reflections in the range $11 < \theta < 14°$. A summary of crystal and intensity collection data is given in Table V. A total of 2465 reflections (*hkl* and *hkl*) were recorded at a 2θ (Mo) maximum of 60° by procedures described elsewhere.[32] Data reduction was then performed.[33] Intensity standards, monitored every 2 h, showed no significant variation. From a ψ scan on four reflections having $\chi > 80°$, empirical absorption corrections[34] were made (μ = 9.8 cm^{-1}, T_{min} = 0.91, T_{max} = 1.00). Equivalent reflections (0*kl* and 0*kl*) were merged (R_{av} = 0.012).

Structure Solution and Refinement. The structure was solved by the heavy-atom method. The Ru atom was located. The full-matrix least-squares refinement and difference Fourier processes were achieved with the SHELX76 program[35] with 1722 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. Space group *C*2/*c* implies that the B atom is in a special position, the four F atoms being thus disordered. The structure was then refined in the noncentrosymmetric space group *Cc*. Correlations being greater than 0.9 between parameters of C atoms and the disorder of the BF_4 anion being always present, space group *C*2/*c* was then considered as the correct one. The four F atoms were assigned an occupancy factor of 0.5. The BF_4 anion was refined isotropically. Ru and C atoms were refined anisotropically. All H atoms were located on a difference Fourier map except that bonded to Ru atom; they were introduced in calculations in idealized positions (C-H = 0.97 Å) with the isotropic temperature factor *U* = 0.09 Å kept fixed.

The terminal Ru hydride, located on a difference Fourier map at a height of 0.65 e/Å^3, was refined isotropically. Its location is in agreement with molecular mechanic calculations.[36]

The atomic scattering factors used were those proposed by Cromer and Waber[37] with anomalous dispersion effects.[38] Scattering factors for the hydrogen atoms were taken from Stewart et al.[39]

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to R = 0.031 and R_w = 0.033 with $w = [\sigma^2(F_o) + (0.02F_o)^2]^{-1}$. The error in an observation of unit weight was S = 1.34 with 1722 observations and 98 variables. An analysis of variance showed no unusual trends. In the last cycle of refinement, the mean parameter shift was 0.03σ (maximum value being 0.41σ on *F* parameters). A final difference Fourier map showed a residual electron density of 0.3 e/Å.

All calculations were performed on a VAX-11/730 DEC computer.

The final fractional atomic coordinates are listed in Table VI. An ORTEP plot[40] of the $[RuH(C_8H_{11})_2]$ cation is shown in Figure 1.

Acknowledgment. We thank CNRS for support, Dr. Y. S. Huang for experimental assistance, and Dr. D. Neibecker for helpful discussions.

Supplementary Material Available: Tables listing atomic coordinates, thermal parameters, bond lengths and angles, and least-squares plane equations (5 pages); a table listing observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

[32] Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr.* **1977**, *B33*, 2639.

[33] Frenz, B. A. *SDP. Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1082.

[34] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[35] Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination. University of Cambridge England, 1976.

[36] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

[37] Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99-101.

[38] Cromer, D. T. Reference 37, Table 2.3.1, p 149.

[39] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[40] Johnson, C. K. ORTEP. Report ORNL-3794, 1965; Oak Ridge National Laboratory: Oak Ridge, TN.

Hydrosilylation of Phenylacetylene via an $Os(SiEt_3)(\eta^2\text{-}H_2)$ Intermediate Catalyzed by $OsHCl(CO)(P^iPr_3)_2$

M. A. Esteruelas, L. A. Oro,* and C. Valero

Departamento de Química Inorgânica, Instituto de Ciencia de Materiales de Aragôn, Universidad de Zaragoza—CSIC, 50009 Zaragoza, Spain

Received May 15, 1990

$OsHCl(CO)(P^iPr_3)_2$ is found to be a very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene. *trans*- and *cis*-PhHC=CH($SiEt_3$) are selectively obtained in high yields depending on the reaction conditions. Although the vinyl compound $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$ is the main species under hydrosilylation conditions, the catalytic reaction proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ according to the following set of reactions: $OsHCl(CO)(P^iPr_3)_2 + HSiEt_3 \rightarrow Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ and $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2 + PhC_2H \rightarrow OsHCl(CO)(P^iPr_3)_2$ + *trans* and *cis*-PhHC=CH($SiEt_3$) in which the reaction between $OsHCl(CO)(P^iPr_3)_2$ and triethylsilane is the rate-determining step.

