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Reactions of the Trigonal-Bipyramidal Cobalt(I) Hydride $[\{P(CH_2CH_2PPh_2)_3\}CoH]$ with 1-Alkynes. Synthesis and Reactivity of Acetylide, Alkenyl, and Vinylidene Complexes

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The reactions of $HC{\equiv}CR$ (R = CO_2Et, Ph, *n*-C_5H_{11}) with the Co(I) hydride $[(PP_3)CoH]$ (**1**) are influenced by a number of factors, including stoichiometry, alkyne substituent, and temperature ($PP_3 = P(CH_2CH_2PPh_2)_3$). The only 1-alkyne that reacts with **1** at room temperature is ethyl propiolate. The stoichiometric reaction yields a mixture of three components, namely the starting hydride, the σ-acetylide $[(PP_3)Co(C{\equiv}CCO_2Et)]$ (**3**), and the σ-alkenyl $[(PP_3)Co\{gem\text{-}C(CO_2Et){=}CH_2\}]$ (**4**). Ethyl acrylate forms in an amount corresponding to that of the σ-acetylide. When a 10-fold excess of $HC{\equiv}CCO_2Et$ is used, **1** quantitatively converts into **3** while 1 equiv of alkyne is hydrogenated to alkene. No reaction is observed between **1** and excesses of $HC{\equiv}CPh$ or $HC{\equiv}CC_5H_{11}$ in both room-temperature and refluxing THF solutions. In contrast, a reaction occurs with phenylacetylene in toluene at reflux temperature to give the σ-acetylide $[(PP_3)Co(C{\equiv}CPh)]$ (**5**). The reactions between **1** and $HC{\equiv}CR$ (R = CO_2Et, Ph) in a 1:100 ratio in toluene at reflux temperature consume all of the organic reagent, which is converted into cyclic and linear oligomers. The termination products of the catalysis cycles are the σ-acetylides **3** and **5**, which, in turn, catalyze themselves the oligomerization of 1-alkynes. The redox behavior of the Co(I) σ-acetylides **3** and **5** have been investigated by electrochemical methods. Upon one-electron oxidation, **3** and **5** are transformed into the corresponding Co(II) derivatives. The phenylacetylide **5** is protonated by strong protic acids to give $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$ (**8**), which represents the first cobalt vinylidene complex. The chemistry and redox properties of the latter compound have been investigated, particularly the one-electron reduction, some ligand-substitution reactions, and the reactions with nucleophiles. The carbethoxyacetylide **3** reacts with protic acids to give the vinylphosphonium complex $[\{(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)\}Co\{C{=}C(H)C(O)OEt\}]BPh_4$ (**9**). Unlike the vinylidene complex **8**, **9** is not deprotonated by bases but adds H^- from $NaBH_4$ to give the alkenyl complex $[(PP_3)Co\{(E)\text{-}CH{=}C(H)CO_2Et\}]$ (**11**). Compound **11** reacts with H^+ under nitrogen, liberating ethyl acrylate and forming the dinitrogen derivative $[(PP_3)Co(N_2)]BPh_4$.

Introduction

We have recently shown that terminal alkynes react with the Rh(I) hydride $[(PP_3)RhH]$ by several different routes ($PP_3 = P(CH_2CH_2PPh_2)_3$). The organometallic products of such reactions include π-complexes, cis hydride acetylide complexes, σ-acetylide complexes, σ-alkenyl complexes, terminal vinylidene complexes, and vinylphosphonium complexes.[1-3,4a] When the reactions are carried out in the presence of an excess of 1-alkyne, a variety of linear and cyclic oligomers are catalytically formed.[4] Also, the rhodium hydride is an excellent catalyst precursor for the regioselective addition of carboxylic acids to terminal alkynes to give enol esters.[5]

The remarkable ability of $[(PP_3)RhH]$ to activate 1-alkynes prompted us to investigate the chemistry of the related Co(I) hydride $[(PP_3)CoH]$ (1). Indeed, we were intrigued by the possibility of replacing rhodium with the more common cobalt.

In the present paper, we describe in detail the reactions of **1** with 1-alkynes bearing both electron-withdrawing and electron-releasing substituents. From our study, it is concluded that **1** can effectively replace the rhodium analogue in several stoichiometric and catalytic reactions of 1-alkynes.

Results and Discussion

The preparations and the principal reactions of the complexes described in this paper are summarized in Schemes I and II. The $^{31}P\{^1H\}$ and ^1H NMR spectral data for all of the new complexes are reported in Tables I and II. The phosphorus spectra are strongly affected by the cobalt quadrupole moment, which broadens the room-temperature resonances. Accordingly, well-resolved spectra were obtained at low temperature (188–220 K). Details of the solvent and of the temperature used in each experiment are given in Table I.

