Crystal Structure of 9. Crystal data are as follows: monoclinic; space group $P2_1/n$; $a = 20.125$ (5), $b = 16.679$ (4), $c = 9.616$ (3) Å; $\beta = 99.76$ (2)°; $V = 3181.0$ Å^3, $Z = 4$; $\rho_{calcd} = 1.289$ gcm^{-3}; $\lambda = 1.5418$ Å; $\mu = 7.049$ cm^{-1}; 4136 independent data collected (Phillips PW 1100/16 diffractometer, $\theta/2\theta$ flying step scan, 3° < θ < 53°) at −100 °C using a local-built gas-flow device. The structure was solved by using MULTAN[10] and refined by full-matrix least squares by using 2873 observed reflections ($I > 3\sigma(I)$). The hydrogen atoms were introduced in structure factor calculations at their computed coordinates (C–H = 0.95 Å, B(H) = 1.3B_{eqv}(C) Å^2) but not refined. No absorption corrections were applied since face indexation was not possible under the cold gas stream and in view of the small absorption coefficient. A final difference map revealed no significant maxima. The scattering factor coefficients come from ref 11. $R(F) = 0.035$; $R_W(F) = 0.036$. Crystal data are listed in Tables I–III.

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Supplementary Material Available: Tables of positional parameters of the hydrogen atoms and anisotropic thermal parameters for 9 (4 pages); a listing of observed and calculated structure factors for 9 (11 pages). Ordering information is given on any current masthead page.

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Metal–Hydride Alkynyl → Metal–Vinylidene Rearrangements Occurring in both Solid State and Solution. Role of the 1-Alkyne Substituent in Determining the Relative Stability of π-Alkyne, Hydride Alkynyl, and Vinylidene Forms at Cobalt

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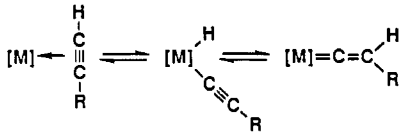
The 16-electron fragment $[(PP_3)Co]^+$ obtained in situ from the dinitrogen complex $[(PP_3)Co(N_2)]BPh_4$ (2) reacts in tetrahydrofuran with terminal alkynes, HC≡CR, yielding π-alkyne adducts of the type $[(PP_3)Co(\pi\text{-}HC{\equiv}CR)]^+$ and vinylidene complexes $[(PP_3)Co\{C{=}C(H)R\}]^+$ as kinetic and thermodynamic products, respectively (R = H, Ph, n-C_3H_7, n-C_5H_{11}, CMe_3, $SiMe_3$; $PP_3 = P(CH_2CH_2PPh_2)_3$). Between the π-alkyne and vinylidene forms, the system evolves through a third species, namely the Co(III) hydride alkynyl complexes $[(PP_3)Co(H)(C{\equiv}CR)]^+$, which are thermodynamically favored over the π-alkyne complexes and disfavored over the vinylidene ones. The sequence $Co(\pi\text{-}HC{\equiv}CR) \rightarrow Co(H)(C{\equiv}CR) \rightarrow Co\{C{=}C(H)R\}$ is controlled by the temperature, so that by a judicious choice of this parameter it is possible to freeze the reactions at any of the three steps. Spectroscopic evidence is provided for the formation of the π-alkyne adducts whereas both the hydride alkynyl and vinylidene complexes have been isolated in the solid state and completely characterized by spectroscopic and X-ray diffraction techniques. The conversion of the hydride alkynyl complexes to the vinylidene isomers is affected inter alia by the nature of the alkyne substituent. In particular, the temperature at which the conversion occurs increases in the order $SiMe_3 > Ph > H \gg CMe_3 > n\text{-}C_3H_7 \cong n\text{-}C_5H_{11}$. Accordingly, the electronic effects seem to prevail over the steric ones in governing the tautomeric rearrangement. Kinetic and thermodynamic studies show that (i) the hydride alkynyl to vinylidene rearrangement is first order in the Co(III) hydride alkynyl complexes and (ii) the rearrangement most likely proceeds via a dissociative intramolecular 1,3-hydrogen shift pathway. The hydride alkynyl to vinylidene rearrangement occurs also in the solid state at relatively low temperatures (from 303 K for R = CMe_3 to 363 K for R = $SiMe_3$) and depends again on the nature of the 1-alkyne terminal substituent.

Introduction

Scheme I



The 1-alkyne to vinylidene tautomerization (Scheme I) occurs widely throughout organometallic chemistry,[1] homogeneous and heterogeneous catalysis,[2] and biochemistry.[3] In recent years, much has been learned about the mechanism of this important reaction, which can be pro-

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[1] For leading references on this subject see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* 1983, *22*, 59. (b) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. C. *J. Am. Chem. Soc.* 1988, *110*, 6096. (c) Schubert, U.; Grönen, J. *Chem. Ber.* 1989, *122*, 1237. (d) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* 1987, 3049. (e) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* 1985, *107*, 4474. (f) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* 1982, *1*, 628. (g) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1979, *101*, 7232. (h) Höhn, A.; Werner, H. *J. Organomet. Chem.* 1990, *382*, 255. (i) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev. (Engl. Transl.)* 1989, *58*, 693; *Usp. Khim.* 1989, *58*, 1197. (j) Miller, D. C.; Angelici, R. J. *Organometallics* 1991, *10*, 79.

[2] (a) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1985, *107*, 6739. (b) Katz, T. J.; Ho, T.-H.; Shih, N.-Y.; Ying, Y.-C.; Stuart, V. I. W. *J. Am. Chem. Soc.* 1984, *106*, 2659. (c) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* 1986, 790. (d) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* 1989, *54*, 1518. (e) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* 1990, *112*, 7809.

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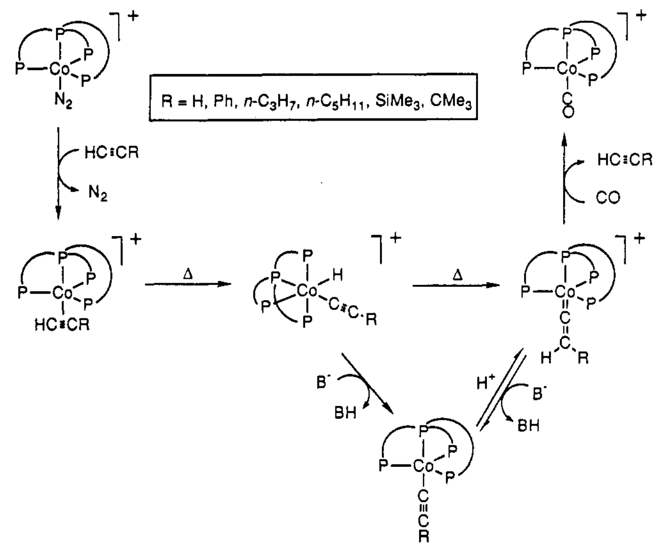
Scheme II



moted by both mononuclear[1,4] and polynuclear[1,5] metal systems. It is generally agreed that in the initial step the alkyne molecule coordinates in a η^2 mode to the metal center. From this π-intermediate, the system can eventually convert into hydride alkynyl (C–H oxidative addition) and/or vinylidene (1,3-hydrogen shift/1,2-hydrogen shift) derivatives.[6] Evidence has been provided for the reversible interconversion of the three isomers of Scheme I, and some kinetic and thermodynamic data have been obtained by spectroscopic methods.[4,5]

In spite of the large body of mechanistic information and the efforts for theoretical interpretation, the factors that may affect the conversion of 1-alkynes into vinylidene ligands at transition metals are not fully elucidated.[4c] In particular, the roles of the metal center and of the alkyne substituent need to be further explored.

This work addresses these limitations by examining the reactions of 16-electron metal fragments with 1-alkynes bearing as many different substituents as possible. The results obtained with the cobalt fragment $[(PP_3)Co]^+$ are described and compared with those previously reported for the rhodium analogue $[(PP_3)Rh]^+$ (PP_3 = $P(CH_2CH_2PPh_2)_3$).[7] From our studies it is concluded that both the alkyne substituent and the metal play a role of primary importance in determining the relative stability of the final products of the reaction, namely hydride alkynyl and vinylidene species, as well as the rate of their interconversion. Also, we describe here the first examples of metal–hydride alkynyl to metal–vinylidene rearrangements occurring in the solid state. This finding is intriguing since several surface-catalyzed reactions involving alkynes,[2a,b] in addition to the well-known Fischer–Tropsch polymerization reaction,[8] have been *suggested* to proceed via vinylidene intermediates.

Results

The principal preparations and reactions of the complexes described in this paper are reported in Scheme II. Selected NMR data ($^{31}P\{^1H\}$ and ^1H spectra) are collected in Table I. Significant IR absorptions and $^{13}C\{^1H\}$ NMR data are given in the Experimental Section.

Reactions of the 16-Electron Fragment $[(PP_3)Co]^+$ with Terminal Alkynes. The trigonal-bipyramidal (TBP) Co(I) monohydride $[(PP_3)CoH]$[9,10] (1) in tetrahydrofuran (THF) under argon undergoes electrophilic attack by CH_3^+ from methyl triflate, to produce, following the reductive elimination of methane, the 16-electron system $[(PP_3)Co]^+$. The latter fragment may be stabilized by a variety of organic and inorganic ligands, including molecular dinitrogen, which favors the quantitative formation of the brick red complex $[(PP_3)Co(N_2)]BPh_4$ (2).[11] Since dinitrogen is weakly bound to cobalt and can be readily displaced by dihydrogen and olefins,[10,11] 2 provides an excellent entry to study the reactions of the 16-electron fragment $[(PP_3)Co]^+$ with terminal alkynes. As will be apparent in forthcoming pages, the products of such reactions are strongly dependent on both the temperature and the nature of the substituents at the alkynes. Therefore, the results obtained will be conveniently classified according to these two parameters.

Room-Temperature Reactions. (a) $HC{\equiv}CSiMe_3$. Stirring 2 in THF with a slight excess of (trimethylsilyl)acetylene for 30 min yields off-white crystals of the cis hydride alkynyl complex $[(PP_3)Co(H)(C{\equiv}CSiMe_3)]BPh_4$ (3) after addition of $NaBPh_4$ in ethanol. No formation of other products than 3 is observed on increasing the reaction time up to 24 h.