Introduction

The addition of silanes to acetylenes is a reaction of considerable interest in connection with important industrial processes.[1] This reaction is catalyzed by several nickel,[2] palladium,[3] platinum,[4] cobalt,[2] rhodium,[5] iridium,[6] iron,[2] and ruthenium[7] complexes, but to the best of our knowledge, no osmium compounds have been reported

---

[1] Noels, A. F.; Hubert, A. J. In *Industrial Applications of Homogeneous Catalysis*; Mortreux, A., Petit, F., Eds.; D. Reidel Publishing Company: Boston, 1988; Chapter 3.1.3.

[2] Lappert, M. F.; Nile, T. A.; Takahashi, S. *J. Organomet. Chem.* **1974**, *72*, 425.

[3] (a) Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 1807. (b) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.

[4] (a) Green, M.; Spencer, J. L.; Gordon, F.; Stone, A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525. (b) Iovel, I. G.; Goldberg, Y. Sh.; Shymanska, M. V.; Lukevics, E. *Organometallics* **1987**, *6*, 1410. (c) Licchelli, M.; Greco, A. *Tetrahedron Lett.* **1987**, *28*, 3719. (d) Ohshita, J.; Ishikawa, M. *Chem. Express* **1988**, *3*, 179. (e) Caseri, W.; Pregosin, P. S. *Organometallics* **1988**, *7*, 1373.

0276-7333/91/2310-0462$02.50/0

Table I. Hydrosilylation of Phenylacetylene Catalyzed by $OsHCl(CO)(P^iPr_3)_2$[a]

T, °C	$[HSiEt_3]$, M	$[PhC_2H]$, M	t, h	$[PhHC{=}CH(SiEt_3)]$, M	% $PhHC{=}CH(SiEt_3)$ cis	trans	ratio cis/(cis + trans)
70	0.24	0.26	4.5	0.24	83	17	0.83
60	0.63	0.25	17.0	0.22	1	99	0.01
	0.38	0.25	16.0	0.22	1	99	0.01
	0.23	1.55	23.0	0.04	98	2	0.98
	0.24[b]	0.76	23.0	0.12	85	15	0.85
	0.24[b]	0.25	1.0	0.14	70	30	0.70
			4.5	0.24	74	26	0.74
	0.25	0.16	1.0	0.15	6	94	0.06
			16.0	0.16	2	98	0.02
50	0.24	0.26	8.0	0.22	62	38	0.62
40	0.24	0.26	5.0	0.22	60	40	0.60
32	0.24	0.26	5.0	0.16	65	35	0.65
			12.5	0.19	62	38	0.62
24	0.24	0.25	7.0	0.17	68	32	0.68
			9.8	0.18	69	31	0.69
			23.5	0.20	64	36	0.64

[a] $[OsHCl(CO)(P^iPr_3)_2]$: 2.4×10^{-3} M. [b] In the presence of hydroquinone, similar results were obtained.

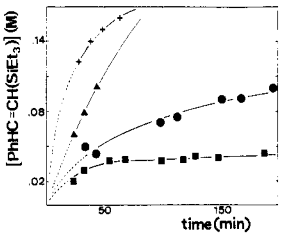


Figure 1. Formation of $PhHC{=}CH(SiEt_3)$ as a function of time in the hydrosilylation of phenylacetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$ in 1,2-dichloroethane at 60 °C (0.24 M $HSiEt_3$; 2.4×10^{-3} M $OsHCl(CO)(P^iPr_3)_2$). $[PhC_2H]$: (+) 0.16 M; (▲) 0.25 M; (●) 0.76 M; (■) 1.55 M; (- - -) extrapolated to initial time.

