137259-18-8; **9**, 137202-67-6; **10**, 67420-82-0; **11**, 137259-20-2; **12**, 137202-69-8; **13**, 137202-71-2; **14**, 137202-73-4; **15**, 137202-75-6; **16**, 137202-77-8; Ru(η-C_6Me_6)(η^4-2,3-C_6H_{10}), 71896-90-7; Ru(η-$C_6H_3Me_3$)(η^4-2,3-C_6H_{10}), 137202-83-6; Ru(η-C_6H_6)(η^4-2,3-C_6H_{10}), 137202-84-7; Ru(η-C_6Me_6)(η^4-2,4-C_6H_{10}), 137202-78-9; Ru(η-C_6Me_6)(η^4-3,4-C_6H_{10}), 137202-79-0; Ru(η-C_6Me_6)(η^4-C_5H_8), 137259-21-3; Os(η-C_6H_6)(η^4-C_6H_8), 95514-96-8; Os(η-C_6H_3Me)(η^4-C_6H_8), 137202-85-8; Os(η-C_6H_6)(η^4-2,3-C_6H_{10}), 137202-86-9; Os(η-C_6H_3)(η^4-2,3-C_6H_{10}), 137202-87-0; Os(η-C_6H_6)(η^4-1,5-C_8H_{12}), 137202-88-1; Os(η-$C_6H_3Me_3$)(η^4-1,5-C_8H_{12}), 137202-80-3; [RuH(R-C_6H_6)(η^4-C_8H_{12})]PF_6, 137202-90-5; [RuH(η-$C_6H_3Me_3$)(η^4-C_8H_{12})]PF_6, 135585-15-8; [RuH(η-C_6Me_6)(η^4-C_8H_{12})]PF_6, 135585-17-0; [OsH(η-C_6H_6)(η^4-C_8H_{12})]PF_6, 137202-92-7; [OsH(η-$C_6H_3Me_3$)(η^4-C_8H_{12})]PF_6, 137202-82-5; [Rh(η-C_5Me_5)(η^3-C_6H_9)(CN-*t*-Bu)]BF_6, 137259-23-5; [Ir(η-C_5Me_5)(η^3-C_6H_9)(CN-*t*-Bu)]BF_6, 137202-94-9; [Os(η-C_6H_6)(η^3-C_6H_9){P(OMe)$_3$}]PF_6, 137202-96-1; [Os(η-$C_6H_3Me_3$)(η^3-C_6H_9)(CN-*t*-Bu)]PF_6, 137202-98-3; [Os(η-C_6H_6)(η^3-1,1,2-C_6H_{11}){P(OMe)$_3$}]PF_6, 137203-00-0; [Os(η-$C_6H_3Me_3$)(η^3-1,1,2-C_6H_{11})(CN-*t*-Bu)]PF_6, 137203-02-2; [Ru(η-C_6H_6)(η^3-C_6H_9)(CN-*t*-Bu)]PF_6, 137203-04-4; [Ru(η-C_6H_6)(η^3-C_6H_9){P(OMe)$_3$}]PF_6, 137203-06-6; [Ru(η-C_6Me_6)(η^3-C_6H_9)(CN-*t*-Bu)]PF_6, 137203-08-8; [Ru(η-C_6Me_6)(η^3-C_8H_{13})(CO)]PF_6, 137203-10-2; [Ru(η-C_6Me_6)(η^3-C_8H_{13}){P(OMe)$_3$}]PF_6, 137203-12-4; [Ru(η-C_6Me_6)(η^3-C_8H_{13})(CN-*t*-Bu)]PF_6, 137203-14-6; [Ru(η-C_6H_6)(η^3-C_8H_{13})(CN-*t*-Bu)]PF_6, 137203-16-8; [Ru(η-C_6Me_6)(η^3-1,1,2-C_6H_{11})(CN-*t*-Bu)]PF_6, 137203-18-0; [Ru(η-C_6Me_6)(η^3-1,1,2-C_6H_{11})(CO)]PF_6, 137203-20-4; [Ru(η-$C_6H_3Me_3$)(η^3-1,1,2-C_6H_{11})(CO)]PF_6, 137203-22-6; [Ru(η-C_6H_6)(η^3-1,1,2-C_6H_{11})(CO)]PF_6, 137203-24-8; [Ru(η-C_6Me_6)(η^3-1,1-C_5H_9)(CO)]PF_6, 137203-26-0; [Ru(η-C_6Me_6)(η^3-1,1,3-C_6H_{11})(CO)]PF_6, 137203-28-2; [Ru(η-C_6Me_6)(η^3-1-*anti*,*syn*-1,2,3-C_6H_{11})(CO)]PF_6, 137203-30-6; [$RhCl_2$(η-C_5Me_5)]$_2$, 12354-85-7; [$IrCl_2$(η-C_5Me_5)]$_2$, 12354-84-6; [$RuCl_2$(η-C_6H_6)]$_2$, 37366-09-9; [$RuCl_2$(η-$C_6H_3Me_3$)]$_2$, 52462-31-4; [$RuCl_2$(η-C_6Me_6)]$_2$, 67421-02-7; [OsI_2(η-C_6H_6)]$_2$, 75353-15-0; [$OsCl_2$(η-$C_6H_3Me_3$)]$_2$, 94957-59-2; Rh(η-C_5Me_5)(η^4-C_6H_8), 33519-75-4; Ir(η-C_5Me_5)(η^4-C_6H_8), 32697-43-1; Rh(η-C_5Me_5)(η^4-2,3-C_6H_{10}), 58355-12-7; Ir(η-C_5Me_5)(η^4-2,3-C_6H_{10}), 58355-13-8; 1,5-COD, 111-78-4; Ru(η-C_6Me_6)(1,5-COD), 71896-91-8.

Supplementary Material Available: Tables of elemental analyses and parent ions in mass spectra of (arene)ruthenium diene and (arene)osmium diene complexes and elemental analyses and decomposition points of protonated diene complexes and of their ligand derivatives (4 pages). Ordering information is given on any current masthead page.

Selective Hydrogenation of 1-Alkynes to Alkenes Catalyzed by an Iron(II) *cis*-Hydride η^2-Dihydrogen Complex. A Case of Intramolecular Reaction between η^2-H_2 and σ-Vinyl Ligands

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The reactions of the *cis*-hydride η^2-dihydrogen complex [(PP_3)Fe(H)(H_2)]BPh_4 (1) and of the dinitrogen derivative [(PP_3)Fe(H)(N_2)]BPh_4 (2) with a variety of 1-alkynes have been investigated. From this study, it is apparent that the insertion of the alkyne across the Fe–H bond in 1 to give a σ-alkenyl intermediate proceeds via decoordination of a phosphine arm of PP_3 rather than via H_2 decoordination. Terminal alkynes are selectively and catalytically hydrogenated to alkenes by 1 in tetrahydrofuran or 1,2-dichloroethane solutions under mild conditions. A kinetic study on the hydrogenation reaction of $HC\equiv CPh$ to $H_2C{=}CHPh$ has shown that the reduction is first order in catalyst and alkyne concentrations and zero order in hydrogen pressure. Incorporation of a large body of experimental data leads to the conclusion that (i) the dihydrogen ligand does not leave the metal prior to alkyne coordination and (ii) the reduction of the substrate most likely occurs via an intramolecular acid/base reaction involving η^2-H_2 and σ-vinyl ligands mutually cis disposed.