Antecedent Facts. The cobalt hydride **1** was synthesized as the hemiacetonate adduct by Sacconi and coworkers in the early 1970s[6] during a systematic study on the coordination chemistry of tripodal polyphosphines toward transition metals.[7] The original synthesis provides a high yield of **1** and agrees well with our large-scale preparative purposes.

Compound **1** was characterized by a complete X-ray analysis and was assigned a regular trigonal-bipyramidal

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(4) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146. (b) Oligomerization reactions of 1-alkynes catalyzed by $[(PP_3)RhH]$ or $[(PP_3)Rh(C{\equiv}CR)]$ (R = CO_2Et, Ph) (catalyst, 0.2 mmol; 1-alkyne, 2 mmol; THF, 10 mL; time, 3 h; reflux temperature) are as follows. $[(PP_3)RhH]$–$HC{\equiv}CCO_2Et$: conversion, 92 (2)%; 1,2,4-tricarbethoxybenzene, 50 (2)%; 1,3,5-tricarbethoxybenzene, 38 (2)%; other, 4 (1)%. $[(PP_3)RhH]$–$HC{\equiv}CPh$: conversion, 70 (2)%; 1,2,4-triphenylbenzene, 6 (1)%; 1,3,5-triphenylbenzene, 3 (1)%; diphenylbutenynes, 39 (2)%; 1,4-diphenylbutadiyne, 17 (2)%; other, 5 (1)%. $[(PP_3)Rh(C{\equiv}CCO_2Et)]$–$HC{\equiv}CCO_2Et$: no conversion. $[(PP_3)Rh(C{\equiv}CPh)]$–$HC{\equiv}CPh$: conversion, 50%; 1,4-diphenylbutadiyne, 15%; diphenylbutenynes, 28%; cyclic trimers 2%; other, 5%.