before. From a mechanistic point of view, it is generally assumed that hydrosilylation proceeds similar to that of hydrogenation.[8]

Recently, it has been reported that the complex $OsHCl(CO)(P^iPr_3)_2$ catalyzes the sequential hydrogenation of phenylacetylene via the vinyl intermediate $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$; the kinetic study of the reaction reveals that the rate and selectivity of the process are determined by the thermodynamic stability of $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$.[9]

This paper reports the addition of triethylsilane to phenylacetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$. This hydrosilylation reaction proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, which we believe is of interest not only because it appears to be intermediate in the catalytic reaction but also because it is the first example of a silyl dihydrogen metal complex. On the other hand, recent work has suggested that adducts of type $MH(\eta^2\text{-}HSiR_3)$ are preferred over the ones of type $M(SiR_3)(\eta^2\text{-}H_2)$.[10]

Results and Discussion

The catalytic addition of triethylsilane to phenylacetylene was performed in a 1,2-dichloroethane solution. The results are listed in Table I. Deactivation of the catalyst was observed when the catalytic solution was exposed to air. It is interesting to note that the rate and extent of the reaction are unaffected by the presence of hydroquinone, suggesting that in this reaction the possible participation of radical-like species as catalytic intermediates is not significant. Thus, at first glance, two general no-radical mechanisms could be proposed:

mechanism 1

$$[Os]H + PhC_2H \rightarrow [Os]((E)\text{-}HC{=}CHPh) \qquad (1)$$

$$[Os]((E)\text{-}HC{=}CHPh) + HSiEt_3 \rightarrow [Os]H + PhHC{=}CH(SiEt_3) \qquad (2)$$

mechanism 2

$$[Os]H + HSiEt_3 \rightarrow \text{“}[Os]HHSiEt_3\text{”} \qquad (3)$$

$$\text{“}[Os]HHSiEt_3\text{”} + PhC_2H \rightarrow [Os]H + PhHC{=}CH(SiEt_3) \qquad (4)$$

Mechanism 1 is similar to that previously reported for the hydrogenation of phenylacetylene to styrene; the insertion reaction of phenylacetylene into the Os–H bond of the carbonyl hydrido complex $OsHCl(CO)(P^iPr_3)_2$ has been recently studied[9,11] and the molecular structure of the vinyl complex $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$ determined by X-ray diffraction.[11] Mechanism 2 implies the initial formation of a silane adduct, which can be formed by oxidative addition of $HSiEt_3$ on the osmium atom in $OsHCl(CO)(P^iPr_3)_2$.

In order to determine the possible mechanism of the catalysis, a careful spectroscopic study of the catalytic reaction was carried out.

The ^{31}P NMR spectra of the catalytic solutions show only one signal at 24.50 ppm, assigned to the vinyl complex $Os((E)\text{-}HC{=}CHPh)Cl(CO)(P^iPr_3)_2$ by comparison of these spectra with a pure sample. This indicates that the vinyl compound is the main species under catalytic conditions.

---

(5) (a) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293. (b) Watanabe, H.; Kitahara, T.; Motegui, T.; Nagai, Y. *Ibid.* **1977**, *139*, 215. (c) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *Ibid.* **1978**, *161*, 91. (d) Cornish, A. J.; Lappert, M. F.; Filatovs, G. L.; Nile, T. A. *Ibid.* **1979**, *172*, 153. (e) Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1979**, 308. (f) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299. (g) Lappert, M. F.; Maskell, R. K. *Ibid.* **1984**, *264*, 217. (h) Marciniec, B.; Foltynowicz, Z.; Urbaniak, W. *Appl. Organomet. Chem.* **1987**, *1*, 459. (i) Chance, J. M.; Nile, T. A. *J. Mol. Catal.* **1987**, *42*, 91. (j) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Sakakibara, J.; Itoh, K. *Organometallics* **1989**, *8*, 2495.