Introduction

In 1984 an X-ray analysis revealed the presence of an intact H_2 ligand in Kubas' complex [W(η^2-H_2)$(CO)_3$-$(PCy_3)_2$].[1] Since then, essentially due to the development of improved diagnostic tools for distinguishing classical from nonclassical metal polyhydrides,[2] more than 100 η^2-H_2 complexes have appeared in the literature.[3,4] Most d-block metals, in various oxidation states, can form a stable dihydrogen adduct when assisted by an appropriate ligand set. It is therefore quite reasonable to state that (dihydrogen)metal complexes now constitute a class of compounds.

In comparison with the abundance and variety of compounds, what is known of the chemical properties of coordinated dihydrogen (the H_2 ligand may behave as a good leaving group[5] and may exhibit remarkable acidic char-

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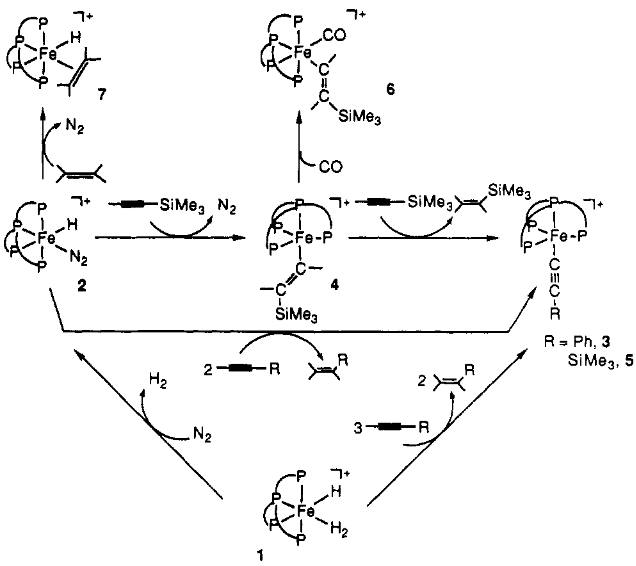
acter)[6] is absolutely inadequate to the increasing role of η^2-H_2 complexes in a number of stoichiometric and catalytic reactions. Important applications of η^2-H_2 complexes in homogeneous catalysis include hydrogenation of alkynes and alkenes,[7] hydrogenation of ketones and arenes,[8] hydrogen production from alcoholic substrates,[9] and selective dimerization of 1-alkynes to *Z*-butenynes.[10]

In the course of our studies on (dihydrogen)metal compounds,[2k,5j,7b,11] we have recently synthesized a (*cis*-hydride)(η^2-dihydrogen)iron(II) complex, namely $[(PP_3)Fe(H)(H_2)]BPh_4$ (1), exhibiting exceptional thermal and chemical stability [$PP_3 = P(CH_2CH_2PPh_2)_3$].[12] In particular, 1 is *fairly stable in refluxing THF under argon and does not undergo H/D exchange when treated for 3 h with* D_2 or D_2O.

Since all of the mechanistic interpretations of the catalytic reactions assisted by (dihydrogen)metal complexes center on the ability of H_2 to be readily displaced by the substrate,[5,7-10] we decided to investigate the potential of 1 as catalyst in homogeneous reactions. In this paper, we report on the ability of 1 and of its dinitrogen derivative $[(PP_3)Fe(H)(N_2)]BPh_4$ (2) to function as catalyst for the selective reduction of 1-alkynes to alkenes. Besides providing evidence of the unique reactivity of acidic η^2-H_2 toward σ-vinyl ligands in the catalysis cycle, the results obtained exhibit their own practical interest due to the low cost of iron as compared with the metals that are generally used to accomplish homogeneous hydrogenation reactions.[13,14] Finally, it is worth mentioning that the selective reduction of alkynes to alkenes is a relevant reaction, largely employed in the preparation of organic intermediates for the synthesis of several pharmaceuticals. As an example, the synthesis of vitamin A (BASF method) requires the selective reduction of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol.[15]

Scheme I



A preliminary communication of part of this work has already appeared.[16]

Results and Discussion

Reactivity of 1 and 2 with Terminal Alkynes. The *cis*-hydride dihydrogen complex 1[12] or its dinitrogen derivative 2[17] react with 1-alkynes in THF under argon to give σ-alkynyl complexes of the general formula $[(PP_3)Fe(C{\equiv}CR)]BPh_4$ (R = Ph, n-C_3H_7, n-C_5H_{11}, $SiMe_3$, $CH{=}CH(OMe)$). A detailed description of the chemicophysical properties of each σ-alkynyl complex is not in order since the information already available in the literature on such compounds is adequate for the purpose of this paper.[16] An X-ray analysis on the phenylalkynyl derivative $[(PP_3)Fe(C{\equiv}CPh)]BPh_4$ (3) has been recently carried out and has confirmed the trigonal-bipyramidal (TBP) structure of the complex as it was inferred by spectroscopic techniques.[18]

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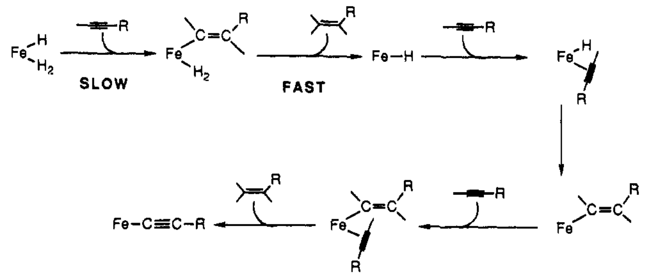
To summarize, all of the σ-alkynyls are paramagnetic with magnetic moments corresponding to two unpaired spins (μ_{eff}(ave) = 3.3 μ_B) and exhibit an almost regular TBP structure in both solid state and solution. In contrast, both the chemistry of the σ-alkynyl complexes and the mechanism leading to their formation are points that need to be clarified.

When the dinitrogen complex **2** is reacted with a stoichiometric amount of $HC{\equiv}CR$ (R = Ph, n-C_3H_7, n-C_5H_{11}, $SiMe_3$, $CH{=}CH(OMe)$), a reaction occurs which completes in a few minutes and transforms 50% of the starting complex into the corresponding σ-alkynyl.[16] Regardless of the substituent, all reactions produce 0.5 equiv of free alkene, dinitrogen but not dihydrogen. Complete conversion of **2** to σ-alkynyl requires the use of 2 equiv of 1-alkyne, in which case 1 equiv of alkene is produced (Scheme I). Substitution of the dihydrogen complex **1** for **2** does not change the nature of the products whereas both the rate and the stoichiometry of the reactions are significantly affected: A complete conversion of **1** to the corresponding σ-alkynyl occurs in 3–4 h and requires the use of 3 equiv of 1-alkyne producing 2 equiv of free alkene. No evolution of dihydrogen is detected in the course of the reactions by NMR or GC. The relatively low rate of conversion allows one to monitor the reactions between **1** and variable amounts of 1-alkynes by NMR spectroscopy. In a typical procedure, ^{31}P and ^1H NMR spectra are recorded immediately after neat alkyne is added to a THF-d_8 solution of **1** in the NMR tube, and then every 15 min until total consumption of the dihydrogen complex has occurred. In the course of the transformations, **1** is the only detectable product by ^{31}P NMR spectroscopy as the paramagnetic σ-alkynyls are NMR silent over 1850 ppm (most likely, this is due to extensive broadening of the phosphorus resonances that practically disappear into the base line). The rate of the disappearance of **1** increases with the temperature and with the 1-alkyne concentration (a precise rate dependence cannot be found since the presence of paramagnetic species in the reaction mixtures prevents a reliable integration of the signals). Appreciable formation of paramagnetic species (X-band ESR and Evans' method)[19] occurs within a few minutes after the addition of the 1-alkyne to the solution of **1**; obviously, the paramagnetism increases as the concentration of **1** decreases. Quantitative measurements of the magnetic moment in solution have been carried out for the reaction of **1** with $HC{\equiv}CPh$. Taken for granted that all **1** has been converted to the Fe(II) σ-alkynyl **3**, a μ_{eff} value of 3 ± 0.2 μ_B is obtained which matches well the value (3.42 μ_B) for a solid sample of **3**. ^1H NMR spectroscopy shows that the reaction of **1** with $HC{\equiv}CPh$ produces styrene (2 equiv at total consumption of **1**) while no dihydrogen is evolved even at high temperature (60 °C).

