (14.1 kcal/mol).[20] Alternatively, the stereomutation of **16** and **17** could proceed on the two spin surfaces via **28**, an analogue of **TS$_B$**, but now a minimum with triplet Co. Starting from **16**, it requires 22.6 kcal/mol to reach **CP$_2$**, whereas, starting from **17**, 21.9 kcal/mol are needed to reach **CP$_3$**. Thus, the singlet course for the interconversion seems favored.

To summarize this section, we have shown that it is triplet cobalt that activates Si–H bonds to generate eventually singlet silylcobalt hydrides without the intervention of σ-silanes. These

compounds are quite deformable, blurring their operational distinction as Co^{III} silyl hydride or Co^{I} η^2-silane σ-complexes. The cobalt is configurationally unstable, as evidenced by the diastereoisomerization of derivatives bearing chiral silyl ligands. Inversion at the metal proceeds in the singlet state via a bridging hydride **TS$_B$**. We will now show how such species further transform in the presence of an excess of silane or alkene.

Reactivity of the Cobalt Silyl Hydride Complexes. We studied next the reactivity of the silylhydride **27a**. Our calculations indicate that this species prefers insertion of the ethene ligand into the Co–H (Chalk–Harrod mechanism) rather than the Co–Si bond (modified Chalk–Harrod mechanism). The required energy of activation for the latter was 22.5 kcal/mol (Scheme 10, **TS$_D$**), whereas only 6.0 kcal/mol suffice for the former (**TS$_C$**).[51] The step to the product ethyl(silyl)cobalt complex **30** is endothermic ($\Delta E = 5.0$ kcal/mol). The ethyl group displays a β-H agostic interaction, as shown by the very long β-C–H distance of 1.24 Å. Consequently, the Cp$_{centroid}$, the Si, Co, and internal ethyl carbon are not coplanar but define a dihedral angle of −143.6°. The small Co–C$_\alpha$–C$_\beta$ angle of 73.8° of the cobalt-ethyl fragment compares well with the corresponding geometrical data obtained by X-ray analyses of related phosphine-stabilized β-agostic structures [see ref 18b: 74.4(5)° and 75.16(19)°]. Two options are now possible for that complex. The first is α-H-elimination to give the corresponding silene followed by ethyl migration.[52] Computational generation of a cobalt silene (**31**, Co–Si 2.10 Å) requires 14.0 kcal/mol and is endothermic by 6.7 kcal/mol. However, we were not able to connect this species with a singlet cobalt hydride.[53] Thus, this pathway seems to be a dead-end on the potential energy surfaces.[54] Alternatively, **30** might transform into its triplet analogue **32**. We therefore turned to the possibility of triplet **32** as a viable intermediate on route to hydrosilylation products.

(49) With the B3LYP functional, this transformation is endothermic by 2.6 kcal/mol, which is at odds with experiment (ref 20). We thank the referees for stressing this point.
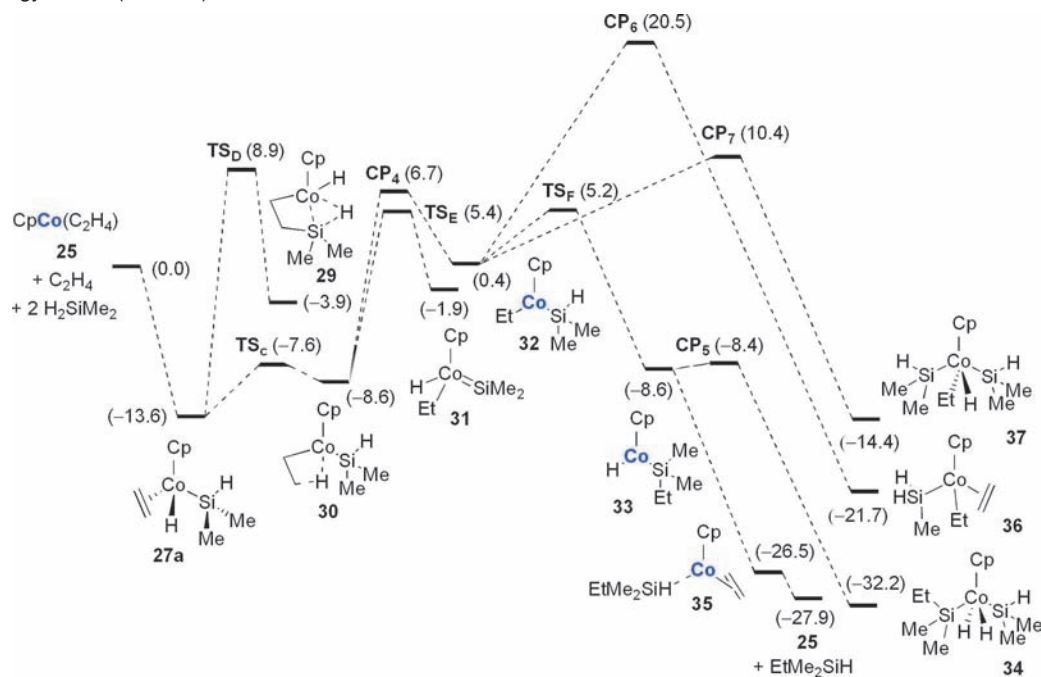
(50) The apparent discrepancy between solution and gas phase (calculated) values for the $^2J_{Si-H}$ coupling constants is discussed in the Supporting Information (Figure 1).