Compound 3 is air-stable in the solid state and in deoxygenated solutions, in which it behaves as a 1:1 electrolyte. The IR spectrum contains a strong, sharp absorption at 2023 cm^{-1} and a weaker, broad band at 1951 cm^{-1}, which are assigned to $\nu(C{\equiv}C)$ of a terminal alkynyl ligand and to $\nu(Co{-}H)$, respectively.[7,10] Finally, the typical bands at 851 and 612 cm^{-1} diagnose the presence of the $SiMe_3$ substituent and of the tetraphenylborate anion, respectively. The occurrence of oxidative addition of the alkyne C—H bond at cobalt is clearly confirmed by the ^{31}P and ^1H NMR spectra of 3.

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Table I. NMR Spectral Data for the Complexes

		^1H[b]				$^{31}P\{^1H\}$[c]					
compd	solvent[a]	assignt	chem shift	coupling const, J		temp	pattern	chem shift		coupling const, J	
3	A	Co–H	−13.21 dpq	HP_{trans}	79.6	188	AM_2Q	P_A	157.82	P_AP_M	18.5
				HP_{cis}	51.5			P_M	61.46	P_AP_Q	18.5
		$SiMe_3$	0.24 s					P_Q	60.32	P_MP_Q	*d*
4	A	C=CH	4.34 tqd	HH_α	7.3	213	AM_3	P_A	161.73	P_AP_M	31.8
				HP_M	5.5			P_M	79.97		
				HP_A	1.0						
		H_α	2.36 pqq	$H_\alpha H_\beta$	7.3						
				$H_\alpha P_M$	1.7						
		H_β	1.40 psex	$H_\beta H_\gamma$	7.3						
		H_γ	0.89 t								
5	A	C=CH	4.61 tqd	HH_α	6.9	213	AM_3	P_A	161.85	P_AP_M	31.7
				HP_M	5.7			P_M	79.90		
				HP_A	0.9						
		H_α	2.63 pqq	$H_\alpha H_\beta$	6.8						
				$H_\alpha P_M$	1.5						
		H_β, H_γ, H_δ	2.63–1.50 m								
		H_ϵ	1.16 t	$H_\delta H_\epsilon$	7.0						
6	A	C=CH	3.52 qd	HP_M	5.9	253	AM_3	P_A	155.97	P_AP_M	32.5
				HP_A	0.9			P_M	74.51		
		CMe_3	1.08 s								
7[e]	A	Co–H	−13.22 dpq	HP_{trans}	87.0	248	AM_2Q	P_A	159.1	P_AP_M	*d*
				HP_{cis}	50.2			P_M	59.9	P_AP_Q	*d*
		CC—H	2.49 pqu	HP_{cis}	3.1			P_Q	69.0	P_MP_Q	*d*
8[e]	A	Co—H	−13.16 dpq	HP_{trans}	85.1	253	AM_2Q	P_A	160.7	P_AP_M	*d*
				HP_{cis}	55.7			P_M	64.3	P_AP_Q	*d*
		CC—H	0.99 s					P_Q	61.5	P_MP_Q	*d*
9	A	$C=CH_2$	5.08 qd	HP_M	10.1	248	AM_3	P_A	157.56	P_AP_M	42.7
				HP_A	2.0			P_M	64.57		
10	B	C=CH	5.22 qd	HP_M	6.4	248	AM_3	P_A	157.94	P_AP_M	27.3
				HP_A	0.8			P_M	76.98		
11[e]	A	Co—H	−13.40 dpq	HP_{trans}	86.0	253	AM_2Q	P_A	159.7	P_AP_M	*d*
				HP_{cis}	51.5			P_M	62.1	P_AP_Q	*d*
		CMe_3	0.99 s					P_Q	60.4	P_MP_Q	*d*
13	A	C=CH	3.65 qd	HP_M	9.1	228	AM_3	P_A	163.40	P_AP_M	33.9
				HP_A	1.6			P_M	78.99		
		$SiMe_3$	0.15 s								
14[e]	A	Co—H	−13.33 dpq	HP_{trans}	88.9	233	AM_2Q	P_A	159.44	P_AP_M	*d*
				HP_{cis}	46.9			P_M	60.46	P_AP_Q	*d*
		H_α	*f*					P_Q	62.80	P_MP_Q	*d*
		H_β	1.79 psex	$H_\beta H_\alpha$	7.0						
		H_γ	1.18 t	$H_\beta H_\gamma$	7.0						
15[e]	A	Co—H	−13.28 dpq	HP_{trans}	84.1	253	AM_2Q	P_A	159.50	P_AP_M	*d*
				HP_{cis}	47.9			P_M	62.97	P_AP_Q	*d*
		H_α	2.64 tq	$H_\alpha H_\beta$	7.1			P_Q	60.50	P_MP_Q	*d*
				$H_\alpha P_M$	2.3						
		H_β, H_γ, H_δ	1.85–1.45 m								
		H_ϵ	0.97 t	$H_\delta H_\epsilon$	7.2						
16	B	C≡CH	*g*			253	AM_3	P_A	174.42	P_AP_M	33.9
								P_M	64.00		
17	B	CMe_3	1.16 s			253	AM_3	P_A	174.34	P_AP_M	30.4
								P_M	64.21		
18	C	$SiMe_3$	0.38 s			263	AM_3	P_A	174.20	P_AP_M	32.4
								P_M	65.46		
19	C	CCC_6H_5	*h*			223	AM_3	P_A	173.34	P_AP_M	33.9
								P_M	65.08		
20[e]	B	H_α	2.36 m			183	AM_3	P_A	177.49	P_AP_M	32.2
		H_β	1.42 psex	$H_\alpha H_\beta$	7.1			P_M	63.80		
		H_γ	0.91 t	$H_\beta H_\gamma$	7.1						
21	C	H_α	2.10 m[i]			223	AM_3	P_A	174.53	P_AP_M	31.7
		H_β, H_γ, H_δ	1.50–1.10 m					P_M	67.08		
		H_ϵ	0.82 t	$H_\delta H_\epsilon$	7.2						

[a] Legend: A, acetone-d_6; B, dichloromethane-d_2; C, toluene-d_8. [b] All ^1H NMR spectra were recorded at 299.945 MHz at room temperature unless otherwise stated. The resonances due to the hydrogen atoms of the PP_3 ligand are not reported. Chemical shifts are given in ppm from external TMS. The greek subscripts α, β, γ, δ, and ϵ denote the protons of the n-C_3H_7 and n-C_5H_{11} substituents. Key: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; sex, sextuplet; m, multiplet; p, pseudo. Coupling constants are in Hz. [c] Chemical shifts are given in ppm from external 85% H_3PO_4 with positive values being downfield from the standard. P_A denotes the bridgehead phosphorus atom, while P_M and P_Q refer to the terminal phosphorus atoms of the PP_3 ligand. Coupling constants are in Hz. [d] Because of the quadrupolar broadening of the resonance the coupling constants are not resolved even at low temperature. [e] The ^1H NMR spectrum was recorded at 253 K. [f] Obscured by the aliphatic protons of the PP_3 ligand. [g] Not observed. [h] Obscured by the aromatic protons of the PP_3 ligand and of the BPh_4 anion. [i] Partially masked by the aliphatic protons of the PP_3 ligand.

The $^{31}P\{^1H\}$ NMR spectrum recorded in acetone-d_6 at room temperature consists of an AM_2Q spin system. The low-field signal ($\delta(P_A) = 157.80$) is readily assigned to the bridgehead phosphorus atom of the PP_3 ligand. The high value of its coordination chemical shift ($\Delta(P) = \delta(P_{coord}) - \delta(P_{free\ ligand}) = 122.7$ ppm) is consistent with the highly deshielding $\Delta(R)$ contribution expected for a P atom involved in multiple five-membered metalla rings.[12] The other two resonances, which fall very close to each other ($\delta(P_M) = 61.09$; $\delta(P_Q) = 60.73$), are assigned to the three terminal phosphorus atoms of the tripodal ligand, two of

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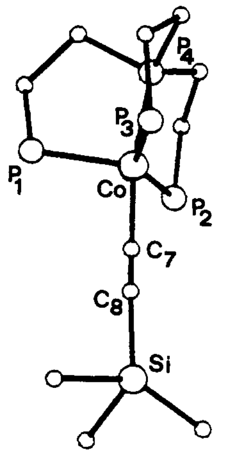

Figure 1. Drawing of the complex cation $[(PP_3)Co(H)(C{\equiv}CSiMe_3)]^+$.

which (P_M), namely those lying mutually trans in the two axial positions of the octahedron, are magnetically equivalent.

The $^{31}P\{^1H\}$ NMR spectra of **3** do not significantly change over the temperature range from 188 to 298 K, showing only a small temperature dependence of the chemical shifts. All the resonances are largely broadened by the cobalt quadrupolar moment and sharpen, but do not completely resolve, into fine structures even at the lowest temperature attained. At low temperature, the coupling constant between the apical and the terminal phosphorus atoms becomes discernible as one enhances the resolution by Gaussian multiplication. The observed value of 18.5 Hz for $J(P_AP_M)$ and $J(P_AP_Q)$ is in line with literature data for octahedral (OCT) complexes of cobalt containing the PP_3 ligand.[10,11,13]

The proton NMR spectrum (acetone-d_6, room temperature) shows a well-resolved doublet of pseudoquartets at −13.21 ppm. This resonance is readily attributed to the terminal hydride ligand. Its multiplicity arises from coupling of the hydride to the trans phosphorus atom ($J(HP_{trans})$ = 79.6 Hz) and to three cis phosphorus nuclei ($J(HP_{cis})$ = 51.5 Hz), which are not magnetically equivalent but exhibit fortuitous coincidence of the coupling constant values to the hydride.