The absence of H_2 evolution (indirectly demonstrated by the formation of 2 equiv of alkene) is of great mechanistic relevance as it clearly indicates that the σ-alkynyl complexes do not form via C–H oxidative addition of 1-alkynes to iron, followed by H_2 reductive elimination.[20] The only alternative mechanism to explain the formation of both σ-alkynyl complex and free alkene implies primary insertion of 1-alkyne across an Fe–H bond to give a σ-alkenyl species, which then reacts with a second alkyne molecule to produce the σ-alkynyl complex via alkene elimination. Indeed, we have been able to isolate an alkenyl derivative, (E)-$[(PP_3)Fe\{CH{=}CH(SiMe_3)\}]BPh_4$ (**4**), as the predominant product of the 1:1 reaction between **2** and $HC{\equiv}CSiMe_3$ (Scheme I). The reaction produces some σ-alkynyl complex, $[(PP_3)Fe(C{\equiv}CSiMe_3)]BPh_4$ (**5**), and free vinyltrimethylsilane (10–15%). The cis addition of the Fe–H bond across the alkyne triple bond has been established by ^1H NMR spectroscopy on the diamagnetic octahedral derivative (E)-$[(PP_3)Fe(CO)\{CH{=}CH(SiMe_3)\}]BPh_4$ (**6**) (J(HH) = 18.6 Hz)[21] prepared by bubbling CO throughout a THF solution of **4**. By treatment of **4** with further 1-alkyne, **5** and $H_2C{=}CH(SiMe_3)$ are obtained quantitatively. Like the σ-alkynyl compounds, the σ-alkenyl **4** is TBP and paramagnetic with a magnetic moment corresponding to two unpaired spins (μ_{eff} = 3.35 μ_B).

Scheme II



Incorporation of all of the above experimental evidence leads to the mechanism shown in Scheme II for the reactions between **1** and excess 1-alkyne. The 1-alkyne slowly interacts with the starting complex to give an insertion product, namely a σ-alkenyl. Since there is no H_2 evolution at any stage of the reaction (**1** *reacts with 1-alkynes to give 2 equiv of alkene even in refluxing THF under a steady stream of argon*), we conclude that *dihydrogen remains coordinated to iron during the insertion reaction.* This means that one phosphine arm of PP_3 must unfasten to create a free coordination site for the activation of the incoming 1-alkyne molecule.[22] Such a motion for metal PP_3 complexes in insertion reactions is well documented.[23] After 1-alkyne has inserted across the Fe–H bond, a σ-alkenyl η^2-dihydrogen intermediate forms, which may be intrinsically unstable as the metal carries acidic (η^2-H_2) and basic (σ-vinyl) ligands in mutual cis position. A fast intramolecular acid/base reaction explains well the formation of the first equivalent of alkene.[6] However, since 2 equiv of alkene is recovered at the end of the reaction, we must assume that a second 1-alkyne molecule inserts across the Fe–H bond of the unsaturated monohydride $[(PP_3)FeH]^+$ to form a σ-alkenyl complex.[2k] From this point, the major aspects of the reaction are relatively clear. We know that Fe σ-alkenyl complexes (recall the **4** to **5** conversion) do react with 1-alkynes, yielding stable σ-alkynyls and alkenes, but a precise mechanism for such a step is still to be proved. Formally, the reaction corresponds to the transfer of a hydrogen atom from an alkyne molecule to

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[18] Manuscript in preparation. Crystallographic data: monoclinic, space group $P2_1/C$ (No. 14), a = 10.339 (6) Å, b = 33.259 (9) Å, c = 19.012 (4) Å, β = 92.13 (3)°, d_{calcd} = 1.24 g cm^{-3}, Z = 4, n_{obsd} = 2145, R = 0.079. Selected distances and angles: Fe–C_α(alkynyl) = 1.88 (2) Å, C_α–C_β(alkynyl) = 1.20 (3) Å, P(apical)–Fe–C_α 177.2 (6)°.

[19] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[20] A mechanism proceeding through C–H bond cleavage has been proposed for the reaction of $[(NP_3)RhH]$ with 1-alkynes to give σ-alkynyl complexes ($NP_3 = N(CH_2CH_2PPh_2)_3$): Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146.

[21] See, for example: (a) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (b) Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1989**, 589.

[22] "Arm-off" mechanisms are well documented in transition-metal polyphosphine chemistry. See, for example: (a) Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664. (b) Thaler, E. G.; Caulton, K. G. *Organometallics* **1990**, *9*, 1871.

[23] Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

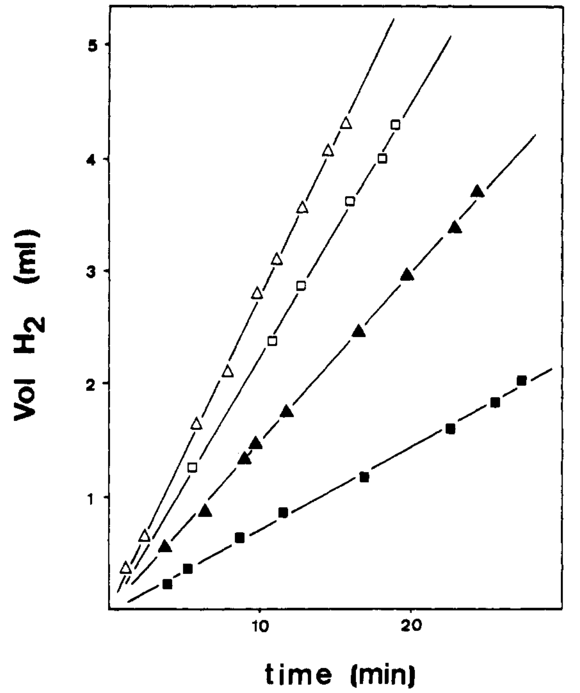

Figure 1. H_2 gas uptake plots for the 1-catalyzed hydrogenation of phenylacetylene to styrene in 1,2-dichloroethane at 30 °C (1 atm of H_2, 1.37×10^{-3} M 1). [HC≡CPh]: (■) 0.10 M, (▲) 0.20 M, (□) 0.30 M, (△) 0.40 M.

coordinated alkenyl ligand, and several, reasonable paths can be proposed (C–H oxidative addition/reductive elimination path; alkyne to vinylidene tautomerization via H 1,2-shift, followed by vinylidene deprotonation by a basic cis vinyl ligand; direct deprotonation of a π-1-alkyne ligand by a basic cis vinyl ligand).