(51) This finding makes it unlikely that intermediates **10** and its successor **12** proposed in Scheme 4 are viable alternatives to options **9** and, hence, **11**.

(52) Corresponding to the conversion of **9** into **13** via **11** in Scheme 4.

(53) Equivalent to postulated **13** in Scheme 4.

(54) Rendering unlikely the occurrence of **11** in Scheme 4.

Scheme 10. Energy Profile (kcal/mol) for Various Transformations of **27a**[a]

Values and structures from the scheme:

CP₆ (20.5), TS_D (8.9), CP₄ (6.7), CP₇ (10.4), TS_E (5.4), TS_F (5.2), CpCo(C₂H₄) **25** + C₂H₄ + 2 H₂SiMe₂ (0.0), **29** (−3.9), (0.4) **32**, CP₅ (−8.4), TS_C (−7.6), (−8.6) **30**, **31** (−1.9), **33** (−8.6), **37** (−14.4), **36** (−21.7), **27a** (−13.6), (−26.5) **35**, **34** (−32.2), **25** + EtMe₂SiH (−27.9).

a Triplet species are depicted in blue.

This complex is less stable than its singlet counterpart by 9.0 kcal/mol, and its formation is achieved through the crossing point **CP₄**, located 15.3 kcal/mol above the singlet. As expected, its structure is very different from that of **30**, lacking the β-H agostic bond and exhibiting the coplanarity of the Cp_centroid and the Si, Co, and internal ethyl carbon (dihedral angle of −176.4°). Species **32** transforms readily into **33** via **TS_F** ($\Delta E^{\ddagger}$ = 4.8 kcal/mol). The formation of **33** is exothermic by 9.0 kcal/mol. A computational search did not reveal any other triplet transition states accessible to **32**. Along the intrinsic reaction coordinates toward **33**, one observes first the reductive elimination of dimethylethylsilane followed by oxidative addition to the Si−H bond.[55] We tried to model the reaction of **32** with the components of the reaction mixture, namely ethene or dimethylsilane, but there was no binding interaction. However, contact of **32** with ethene can promote a spin change to give **36** via **CP₆** lying 20.1 kcal/mol above **32** and ethene. This transformation is exothermic by 22.1 kcal/mol. Similarly, at an energetic cost of 10.0 kcal/mol and exothermic by 16.2 kcal/mol, **32** activates dimethylsilane to result in disilyl species **37** through **CP₇**. Overall, of all the alternatives depicted in Scheme 10 to transform **32**, the path via **TS_F** is the most favored.

In Brookhart's experiment (Scheme 3, eq 2), excess dihydrosilane was used, and the final product was a disilyl dihydride complex. We probed this sequence with **33** at its origin and Me₂SiH₂ as the (continuing) model substrate. We found a crossing point (**CP₅**) from the triplet to singlet surface as the silane approaches, located only 0.2 kcal/mol above **33**. The resulting piano-stool complex **34** displays the expected trans geometry. The distances between the silicon and the hydride atoms are in the range 2.14−2.26 Å. This complex[56] lies 32.2 kcal/mol below [CpCo(C₂H₄)] (**25**) and two molecules of dimethylsilane.