The solid-state structure of **3** has been investigated by X-ray diffraction techniques, an experiment that has been only partially successful.[14] No plate-shaped crystal could be grown thicker than 0.03 mm, and at the same time the diffracting power of the specimen was unusually low. Since two unit formulas of **3** crystallize in the asymmetric unit, the task of refining a minimum number of ca. 400 parameters with only 2207 reflections ($I > 2\sigma(I)$) resulted in a poor structure determination. The poor R factor of ca. 0.11 as well as the large standard deviations associated with bond lengths and angles does not allow us to present a full report of the X-ray structural results, except for two macroscopic aspects that are relevant for understanding the chemistry of the system. In Figure 1 we present a sketch of the complex cation $[(PP_3)Co(H)(C{\equiv}CSiMe_3)]^+$. The quasi-collinearity of the vector P_4–Co–C_7–C_8–Si is a reliable structural feature that, in keeping with the spectroscopic results, confirms the presence of a hydride acetylide complex rather than a vinylidene one. In fact, the angle C_7–C_8–Si with a value of 178° excludes an sp^2 hybridization of C_8. The second feature is that one of the angles at the cobalt atom, determined by two terminal phosphorus donors (P_2, P_3) is opened to a value of ca. 150°. This feature indicates that there is sufficient room for a hydride ligand to sit between the two phosphorus donors. A very similar angle of 153° was found in the closely related complex $[(NP_3)Rh(H)(C{\equiv}CH)]^+$ (NP_3 = $N(CH_2CH_2PPh_2)_3$), having a pseudooctahedral structure with an equatorial hydride ligand.[7b] Also in the dihydride complex $[(PP_3)RhH_2]^+$ the P–M–P angle in question has exactly the same opening,[15] whereas in the cobalt dihydrogen complex $[(PP_3)Co(\eta^2\text{-}H_2)]^+$, which has an almost regular trigonal-bipyramidal structure, the three equatorial P–Co–P angles are in the range 115.5 (7)–121.8 (7)°.[11]

(b) $HC{\equiv}CR$ (R = n-C_3H_7, n-C_5H_{11}, CMe_3). Under the same reaction conditions, the alkyl-substituted acetylenes $HC{\equiv}CR$ (R = n-C_3H_7, n-C_5H_{11}, CMe_3) react with **2**, producing dark red solutions from which separate dark red crystals of the vinylidene complexes $[(PP_3)Co\{C{=}C(H)R\}]BPh_4$ (R = n-C_3H_7 (**4**), n-C_5H_{11} (**5**), CMe_3 (**6**)) after addition of $NaBPh_4$ and ethanol. Compounds **4**–**6** are diamagnetic and fairly stable in the solid state and in deoxygenated solutions, in which they behave as 1:1 electrolytes. The presence of vinylidene ligands in **4**–**6** is unambiguously determined by spectroscopic IR and NMR measurements, although a direct comparison with other mononuclear cobalt vinylidenes is precluded by the lack of such compounds in the literature.[16]

The IR spectra contain no high-energy vibrations typical of either C≡C or Co—H bonds, whereas medium-intensity bands attributable to $\nu(C{=}C)$ of the vinylidene moiety are exhibited in the 1645–1660-cm^{-1} range.[1] The ^1H NMR spectra (acetone-d_6, room temperature) show well-resolved multiplets (1 H) which fall in the proper range for vinylidene hydrogens ($3.52 \le \delta \le 4.61$ ppm),[1] each of which couples to the four phosphorus atoms of the PP_3 ligand and, for compounds **4** and **5**, also to the two hydrogens of the CH_2 group proximal to the alkyl substituent. The $^{31}P\{^1H\}$ NMR spectra in acetone-d_6 exhibit AM_3 patterns with chemical shifts and coupling constants in line with those previously reported for a variety of TBP complexes containing polydentate phosphines.[10,13,17,18] Due to the cobalt quadrupolar moment, well-resolved spectra are obtained below 260 K. The spectra are invariant down to 175 K, thus indicating that, also at low temperature, the

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(13) (a) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266. (b) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616. (c) DuBois, D. L.; Miedaner, A. *Inorg. Chem.* **1986**, *25*, 4642.

(14) Crystal data: monoclinic, $P2_1/a$, a = 33.118 (7) Å, b = 19.481 (4) Å, c = 19.533 (4) Å, β = 94.90 (8)°, V = 12602 Å^3, Z = 4. Data collection was on a Philips PW1100 diffractometer with Mo Kα radiation. Only 2207 reflections having $I \ge 2\sigma(I)$ could be considered observed out of the ca. 13000 collected reflections. The structure was solved by Patterson and Fourier techniques and refined to R = 0.11. Anisotropic temperature factors for Co, Si, and P atoms were used in the least-squares refinement. Phenyl rings were treated as rigid bodies of D_{6h} symmetry.

(15) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. A complete report of structural data is to be published.

(16) Few cobalt complexes containing bridging μ_2- or μ_3-vinylidene ligands have been described: (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97 and references therein. (b) Albiez, T.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 572. (c) Bernhardt, W.; Schacht, H.-T.; Vahrenkamp, H. *Z. Naturforsch.* **1989**, *44B*, 1060. (d) Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 141. (e) Vahrenkamp, H. *J. Mol. Catal.* **1983**, *21*, 233. (f) Horváth, I. I.; Pályi, G.; Markó, L.; Andretti, G. *J. Chem. Soc., Chem. Commun.* **1979**, 1054. See also ref 5g. (g) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329. (h) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (i) Herrmann, W.; Weber, C.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1985**, *297*, 245.

(17) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

(18) (a) Bianchini, C.; Laschi, F.; Ottaviani, M. F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146.

Table II. Summary of Crystal Data for $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$

formula	$C_{74}H_{68}P_4BCo$
mol wt	1151.01
cryst dimens, mm	0.25 × 0.20 × 0.05
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	22.459 (4)
b, Å	19.565 (4)
c, Å	17.444 (4)
α, deg	79.12 (9)
β, deg	67.49 (8)
γ, deg	60.76 (9)
V, Å^3	6178.81
Z	4
d_{calc}, g cm^{-3}	1.24
μ(Cu Kα), cm^{-1}	35.82
radiation	graphite-monochromated Cu Kα, λ = 1.5418 Å
scan type	ω–2θ
2θ range, deg	5–110
scan width, deg	0.7 + 0.15 (tan θ)
scan speed, deg s^{-1}	0.04
total no. of data	13 376
no. of unique data, $I > 2\sigma(I)$	3884
no. of params	430
R	0.087
R_w	0.087
abs cor, min–max	0.51–0.79

vinylidene fragment is freely rotating in solution around the metal–carbon axis. Such behavior is common for vinylidene complexes and is ascribed to a very low energy barrier for interconversion of rotational isomers.[1,4,7a]

Conclusive spectroscopic evidence for the vinylidene structure of **4–6** is provided by $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2, 298 K) recorded with use of pulse delays up to 4 s in order to enhance the sensitivity toward the unsubstituted C_α carbon of the vinylidene moiety. In this way, a well-resolved doublet of quartets between 327.2 and 332.6 ppm was observed for each complex with chemical shifts and coupling constants, J(CP), characteristic for the electron-deficient α-carbons of terminal vinylidene ligands.[1a,i,7] The dq multiplicity is consistent with the solution structure of the complexes (the vinylidene C_α carbon atom is close to three equivalent terminal phosphorus nuclei). In particular, we observe a stronger coupling to the bridgehead phosphorus atom ($J(C_\alpha P_{ap})_{av}$ = 45.6 Hz) than to the terminal P donors ($J(C_\alpha P_{eq})_{av}$ = 23.0 Hz). The C_β resonances for compounds **4–6** appear as broad doublets at relatively high field (121.6–132.8 ppm, $J(C_\beta P)_{av}$ = 15.4 Hz).[1i]

(c) Reactions with HC≡CH and HC≡CPh. Under the same conditions and after the usual workup, the reactions of **2** with ethyne or phenylacetylene produce mixtures of hydride alkynyl, $[(PP_3)Co(H)(C{\equiv}CR)]BPh_4$ (R = H (**7**), Ph (**8**)), and vinylidene, $[(PP_3)Co\{C{=}C(H)R\}]BPh_4$ (R = H (**9**), Ph (**10**)), complexes. Like **3**, the compounds **7** and **8** are hexacoordinated Co(III) species with hydride and alkynyl ligands mutually cis disposed. A vinylidene structure can be readily assigned to **9** and **10** on the basis of their IR and NMR properties, which are quite comparable with those of **4–6**.

The detailed structural features of the phenylvinylidene derivative **10** have been determined by an X-ray diffraction analysis. Crystal data are presented in Table II. There are two complex cations $[(PP_3)Co\{C{=}C(H)Ph\}]^+$ and two BPh_4^- anions in the asymmetric unit of **10**. A drawing of the complex cation a is presented in Figure 2, cation b being only marginally different. Selected bond lengths and angles are reported in Table III. The coordination geometry at the cobalt atom is approximately TBP, although one equatorial P–Co–P angle is as large as 140 (5)° (average value) and the angle determined at cobalt by the trans-axial ligands (P_4–Co–C_7) deviates significantly from 180° (167 (1) and 162 (1)° in cations a and b, respectively). The presence of a vinylidene ligand in **10** is transparent from structural data. In fact, the angle at the β-carbon atom (C_7–C_8–C_{Ph}) has a value of 128 (3)° (131 (3)° in b), still reasonable for sp^2 hybridization. Interestingly, the four-atom sequence P_4–Co–C_7–C_8 is not linear; the P_4–Co–C_7 angle is 167 (1) and 162 (1)° (in a and b, respectively), bent toward the cradle of the P_2–Co–P_3 angle. A slight bending at the α-carbon (C_7) is not unusual for vinylidene complexes, and it has been observed in other cases.[19] To our knowledge, the only other X-ray-authenticated mononuclear vinylidene complexes of a first-row transition element are the two iron compounds $[CpFe\{C{=}C(Me)CS_2Me\}]I$[20] and $[\{P(OMe)_3\}_2Fe(CO)_2\{C{=}C(H)CHO\}]$.[21]