In contrast, we can offer an explanation for the unique stability of the (trimethylsilyl)vinyl complex 4, which is the only σ-alkenyl derivative of the Fe–PP_3 family to be isolated. The presence of a trimethylsilyl substituent on the C–C double bond decreases the electron density at the C_β atom.[24] In the case at hand, this effect may stabilize the σ-alkenyl ligand in 4 by lessening its nucleophilic character.

Hydrogenation of Phenylacetylene Catalyzed by 1. The ability of 1 to reduce 1-alkynes to alkenes by using its η^2-H_2 ligands has prompted us to study in detail the potential of 1 and 2 as catalysts for the homogeneous hydrogenation of 1-alkynes. Here, we focus our attention on phenylacetylene, but comparisons with a variety of 1-alkynes are given in the text showing the wide applicability of the PP_3–Fe system to the selective hydrogenation of 1-alkynes to alkenes.

The hydrogenation of HC≡CPh to H_2C=CHPh has been studied in 1,2-dichloroethane solution where 1 is quite stable. Initial hydrogenation rates were obtained from gas-uptake experiments, as shown in Figure 1.

A simple rate law for this catalytic reaction is

$$-d[HC{\equiv}CPh]/dt = -d[H_2]/dt = d[H_2C{=}CHPh]/dt = k[HC{\equiv}CPh]^m[1]^n(P_{H_2})^q \quad (1)$$

At constant temperature and with a large excess of phenylacetylene, the rate law is further simplified to

$$-d[HC{\equiv}CPh]/dt = -d[H_2]/dt = d[H_2C{=}CHPh]/dt = k_{obs}[1]^n(P_{H_2})^q \quad (2)$$

Table I. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by 1

T, K	P_{H_2}, atm	[Fe/H_2], 10^3 M	[PhC≡CH], M	dV/dt, 10^7 L s^{-1}	k_{obs}, 10^3 s^{-1}	k, 10^2 M^{-1} s^{-1}
303	1	0.60	0.3	17.0	4.2	4.7
	1	0.80	0.3	25.5	16.0	5.3
	1	1.00	0.3	29.0	14.6	4.9
	1	1.20	0.3	33.2	13.9	4.6
	1	1.37	0.3	37.5	13.8	4.6
	1	1.37	0.4	46.3	17.0	4.2
	1	1.37	0.2	24.8	9.1	4.6
	1	1.37	0.1	12.0	4.4	4.4
	0.78	1.00	0.3	28.7	14.4	4.8
	0.59	1.00	0.3	27.5	13.8	4.6
313	1	1.00	0.3	70.7	34.4	11.5
323	1	1.00	0.3	157.3	74.2	24.7
333	1	1.00	0.3	204.2	93.5	31.1

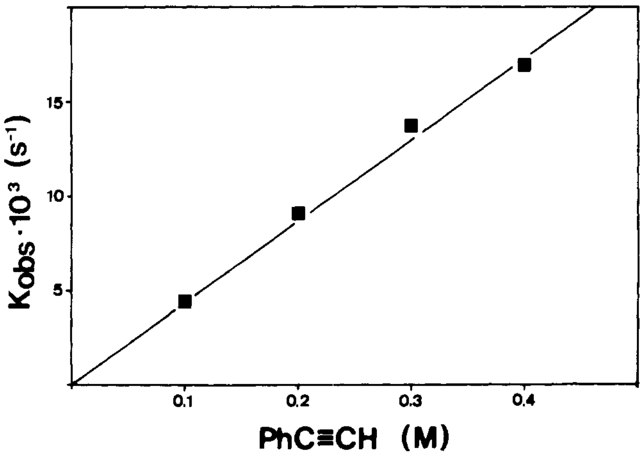

Figure 2. Rate constant for the hydrogenation of phenylacetylene to styrene catalyzed by 1 in 1,2-dichloroethane at 30 °C (1 atm of H_2, 1.37×10^{-3} M 1).

The reactions were followed by mesuring the hydrogen consumption as a function of time. The volume of H_2 corrected to 1 atm was converted into a pseudo-zero-order constant (k_{obs}) by using eq 3, where $-dV/dt$ is the initial rate measured from gas-uptake experiments, R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume of the reacting solution.

$$-(dV/dt)RTV_{sol} = k_{obs}[1]^n(P_{H_2})^q \quad (3)$$

In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst and substrate concentrations and at different hydrogen pressures (Table I). Plots of log ($-dV/dt$) vs log [1] and log ($-dV/dt$) vs log (P_{H_2}) yield straight lines of slopes 1.09 and 0.03, respectively, showing that the reduction of phenylacetylene is first order in catalyst concentration and zero order in hydrogen pressure. The values of k_{obs} shown in Table I were thus obtained from eq 3 with $n = 1$ and $q = 0$. Plots of log ($-dV/dt$) vs log [HC≡CPh] yield a straight line of slope 0.91, demonstrating that the reaction is first order in substrate concentration (i.e., $m = 1$ in eq 1).

Therefore, the catalytic rate law is

$$-d[HC{\equiv}CPh]/dt = -d[H_2]/dt = d[H_2C{=}CHPh]/dt = k_4[HC{\equiv}CPh][1] \quad (4)$$

and

$$k_{obs} = k_4[HC{\equiv}CPh] \quad (5)$$

A plot of k_{obs} vs [HC≡CPh] (Figure 2) provides a value of $(4.3 \pm 0.2) \times 10^{-2}$ M^{-1} s^{-1} for k_4 at 303 K.

Under the catalytic conditions employed for 1, the dinitrogen derivative 2 is able to catalyze the selective hydrogenation of HC≡CPh to H_2C=CHPh. In order to

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[24] (a) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1989**, *111*, 6137. (b) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333.

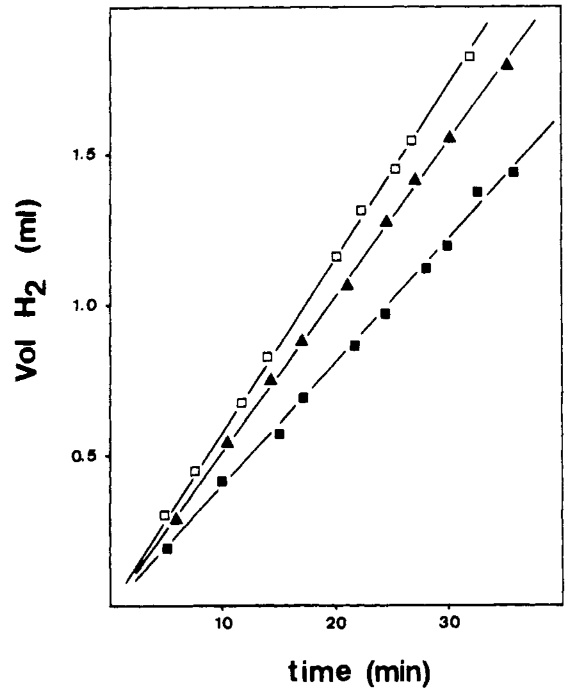


Figure 3. H_2 gas uptake plots for the 2-catalyzed hydrogenation of phenylacetylene to styrene in 1,2-dichloroethane at 20 °C (1 atm of H_2, 0.60 × 10^{-3} M 2). [HC≡CPh]: (■) 0.13 M, (▲) 0.15 M, (□) 0.20 M.