(6) (a) Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, F. A. *J. Mol. Catal.* **1985**, *29*, 55. (b) Fernândez, M. J.; Oro, L. A.; Manzano, B. R. *Ibid.* **1988**, *45*, 7.

(7) Marciniec, B.; Foltynowicz, Z.; Urbaniak, W.; Perkowski, J. *Appl. Organomet. Chem.* **1987**, *1*, 267.

(8) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(9) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.

(10) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

(11) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

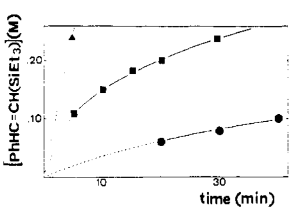


Figure 2. Formation of PhHC=CH(SiEt$_3$) as a function of time in the hydrosilylation of phenylacetylene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ inn 1,2-dichloroethane at 60 °C (0.25 M [PhC$_2$H]; 2.4 × 10^{-3} M OsHCl(CO)(P^{i}Pr$_3$)$_2$). [HSiEt$_3$]: (●) 0.24 M; (■) 0.38 M; (▲) 0.63 M; (- - -) extrapolated to initial time.

On the other hand, it was observed that this vinyl complex is inert in the presence of triethylsilane. Thus, the ^{31}P NMR spectra of Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ performed in a 0.4 M solution of triethylsilane in 1,2-dichloroethane show the singlet at 24.50 ppm, which is unchanged after keeping the solutions at 60 °C for 4 days. This suggests that the vinyl complex represents a thermodynamic sink that causes virtually all osmium present in solution to be tied up in this form, but it is not an authentic catalytic intermediate. In accord with this, it was found that the rate of the catalytic proceeding decreases as the concentration of phenylacetylene increases (Figure 1). These observations indicate clearly that the hydrosilylation of phenylacetylene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ does not proceed by mechanism 1. So, mechanism 2 should be the far more dominant pathway, since we have observed that the rate of the catalytic reaction rises as the concentration of triethylsilane increases (Figure 2). In order to support this hypothesis, we have carried out the spectroscopic investigation of the reaction of the hydride OsHCl(CO)(P^{i}Pr$_3$)$_2$ with triethylsilane.

Reaction of HSiEt$_3$ with OsHCl(CO)(P^{i}Pr$_3$)$_2$. If mechanism 2 is correct, we may be able to observe the silane derivative. This prompted us to examine the reaction of OsHCl(CO)(P^{i}Pr$_3$)$_2$ with HSiEt$_3$ in the absence of PhC$_2$H. Addition of an excess of HSiEt$_3$ (ca. 4 equiv) to OsHCl(CO)(P^{i}Pr$_3$)$_2$ in 1,2-dichloroethane at 60 °C in a NMR tube under argon yields an orange solution after 12 h. The ^{31}P NMR spectrum shows only one signal at 37.1 ppm. After the solution was cooled at −20 °C, orange crystals were formed. The ^{1}H NMR spectrum of the crystals in C$_6$D$_6$ at 20 °C exhibits phosphine protons as a multiplet at 2.80 ppm plus two doublets of virtual triplets at 1.44 and 1.42 ppm (N = 13.5 Hz, J_{H-H} = 8.0 Hz) along with peaks for SiEt$_3$ (1.23, t; 0.80, q; J_{H-H} = 8.0 Hz), and in the hydride region, a relatively broad resonance appears at −1.70 ppm (T_1 = 17 ms), characteristic of a η^2-bonded H$_2$ ligand.[12] The signals at 1.23, 0.80, and −1.70 ppm indicate that the obtained compound by reaction of OsHCl(CO)(P^{i}Pr$_3$)$_2$ with HSiEt$_3$ is the dihydrogen complex Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ (2), which can be formed according to eq 5.

$$\begin{aligned} &\mathrm{OsHCl(CO)(P^iPr_3)_2 + HSiEt_3} \rightarrow \\ &\qquad \underset{1}{\mathrm{OsH_2(SiEt_3)Cl(CO)(P^iPr_3)_2}} \rightleftarrows \\ &\qquad\qquad \underset{2}{\mathrm{Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2}} \quad (5) \end{aligned}$$