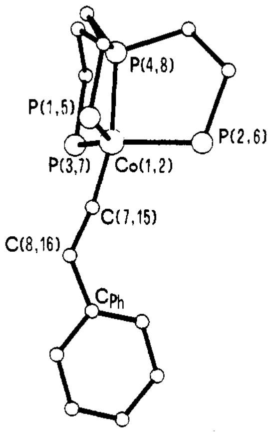

Figure 2. Drawing of the complex cation $[(PP_3)Co\{C{=}C(H)Ph\}]^+$. For the sake of clarity, the phenyl rings are omitted. The labeling (double numbers in parentheses) refer to atoms of the two independent molecules in the asymmetric unit.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$[a]

	molecule a	molecule b
$Co_{1,2}$–$P_{1,5}$	2.197 (7)	2.202 (8)
$Co_{1,2}$–$P_{2,6}$	2.19 (1)	2.23 (1)
$Co_{1,2}$–$P_{3,7}$	2.20 (8)	2.21 (1)
$Co_{1,2}$–$P_{4,8}$	2.190 (9)	2.180 (8)
$Co_{1,2}$–$C_{7,15}$	1.71 (3)	1.71 (3)
$C_{7,15}$–$C_{8,16}$	1.35 (4)	1.33 (5)
$C_{8,16}$–C_{Ph}	1.48 (4)	1.43 (3)
$P_{1,5}$–$Co_{1,2}$–$P_{2,6}$	104.8 (4)	112.8 (5)
$P_{1,5}$–$Co_{1,2}$–$P_{3,7}$	139.4 (6)	140.5 (4)
$P_{3,7}$–$Co_{1,2}$–$P_{2,6}$	113.7 (5)	104.4 (4)
$P_{4,8}$–$Co_{1,2}$–$P_{1,5}$	85.1 (4)	84.9 (4)
$P_{4,8}$–$Co_{1,2}$–$P_{2,6}$	87.6 (4)	86.4 (4)
$P_{4,8}$–$Co_{1,2}$–$P_{3,7}$	84.0 (4)	84.5 (5)
$P_{4,8}$–$Co_{1,2}$–$C_{7,15}$	167 (1)	162 (1)
$P_{1,5}$–$Co_{1,2}$–$C_{7,15}$	90 (1)	93 (1)
$P_{2,6}$–$Co_{1,2}$–$C_{7,15}$	105 (1)	110 (1)
$P_{3,7}$–$Co_{1,2}$–$C_{7,15}$	92 (1)	86 (1)
$Co_{1,2}$–$C_{7,15}$–$C_{8,18}$	170 (3)	167 (3)
$C_{7,15}$–$C_{8,16}$–C_{Ph}	129 (3)	131 (3)

[a] The subscript numbers, separated by commas, refer to the first and second molecule, respectively, in the asymmetric unit.

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(19) Pombeiro, A. L.; Almeida, S. S. P. R.; Silva, M. F. C. G.; Jeffrey, J. C.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 2387 and references therein.

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(21) Löwe, C.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, *372*, 295.

The Co–C$_\alpha$ distance of 1.715 (25) Å is somewhat shorter than the related Fe–C distance in the two iron vinylidenes (1.74 (2) and 1.749 (5) Å, respectively). In any case the M–C$_\alpha$ distance is shorter than that found in σ-alkyl and in σ-aryl complexes (for cobalt, these range between 1.931 and 2.086 Å),[22] thus confirming a good percentage of M=C double-bond character in vinylidene complexes. The C–C distance within the vinylidene ligand (1.34 (5) Å, average) in **10** is similar to that in the two iron analogues (1.31 (2) and 1.335 (7) Å) and is in agreement with the value expected for a C(sp^2)–C(sp) double bond.[23,24]

The composition of the hydride alkynyl and vinylidene mixtures obtained from the reactions between **2** and ethyne or phenylacetylene (mixtures of **7**–**9** and **8**–**10**, respectively) has been determined by ^{31}P NMR integration. For equal reaction conditions (30 min, 295 K), the product composition is exceedingly reproducible over several experiments. In particular, the reaction with ethyne gives **7** and **9** in a 4:1 ratio, whereas the vinylidene complex **10** is the predominant product of the reaction with $HC\equiv CPh$ (ca. 70%). Interestingly, increasing the reaction time increases the amount of vinylidene products **9** and **10**. At room temperature, the hydride alkynyl to vinylidene transformation is much faster for R = H than for R = Ph. Moreover, we have found that this conversion is greatly accelerated by increasing the temperature of the reactions. At 318 K, stirring **2** in THF for 30 min with either $HC\equiv CH$ or $HC\equiv CPh$ produces only vinylidene derivatives (traces of **7** were detected by ^{31}P NMR spectroscopy). *These results suggested the hydride acetylide species to be the precursor (kinetic products) to the vinylidene species (thermodynamic products).* We decided therefore to study the reactions between **2** and terminal alkynes at different temperatures.

Variable-Temperature Reactions. $HC\equiv CR$ (R = H, $SiMe_3$, Ph, *n*-C_3H_7, *n*-C_5H_{11}, CMe_3). In a typical experiment a weighed amount of **2** is dissolved in acetone-d_6 and the solution transferred into an NMR tube cooled to 195 K. A slight excess of the appropriate alkyne is then added with a microsyringe, and the NMR tube is immediately inserted into the spectrometer precooled to 213 K. In all cases, no reaction is observed below this temperature, the only ^{31}P signals being those of the starting dinitrogen complex. At higher temperature, reactions take place as evidenced by the appearance of new resonances in the spectra. The temperature at which each reaction starts depends on the nature of the alkyne substituent. As an example, while $HC\equiv CSiMe_3$ does not react at all with **2** at 268 K within 30 min, at this temperature and after the same time $HC\equiv CCMe_3$ converts more than 90% of **2** into a 1:4 mixture of vinylidene **6** and of the cis hydride alkynyl $[(PP_3)Co(H)(C\equiv CCMe_3)]BPh_4$ (**11**) (for the synthesis and spectroscopic characterization of **11**, see below and Table I).

A detailed variable-temperature ^{31}P NMR study is herein described for the reaction of $HC\equiv CPh$ with **2**.

As mentioned above, no reaction occurs at 213 K in acetone-d_6 between **2** and phenylacetylene even in a large excess. The resonances due to **2** remain the only signals up to 223 K. Above this temperature, the AM_2Q spin system ($\delta(P_A)$ = 160.7, $\delta(P_M)$ = 64.3, $\delta(P_Q)$ = 61.5) of the cis hydride acetylide **8** begins to appear together with another couple of broad resonances constituting an AM_3 spin system with $\delta(P_A)$ = 138.1, $\delta(P_M)$ = 58.0, and $J(P_AP_M)$ = 27.9 Hz. At 228 K, the product composition is roughly as follows: **2**, 70%; **8**, 5%; compound responsible for the AM_3 pattern, from now on designated as **12**, 25%. On a further increase in the temperature (263 K), the concentration of **2** in the reaction mixture significantly decreases and **12** becomes the prevalent species (48%). Slightly over 273 K, **2** disappears while **12** has almost completely converted into the octahedral hydride phenylacetylide **8**. At this temperature, no trace of vinylidene **10** is present in solution. The vinylidene complex begins to form at 288 K at the expense of **8**, the concentration of which progressively decreases as the temperature is increased until only **10** is present in the reaction mixture above 303 K.

All our attempts to isolate pure samples of **12**, the intermediate product obtained from phenylacetylene, were unsuccessful. However, valuable information on the structure of **12** is provided by NMR spectroscopy. The proton NMR spectrum recorded at 263 K in acetone-d_6 contains a multiplet at 5.94 ppm which could be assigned to a terminal alkyne C–H hydrogen. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum of **12** is temperature-dependent. Below 263 K, the high-field component of the AM_3 pattern broadens and at ca. 223 K coalesces with the base line. On a further decrease in the temperature, decoalescence occurs and two broad resonances of 2:1 relative intensity appear in the spectrum. Although no fine structure is discernible even at the lowest temperature attained (188 K), there is little doubt that the limiting pattern is of the AM_2Q type ($\delta(P_A)$ = 141.0 (br), $\delta(P_M)$ = 52.8 (br), and $\delta(P_Q)$ = 74.8 (br)). The fluxional behavior exhibited by **12** is consistent with a π-alkyne structure, namely $[(PP_3)Co(\pi\text{-}HC\equiv CPh)]^+$. In fact, quite comparable NMR features have been found for the π-alkyne complex $[(PP_3)Rh(\pi\text{-}HC\equiv CCO_2Et)]BPh_4$, which can be isolated as the kinetic product of the reaction of the 16-electron fragment $[(PP_3)Rh]^+$ with ethyl propiolate.[7b]

In light of the NMR evidence, a pure sample of the hydride acetylide **8** was obtained by simply accomplishing the reaction between **2** and $HC\equiv CPh$ at 0 °C. Off-white microcrystals of **8** were obtained by adding a cold ethanol/*n*-hexane mixture. The compound exhibits IR and ^{1}H and ^{31}P NMR properties quite similar to those of **3**. It is therefore reasonable to assign to **8** a structure where the cobalt center is octahedrally coordinated by the four phosphorus donors of PP_3, by a terminal $C\equiv CPh$ ligand, and by hydride.

Variable-temperature studies on the reactions between **2** and the other 1-alkynes examinated in this work have provided results qualitatively similar to those found for phenylacetylene. In all cases, evidence has been obtained for π-coordination of 1-alkynes to cobalt prior to C–H bond cleavage. By a purposeful choice of the reaction temperature, the hydride alkynyl complexes $[(PP_3)Co(H)(C\equiv CR)]BPh_4$ (R = H (**7**), CMe_3 (**11**)) and the vinylidene derivative $[(PP_3)Co\{C{=}C(H)(SiMe_3)\}]BPh_4$ (**13**) have been prepared and properly characterized. In particular, the last compound has been synthesized by heating at reflux temperature a 1,4-dioxane solution of the corresponding hydride alkynyl **3**. For R = *n*-C_3H_7 or *n*-C_5H_{11}, no pure sample of the corresponding hydride alkynyl complex was obtained. The reactions invariably gave mixtures of the starting dinitrogen complex **2**, of vinylidenes **4** or **5**, and of hydride alkynyl derivatives $[(PP_3)Co(H)(C\equiv CR)]BPh_4$ (R = *n*-C_3H_7 (**14**), *n*-C_5H_{11} (**15**)).

Kinetic and Thermodynamic Studies on the Hydride Alkynyl → Vinylidene Conversion. As shown in

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[22] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

[23] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

[24] See for example: (a) Almenninger, A.; Bustiansen, O.; Traettenberg, M. *Acta Chem. Scand.* **1959**, *13*, 1699. (b) Maki, A. G.; Toth, R. A. *J. Mol. Spectrosc.* **1965**, *17*, 136.