Table II. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by 2

T, K	P_{H_2}, atm	[Fe/N$_2$], 10^3 M	[PhC≡CH], M	dV/dt, 10^7 L s^{-1}	k_{obs}, 10^3 s^{-1}	k, 10^2 M^{-1} s^{-1}
293	1	0.60	0.10	5.2	4.5	4.5
	1	0.93	0.10	8.3	4.7	4.7
	1	1.19	0.10	8.3	3.6	3.6
	1	1.40	0.10	13.3	4.9	4.9
	1	1.63	0.10	16.3	5.2	5.2
	1	0.60	0.13	6.8	5.9	4.5
	1	0.60	0.15	8.7	7.5	5.0
	1	0.60	0.18	9.3	8.1	4.5
	1	0.60	0.20	9.7	8.4	4.2
	0.90	0.60	0.13	7.0	6.1	4.7
	0.74	0.60	0.13	7.3	6.4	4.9
	0.69	0.60	0.13	7.2	6.2	4.8
	0.51	0.60	0.13	6.7	5.8	4.4
314	1	0.60	0.10	17.8	14.4	14.4
324	1	0.60	0.10	31.2	24.4	24.4
333	1	0.60	0.10	70.0	53.4	53.4

determine the mechanism of the hydrogenation reaction in the presence of 2, the kinetics of the reaction was studied. Typical gas-uptake measurements are shown in Figure 3. Following a kinetic analysis analogous to that described above for 1, we deduce from the data reported in Table II that the rate law for the hydrogenation of phenylacetylene to styrene catalyzed by 2 is

$$-d[HC{\equiv}CPh]/dt = -d[H_2]/dt = d[H_2C{=}CHPh]/dt = k_6[HC{\equiv}CPh][\mathbf{2}] \quad (6)$$

with a value of k_6 of (4.4 ± 0.3) × 10^{-2} M^{-1} s^{-1} at 293 K.

The activation parameters for the catalytic reactions (Table III) were obtained from the temperature dependence of k_4 and k_6. The values are essentially identical (Figure 4) and therefore suggest that the same mechanism is operating for both catalysts, a fact that is readily explained by the almost immediate conversion of 2 to 1 in solution under H_2.

It is interesting to note that the nondependence of the reaction rate on H_2 pressure holds also in the range from 5 to 105 atm (Table IV) where no appreciable formation of ethylbenzene (GC) is produced after complete conversion of HC≡CPh to $H_2C{=}CHPh$ and further (48 h).

Table III. Activation Parameters[a] for the Selective Hydrogenation of Phenylacetylene to Styrene

	a	b	c
E_a (kcal mol^{-1})	11.8 ± 0.8	13 ± 2	12 ± 1
$\Delta H^{\ddagger}$ (kcal mol^{-1})	11.2 ± 0.8	12 ± 2	11 ± 1
$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})	−27 ± 3	−24 ± 6	−27 ± 3
ΔG (kcal mol^{-1})	19 ± 1	19 ± 4	19 ± 4

[a] Activation parameters were calculated in standard conditions (T = 298 K, P = 1 atm): (a) calculated from the plot ln k_6 vs 1/T; (b) calculated from the plot ln k_4 vs 1/T; (c) calculated from the plot shown in Figure 4.

Table IV. Hydrogenation of Phenylacetylene in the Presence of 1[a]

P_{H_2}, atm	product (tof)[b] $H_2C{=}CHPh$	P_{H_2}, atm	product (tof)[b] $H_2C{=}CHPh$
5	7.9	28	8.7
15	9.3	105	7.6

[a] Reaction conditions: catalyst, 0.02 mmol; substrate, 20 mmol; THF (solvent), 50 mL; T, 60 °C; time, 3 h. [b] Moles of substrate transformed per mole of catalyst per hour.

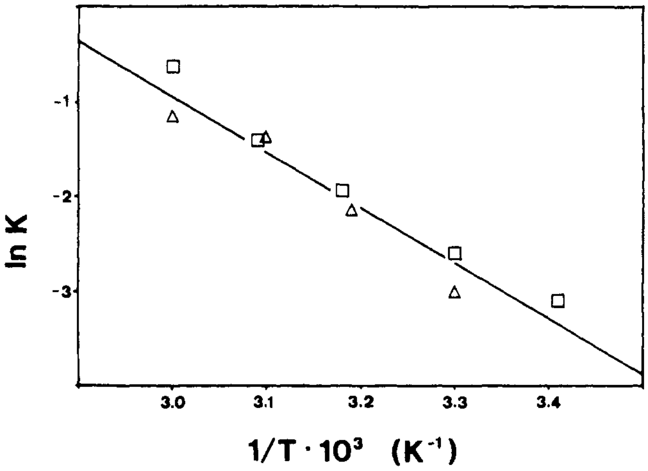


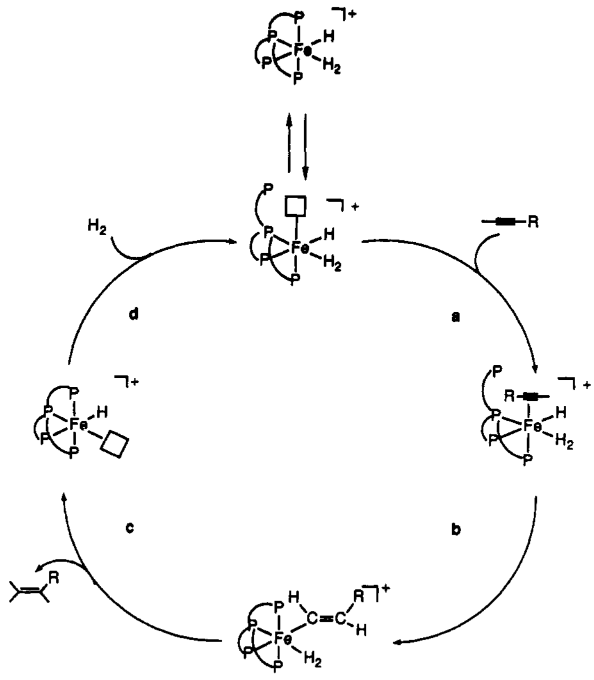
Figure 4. Plot of ln k vs 1/T × 10^3 for the hydrogenation of phenylacetylene catalyzed by 1 (△) and 2 (□).

When the hydrogenation reactions of HC≡CPh catalyzed by 1 or 2 are monitored by either $^{31}P\{^1H\}$ NMR or X-band ESR spectroscopy, we observe that (i) the hydride η^2-dihydrogen complex 1 is the only NMR-detectable species during the catalysis cycle and the termination product as well and (ii) no paramagnetic compound forms in the course of the reaction. In contrast, when the reactions are carried out by using more alkyne than dihydrogen, the paramagnetic σ-alkynyl 3 is found as the termination product of the catalysis cycle.

Mechanistic Considerations. All of the experimental observables reported in the previous sections can be translated into precious information on the mechanism of hydrogenation.