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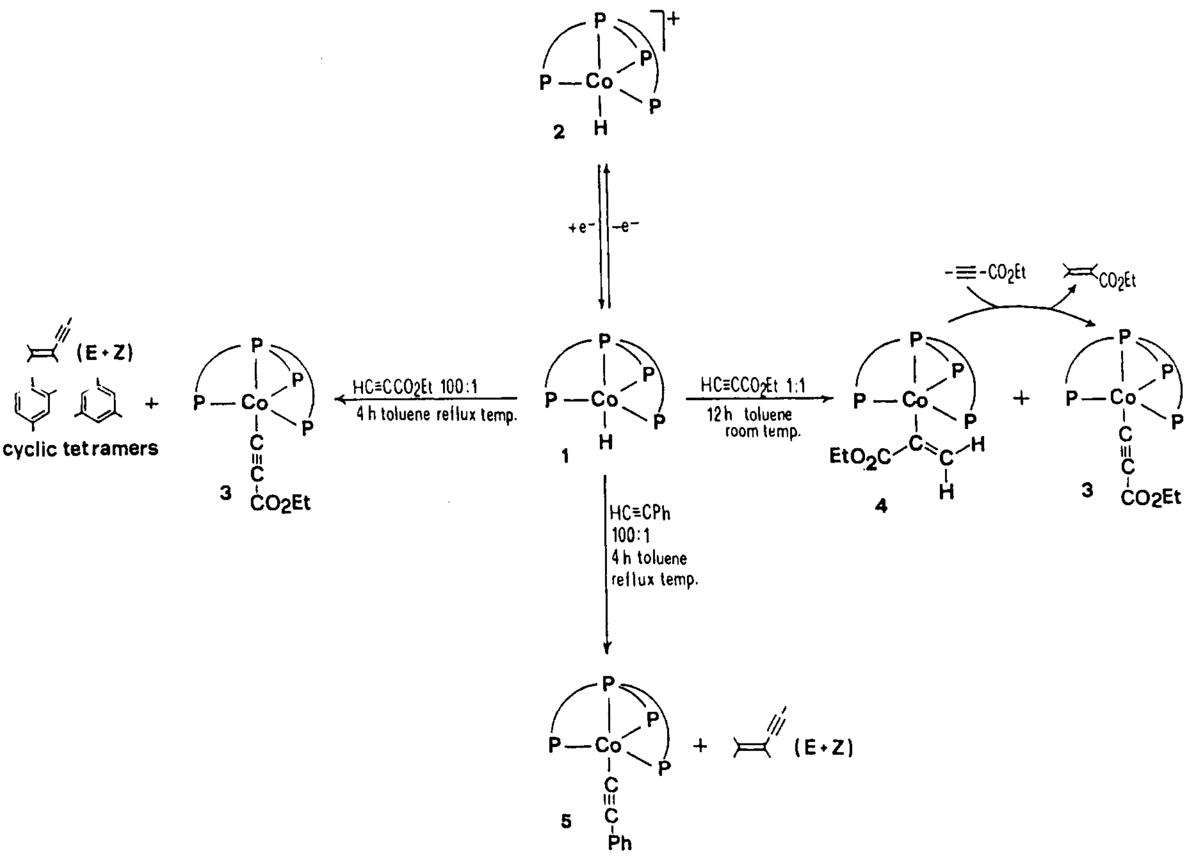
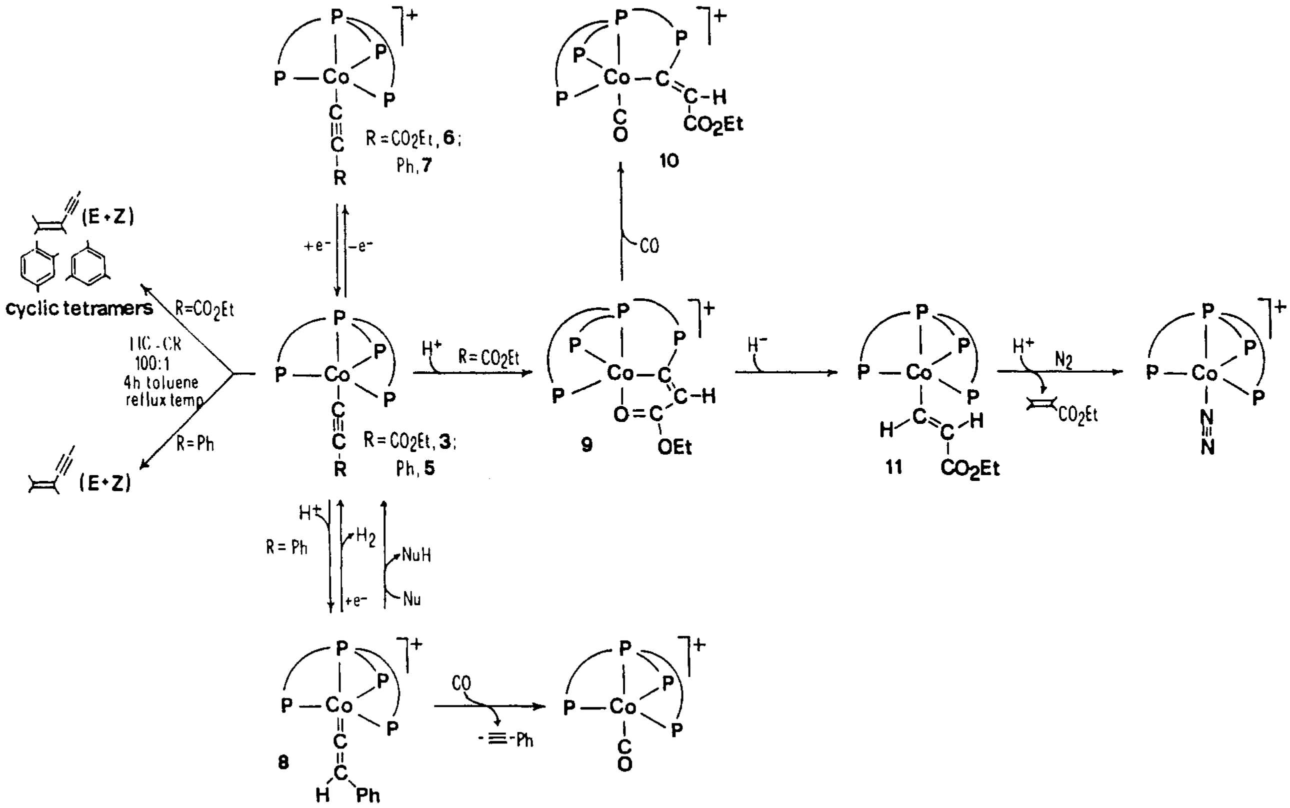
Scheme I



Scheme II



(TBP) geometry in which the bridgehead phosphorus atom and the hydride ligand lie on the 3-fold crystallographic axis.[6,8] However, compound 1 neither was characterized by NMR techniques nor was its chemistry explored in detail.