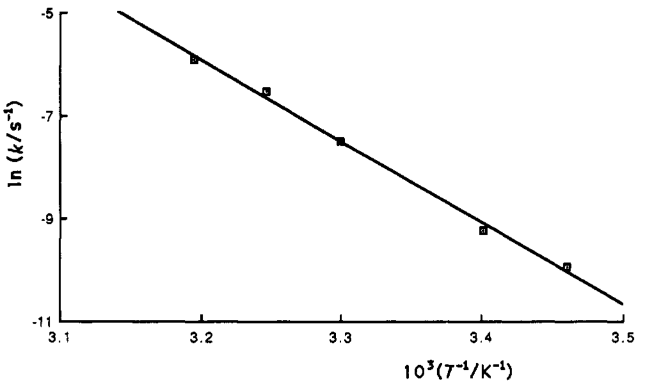


Figure 3. Arrhenius plot for the rate constants obtained from ^{31}P{^{1}H} NMR data relative to the rearrangement of 8 to 10.

the preceding section, ^{31}P{^{1}H} NMR spectroscopy provides a powerful tool to monitor the course of the reactions between terminal alkynes and the 16-electron fragment $[(PP_3)Co]^+$. NMR spectroscopy provides also a reliable method for evaluating the kinetic and thermodynamic parameters associated with the hydride alkynyl to vinylidene transformation (1,3-H shift).[25] In fact, the hydride alkynyl and vinylidene isomers show readily distinguishable splitting patterns (AM_2Q vs AM_3) and, in some cases, well-separated resonances of the PP_3 phosphorus nuclei. This is particularly true for the Co(H)(C≡CR) → Co{C=C(H)(R)} (R = Ph, n-C_5H_{11}) rearrangements, which occur within the temperature window of acetone-d_6 solutions and exhibit a favorable isomerization rate.

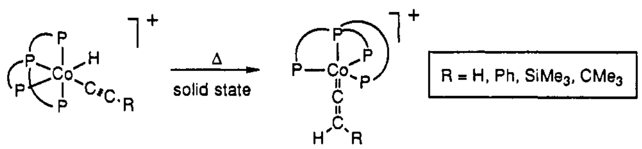
The rate law has been determined at a fixed temperature by varying the starting concentration of the hydride alkynyl complexes **10** and **15**. The results obtained for both compounds indicate that the Co(H)(C≡CR) → Co{C=C(H)(R)} conversion is first order in the hydride alkynyl complexes. The $t_{1/2}$ parameters significantly decrease, with the temperature going from a value of 4 h at 289 K to a value of 4 min at 313 K for R = Ph and from a value of 44 min at 273 K to a value of 4 min at 288 K for R = n-C_5H_{11}. Values of the rate constants as a function of temperature are reported in Figure 3 for R = Ph. From the Arrhenius plots, we determined the activation parameters, which are as follows: R = Ph, $\Delta H^{*} = 31 \pm 1$ kcal mol^{-1}, $\Delta S^{*} = 28 \pm 4$ cal K^{-1} mol^{-1}, and $\Delta G^{*}_{298\,K} = 22 \pm 2$ kcal mol^{-1}; R = n-C_5H_{11}, $\Delta H^{*} = 26 \pm 2$ kcal mol^{-1}, $\Delta S^{*} = 20 \pm 4$ cal K^{-1} mol^{-1}, and $\Delta G^{*}_{298\,K} = 20 \pm 2$ kcal mol^{-1}.

Despite the apparent uncertainty affecting the thermodynamic functions, particularly ΔS^{*}, due to the narrow temperature range within which the rearrangement occurs, these data provide some useful mechanistic information. In particular, the positive entropy of activation indicates a dissociative mechanism while the first-order law is consistent with an intramolecular process. Also, the activation energy of the rate-determining step seems to be influenced by the 1-alkyne substituent.

A comparison of the present values of the thermodynamic functions with those associated with other hydride alkynyl to vinylidene rearrangements is precluded by the lack of such data in the literature.

Solid-State Reactions. As often occurs in chemistry, a new chemical reaction can be discovered by accident. This is just the case for the solid-state conversion of the present cis hydride alkynyl complexes into the corresponding vinylidene derivatives. In the course of the determination of the melting points of the hydride alkynyl compounds with a Büchi SMP-20 apparatus in sealed capillaries under nitrogen, we observed that compounds **3**, **7**, **8**, and **11** changed color (off-white or pale yellow) to red before melting or decomposing with no apparent loss of the crystalline aspect (see the Experimental Section). The temperature at which the color changes depends on the alkynyl substituent and decreases in the order $SiMe_3$ > Ph ≈ H ≫ CMe_3. In light of these findings, an appreciable sample (ca. 200 mg) of each of the four hydride alkynyl complexes was placed into a Schlenk tube under N_2 and then gently heated with an oil bath for 2 h at the temperature at which the corresponding color change had been observed. Red crystalline products were obtained which were authenticated as vinylidenes **13**, **9**, **10**, and **6**, respectively, by means of IR and NMR (^{1}H and ^{31}P{^{1}H}) spectroscopies.

Scheme III



Like the analogous hydride alkynyl to vinylidene rearrangement occurring in solution, the solid-state conversion illustrated in Scheme III is irreversible and shows a similar dependence on the 1-alkyne substituent.

Deprotonation Reactions of the Hydride Alkynyl and Vinylidene Complexes. Experimental evidence for the weak acidic character of the Co–H bond is provided by the reactions of the hydride alkynyl complexes with a stoichiometric amount of KOBu^t in THF solution below the temperature at which each hydride alkynyl complex transforms into the corresponding vinylidene form. In all cases, a fast deprotonation reaction occurs which converts the Co(III) hydride alkynyls into the neutral Co(I) σ-acetylides $[(PP_3)Co(C{\equiv}CR)]$ (R = H (**16**), CMe_3 (**17**), $SiMe_3$ (**18**), Ph (**19**)). In contrast, no reaction occurs with weaker bases such as NEt_3.

The σ-alkynyl compounds **16**–**19** are air-stable orange to yellow diamagnetic crystalline compounds which behave as nonelectrolytes in nitroethane solutions. On the basis of spectroscopic data, all of the compounds are assigned TBP structures in which the σ-alkynyl ligands are located trans to the bridgehead phosphorus atom of PP_3. In particular, the IR spectra exhibit typical medium to strong ν(C≡C) absorptions in the 1926–2092-cm^{-1} region,[7b,10b,26] while the ^{31}P{^{1}H} NMR spectra are temperature-invariant and consist of AM_3 splitting patterns quite comparable with those of the corresponding TBP vinylidene derivatives (see Table I).

Whereas **16**–**18** are new, the phenylacetylide complex **19** has previously been isolated as the termination product of the oligomerization reaction of phenylacetylene catalyzed by **1**.[10]

Alternatively, compounds **16**–**19** are quantitatively prepared by deprotonation of vinylidenes **4**–**6**, **9**, **10**, and **13** in THF at room temperature with KOBu^t. By this procedure, it is also possible to synthesize the alkylalkynyl derivatives $[(PP_3)Co(C{\equiv}CC_3H_7)]$ (**20**) and $[(PP_3)Co(C{\equiv}CC_5H_{11})]$ (**21**).

Synthesis of Vinylidene Complexes by Protonation of Co(I) σ-Alkynyl Compounds. The σ-alkynyl compounds **16**–**21** belong to a large family of PP_3 TBP complexes of d^8 metals which are highly nucleophilic at the metal center.[17,18,27] Reactions of these electron-rich species

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with protic acids almost invariably result in the formation of d^6 hydride derivatives. On the other hand, it is well-known that the β-carbon of σ-alkynyl ligands may be a nucleophilic center susceptible to protonation by acids to give vinylidene derivatives.[1,7,28] Accordingly, at least in principle, the protonation of the Co(I) σ-alkynyls **16**–**21** was expected to give either Co(III) cis hydride alkynyl or Co(I) vinylidene products. We have found that, *independent of the temperature* (from 195 to 313 K), **16**–**21** in THF are protonated by triflic acid at the C_β carbon atom of the alkynyl ligands to give vinylidenes **4**–**6**, **9**, **10**, and **13**. In other words, the vinylidene complexes are both the kinetic and thermodynamic products of the reaction between the σ-alkynyl complexes and H^+.

Reactions of Vinylidene Complexes with CO. The vinylidene complexes **4**–**6**, **9**, **10**, and **13** are thermally robust and can be refluxed in deareated THF with no apparent decomposition. However, in the presence of CO, a reaction takes place to give the known carbonyl derivative $[(PP_3)Co(CO)]BPh_4$ (**22**)[9] and the corresponding 1-alkyne (determined by GC). The reactions need to be carried out in refluxing THF and are generally slow. Also, the conversion rate depends on the 1-alkyne substituent. Over a reflux time of 12 h, the lowest conversion was observed for the Me_3Si derivative (ca. 6%) and the highest conversion for the alkyl-substituted vinylidenes (ca. 50%).

Displacement of vinylidene ligands by other monofunctional ligands has been observed for very few cases.[29] In the absence of a chemical trap, viz. a coordinatively unsaturated complex,[4k] the free vinylidene moiety readily rearranges to acetylene (recall that the lifetime of $C{=}CH_2$ is ca. 10^{-12} s).[30]

Discussion

The reactions between the 16-electron fragment $[(PP_3)Co]^+$ and 1-alkynes give the π-alkyne adducts $[(PP_3)Co(\pi\text{-}HC{\equiv}CR)]^+$ and the vinylidenes $[(PP_3)Co\{C{=}C(H)R\}]^+$ as the kinetic and thermodynamic products, respectively. Between the π-alkyne and vinylidene forms, the system evolves through a third species, namely the Co(III) hydride alkynyl complexes $[(PP_3)Co(H)(C{\equiv}CR)]^+$, which are thermodynamically favored over the π-alkyne complexes and disfavored over the vinylidene ones.

The π-alkyne complexes can be properly characterized in solution by NMR techniques. However, we failed to isolate them in the solid state, most likely due to the small amount of energy required to promote the insertion of the metal across the sp C–H bnd. In contrast, both the hydride alkynyl and vinylidene complexes can be isolated and characterized in the solid state and their reactivity has been carefully studied. As is often the case in chemistry, one cannot definitely exclude either of the two possible intramolecular mechanisms through which the 1-alkyne to vinylidene tautomerization may proceed, i.e. a 1,3-H shift in Co(III) hydride alkynyls or a 1,2-H shift in Co(I) π-alkyne complexes. However, in light of the experimental results, the occurrence of a 1,3-H shift mechanism appears much more probable. In fact, the 1,2-H shift path would imply the hydride alkynyls to be in an equilibrium with the π-alkyne complexes and we have no VT-NMR evidence of the formation of equilibrium concentrations of π-alkyne species when pure samples of the hydride alkynyls are dissolved in THF. Furthermore, the $Co(H)(C{\equiv}CR) \rightarrow Co\{C{=}C(H)R\}$ rearrangements are first order in the hydride alkynyl complexes (intramolecular process) with activation parameters, particularly the largely positive entropy, which are consistent with a disordered transition state ($\Delta S^{\ddagger} = 28 \pm 4$ and 20 ± 4 cal K^{-1} mol^{-1} for R = Ph and $n\text{-}C_5H_{11}$, respectively). In other words, were the π-alkyne complexes in an equilibrium with the corresponding hydride alkynyls on the way to vinylidene formation, the $Co(H)(C{\equiv}CR) \rightarrow Co(\pi\text{-}HC{\equiv}CR)$ conversion would be the rate-determining step. This is not reasonable in light of either the VT-NMR results or the activation parameters (a negative $\Delta S^{\ddagger}$ value would be expected). Finally, the occurrence of the $Co(H)(C{\equiv}CR) \rightarrow Co\{C{=}C(H)R\}$ rearrangements *also in the solid state* tips the balance in favor of the 1,3-H shift mechanism, as it rules out a complicated two-step pathway involving the formation of an intermediate π-alkyne complex followed by a 1,2-H shift.