A catalysis cycle that nicely fits the chemical, spectroscopic, kinetic, and thermodynamic data is the one shown in Scheme III. In accord with the chemistry of 1 as well as the nondependence of the reaction rate on the H_2 pressure, no decoordination of H_2 is required at any stage of the cycle. The catalyst is just 1 which can provide room for an incoming alkyne molecule by unfastening a terminal phosphine arm.[22,23] Since 1 is the only phosphorus-containing product detected by ^{31}P NMR during the catalysis cycle, reasonably this compound is a reagent in the rate-determining step as indicated also by eqs 4 and 6. On the other hand, these equations suggest that also the 1-alkyne

Scheme III



substrate can play a role in the rate-determining step. Indeed, according to the largely negative $\Delta S^{\ddagger}$ value (−27 ± 3 cal K^{-1} mol^{-1}), the coordination of the substrate to the metal center is an excellent candidate to the role of rate-determining step. If so, it can be concluded that the alkene is liberated via a fast intramolecular reaction between cis η^2-H_2 and σ-vinyl ligands (step c). Actually, step c might proceed via oxidative addition of H_2 to iron(II) to give an iron(IV) classical dihydride, followed by reductive elimination of alkene. This reaction sequence is highly improbable, particularly as one considers that (i) iron(II) has a low tendency to be oxidized to iron(IV), (ii) such a complicated reaction sequence would reasonably constitute the rate-determining step and this is ruled out by the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values which are consistent with an ordered transition state, and (iii) the stoichiometric hydrogenation reactions are altogether slow (3–4 h) (Scheme II) but alkene formation (^{1}H NMR, GC) occurs within a few miutes after combination of the reagents.

Extension to Other 1-Alkynes and Selectivity. Preliminary studies show that 1 and 2 can be used as homogeneous catalysts for the selective hydrogenation (1 atm of H_2) of a variety of 1-alkynes to alkenes in either THF or 1,2-dichloroethane solution. As is evident from a perusal of Table V, the conversion decreases by increasing the bulkiness of the alkyne substituent which, in turn, does not at all affect the selectivity. The only exception is constituted by $HC{\equiv}CSiMe_3$ which, at high temperature (63 °C), is preferentially converted to 1,4-bis(trimethylsilyl)buta-1,3-diene. This finding is not completely surprising as one recalls that the trimethylsilyl substituent decreases the nucleophilicity of the C_β atom in olefinic moieties.[24] In the case at hand, this effect may contribute to stabilize a σ-alkenyl intermediate, making the vinyl ligand insufficiently basic to deprotonate a cis H_2 ligand. Indeed, the σ-alkenyl 4 in THF at room temperature reacts with $HC{\equiv}CSiMe_3$, yielding the σ-alkenyl 5 and vinyltrimethylsilane, whereas at reflux temperature some $(Me_3Si)HC{=}CHCH{=}CH(SiMe_3)$ (2–3%) is produced, indicating that the temperature favors the reductive dimerization of the alkyne to butadiene at iron. Studies are presently under way to try to understand the mechanism of the present 1-alkyne dimerization that might proceed via a vinylidenealkenyl intermediate.

Table V. Catalytic Hydrogenation of Terminal Alkynes in the Presence of 1[a]

substrate RC≡CH	T, °C	product (tof[b]) CH₂=CHR	RCH=CHCH=CHR
Ph	20	7.6	
	63	45.2	
SiMe₃	20	7.6	
	63	5.2	23.0
n-C₃H₇	20	7.9	
	63	36.7	
n-C₅H₁₁	20	6.4	
	63	24.5	
CH=CH(OMe)	20	2.8	
	63	21.2	

[a] Reaction conditions: alkyne, 2 mmol; catalyst, 0.02 mmol; H_2 pressure, 1 atm; time, 2 h; THF (solvent), 12 mL. [b] Moles of substrate transformed per mole of catalyst per hour.

As a final consideration, we briefly comment on the nature of the selectivity in the present hydrogenation reactions of 1-alkynes to alkenes.

It is well-known that in alkyne/alkene mixtures the alkyne functionality can be preferentially reduced because of the better bonding capabilities of the triple bond.[13,14] However, in general, when most of the alkyne has been consumed, the reduction of alkene occurs. This does not happen by using 1 as catalyst, and in fact, we do not detect formation of alkane (GC) over long reaction times (48 h). The larger size of alkenes vs corresponding alkynes may play a role as shown by the fact that 1 and 2 in THF under argon do not react with styrene whereas both complexes form a stable adduct, $[(PP_3)Fe(H)(C_2H_4)]BPh_4$ (7), with the smallest alkene, namely ethylene. As expected, the reaction of ethylene with the dinitrogen complex 2 is much faster (20 min) than that with the dihydrogen complex, which is completed in 3–4 days. Interestingly, no ethane is produced under catalytic conditions (1 atm of H_2, 1 atm of C_2H_4). This result and the observation that the terminal hydride in 7 does not migrate to ethylene even when forced by an excess of ethylene or of CO (carbon monoxide simply displaces C_2H_4 to give the known hydride carbonyl complex $[(PP_3)Fe(H)(CO)]BPh_4$)[17] indicate that also the electronic factors associated with the nature of the iron–olefin bond are responsible of the selectivity of the hydrogenation reactions catalyzed by 1.

An analogous result has been recently reported by some of us for the hydrogenation of $HC{\equiv}CPh$ catalyzed by $[OsHCl(H_2)(PR_3)_2]$ (PR_3 = PMe-*t*-Bu_2, P-*i*-Pr_3);[7e] the selectivity for the reduction to the alkene is determined by the tendency of the alkyne to undergo insertion to give a vinyl intermediate rather than by the difference in the coordinating ability between $HC{\equiv}CPh$ and $H_2C{=}CHPh$.

Conclusions

The present study has revealed that the *cis*-H η^2-H_2 complex $[(PP_3)Fe(H)(H_2)]BPh_4$ is an effective homogeneous catalyst for the selective hydrogenation of 1-alkynes to alkenes and have served to shed some light on the mechanism of the reaction in which *the formation of a metal hydride from molecular hydrogen is not an obligatory step.* In particular, we believe that this is the first documented example of a catalytic reaction in which (i) the dihydrogen ligand does not leave the metal prior to alkyne coordination and (ii) the reduction of the substrate occurs via an intramolecular acid/base reaction involving η^2-H_2 and σ-vinyl ligands mutually cis disposed. Point ii is of particular interest as it suggests that other hydrogenations could involve protonation by η^2-H_2 intermediates of adjacent organyl ligands in a σ-bond metathesis or heterolytic cleavage reaction.[25]

Experimental Section

General Data. Tetrahydrofuran (THF) and halogenated solvents (dichloromethane and 1,2-dichloroethane) were purified under argon just prior to use by distillation over $LiAlH_4$, and P_2O_5, respectively. 1-Alkynes were purchased from either Fluka or Aldrich and checked by ^1H NMR. When necessary, they were distilled prior to use. All the other solvents and chemicals were reagent grade and, unless otherwise stated, were used as received by commercial suppliers. Deuterated solvents for NMR measurements (Janssen) were dried over molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 or at 200.131 MHz on a Bruker 200-ACP spectrometers. Peak positions are relative to tetramethylsilane as external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instruments operating at 121.421 and 81.015 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4, with downfield values reported as positive. Conductivities were measured with an ORION Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 1×10^{-3} M in nitroethane solutions at room temperature (20 °C). X-band ESR spectra were recorded on a ER-200 DSRC Bruker spectrometer operating at $w_0 = 9.78$ GHz. The control of the external magnetic field was obtained with a microwave bridge ER 041 MR Bruker wavemeter. Magnetic susceptibilities of solid samples were measured on a Faraday balance. High-pressure experiments were performed using a Parr Model 4564 stainless steel minireactor (volume 160 mL) with a magnetic drive stirrer and an electrical mantle as heating source. Analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8500 gas chromatograph with a FFAP on Chromosorb GHP 80/100 mesh ($3.6 \times {}^1/_8$ in.) column at 160 °C and on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and with a 10-ft 100/120 Carbosieve-SII or a 6-ft 0.1% SP-1000 80/100 Carbopack C stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method. GC–MS spectra were collected with a Shimadzu QP-2000 fitted with a 30-m (i.d. 0.25 mm) capillary column, SUPELCO SPB-1.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a dry argon atmosphere by using Schlenk tube techniques. The solid compounds were collected on sintered-glass frits and washed with ethanol and petroleum ether (bp 50–70 °C) before being dried in a stream of argon. Complexes **1** and **2** were synthesized according to the methods reported in the literature.[12,17]