The intermediate OsH$_2$(SiEt$_3$)Cl(CO)(P^{i}Pr$_3$)$_2$ (1) is identified by a triplet at −8.48 ppm with a P–H coupling constant of 10 Hz, which can be detected when the above spectrum is strongly amplified (Figure 3). A similar P–H coupling constant has been previously observed in the related complex OsH$_4$(CO)(P^{i}Pr$_3$)$_2$.[13] The oxidative addition of silanes to platinum group metal compounds has been extensively studied and is generally viewed as a concerted cis addition.[14,15] The concerted mechanism must involve an intermediate of type MH(η^2-HSiR$_3$). In our case, this intermediate has not been detected, most probably due to the great weakness of the Si–H bond relative to H–H. So we believe that for our system the type A adducts are preferred over the B type ones, in contrast with a previous proposal.[10]

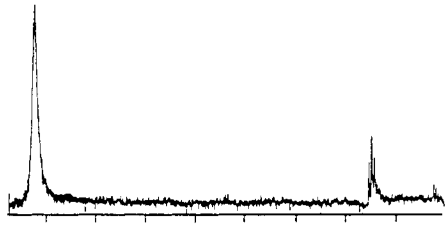


Figure 3. ^{1}H NMR spectrum of the silyl dihydrogen compound Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ in the hydride region.

A B

The solutions of OsHCl(CO)(P^{i}Pr$_3$)$_2$ are rapidly decolorized upon contact with H$_2$ under ambient conditions; their NMR spectra are consistent with the formation of the dihydrogen compound OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$.[16] However, detectable formation of OsH$_3$Cl(CO)(PiPr$_3$)$_2$ does not occur from −75 to 85 °C. The higher stability of the η^2-H$_2$ ligand in OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ relative to its silyl analogue can be assigned to the higher electronegativity of the hydride ligand. In this context, theoretical studies[17] have indicated that the presence of good donor ligands at metal centers promotes charge transfer (i.e., backbonding) from M to the σ^* orbital of H$_2$ and thus favors the cleavage of the H$_2$ molecule with the formation of two M–H bonds.

Hydrosilylation Mechanism. A further reaction of interest in connection with our catalytic investigations is that of the silyl dihydrogen complex Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ with PhC$_2$H. When an excess of PhC$_2$H (ca. 2 equiv) was added to a NMR tube containing a solution of Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ in C$_6$D$_6$ under argon at 20 °C, the solution changed from orange to dark blue. The ^{31}P NMR spectrum of this solution shows only the signal of the vinyl derivative Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ at 23.8 ppm, and the gas chromatography

---

(12) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17.

(13) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

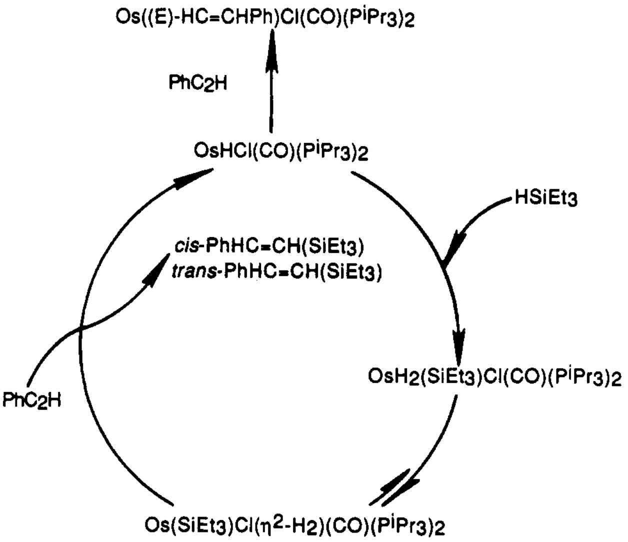
(14) (a) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531. (b) Fernández, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751. (c) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Ibid.* **1988**, *7*, 1939. (d) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Ibid.* **1989**, *8*, 1158. (e) Schubert, U.; Knorr, M. *Inorg. Chem.* **1989**, *28*, 1765.