If one takes for granted that the $Co(H)(C{\equiv}CR) \rightarrow Co\{C{=}C(H)R\}$ conversion proceeds via a 1,3-H shift, two limiting mechanisms can be proposed. In the first mechanism, the hydrogen atom moves from cobalt to the C_β carbon atom of the alkynyl ligand with retention of contact with the metal. The second mechanism involves cleavage of the Co—H bond, followed by a migration of the hydrogen to the alkynyl C_β carbon atom. Indeed, a dissociative mechanism is supported by the largely positive entropy of activation.

From the results obtained, it is evident that the electronic nature of the substituent on the alkyne determines the temperature at which the hydride alkynyl to vinylidene rearrangement occurs and therefore determines the activation energy for this isomerization. In particular, the stability of the hydride alkynyl form decreases as a function of the 1-alkyne substituent in the order $SiMe_3 \gg Ph > H \gg CMe_3 > n\text{-}C_3H_7 \cong n\text{-}C_5H_{11}$. The steric bulkiness of the substituent apparently does not affect the rearrangement, as one may infer from the observation that CMe_3 and $SiMe_3$ groups lie at almost opposite ends of the scale.

At this point, two important questions need to be addressed for understanding the overall mechanism of the $M(\pi\text{-}C{\equiv}CR) \rightarrow M(H)(C{\equiv}CR) \rightarrow M\{C{=}C(H)R\}$ reaction sequence. The first question is concerned with the nature of the migrating hydrogen: *hydridic or protic*? The second question concerns the role played by the 1-alkyne substituent. In particular, it should be rationalized why the $SiMe_3$ group disfavors the 1,3-H shift as compared to the stereochemically similar CMe_3 group. Both of these questions cannot be definitely answered on experimental grounds only. Most likely, a theoretical analysis of the present 1-alkyne to vinylidene tautomerizations would help in understanding these reactions.

Concerning the first question, it would be tempting to conclude that the hydrogen migrates as a proton from cobalt to the C_β atom of the alkynyl. In fact, the hydride alkynyl complexes are deprotonated by a strong base to form the neutral σ-alkynyls which, in turn, convert to the

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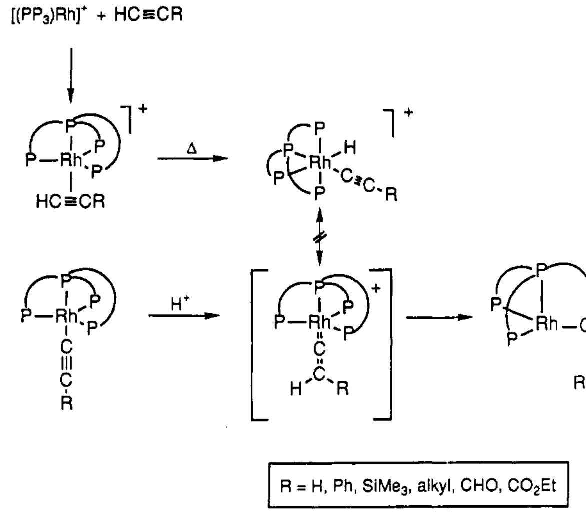
Scheme IV



corresponding vinylidene complex by treatment with a protic acid. On the other hand, the movement of protons among transition-metal cationic complexes in lattices is well documented.[31]

It has been recently reported that, regardless of the alkyne substituent, the rhodium fragment $[(PP_3)Rh]^+$ reacts with HC≡CR (R = H, alkyl, $SiMe_3$, Ph), yielding Rh(III) hydride alkynyl complexes $[(PP_3)Rh(H)(C{\equiv}CR)]BPh_4$ as thermodynamically favored products (Scheme IV).[7b] In particular, no conversion into Rh(I) vinylidenes was observed as a function of the temperature. This result was surprising, since the vinylidene complexes $[(PP_3)Rh\{C{=}C(H)R\}]^+$ are the only products of the reactions between the neutral σ-alkynyl complexes $[(PP_3)Rh(C{\equiv}CR)]$ and strong protic acids.[7] In light of the evidence presented, one may conclude that the Rh compounds get stuck at the hydride alkynyl stage due to the greater strength of the Rh–H bond as compared to that of the Co–H bond.

Experimental Section

General Data. Tetrahydrofuran (THF) was purified by distillation over $LiAlH_4$, under nitrogen, just prior to use; 1,4-dioxane, *n*-hexane, and *n*-heptane were purified by distillation over sodium. 1-Alkynes were purchased from Aldrich and Fluka and checked by proton NMR analysis; when necessary, they were distilled prior to use. All the other solvents and chemicals were reagent grade and were used as received by commercial suppliers. The ligand PP_3 was purchased from Pressure Co. and used without further purification. Deuterated solvents for NMR measurements (Aldrich and Jensen) were dried over molecular sieves. The compounds $[(PP_3)CoH]$ (**1**)[9,10] and $[(PP_3)Co(N_2)]BPh_4$ (**2**)[11] were prepared according to literature methods. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded at 299.945 and 75.429 MHz, respectively, on a Varian VXR 300 spectrometer. Peak positions are relative to tetramethylsilane as external reference. $^{31}P\{^1H\}$ NMR spectra were recorded on the same instrument operating at 121.42 MHz. 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 (295 K). Melting points were determined in capillary tubes sealed under nitrogen with a Büchi SMP-20 apparatus and are uncorrected. GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector an a 10-ft 100/120 Carbosieve-SII or a 6-ft 0.1% SP-1000 on Carbopack C stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled to the chromatograph, operating with an automatic correct area normalization method. The kinetic and thermodynamic parameters associated with the hydride alkynyl to vinylidene rearrangements were determined by integration of the ^{31}P NMR spectra in acetone-d_6 solutions. The reactions were run in NMR tubes in thermostats at fixed temperatures. At regular time intervals, a tube was removed and the reaction quenched at 213 K. The hydride alkynyl/vinylidene ratio was then calculated by integration of the relative resonances.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using Schlenk-tube techniques. The solid compounds were collected on sintered-glass frits and washed with ethanol and petroleum ether (bp 323–343 K) before being dried under a stream of nitrogen.

Reaction of 2 with $HC{\equiv}CSiMe_3$. (A) At Room Temperature. A slight excess of (trimethylsilyl)acetylene (85 μL, 0.60 mmol) was syringed into a stirred THF solution (25 mL) of **2** (0.50 g, 0.46 mmol) at room temperature. Within a few minutes, the starting red color disappeared to produce a clear solution, which was stirred for 30 min more. On addition of solid $NaBPh_4$ (0.40 g, 1.17 mmol) and of an ethanol/*n*-hexane mixture (2:1 v/v, 30 mL), off-white crystals of $[(PP_3)Co(H)(C{\equiv}CSiMe_3)]BPh_4$ (**3**) separated: yield 90%; $\Lambda_M = 60\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C≡C) 2023 cm^{-1} (s); ν(Co—H) 1951 cm^{-1} (w); ν(Si—C) 851 cm^{-1} (s). Anal. Calcd for $C_{71}H_{72}BCoP_4Si$: C, 74.34; H, 6.33; Co, 5.14. Found: C, 74.09; H, 6.28; Co, 5.01.

(B) At High Temperature. A mixture of (trimethylsilyl)acetylene and **2** in 1,4-dioxane (25 mL) prepared as above was refluxed for 30 min. After the mixture was cooled to room temperature, solid $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol (30 mL) were added. On slow evaporation of the solvents, the complex $[(PP_3)Co\{C{=}C(H)SiMe_3\}]BPh_4$ (**13**) separated as dark red crystals: yield 68%; $\Lambda_M = 52\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C=C) 1628, 1602 cm^{-1} (m); ν(Si—C) 843 cm^{-1} (s). $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 322.3 ppm (dq, C_α, $J(C_\alpha P_{ap}) = 46.9$ Hz, $J(C_\alpha P_{eq}) = 23.2$ Hz); 110.9 ppm (d, C_β, $J(C_\beta P) = 16.0$ Hz); 1.1 ppm (s, $Si(CH_3)_3$). Anal. Calcd for $C_{71}H_{72}BCoP_4Si$: C, 74.34; H, 6.33; Co, 5.14. Found: C, 74.23; H, 6.37; Co, 5.04.

Reactions of 2 with HC≡CR (R = *n*-C_3H_7, *n*-C_5H_{11}, CMe_3). (A) At Room Temperature. A slight excess (ca. 0.60 mmol) of the appropriate terminal alkyne was added to a THF solution (30 mL) of **2** (0.50 g, 0.46 mmol). A workup similar to that above described for the trimethylsilyl derivative gave dark red crystals of the vinylidene complexes $[(PP_3)Co\{C{=}C(H)R\}]BPh_4$ (R = C_3H_7 (**4**), C_5H_{11} (**5**), CMe_3 (**6**)).

4: yield 86%; $\Lambda_M = 54\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C=C) 1650 cm^{-1} (m). $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 332.6 ppm (dq, C_α, $J(C_\alpha P_{ap}) = 46.8$ Hz, $J(C_\alpha P_{eq}) = 23.1$ Hz); 128.4 ppm (d, C_β, $J(C_\beta P) = 14.9$ Hz); 31.8 ppm (s, $\mathit{C}H_2CH_2CH_3$); 29.9 ppm (s, $CH_2\mathit{C}H_2CH_3$); 14.8 ppm (s, $CH_2CH_2\mathit{C}H_3$). Anal. Calcd for $C_{71}H_{70}BCoP_4$: C, 76.35; H, 6.32; Co, 5.28. Found: C, 76.28; H, 6.40; Co, 5.27.