Reaction of 2 with Phenylacetylene. (A) 1:1 Reaction. A 250-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **2** (0.50 g, 0.47 mmol) in THF (50 mL) and 1 equiv of $HC{\equiv}CPh$ (110 μL) and closed under argon. The mixture was stirred for 15 min at room temperature. Addition of ethanol (50 mL) and slow evaporation of the solvent gave orange crystals in ca. 90% yield. GC analysis of the solution revealed the total consumption of the alkyne and the formation of 0.5 equiv of styrene. The orange solid was chromatographed under nitrogen on silica gel column (eluent THF/*n*-hexane, 2:1) to give, together with the starting complex **2**, the σ-acetylide complex $[(PP_3)Fe(C{\equiv}CPh)]BPh_4$ (**3**) in ca. 1:1 ratio. Compound **3** can be recrystallized from CH_2Cl_2/C_2H_5OH. IR: $\nu(C{\equiv}C)$ 2035 cm^{-1} (w), phenyl-reinforced vibration 1580 cm^{-1}. Raman (CH_2Cl_2 solution): $\nu(C{\equiv}C)$ 2040 cm^{-1} (s). μ_{eff}: 3.42 μ_B. X-band ESR spectrum (THF glass, 100 K): $\langle g \rangle = 2.030$, $\langle \Delta H \rangle = 175$ G. Anal. Calcd for $C_{74}H_{67}BFeP_4$: C, 77.50; H, 5.89; Fe, 4.87. Found: C, 77.34; H, 6.01; Fe, 4.80.

(B) 1:2 Reaction. When a double proportion of $HC{\equiv}CPh$ is employed in the above reaction, all of the starting hydride **2** disappeared within 15 min. Addition of ethanol and workup as above gave a pure crop of **3** as yellow-orange crystals. Yield: 87%. The mother liquor was analyzed by GC–MS, showing the presence of 1 equiv of styrene.

Reaction of 1 with Phenylacetylene. Substitution of the dihydrogen complex **1** for **2** in the reaction with phenylacetylene does not change the nature of the products whereas both the rate and the stoichiometry are significantly affected. In fact, the reaction completes within 3–4 h to give **3** and 2 equiv of styrene only by using 3 equiv of $HC{\equiv}CPh$.

A weighted amount of $HC{\equiv}CPh$ (1, 2, or 3 equiv) was introduced via syringe into a THF-d_8 solution (24 mL) of **1** (0.8 mmol) under argon. Samples were withdrawn via syringe every 15 min and checked by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy after being quenched in a liquid nitrogen bath. ^{31}P NMR showed **1** to be the only diamagnetic product present in the solution at any stage of the reactions. The formation of paramagnetic species, most likely **3** ($\langle g \rangle = 2.030$ at 100 K) was determined by X-band ESR spectroscopy. ^1H NMR and GC revealed increasing formation of styrene in the course of the transformation and no evolution of H_2. At complete disappearance of **1**, the formation of 2 equiv of styrene was determined.

Preparation of (*E*)-$[(PP_3)Fe\{CH{=}CH(SiMe_3)\}]BPh_4$ (4). A mixture of **2** (1.07 g, 1.0 mmol) and $HC{\equiv}CSiMe_3$ (145 μL, 1.0 mmol) in THF (80 mL) was stirred at room temperature for 1 h under an argon atmosphere. Addition of ethanol (100 mL) and slow concentration of the solution led to the precipitation of yellow-orange crystals. GC analysis of the solution revealed the formation of vinyltrimethylsilane (10–15%) and complete disappearance of the alkyne. The orange solid contains, together with a small amount of unreacted **2** (<5%), two novel, paramagnetic iron complexes: the σ-alkenyl (*E*)-$[(PP_3)Fe\{CH{=}CH(SiMe_3)\}]BPh_4$ (**4**) (80–85%) and the σ-alkynyl $[(PP_3)Fe(C{\equiv}CSiMe_3)]BPh_4$ (**5**) (10–15%). A pure sample of **4** was obtained by repeated recrystallizations from THF/1-butanol of the crude product. Yield: 71% based on **2**. IR: $\nu(C{=}C)$ 1605 cm^{-1} (m), $\nu(SiC)$ 850 cm^{-1} (s). μ_{eff}: 3.35 μ_B. ESR silent. Anal. Calcd for $C_{71}H_{73}BFeP_4Si$: C, 74.48; H, 6.43; Fe, 4.88. Found: C, 74.22; H, 6.36; Fe, 4.79.

Preparation of $[(PP_3)Fe(C{\equiv}CSiMe_3)]BPh_4$ (5). Treatment of **4** in THF with 1 equiv of $HC{\equiv}CSiMe_3$ and workup as described above gave pure **5** as orange crystals. Yield: 85%. Alternatively, **5** was prepared by reacting **2** in THF with 2 equiv of $HC{\equiv}CSiMe_3$. In both cases, GC analysis of the solution showed the formation of 1 equiv of vinyltrimethylsilane. IR: $\nu(C{\equiv}C)$ 1990 cm^{-1} (m), $\nu(SiC)$ 850 cm^{-1} (vs). μ_{eff}: 3.28 μ_B. X-band ESR spectrum (THF glass, 100 K): $\langle g \rangle = 2.018$, $\langle \Delta H \rangle = 200$ G. Anal. Calcd for $C_{71}H_{71}BFeP_4Si$: C, 74.61; H, 6.26; Fe, 4.89. Found: C, 74.44; H, 6.15; Fe, 4.78.

Preparation of (*E*)-$[(PP_3)Fe(CO)\{CH{=}CH(SiMe_3)\}]BPh_4$ (6). Carbon monoxide was bubbled throughout a THF solution (20 mL) of **4** (0.25 g, 0.22 mmol) for 15 min. Addition of ethanol (20 mL) and slow evaporation of the solvent gave **6** as pale yellow crystals. Yield: 90%. Λ_M: 53 Ω^{-1} cm^2 mol^{-1}. IR: $\nu(C{\equiv}O)$ 1980 cm^{-1} (s), $\nu(C{=}C)$ 1520 cm^{-1} (m), $\nu(SiC)$ 852 cm^{-1} (s). ^1H NMR (CD_2Cl_2, 20 °C): δ 0.73 (s, 9 H, $SiMe_3$), 5.67 (tdd, 1 H, $CH{=}C\mathit{H}SiMe_3$, $J(HH) = 18.6$ Hz, $J(HP) = 4.3$ Hz, $J(HP) = 5.6$ Hz), 6.54 (m, 1 H, $C\mathit{H}{=}CHSiMe_3$, $J(HP) = 9$ Hz, $J(HP) < 4$ Hz). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): AM_2Q spin system, $\delta(P_A) = 172.29$, $\delta(P_M) = 79.95$, $\delta(P_Q) = 77.79$, $J(P_AP_M) = 28.5$ Hz, $J(P_AP_Q) = 11.5$ Hz, $J(P_MP_Q) = 11.7$ Hz. Anal. Calcd for $C_{72}H_{73}BFeOP_4$: C, 73.67; H, 6.27; Fe, 4.76. Found: C, 73.58; H, 6.24; Fe, 4.69.