In keeping with the X-ray analysis, the $^{31}P\{^{1}H\}$ NMR spectrum of 1 exhibits an AM_3 splitting pattern, which points to the equivalence of the three terminal phosphorus atoms of the tripodal ligand. Such a pattern is fully con-

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Table I. $^{31}P\{^1H\}$ NMR Data for the Complexes[a]

				chem shift, ppm[b]			coupling const, J, Hz		
compd	solvent	temp, K	pattern	$\delta(P_A)$	$\delta(P_M)$	$\delta(P_Q)$	P_AP_M	P_AP_Q	P_MP_Q
1	C_7H_8	188	AM_3	183.83	84.62		18.5		
3	C_7H_8	220	AM_3	171.26	65.81		35.4		
4	C_7H_8	220	AM_3	161.06	59.32		33.3		
5	C_7H_8	220	AM_3	173.34	65.08		33.9		
8	CH_2Cl_2	220	AM_3	157.94	76.98		27.3		
9	CH_2Cl_2	250	AM_2Q	97.37	72.44	15.05	22.3	28.5	6.3
10	CH_2Cl_2	193	AM_2Q	95.46	71.05	14.55	21.2	27.5	6.0
11	CH_2Cl_2	197	AM_3	168.23	62.02		25.8		

[a] Recorded at 121.421 MHz. [b] The chemical shift values (δ's) are relative to 85% H_3PO_4 with positive values being downfield from the standard. P_A refers to the bridgehead phosphorus atom of the PP_3 ligand, whereas P_M denotes the equatorial phosphorus atoms of the tripodal phosphine. Finally, P_Q is the PPh_2 group that is bonded to the C_α atom in the vinylphosphonium complexes **9** and **10**.

Table II. Selected ^1H NMR Data for the Complexes[a]

compd	solvent	δ, ppm[b]	assignt[c]	coupling const, Hz[c,d]
1	C_6D_6	−9.38 dq	Co–H	71.3 ($^2J(HP_A)$) 41.9 ($^2J(HP_M)$)
3	C_6D_6	3.99 q	OCH_2CH_3	7.0 ($^3J(HH)$)
		1.17 t	OCH_2CH_3	
4	C_6D_6	5.72 ddq	H_A	8.3 ($^4J(H_AP_A)$) 2.9 ($^3J(H_AH_B)$) 1.2 ($^4J(H_AP_M)$)
		4.91 br d	H_B	
		3.21 q	OCH_2CH_3	6.9 ($^3J(HH)$)
		0.74 t	OCH_2CH_3	
8	CD_2Cl_2	5.22 qd	C=CH	6.4 ($^4J(HP_M)$) 0.8 ($^4J(HP_A)$)
9[e]	CD_2Cl_2	6.52 d	C=CH	20.0 ($^3J(HP_Q)$)
		4.30 q	OCH_2CH_3	7.0 ($^3J(HH)$)
		1.18 t	OCH_2CH_3	
10[f]	CD_2Cl_2	6.53 d	C=CH	20.9 ($^3J(HP_Q)$
		4.21 q	OCH_2CH_3	7.3 ($^3J(HH)$)
		1.19 t	OCH_2CH_3	
11[g]	CD_2Cl_2	10.77 m	H_A	
		6.10 br d	H_B	15.9 ($^3J(H_AH_B)$)
		3.92 q	OCH_2CH_3	6.9 ($^3J(HH)$)
		1.17 t	OCH_2CH_3	

[a] Ambient temperature (294 K) unless otherwise stated; recorded at 299.945 MHz. The resonances due to the hydrogen atoms belonging to the PP_3 ligand and to the BPh_4^- counteranion are not reported. [b] The chemical shift values (δ's) are relative to tetramethylsilane as external standard. Key: d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [c] The subscripts A and B denote the vinyl protons of the alkenyl ligands. [d] P_A refers to the bridgehead phosphorus atom of the PP_3 ligand. P_M denotes the equatorial phosphorus atoms of the PP_3 ligand. P_Q is the C_α-bonded phosphorus atom of the vinylphosphonium complexes **10** and **11**. [e] At 250 K. [f] At 220 K. [g] At 197 K.

sistent with the solid-state TBP geometry of the complex, which is thus maintained in solution.[9-13] At 188 K the expected fine structures of the two resonances are fully resolved ($J(PP)$ = 18.5 Hz). The room-temperature ^1H NMR spectrum shows a high-field doublet of quartets centered at −9.38 ppm, which is assigned to the hydride ligand trans to the bridgehead phosphorus. The observed multiplicity arises from coupling of the hydride to the trans P atom ($J(HP_{trans})$ = 71.3 Hz) and to the three equivalent terminal P donors ($J(HP_{cis})$ = 41.9 Hz) that reside on the equatorial plane of the trigonal bipyramid.