5: yield 88%; $\Lambda_M = 56\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C=C) 1645 cm^{-1} (m). $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 331.0 ppm (dq, C_α, $J(C_\alpha P_{ap}) = 43.3$ Hz, $J(C_\alpha P_{eq}) = 23.8$ Hz); 121.6 ppm (d, C_β, $J(C_\beta P) = 15.7$ Hz); 32.0 ppm (s, $\mathit{C}H_2(CH_2)_3CH_3$); 30.9 ppm (s, $CH_2\mathit{C}H_2(CH_2)_2CH_3$); 24.9 ppm ($CH_2CH_2\mathit{C}H_2CH_2CH_3$); 23.0 ppm ($CH_2(CH_2)_2\mathit{C}H_2CH_3$); 14.3 ppm (s, $CH_2(CH_2)_3\mathit{C}H_3$). Anal. Calcd for $C_{73}H_{74}BCoP_4$: C, 76.57; H, 6.51; Co, 5.15. Found: C, 76.52; H, 6.49; Co, 5.11.

6: yield 82%; $\Lambda_M = 50\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(C=C) 1660, 1630 cm^{-1} (m). $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 327.2 ppm (dq, C_α, $J(C_\alpha P_{ap}) = 46.8$ Hz, $J(C_\alpha P_{eq}) = 22.1$ Hz); 132.8 ppm (d, C_β, $J(C_\beta P) = 15.7$ Hz); 33.2 ppm (s, $\mathit{C}(CH_3)_3$); 32.2 ppm (s, $C(\mathit{C}H_3)_3$). Anal. Calcd for $C_{72}H_{72}BCoP_4$: C, 76.46; H, 6.42; Co, 5.21. Found: C, 76.27; H, 6.36: Co, 5.17.

(B) At Low Temperature. When the above reactions were carried out at low temperature (from 263 to 278 K), different results were obtained depending on the 1-alkyne employed.

For *tert*-butylacetylene, the standard workup at low temperature (ca. 263 K) yielded the hydride alkynyl complex $[(PP_3)Co(H)(C{\equiv}CCMe_3)]BPh_4$ (**11**) contaminated with less than 10%

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of **6**. Careful recrystallization at 245 K (dry ice/2-propanol bath) from an acetone/*n*-hexane mixture gave a pure sample of **11** as white crystals. The product is highly temperature-sensitive but can be indefinitely stored at low temperature with no decomposition.

In contrast, when the *n*-alkylacetylenes $HC{\equiv}CC_3H_7$ and $HC{\equiv}CC_5H_{11}$ were used, no pure sample of the hydride alkynyls $[(PP_3)Co(H)(C{\equiv}CR)]BPh_4$ was obtained even at low temperature ($R = n\text{-}C_3H_7$ (**14**), $n\text{-}C_5H_{11}$ (**15**)). Mixtures of the starting dinitrogen complex **2**, the vinylidene **4** or **5**, and the hydride alkynyl **14** or **15** were invariably obtained. Because of the thermal instability of **14** and **15**, as well as their relatively low concentration in the crude products (ca. 10–20%), no attempt was made to separate them from the other products.

11: yield 67%. IR: $\nu(C{\equiv}C)$ 2101 cm^{-1} (w); $\nu(Co{-}H)$ 1952 cm^{-1} (w). Anal. Calcd for $C_{72}H_{72}BCoP_4$: C, 76.46; H, 6.42; Co, 5.21. Found: C, 76.32; H, 6.33; Co, 4.98.

14: IR: $\nu(C{\equiv}C)$ 2085 cm^{-1} (w); $\nu(Co{-}H)$ 1960 cm^{-1} (w).

15: $\nu(C{\equiv}C)$ 2090 cm^{-1} (w); $\nu(Co{-}H)$ 1955 cm^{-1} (w).

Reactions of 2 with $HC{\equiv}CH$. (A) At Room Temperature. Ethyne was bubbled into a stirred solution of **2** (0.50 g, 0.46 mmol) in THF (20 mL) until the solution became purple (ca. 15 min). At this point, ethyne was replaced by N_2, and after 15 min, solid $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol (30 mL) were added. $^{31}P\{^1H\}$ NMR analysis on the crude filtered product showed it to be a mixture of $[(PP_3)Co(H)(C{\equiv}CH)]BPh_4$ (**7**) and $[(PP_3)Co\{C{=}CH_2\}]BPh_4$ (**9**) in a ca. 4:1 ratio; total yield based on **2** ca. 90%.

(B) At Low Temperature. When the reaction of **2** with ethyne was accomplished at ca. 283 K or below, a pure sample of **7** was obtained as cream-colored crystals: yield 82%; Λ_M = 57 Ω^{-1} cm^2 mol^{-1}. IR: $\nu(C{-}H)$ 3285 cm^{-1} (w); $\nu(Co{-}H)$ 1995 cm^{-1} (w); $\nu(C{\equiv}C)$ 1975 cm^{-1} (m). Anal. Calcd for $C_{68}H_{64}BCoP_4$: C, 75.98; H, 6.00; Co, 5.48. Found: C, 75.82; H, 6.07; Co, 5.40.

(C) At High Temperature. Ethyne was bubbled through a warm THF solution of **2** (ca. 318 K) for 30 min. After the usual workup, red crystals of **9** were obtained: yield 75%; Λ_M = 49 Ω^{-1} cm^2 mol^{-1}. IR: $\nu(C{=}C)$ 1620 cm^{-1} (m). $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 324.4 ppm (dq, C_α, $J(C_\alpha P_{ap})$ = 45.6 Hz, $J(C_\alpha P_{eq})$ = 23.3 Hz); 121.9 ppm (d, C_β, $J(C_\beta P)$ = 16.0 Hz). Anal. Calcd for $C_{68}H_{64}BCoP_4$: C, 75.98; H, 6.00; Co, 5.48. Found: C, 75.76; H, 5.99; Co, 5.23.

Reaction of 2 with $HC{\equiv}CPh$. (A) At Room Temperature. Neat phenylacetylene (100 μL, 0.9 mmol) was syringed into a stirred THF solution (35 mL) of **2** (0.79 g, 0.73 mmol). Within a few minutes the solution became deep purple. Stirring was continued for 30 min. Solid $NaBPh_4$ (0.40 g, 1.17 mmol) and ethanol (50 mL) were added to precipitate a 3:7 mixture of $[(PP_3)Co(H)(C{\equiv}CPh)]BPh_4$ (**8**) and $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$ (**10**) (as determined by $^{31}P\{^1H\}$ NMR integration). Total yield based on **2** ca. 95%.

(B) At Low Temperature. When the reaction of **2** with $HC{\equiv}CPh$ was performed at 273 K, a pure sample of the hydride alkynyl complex **8** was obtained as white crystals: yield 89%; Λ_M = 54 Ω^{-1} cm^2 mol^{-1}. IR: $\nu(C{\equiv}C)$ 2085 cm^{-1} (m); $\nu(Co{-}H)$ 1952 cm^{-1} (w); phenyl reinforced vibration 1595 cm^{-1}. Anal. Calcd for $C_{74}H_{68}BCoP_4$: C, 77.22; H, 5.95; Co, 5.12. Found: C, 77.04; H, 6.02; Co, 4.97.

(C) At High Temperature. A pure sample of the vinylidene **10** was prepared just heating the above solution to ca. 318 K for 30 min.

Deep purple crystals of **10** were obtained after the usual workup: yield 83%; Λ_M = 49 Ω^{-1} cm^2 mol^{-1}. IR: $\nu(C{=}C)$ 1640, 1615 cm^{-1} (m); phenyl reinforced vibration 1595 cm^{-1}. $^{13}C\{^1H\}$ NMR (75.429 MHz, CD_2Cl_2, 295 K, TMS reference): 336.8 ppm (dq, C_α, $J(C_\alpha P_{ap})$ = 48.2 Hz, $J(C_\alpha P_{eq})$ = 24.1 Hz); 127.4 ppm (d, C_β, $J(C_\beta P)$ = 15.5 Hz). Anal. Calcd for $C_{74}H_{68}BCoP_4$: C, 77.22; H, 5.95; Co, 5.12. Found: C, 77.06; H, 6.02; Co, 5.10.

Variable-Temperature Experiments. An acetone-d_6 solution of **2** was prepared under nitrogen and transferred into a 10-mm tube cooled at 195 K. A slight excess (1.5 equiv) of the appropriate 1-alkyne $HC{\equiv}CR$ ($R = n\text{-}C_3H_7$, $n\text{-}C_5H_{11}$, CMe_3, $SiMe_3$, Ph) was syringed into the NMR tube, which was then inserted into the spectrometer precooled to 213 K. No reaction was observed at this temperature. The sample was then removed from the spectrometer and placed into a thermostat at a fixed temperature for 15 min. After this time the NMR tube was inserted again into the spectrometer cooled to ca. 233 K and the $^{31}P\{^1H\}$ NMR spectrum was recorded. All of the ^{31}P NMR spectra were recorded at this temperature because of the cobalt quadrupole moment and because the reactions were quenched as well. The above operations were done for temperatures in the range 233–283 K. In all cases, the kinetic products are π-alkyne adducts of the type $[(PP_3)Co(\pi\text{-}HC{\equiv}CR)]^+$ ($R = n\text{-}C_3H_7$, $n\text{-}C_5H_{11}$, CMe_3, $SiMe_3$, Ph). All our attempts to isolate pure samples of the π-adduct species from low-temperature reactions were unsuccessful (see text). However, the π-complexes could be characterized by ^{31}P NMR spectroscopy.

$^{31}P\{^1H\}$ NMR Characterization of the π-Alkyne Complexes in Acetone-d_6 at 233 K. $[(PP_3)Co(\pi\text{-}HC{\equiv}CPh)]^+$: AM_3 spin system, $\delta(P_A)$ = 138.1 (br q, $J(P_AP_M)$ = 27.9 Hz), $\delta(P_M)$ = 58.0 ppm (br d).

$[(PP_3)Co(\pi\text{-}HC{\equiv}CC_3H_7)]^+$: AM_3 spin system, $\delta(P_A)$ = 137.3 (br q, $J(P_AP_M)$ = 29.9 Hz), $\delta(P_M)$ = 59.2 (br d).

$[(PP_3)Co(\pi\text{-}HC{\equiv}CC_5H_{11})]^+$: AM_3 spin system, $\delta(P_A)$ = 144.2 (br q, $J(P_AP_M)$ = 30.5 Hz), $\delta(P_M)$ = 52.1 (br d).