Preparation of $[(PP_3)Fe(H)(CH_2{=}CH_2)]BPh_4$ (7). Ethylene was bubbled throughout a stirred THF (25 mL) solution of **2** (0.42 g, 0.39 mmol) for 20 min. Addition of ethanol and slow evaporation of the solvent gave **7** as deep yellow crystals. Yield: 79%. Compound **7** can be prepared also by reacting **1** in THF with ethylene, but much longer times are required for a complete conversion (0.4 mmol of **1** transforms into **7** in 72 h). IR: $\nu(FeH)$ 1942 cm^{-1} (br). ^1H NMR (CD_2Cl_2, −20 °C): δ 3.43 (br q, 4 H, C_2H_4, $J(HP) = 3.0$ Hz), −8.43 (dt, 1 H, FeH, $J(HP_A) = 65.3$ Hz, $J(HP_Q) < 2$ Hz, $J(HP_M) = 52.1$ Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8/1,2-dichloroethane, 1:1, 0 °C): AM_2Q spin system, $\delta(P_A) = 161.85$, $\delta(P_M) = 79.64$, $\delta(P_Q) = 70.55$ $J(P_AP_M) = 23.1$ Hz, $J(P_AP_Q) = 42.6$ Hz,

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$J(P_MP_Q)$ = 15.5 Hz. Anal. Calcd for $C_{68}H_{67}BFeP_4$: C, 75.99; H, 6.28; Fe, 5.20. Found: C, 75.82; H, 6.22; Fe, 5.07.

Catalytic Hydrogenation Reactions. Low-Pressure Experiments. The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256).

The catalyst was carried with a degassed solution of the substrate in 1,2-dichloroethane (8 mL) into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenk manifold. The flask was closed by a silicone septum. The system was evacuated and refilled with dihydrogen six times, and the flask was immersed in a constant-temperature bath. The mixture was vigorously shaken during the run. Plots of the kinetic data were fitted by use of conventional linear regression programs.

Alternatively, the substrate (2 mmol), THF (12 mL), and a stirring bar were placed in a reaction vessel fitted with a reflux condenser and with a side arm with a rubber septum under a constant 1 atm of H_2. The vessel was immersed in a constant-temperature oil bath (20 or 63 °C). The catalyst (0.02 mmol) was then added. The solution was sampled after 2 h, and the samples were analyzed by GC and GC–MS.

High-Pressure Experiments. Air was evacuated from the autoclave; then, the solution containing the catalyst, the substrate, and the solvent, prepared in a Schlenk tube, was introduced by suction. Hydrogen was added up to the desired pressure, and the solution in the autoclave was stirred at the selected temperature. At the end of the reaction, the autoclave was cooled, the gas vented out, and the solution collected. The conversion was determined from the crude product by GC analysis with a 2-m packed column containing free fatty acid phase (5%) on Chromosorb G AW-DMCS.

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Registry No. **1**, 123122-81-6; **2**, 54477-71-3; **3**, 123054-72-8; **4**, 123054-68-2; **5**, 123054-70-6; **6**, 123054-78-4; **7**, 137436-45-4; $PhC{\equiv}CH$, 536-74-3; $PhCH{=}CH_2$, 100-42-5; $HC{\equiv}CSiMe_3$, 1066-54-2; $PhCH{=}CHSiMe_3$, 754-05-2; $CH_2{=}CH_2$, 74-85-1; n-$C_3H_7C{\equiv}CH$, 627-19-0; n-$C_5H_{11}C{\equiv}CH$, 628-71-7; $(MeO)CH{=}CHC{\equiv}CH$, 2798-73-4; n-$C_3H_7CH{=}CH_2$, 109-67-1; n-$C_5H_{11}CH{=}CH_2$, 592-76-7; $(MeO)CH{=}CHCH{=}CH_2$, 3036-66-6; $Me_3SiCH{=}CHCH{=}CHSiMe_3$, 13625-90-6.

Syntheses and Structures of Isopropyl- and (Bis(trimethylsilyl)methyl)antimony Rings and *catena*-Tri- and *catena*-Tetrastibanes by Reaction of Organoantimony Rings with Distibanes

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The syntheses and the structures of selected organoantimony rings $(RSb)_n$ and the formation of *catena*-stibanes by reaction of organoantimony rings with distibanes are reported. The syntheses include the preparation of i-$PrSbBr_2$ and the reaction of this intermediate with magnesium to form $(i\text{-}PrSb)_4$ and $(i\text{-}PrSb)_5$. The isopropylantimony rings are stable in solution but polymerize in the absence of solvent. $[(Me_3Si)_2CHSb]_4$ is, however, stable in the solid state with respect to polymerization. This four-membered ring has been obtained in the form of orange crystals from a solution of the dehalogenation products of the corresponding dichloride. The ^1H NMR data of $(i\text{-}PrSb)_4$ and $(i\text{-}PrSb)_5$ in solution are in accordance with the cyclic structures with the substituents adopting a maximum of trans positions. The structure of $[(Me_3Si)_2CHSb]_4$ has been determined by single-crystal X-ray diffractometry as that of a strongly folded cyclotetrastibane (115.4°) in the all-trans configuration. The Sb–Sb distances alternate between short and long (2.83, 2.87 Å), and the molecule on the whole approximates C_2 symmetry. The crystal data with Mo Kα radiation are as follows: triclinic, space group $P\bar{1}$, a = 12.361 (1) Å, b = 12.981 (1) Å, c = 17.337 (2) Å, α = 108.18 (1)°, β = 90.82 (1)°, γ = 102.82 (1)°, Z = 2, and R = 0.0362. The study of the reactivity of organoantimony rings with distibanes led to the formation of the first examples of *catena*-tri- and *catena*-tetrastibanes. The tristibanes $(Me_2Sb)_2SbR$, with R = Et, Pr, t-Bu, $[Me_3Si]_2CH$, and 2,4,6-$Me_3C_6H_2$, are formed by reaction of an excess of Me_4Sb_2 with the corresponding rings $(RSb)_n$. Action of an excess of Et_4Sb_2 with $(EtSb)_5$ or $(PrSb)_5$ gives $(Et_2Sb)_2SbEt$ or $(Et_2Sb)_2SbPr$. $(Ph_2Sb)_2SbEt$ and $(Ph_2SbSbEt)_2$ are formed by the reaction of Ph_4Sb_2 with $(EtSb)_5$. *catena*-Stibanes derived from difficulty accessible antimony rings are better obtained by dehalogenation of appropriate mixtures of organoantimony bromides or by salt elimination; Me_2SbBr and $MeSbBr_2$ react with magnesium to give $(Me_2Sb)_2SbMe$, and Ph_5Sb_3 is obtained by reaction of $PhSbCl_2$ and Ph_2SbLi or Ph_2SbNa in liquid NH_3. The novel *catena*-tri- and *catena*-tetrastibanes have been characterized by ^1H NMR and mass spectra. They exist in equilibrium with distibanes and cyclostibanes.

Introduction

In the context with recent results on the syntheses of organoantimony rings, $(RSb)_n$ (with R = Et, Pr, Bu, Mes; n = 4, 5),[3] we reinvestigated the chemistry of isopropylantimony, which had been reported[4] as black solid polymer, and of (bis(trimethylsilyl)methyl)antimony,[5] a trimer

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