Compound **1** is a diamagnetic low-spin cobalt(I) species that can be oxidized to the corresponding cobalt(II) derivative $[(PP_3)Co(H)]PF_6$ (**2**) by treatment in tetrahydrofuran (THF) with 1 equiv of the one-electron oxidant $[(C_5H_5)_2Fe]PF_6$. Alternatively, **2** can be prepared by controlled-potential macroelectrolysis in THF starting either from the monohydride **1** or from the molecular hydrogen complex $[(PP_3)Co(\eta^2\text{-}H_2)]PF_6$.[14]

Compound **2** is paramagnetic[15-17] with the magnetic moment μ_{eff} = 2.01 μ_B corresponding to one unpaired electron (d^7 low-spin configuration). The Co(II) hydride has been characterized by an X-ray diffraction analysis.[18] In the solid state the complex retains the TBP structure of the parent Co(I) derivative, although the coordination polyhedron appears remarkably expanded as a result of the lengthening of the bonds between the metal and the surrounding donor atoms. As an example, the Co–H distance is significantly elongated in the Co(II) derivative (1.53 vs 1.43 Å).

Reaction of 1 with Terminal Alkynes at Room Temperature. The reactivity of **1** toward 1-alkynes bearing CO_2Et, Ph, and C_5H_{11} substituents was studied under different conditions of temperature and stoichiometry.

At room temperature in THF, benzene, or toluene, $HC\equiv CPh$ and $HC\equiv CC_5H_{11}$ do not react at all with **1** even when a large excess of alkyne is employed. GC analysis of the reaction mixture does not reveal the formation of organic compounds other than the original alkyne. In contrast, a slow reaction occurs when the more acidic alkyne ethyl propiolate is used. Regardless of the solvent, stirring equimolar amounts of **1** and $HC\equiv CCO_2Et$ for 12 h gives a mixture of three different products: the starting hydride and the two novel compounds $[(PP_3)Co(C\equiv CCO_2Et)]$ (**3**) and $[(PP_3)Co\{gem\text{-}C(CO_2Et)=CH_2\}]$ (**4**) in a 2:1:1 ratio (based on ^{31}P NMR integration). The three components of the mixture can be separated from each other by column chromatography on silica gel by eluting

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with benzene–*n*-hexane mixtures. GC analysis of the gas phase shows no evolution of dihydrogen, while ethyl acrylate is found as the only new organic product of the reaction in an amount which practically corresponds to that of the acetylide **3**.

Both the acetylide **3** and the alkenyl **4** are yellow diamagnetic, nonconducting compounds that are fairly stable in the solid state and in deareated solutions. The $^{31}P\{^1H\}$ NMR spectrum of **3** recorded in toluene-d_8 at 220 K shows an AM_3 pattern that is typical of a TBP geometry around the metal center.[9-12] The IR spectrum exhibits $\nu(C{\equiv}C)$ at 2020 cm^{-1}, which is consistent with the presence of a terminal acetylide ligand. Strong IR absorptions at 1645 and 1185 cm^{-1} are readily assigned to $\nu(C{=}O)$ and $\nu(COC)$ of a carbethoxy substituent not engaged in bonding to the metal. The ^1H NMR spectrum shows the ethoxy hydrogens to constitute an A_2M_3 spin system ($\delta(H_A)$ 3.99 ppm; $\delta(H_M)$ 1.17 ppm; $J(HH) = 7.0$ Hz).

A TBP structure can be safely assigned also to the σ-alkenyl complex **4** as its $^{31}P\{^1H\}$ NMR spectrum exhibits a temperature-invariant AM_3 spin system. Conclusive evidence for the presence of a σ-alkenyl ligand in **4** is obtained from IR and ^1H NMR measurements. The IR spectrum contains no band attributable to a $\nu(C{\equiv}C)$ vibration, whereas, besides the typical absorptions of the carbethoxy group, a weak-intensity band at 1535 cm^{-1} can be assigned to the stretching of a C=C bond. The ^1H NMR spectrum shows two mutually correlated resonances at 5.72 and 4.91 ppm, which fall in the expected region for σ-alkenyl protons.[4,19,20] Also, the spectrum provides valuable information on the stereochemistry of the metal σ-alkenyl moiety and consequently on the type of insertion of $HC{\equiv}CCO_2Et$ across the Co–H bond. The lower field resonance appears as a couple of doublets of quartets and constitutes the A part of an $ABMX_3$ spin system, which can be properly simulated with use of the following parameters: $J(H_AH_B) = 2.9$ Hz, $J(H_AP_M) = 8.3$ Hz, $J(H_AP_X) = 1.2$ Hz. The higher field signal, assigned to the H_B proton, consists of a broad doublet. Both the chemical shifts and the $J(HH)$ value are diagnostic for a *gem* stereochemistry of the alkenyl group.[4a,19] In this respect, it is worth mentioning that the insertion of $HC{\equiv}CCO_2Et$ across the Co–H bond in the related hydride $[(NP_3)CoH]$ was observed to proceed in a similar way, yielding $[(NP_3)Co\{gem\text{-}C(CO_2Et){=}CH_2\}]$, which was authenticated by an X-ray analysis ($NP_3 = N(CH_2CH_2PPh_2)_3$).[20a]