(15) (a) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I, Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 673. (b) Ojima, I.; Yamamoto, K.; Kumada, M. In *Aspects of Homogeneous Catalysis*; Ugo, R.; Ed.; D. Reidel: Boston, 1977; Vol. 3, p 185. (c) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; Chapters 4, 6.

(16) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem.* **1988**, *100*, 1621; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563.

(17) (a) Sailar, J. Y.; Hoffman, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Jean, Y.; Einsenstein, O.; Volatron, F. Maouche, B.; Sefta, F. *Ibid.* **1986**, *108*, 6587. (c) Hay, P. J. *Ibid.* **1987**, *109*, 705. (d) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684.

Scheme I. Catalytic Cycle for the Addition of Triethylsilane to Phenylacetylene



(GC) analysis indicates the presence of *cis*- and *trans*-PhHC=CH(SiEt$_3$) in similar relative amounts to that observed for the catalytic reaction at 24 °C. This reaction together with the formation of the silyl dihydrogen compound Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ constitutes a catalytic cycle for the addition of triethylsilane to phenylacetylene (Scheme I).

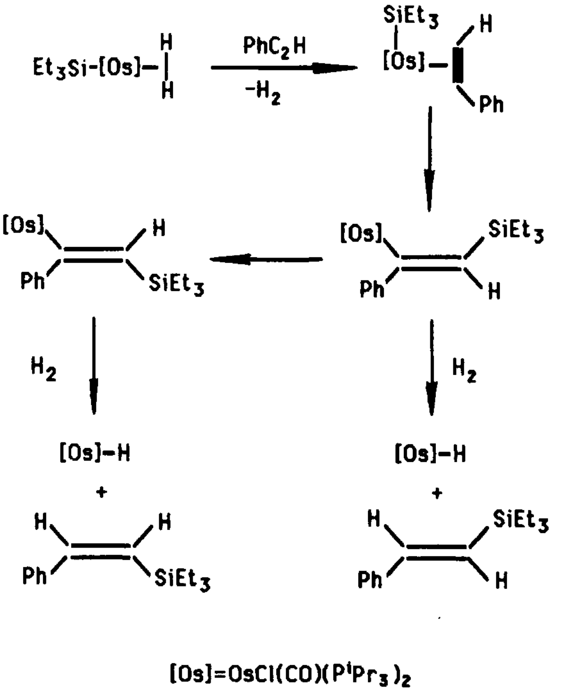
The reaction between Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ and PhC$_2$H occurs in a flash, while this dihydrogen complex is obtained after 12 h, so the slow step of the catalytic cycle is the reaction of OsHCl(CO)(P^{i}Pr$_3$)$_2$ with HSiEt$_3$. In accord with this, we have mentioned above that the rate of the catalytic proceeding rises as the HSiEt$_3$ concentration increases, while the rate decreases as the PhC$_2$H concentration inceases.

The mechanism of the hydrogenation of phenylacetylene to styrene involves the initial formation of the vinyl intermediate Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ and subsequent reaction of this intermediate with hydrogen.[9] Under hydrosilylation conditions, this vinyl intermediate is also formed; however, it does not react with HSiEt$_3$. Although Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ undoubtedly is a 16-electron complex and thus coordinatively unsaturated, the sixth position of the octahedron around the osmium atom is well shielded. Four of the 12 methyl groups of the phosphine ligands surround the metal like an umbrella,[11] which may explain why the vinyl compound does not react with HSiEt$_3$ being more bulky than H$_2$.