With respect to the potential establishment of a catalytic hydrosilylation cycle, it was of interest to study the behavior of **33** in the presence of excess ethene instead of dimethylsilane. Interestingly, in the triplet state, ethene adds in a barrierless fashion to **33** to yield the adduct **35**, 17.9 kcal/mol more stable than **33**, in which the silane is H-bonded to [CpCo(C₂H₄)] in its reactive triplet state. This sequence completes the cycle of a possible catalytic hydrosilylation (Scheme 11), finishing at the end point triplet **35**, from which EtMe₂SiH would dissociate to allow reentry of Me₂SiH₂ (to **26**). We surmise that such a process was not observed by Brookhart in Scheme 3, eq 2, because of the volatility of ethene (liberated from **2**) and the excess silane employed.

Cognizant of the fact that monohydridosilanes are the reagents of choice in catalytic hydrosilylations,[1] we turned to HSiMe₃ as a substrate in our computations, assuming that the lack of a second Si−H bond (and hence impossibility of **TS_F**) would lead to a sequence analogous to those going through **CP₆** or **CP₇**. Surprisingly, an alternative was found, as shown in Schemes 12 and 13. Here, the initial Si−H activation process is closely analogous to that described for H₂SiMe₂, the silyl hydride **39** being formed exothermically from **25** and trimethylsilane via **CP₈**. Next, ethene insertion leads to the (ethyl)silylcobalt complex **40** via **TS_G**, and its spin changes to triplet **41** through **CP₉**. However, unlike **32**, in which the presence of a Si−H bond facilitates isomerization to hydride **33**, intermediate **41** is capable of facile reductive elimination to **42**, requiring 5.5 kcal/mol. In **42**, triplet cobalt is bonded to two hydrogen atoms of one methyl group. The back-bonding of the metal to the σ* orbital of the C−H bonds is evidenced by the long distances of 1.14 and 1.15 Å (see Figure 2 in the Supporting Information). Finally, **42** reacts in a barrierless fashion with ethene to give EtSiMe₃ and to regenerate **25**, ready for the next catalytic cycle. This step is strongly exothermic by 30.1 kcal/mol. These results suggest that a CpCo(C₂H₄)₂-catalyzed hydrosilylation of alkenes with monosilanes should be experimentally attainable. The option of ethene induced spin change to give **43** is more

(55) This finding supports the intermediacy of **13** in Scheme 4, but in its triplet state.
(56) Complex **34** corresponds to **3** in Scheme 4. We suspect that the subsequent transformation of **3** into **4** is driven by steric relief.

Scheme 11. Proposed Catalytic Cycle for the Transformation of Ethene and H_2SiMe_2 and Side Reactions[a]
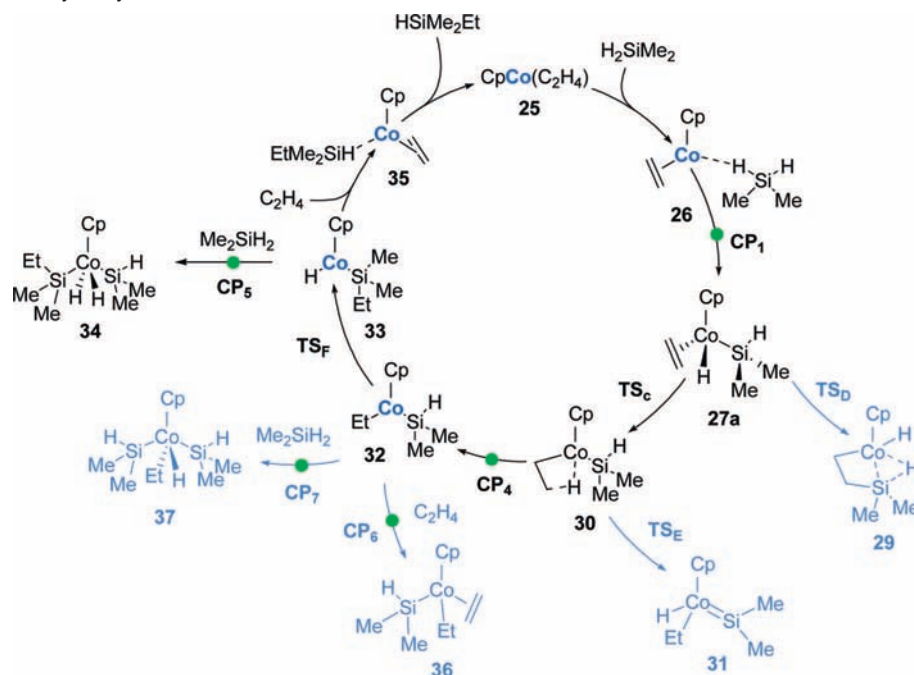
[a] Triplet Co is depicted in blue, crossing points are shown in green, and side reactions are in violet-blue.