When **1** is reacted with a 10-fold excess of $HC{\equiv}CCO_2Et$ in THF for 12 h, the σ-acetylide **3** is quantitatively obtained together with ethyl acrylate. The ethyl acrylate–ethyl propiolate ratio of ca. 1:8 in the reaction mixture (determined by GC and ^1H NMR techniques) indicates the consumption of 2 equiv of alkyne/equiv of starting hydride. The formation of such an amount of alkene suggests that the reaction initially proceeds via insertion of the alkyne across the Co–H bond to give **4**. Successively, the σ-alkenyl complex reacts with a second alkyne molecule, producing **3** and alkene. The σ-alkenyl → σ-acetylide conversion most likely proceeds through C(alkyne)–H oxidative addition to cobalt, followed by the reductive elimination of alkene. As a matter of fact, **4** in THF is rapidly and quantitatively converted into **3** by treatment with a stoichiometric amount of ethyl propiolate while ethyl acrylate is liberated.

Reaction of 1 with Terminal Alkynes at Reflux Temperature. Catalytic Oligomerization Reactions. The hydride **1** in THF does not react with a 10-fold excess of $HC{\equiv}CR$ (R = Ph, C_5H_{11}) at reflux temperature. In contrast, a fast reaction takes place between **1** and phenylacetylene in refluxing toluene. After the reaction is quenched with a cold ethanol–*n*-hexane mixture, yellow crystals of the novel σ-acetylide $[(PP_3)Co(C{\equiv}CPh)]$ (**5**) precipitate in an excellent yield. Compound **5** shares with **3** most of its chemical–physical properties. A strong IR absorption at ca. 1590 cm^{-1} diagnoses the presence of the phenyl substituent on the σ-acetylide ligand, which, in turn, exhibits $\nu(C{\equiv}C)$ at 2050 cm^{-1}. Like all of the cobalt(I) complexes herein described, **5** is assigned a TBP structure on the basis of ^{31}P NMR spectroscopy.

Increasing the temperature up to 110 °C does not significantly affect the course of the reaction of **1** with $HC{\equiv}CC_5H_{11}$, the starting hydride being almost quantitatively recovered after addition of ethanol–*n*-hexane.

Interestingly, the 1:10 reactions between **1** and $HC{\equiv}CR$ (R = CO_2Et, Ph) in refluxing toluene consume all of the organic reagent. In order to elucidate the fate of the alkyne, the reactions were carried out in a catalytic fashion with use of a substrate to catalyst ratio of 100 in toluene at reflux temperature. After 4 h, the mixtures were cooled down to room temperature and the solutions were carefully analyzed by GC–MS and ^{31}P NMR techniques. The organic products were identified by comparison with authentic specimens either prepared by us or purchased from commercial suppliers. Ethyl propiolate is totally converted into the cyclic trimers 1,2,4-tricarbethoxybenzene (52 (2)%) and 1,3,5-tricarbethoxybenzene (29 (2)%), into butenynes (4 (1)%), and into various cyclic tetramers (15 (1)%) (numbers in parentheses are estimated standard deviations). A quite different product composition is found for the reaction with $HC{\equiv}CPh$ since only butenynes form, notably (*E*)-1,4-diphenylbutenyne (97 (2)%). As expected, we observe a very poor conversion of $HC{\equiv}CC_5H_{11}$, ca. 3%, essentially into 1,2,4- and 1,3,5-tri-*n*-pentylbenzenes.

The σ-acetylides **3** and **5** are the termination products of the oligomerization reactions of the corresponding 1-alkyne. On the other hand, both complexes could well play an active role in the catalysis cycles. In fact, under the same reaction conditions, the σ-acetylides catalyze the oligomerization reactions of $HC{\equiv}CPh$ and $HC{\equiv}CCO_2Et$, yielding a rather similar product composition but a lower conversion as compared to the reactions of the parent hydride **1**: $HC{\equiv}CPh$, 23 (1)% conversion into (*E*)-1,4-diphenylbutenyne (96 (3)%) and (*Z*)-1,4-diphenlbutenyne (4 (1)%); $HC{\equiv}CCO_2Et$, 83 (2)% conversion into 1,2,4-tricarbethoxybenzene (43 (1)%), 1,3,5-tricarbethoxybenzene (26 (1)%), butenynes (15 (1)%), and various cyclic tetramers (16 (1)%).