Comments on the Formation of *cis*-PhHC=CH(SiEt$_3$). Table I shows that *trans*-PhHC=CH(SiEt$_3$) can be selectively obtained in 87% yield, but by lowering the HSiEt$_3$ concentration or increasing the PhC$_2$H concentration, the relative amount of *cis*-PhHC=CH(SiEt$_3$) increases. Raising the temperature also increases the yield of the cis isomer. Proposed nonradical pathways for the formation of *cis*-alkenylsilanes with transition-metal complexes involve (i) formation of *trans*-alkenylsilanes followed by isomerization to the cis isomer in the presence of the catalyst and silane,[5c] (ii) isomerization of a vinyl intermediate,[5f,6a] and (iii) formation of a metal alkynyl complex.[6b]

The reaction of Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ and PhC$_2$H to give *cis*- and *trans*-styryltriethylsilane is very fast, and unfortunately, the study of the probable reaction intermediates was not possible. However, in light of the obtained results, some considerations can be made: (i) no significant isomerization was observed when the hydrosilylation of PhC$_2$H was performed in the presence of *trans*- or *cis*-PhHC=CH(SiEt$_3$) and (ii) isomerization of a vinyl intermediate and formation of alkynyl species are two pathways that could potentially explain the formation of *trans*- and *cis*-PhHC=CH(SiEt$_3$). Although the mechanism for the isomerization of vinyl complex is not well established, precedents for this process are known.[18] On the other hand, it has been recently reported that the tetrahydride OsH$_4$(CO)(P^{i}Pr$_3$)$_2$ reacts with phenylacetylene to give Os(C$_2$Ph$_2$)$_2$(CO)(P^{i}Pr$_3$)$_2$.[19] The participation of alkynyl intermediates in the hydrosilylation reaction should, most probably, involve the formation of PhC$_2$SiEt$_3$ as the reaction product. However, detectable amounts of this product were not observed, so we assume that the formation of *cis*-PhHC=CH(SiEt$_3$) occurs by isomerization of a vinyl intermediate (Scheme II). In light of the results of Table I, it can be inferred that the isomerization process is favored in the presence of PhC$_2$H and with high temperature.

Scheme II. Proposed Pathway to the Formation of *cis*-Styryltriethylsilane Isomer



The (*Z*)-vinyl intermediate shown in Scheme II could be formed by displacement of coordinated dihydrogen ligand and subsequent insertion of the alkyne into the Os–SiEt$_3$ bond of Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$. In this context, it is relevant to note that the reaction between the dihydrogen compound OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ and PhC$_2$H leads to the displacement of the dihydrogen ligand with formation of Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$.[9]

Concluding Remarks

This study has revealed that the five-coordinated hydrido carbonyl complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ catalyzes the addition of triethylsilane to phenylacetylene. *cis*- and *trans*-PhHC=CH(SiEt$_3$) can be selectively obtained in good yield depending on the reaction conditions. Although the vinyl compound Os((*E*)-HC=CHPh)Cl(CO)(P^{i}Pr$_3$)$_2$ is

---

[18] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

[19] Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A.; *J. Organomet. Chem.* **1989**, *366*, 187.

the main species under hydrosilylation conditions, the reaction proceeds via the silyl dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$. For this adduct, bonding $M(SiEt_3)(\eta^2\text{-}H_2)$ is preferred over that of $MH(\eta^2\text{-}HSiEt_3)$.

Finally, it is relevant to note that the hydrosilylation of phenylacetylene proceeds via a different mechanism to the one previously reported for the hydrogenation. In light of this result, it is clear that further work needs to be done in order to fully understand the mechanistic aspects of alkyne hydrosilylation by metal hydrides, which have so far remained at the level of speculative extrapolations of our knowledge of alkyne hydrogenation.

Experimental Section

General Considerations. All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. Phenylacetylene (Merck) was purified by distillation, and triethylsilane (Merck) was used without further purification. $OsHCl(CO)(P^iPr_3)_2$ was prepared by reaction of $OsCl_3\cdot nH_2O$ (Degussa) with P^iPr_3 (Strem) in methanol.[20]

Physical Measurements. NMR spectra were recorded on a 200-MHz Varian XL and are reported in ppm from internal $Si(CH_3)_4$ (^1H) and 85% H_3PO_4 (^{31}P) on a δ scale. The T_1 experiments were performed at 20 °C with a standard $180°–\tau–90°$ pulse sequence. The catalytic reactions were followed by measuring the silane consumption as a function of time using C_6H_{12} as the internal standard with a 15% β,β'-oxodipropionitrile on Chromosorb W-HP 80/100-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector. Silicon-containing products were analyzed by using a FFAP on Chromosorb GHP 80/100-mesh column at 175 °C.