Scheme 12. Energy Profile (kcal/mol) for the Transformations of **25** and Me_3SiH[a]
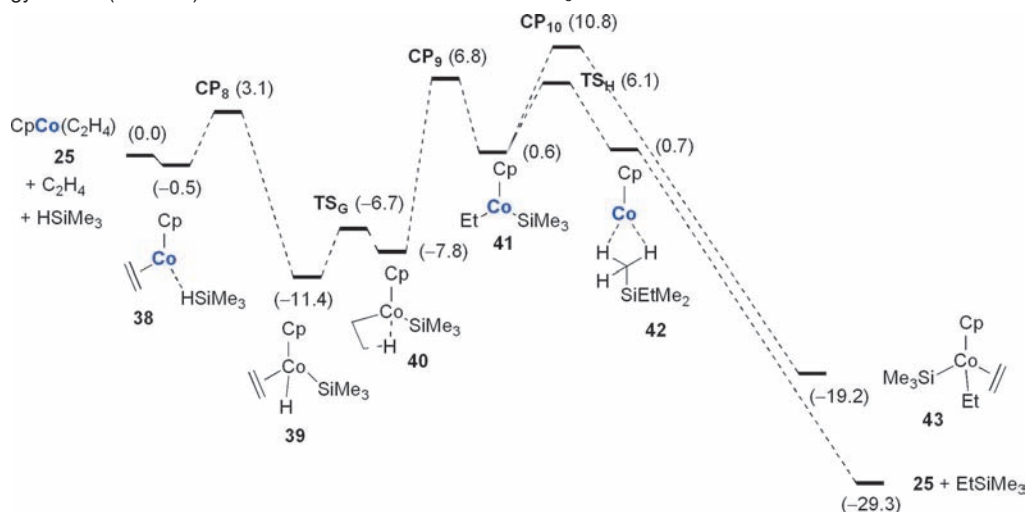
[a] Triplet species are depicted in blue.

difficult,[57] the energy required to reach **CP$_{10}$** being 10.2 kcal/mol. We also probed for the possibility of a spin change during the reaction of **41** with Me_3SiH.[58] However, we could not locate the corresponding MECP, access to which being possibly prohibited by the steric congestion around the metal center. This is also corroborated experimentally, as no disilyl dihydride complexes were observed when using monohydrido silanes.[20]

In this section, we have demonstrated the existence of a two-state mechanism for the transformation of monosilyl hydride into disilyl dihydride cobalt complexes. Similar to other important cobalt-catalyzed transformations,[29−31,59] it connects high- and low-spin species. The key step is the insertion of the

ethene ligand into the Co−H bond, as in the standard Chalk−Harrod mechanism. The resulting (ethyl)silylcobalt complex relaxes to its triplet state which results in the transfer of the alkyl group to silicon to give a silyl hydride complex **33**. In the presence of a second equivalent of silane, oxidative addition gives rise to the piano-stool complexes observed by Brookhart.[15] On the other hand, our calculations predict that, in the presence of an excess of ethene, complex **33** can reductively eliminate to regenerate the active species of a potential hydrosilylation catalytic cycle. In case a monohydridosilane is used, another hydrosilylation catalytic cycle, similar to the Chalk−Harrod mechanism described in Scheme 1, can take place, and the formation of disilyldihydride complexes becomes very difficult. These findings are substantiated by the experiments of Perutz.[20] The overall results are summarized in Scheme 14.

(57) Analogous to the conversion of **31** to **35** in Scheme 10.
(58) Analogous to the conversion of **31** to **36** in Scheme 10.
(59) Dahy, A. A.; Suresh, C. H.; Koga, N. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 792.