$[(PP_3)Co(\pi\text{-}HC{\equiv}CCMe_3)]^+$: AM_3 spin system, $\delta(P_A)$ = 135.9 (br q, $J(P_AP_M)$ = 28.2 Hz), $\delta(P_M)$ = 60.6 (br d).

$[(PP_3)Co(\pi\text{-}HC{\equiv}CSiMe_3)]^+$: AM_3 spin system, $\delta(P_A)$ = 138.4 (br q, $J(P_AP_M)$ = 29.0 Hz), $\delta(P_M)$ = 53.2 (br d).

Hydride Alkynyl to Vinylidene Rearrangement. (A) In Solution. A THF solution (25 mL) of the hydride alkynyl complex **7**, **8**, or **11** (ca. 0.20 g) was gently heated to ca. 323 K for 15 min. During this time the solution became dark red. Adding ethanol (30 mL) and cooling to room temperature gave red to purple crystals of the vinylidene complex **9**, **10**, or **6**, respectively. The yields were higher than 90%. The conversion of the trimethylsilyl derivative **3** into the corresponding vinylidene **13** (70% yield) was achieved by refluxing a 1,4-dioxane solution of **3** for 20 min.

(B) In the Solid State. A Schlenk tube was charged under nitrogen with a weighed amount (ca. 200 mg) of the appropriate hydride alkynyl complex (**3**, **7**, **8**, or **11**). The tube was then placed in an oil bath thermostated at the temperature at which the color change to red had previously been observed by using a Büchi SMP-20 apparatus. After 2 h, the tubes were cooled to room temperature and the red products were analyzed by spectroscopic techniques. A comparison of their IR and NMR spectra with those of authentic specimens of **13**, **9**, **10**, and **6** showed the red products to be the vinylidene complexes. The temperatures at which each hydride alkynyl to vinylidene rearrangement occurs are as follows: transformation **3** → **13**, ca. 363 K (mp 418–423 K dec); transformation **8** → **10**, ca. 348 K (mp 428–433 K dec); transformation **7** → **9**, ca. 338 K (mp 428–433 K dec); transformation **11** → **6**, ca. 303 K (mp 363–368 K dec).

Preparation of the σ-Alkynyl Complexes $[(PP_3)Co(C{\equiv}CR)]$ (R = H (16), CMe_3 (17), $SiMe_3$ (18), Ph (19), $n\text{-}C_3H_7$ (20), $n\text{-}C_5H_{11}$ (21)). Method A. A stoichiometric amount of solid $KOBu^t$ (0.06 g, 0.53 mmol) was added portionwise to a stirred THF solution (20 mL) of the appropriate cis-hydride alkynyl complex **7**, **11**, **3**, or **8** (ca. 0.5 mmol) maintained at 273 K. Immediately, the solutions became yellow and yielded, after addition of an ethanol/*n*-hexane mixture (1:1 v/v, 30 mL), light yellow or orange needles of the corresponding σ-alkynyl derivatives $[(PP_3)Co(C{\equiv}CR)]$ (R = H (**16**), CMe_3 (**17**), $SiMe_3$ (**18**), Ph (**19**)).

Method B. The same products were obtained by substituting the vinylidene complexes **4**–**6**, **9**, **10**, and **13** for the corresponding hydride alkynyls. By this procedure it was possible to synthesize also the two alkylalkynyl complexes $[(PP_3)Co(C{\equiv}CR)]$ ($R = n\text{-}C_3H_7$ (**20**), $n\text{-}C_5H_{11}$ (**21**)).

16: yield 84% (method A), 86% (method B). IR: $\nu(C{-}H)$ 3280 cm^{-1} (w); $\nu(C{\equiv}C)$ 1926 cm^{-1} (s). Anal. Calcd for $C_{44}H_{43}CoP_4$: C, 70.03; H, 5.74; Co, 7.81. Found: C, 69.95; H, 5.74; Co, 7.68.

17: yield 89% (method A), 92% (method B). IR: $\nu(C{\equiv}C)$ 2071 cm^{-1} (m). Anal. Calcd for $C_{48}H_{51}CoP_4$: C, 71.11; H, 6.34; Co, 7.27. Found: C, 70.89; H, 6.30; Co, 7.21.

18: yield 83% (method A), 85% (method B). IR: $\nu(C{\equiv}C)$ 1986 cm^{-1} (s); $\nu(Si{-}C)$ 861 cm^{-1} (s). Anal. Calcd for $C_{47}H_{51}CoP_4Si$: C, 68.27; H, 6.22; Co, 7.13. Found: C, 68.04; H, 6.17; Co, 6.97.

19: yield 90% (method A), 90% (method B). IR: $\nu(C{\equiv}C)$ 2050 cm^{-1} (s); phenyl reinforced vibration 1590 cm^{-1}. Anal. Calcd for $C_{50}H_{47}CoP_4$: C, 72.29; H, 5.70; Co, 7.09. Found: C, 72.14; H, 5.82; Co, 6.97.

20: yield 85% (method B). IR: $\nu(C{\equiv}C)$ 2090 cm^{-1} (m). Anal. Calcd for $C_{47}H_{49}CoP_4$: C, 70.85; H, 6.20; Co, 7.40. Found: C, 70.62; H, 6.13; Co, 7.25.

21: yield 91% (method B). IR: $\nu(C{\equiv}C)$ 2092 cm^{-1} (m). Anal. Calcd for $C_{49}H_{53}CoP_4$: C, 71.36; H, 6.48; Co, 7.14. Found: C, 71.27; H, 6.43; Co, 6.99.

Protonation of the σ-Alkynyls 16–21. A stoichiometric amount of triflic acid (18 μL, 0.20 mmol) was syringed into stirred THF solutions (25 mL) of the σ-alkyne complexes **16–21** (ca. 0.2 mmol) in the temperature range 195–313 K. Regardless of the temperature, the starting yellow or orange solutions immediately turned deep red. Addition of solid $NaBPh_4$ (0.10 g, 0.29 mmol) and ethanol (25 mL) yielded red to purple crystals of vinylidene **4–6**, **9**, **10**, or **13**. The yields were ca. 85%.

Reaction of Vinylidenes 4–6, 9, 10, and 13 with CO. In a typical experiment, a THF solution (20 mL) of the appropriate vinylidene complex (**4–6**, **9**, **10**, or **13**) was saturated with CO and then heated for 12 h at 338 K. The solution was then cooled down to room temperature, and *n*-heptane was added until an orange microcrystalline solid precipitated. In all cases, $^{31}P\{^1H\}$ NMR analysis showed the crude products to contain the carbonyl complex $[(PP_3)Co(CO)]BPh_4$ (**22**) together with unreacted vinylidene complexes. The percentage concentration of **22** in the various preparations is as follows: **4** + CO, 49%; **5** + CO, 38%; **6** + CO, 35%; **9** + CO, 22%; **10** + CO, 7%; **13** + CO, 6%.

X-ray Diffraction Study. A summary of crystal and intensity data for the compound $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$ (**10**) is reported in Table II. All X-ray measurements were performed at room temperature on a Philips PW1100 automated diffractometer using Cu Kα radiation monochromatized with a graphite crystal. The cell parameters were determined by least-squares refinement of the setting angles of 25 randomly selected reflections. Three standard reflections were collected every 2 h (the intensities were corrected for a decay of ca. 10%). The data were also corrected for Lorentz-polarization effects. An empirical absorption correction was made by using the program DIFABS.[32] Atomic scattering factors were those of Cromer and Waber[33] with anomalous dispersion corrections taken from ref 34. The structure was solved by the heavy-atom technique. Refinement was by full-matrix least-squares calculations; initially isotropic thermal parameters were generally applied, and later, anisotropic parameters were used for the Co and P atoms. The phenyl rings were treated as rigid hexagons (C–C distances 1.39 Å), and all of the hydrogen atoms were introduced at calculated positions. The final refinement cycles were performed with use of the weighting scheme $w = k/(\sigma^2(F) + pF^2)$ ($p = 0.0001$), which gave the smallest variations of the mean value of $w(F_o - F_c)^2$. The final Fourier map was practically featureless. Tables of atomic coordinates and temperature factors (including those of hydrogen atoms) are given as supplementary material.

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Supplementary Material Available: Tables of atomic parameters (including coordinates of hydrogen atoms) for the structure of $[(PP_3)\{C{=}C(H)Ph\}]BPh_4$ (**10**) (6 pages); a list of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of (Phenylsilatrane)manganese Tricarbonyl Perchlorate: Molecular Structure of $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$

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$[\{N(CH_2CH_2O)_3SiC_6H_5\}Mn(CO)_3]ClO_4$ (**1**) undergoes regioselective reaction with RMgBr (R = Ph, Me, Et) in CH_2Cl_2 to give $[\eta^5\text{-}1\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**2a**, R = Ph; **2b**, R = Me; **2c**, R = Et), with EtLi in THF to yield $[\eta^5\text{-}2\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**3c**, R = Et), and with RMgBr (R = Ph, Me, Et), $LiCH_2CO_2CMe_3$, $LiCH_2CN$, and $Li\overline{CHS(CH_2)_3S}$ in THF to yield $[\eta^5\text{-}3\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**4a**, R = Ph; **4b**, R = Me; **4c**, R = Et; **4e**, R = $CH_2CO_2CMe_3$; **4j**, R = CH_2CN; **4k**, R = $\overline{CHS(CH_2)_3S}$). However, **1** does not react regioselectively with the carbanions from isobutyronitrile, acetone, or *tert*-butyllithium or with sodium cyanide. The selectivity of the nucleophilic addition to **1** is strongly dependent on the nucleophile and reaction medium. The structure of **2a** has been confirmed by X-ray diffraction: space group $P\bar{1}$; $a = 9.169$ (2) Å, $b = 9.905$ (2) Å, $c = 12.353$ Å, $\alpha = 110.25$ (2)°, $\beta = 97.33$ (1)°, $\gamma = 97.70$ (2)°; final error indices $R = 0.042$, $R_G = 0.043$ for 2856 unique data with $I > 3\sigma(I)$.

Introduction

The structure and the chemical properties of silatranes have been investigated by various methods.[1] Although atrane compounds have been much studied recently,[2] silatrane derivatives have received little attention as π-coordinating ligands for transition metals until we reported the $Cr(CO)_3$ and $Mn(CO)_3^+$ derivatives of phenylsilatrane[3]

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