General Procedure. The hydrosilylation reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. In a typical procedure, 4 mL of a 4.8×10^{-3} M solution of $OsHCl(CO)(P^iPr_3)_2$ in 1,2-dichloroethane was added to an other 1,2-dichloroethane solution (4 mL) containing $HSiEt_3$, PhC_2H, and C_6H_{12}. The flask was then immersed in a bath at 60 °C, and the reaction mixture was magnetically stirred. Silicon-containing products were isolated by column chromatography (Al_2O_3; hexane) and characterized by ^1H NMR. ^1H NMR (*trans*-$PhCH{=}CH(SiEt_3)$, $CDCl_3$): δ 7.40–7.16 (Ph), 6.82 (d, $PhHC{=}$, $J_{H\text{-}H}$ = 19.35 Hz), 6.34 (d, $={CH}(SiEt_3)$, $J_{H\text{-}H}$ = 19.35 Hz), 0.91 (t, $SiCH_2CH_3$, $J_{H\text{-}H}$ = 7.80 Hz), 0.58 (q, $SiCH_2CH_3$, $J_{H\text{-}H}$ = 7.80 Hz). ^1H NMR (*as*-$PhHC{=}CH(SiEt_3)$, $CDCl_3$): δ 7.45 (d, $PhHC{=}$, $J_{H\text{-}H}$ = 15.10 Hz), 7.36–6.94 (Ph), 5.57 (d, $={CH}(SiEt_3)$, $J_{H\text{-}H}$ = 15.10 Hz), 0.86 (t, $SiCH_2CH_3$), $J_{H\text{-}H}$ = 7.60 Hz), 0.58 (q, $SiCH_2CH_3$, $J_{H\text{-}H}$ = 7.60 Hz).

In the presence of hydroquinone, the procedure was as follows: To a solution of $OsHCl(CO)(P^iPr_3)_2$ (11.04 mg, 0.019 mmol) and hydroquinone (8.37 mg, 0.076 mmol) in 4 mL of 1,2-dichloroethane was added an other 1,2-dichloroethane solution (4 mL) containing $HSiEt_3$, PhC_2H, and C_6H_{12}. The flask was then immersed in a bath at 60 °C, and the reaction mixture was magnetically stirred.

Reaction of $OsHCl(CO)(P^iPr_3)_2$ with $HSiEt_3$: Preparation of $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (2). To a NMR tube containing a 1,2-dichloroethane solution of $OsHCl(CO)(P^iPr_3)_2$ (0.052 mmol in 1.5 mL of solution) was added triethylsilane (33.13 μL, 0.208 mmol). The sample was shaken and then immersed in a bath at 60 °C. The reaction was followed by ^{31}P NMR. After 12 h, the ^{31}P NMR shows only one signal at δ 37.1 ppm. The orange solution was cooled at −20 °C, and orange crystals were formed, which were characterized by NMR spectroscopy. ^1H NMR (benzene-d_6, 25 °C): δ −1.70 (br, 2 H, $Os(H_2)$, T_1 = 17 ms), 0.80 (q, $H_{H\text{-}H}$ = 8.0 Hz, 6 H, $SiCH_2CH_3$), 1.23 (t, $J_{H\text{-}H}$ = 8.0 Hz, 9 H, $SiCH_2CH_3$), 1.42 (dvt, N = 13.5 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 18 H, $PCHCH_3$), 1.44 (dvt, N = 13.5 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 18 H, $PCHCH_3$), 2.80 (m, 6 H, $PCHCH_3$). ^{31}P NMR (benzene-d_6, 25 °C): δ 37.1 (s).

Acknowledgment. We thank DGICYT (Project PB 88-0386; Programa de Promoción General del Conocimiento) for financial support.

---

[20] Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* 1986, *303*, 221.