Scheme 13. Proposed Catalytic Cycle for the Transformation of Ethene and HSiMe₃[a]
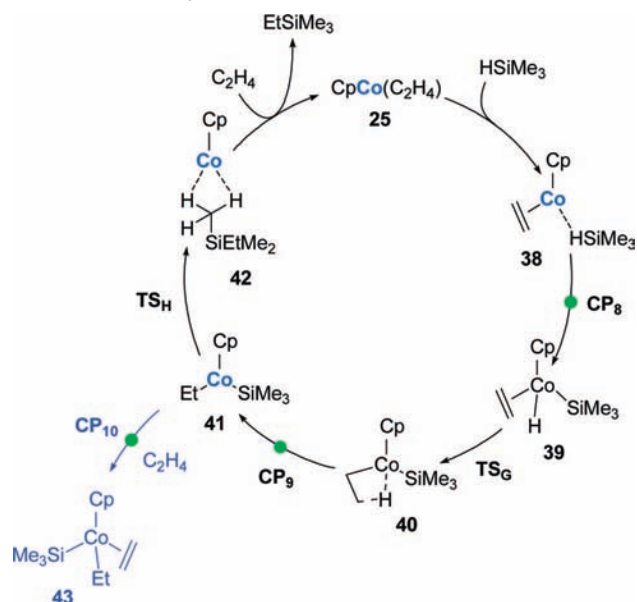
[a] Triplet Co is depicted in blue, crossing points are shown in green, and side reaction is in violet-blue.

Scheme 14. Simplified Overview of Catalytic Cycles for the Hydrosilylation of Ethene by Mono- and Dihydridosilane and of the Path to Disilyl Dihydride CpCo Complexes
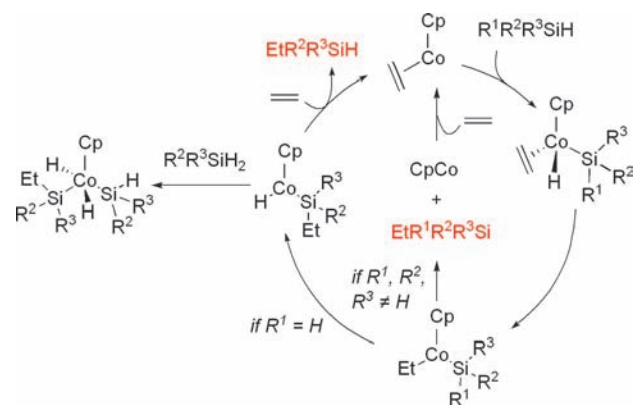
Conclusion

This study has clarified extensively the modes by which CpCo complexes activate Si−H bonds and transform in the presence of ethene. We have shown that triplet [CpCo(C₂H₄)] **25** reacts with silanes to give singlet silylcobalt hydrides **27** (Scheme 8)

that are configurationally unstable (Scheme 9). Perutz actually observed these species and studied their stereomutation.[20] Unexpectedly, our computations show that the interconversion proceeds in a concerted manner, without intervention of σ-silane complexes. The hydride ligand is then transferred to ethene, following a Chalk−Harrod type mechanism, rather than its modified version, to generate a new triplet ethyl silylcobalt(III) species **32** (Schemes 10 and 11) or **41** (Schemes 12 and 13). When the attached Si bears H (i.e., the starting silane is R₂SiH₂), a surprising rearrangement is observed: Complex **32** preferably transforms into a triplet cobalt hydride **33**, which adds ethene to give the hydrosilylation product. This step should be facilitated under high ethene concentration; thus our calculations are highly predictive of a successful cobalt-catalyzed hydrosilylation of alkenes. Alternatively, it may be attacked by another molecule of silane giving rise to a dihydro disilylcobalt complex **34**. This finding is supported by the experiments of Brookhart who isolated such compounds.[15] When the attached Si bears only alkyl groups (i.e., the starting silane is R₃SiH), the ethyl silylcobalt(III) species **41** reductively eliminates to give a tetraalkylsilane coordinated to CpCo (**42**). The reaction of this species with ethene regenerates the catalyst. These results are also corroborated by experimental results of Perutz,[20] who carried out an NMR experiment indicating that [(η⁵-C₅H₅)Co{Si(OMe)₃}(H)(C₂H₄)] may be a catalyst in the conversion of HSi(OMe)₃ and ethene to C₂H₅Si(OMe)₃, by observing the appearance of the signals of the product. Overall, our calculations have led to mechanistic proposals (Schemes 11 and 13) that constitute major revisions of previous postulates (Scheme 4). Among them perhaps most important is the exclusion of the intermediacy of cobalt silenes such as **11** during the formation of dihydro disilylcobalt complexes.

Supporting Information Available: Complete ref 33; computed potential energies; calculations of $^2J_{Si-H}$ coupling constants; structures and selected bond distances; coordinates of computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA809100T