A comparison of the present data with those previously reported for the rhodium analogues $[(PP_3)RhH]$ and $[(PP_3)Rh(C{\equiv}CR)]$ (R = Ph, CO_2Et) shows that the cobalt complexes, especially the hydride, are more efficient than the rhodium ones while the product composition is quite comparable.[4]

Redox Properties of the σ-Acetylides $[(PP_3)Co(C{\equiv}CR)]$. Synthesis of the Co(II) Derivatives $[(PP_3)Co(C{\equiv}CR)]^+$ (R = CO_2Et, Ph). The ability of the parent hydride **1** to lose one electron in a reversible manner

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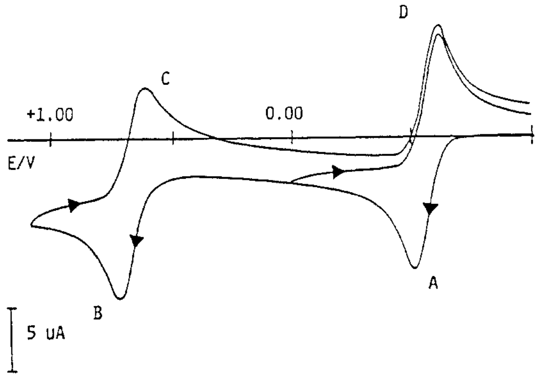


Figure 1. Cyclic voltammogram recorded at a platinum electrode on a deaerated CH_2Cl_2 solution containing **5** (1.02×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Table III. Electrochemical Parameters for the Redox Changes Exhibited by $[(PP_3)Co(C{\equiv}CR)]$ in Nonaqueous Solutions

R	$E°_{Co^{III}/Co^{II}}$, V	ΔE_p,[a] mV	$E°_{Co^{II}/Co^{I}}$, V	ΔE_p,[a] mV	solvent
Ph	+0.68[b]	110	−0.55	66	CH_2Cl_2
Ph	+0.69[c]		−0.49	87	THF
CO_2Et	+0.80[b]	96	−0.41	64	CH_2Cl_2
CO_2Et	+0.90[c]		−0.36	90	THF

[a] Measured at a scan rate of 0.2 V s^{-1}. [b] Measured at scan rates higher than 1 V s^{-1} in order to overcome the coupled chemical complications. [c] Peak potential value for (apparently) irreversible processes measured at 0.2 V s^{-1}.

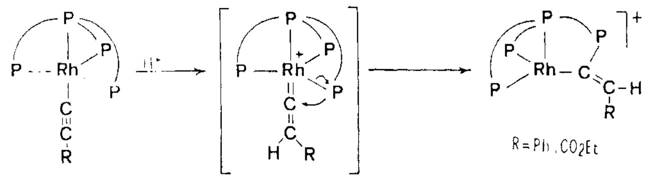
prompted us to investigate the redox behavior of the σ-acetylides **3** and **5**.

Figure 1 illustrates the cyclic voltammetric response exhibited by **5** in CH_2Cl_2 solution. Two subsequent oxidation processes (peaks A and B) are displayed, each of which shows a directly associated rereduction response in the reverse scan (peaks C and D, respectively). Controlled-potential coulometric tests in correspondence to both the first anodic step (E_w = 0.0 V) and the second one (E_w = +1.0 V) indicate that each process involves the consumption of one electron per molecule.

Analysis[21] of the cyclic voltammograms relevant to the peak system A/D with scan rates v varying from 0.02 to 51.20 V s^{-1} shows that (i) the $i_{p(D)}/i_{p(A)}$ ratio is constantly equal to 1, (ii) the difference between the peak potential values ΔE_p varies from 63 to 67 mV up to 0.5 V s^{-1} and then it progressively increases up to 232 mV, and (iii) the ratio $i_{p(A)}v^{-1/2}$ decreases by ca. 10%. All of these data are diagnostic for a chemically reversible one-electron transfer exhibiting a slight departure from the pure electrochemical reversibility (in which case a constant ΔE_p value of 59 mV is expected). In contrast, the cyclic voltammetric responses relevant to the peak system B/C put in evidence that the relevant one-electron-redox change, which is quasireversible in character, is complicated by following, relatively slow chemical reactions. In fact, the $i_{p(C)}/i_{p(B)}$ ratio is 0.4 at 0.02 V s^{-1} and reaches unity only at scan rates higher than 1.0 V s^{-1}. Contemporaneously, ΔE_p progressively increases from 84 mV at 0.02 V s^{-1} to 407 mV at 51.20 V s^{-1}.

When THF is used in place of CH_2Cl_2, the rate of the heterogeneous charge transfer of the first electron removal is lowered while the rate of the homogeneous chemical complication coupled to the second electron removal significantly increases.

Scheme III



Qualitatively similar voltammetric features are displayed by **3**. Table III summarizes the redox parameters for the following electron-transfer sequence exhibited by **3** and **5**:

$$[(PP_3)Co^{I}(C{\equiv}CR)] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(PP_3)Co^{II}(C{\equiv}CR)]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [(PP_3)Co^{III}(C{\equiv}CR)]^{2+}$$
$$\text{decomposition}$$

In view of the electrochemical studies we expected to easily electrogenerate the one-electron-oxidized products. Indeed, exhaustive electrolyses in CH_2Cl_2 of **3** and **5** at E_w = 0.0 V (0.2 mol dm^{-3} $[NBu_4]ClO_4$ as supporting electrolyte) afford red-brown solutions from which crystals of $[(PP_3)Co(C{\equiv}CR)]BPh_4$ (R = CO_2Et (**6**), Ph (**7**)) are obtained after recrystallization of the crude products from CH_2Cl_2–ethanol mixtures in the presence of $NaBPh_4$. Alternatively, both compounds can be prepared by treatment of **3** or **5** in THF with 1 equiv of the one-electron oxidant $[(C_5H_5)_2Fe]PF_6$, followed by addition of $NaBPh_4$ in ethanol.

Compounds **6** and **7** are quite air-stable in both the solid state and solution, in which they behave as 1:1 electrolytes. Both compounds are paramagnetic with magnetic moments of 2.06 (**6**) and 2.11 μ_B (**7**) corresponding to one unpaired spin.[22] The reflectance spectra, showing intense bands at 9950 and 9900 cm^{-1}, are fully comparable with those of several TBP low-spin Co(II) complexes with the PP_3 ligand.[6,23] The presence of a terminal acetylide ligand in complexes **6** and **7** is shown by typical IR $\nu(C{\equiv}C)$ absorptions at 2060 and 2070 cm^{-1}, respectively, that are significantly shifted to higher wavenumbers (ca. 35 cm^{-1}) as compared to those of the Co(I) analogues. The $\nu(C{\equiv}C)$ shift is consistent with a significant dπ(metal) → π*(acetylide) interaction in the HOMO in the starting Co(I) complexes **3** and **5**.[2] The expected IR absorptions for the carbethoxy group in **6** are found in the proper region for $\nu(C{=}O)$ and $\nu(COC)$ vibrations, while a reinforced phenyl vibration at 1595 cm^{-1} is observed in the spectrum of the phenylacetylide **7**.

Reactions of the σ-Acetylides $[(PP_3)Co(C{\equiv}CR)]$ (R = CO_2Et, Ph) with Protic Acids. The β-carbon of terminal acetylide ligands, especially in low-valent transition-metal complexes, is a nucleophilic center susceptible to attack by electrophiles.[24] In most instances, such reactions give terminal vinylidene complexes;[25,26] however, in some cases, the electrophilic attack at the β-carbon is

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followed by addition of a nucleophile at the α-carbon to give vinyl ligands.[27] A particular example is represented by the reactions of the Rh(I) σ-acetylides [(PP$_3$)Rh(C$\equiv$CR)] (R = CO$_2$Et, Ph) with HSO$_3$CF$_3$, which give vinylphosphonium complexes through intramolecular attack by a phosphine arm of PP$_3$ at the α-carbon of a vinylidene intermediate (Scheme III).[3]

To continue comparing the chemistry of the present cobalt acetylides with that of the rhodium congeners, we have reacted **3** and **5** with protic acids.

Synthesis and Chemistry of the Vinylidene [(PP$_3$)Co{C=C(H)Ph}]BPh$_4$ (8). The yellow phenylacetylide **5** reacts in THF with triflic or tetrafluoboric acid, producing a deep purple solution from which purple crystals of [(PP$_3$)Co{C=C(H)Ph}]BPh$_4$ (**8**) precipitate by addition of NaBPh$_4$ in ethanol. Compound **8** is stable in the solid state and in deareated solutions, in which it behaves as a 1:1 electrolyte. The vinylidene nature of the compound was unambiguously determined by spectroscopic (IR and NMR) techniques. In addition to the typical absorptions of the PP$_3$ ligand and of the BPh$_4$ counteranion, the IR spectrum contains a couple of medium-intensity bands (1640 and 1615 cm^{-1}) that fall in the proper region for ν(C=C) absorptions of terminal vinylidene ligands.[3,25,26] A reinforced absorption at 1595 cm^{-1} testifies that the phenyl substituent on the parent acetylide ligand is still present in the complex framework. The proton NMR spectrum recorded in CD$_2$Cl$_2$ at room temperature is fully consistent with the presence of a vinylidene ligand. In fact, the spectrum exhibits a quartet of doublets that falls in the expected region for vinylidene hydrogens (δ +5.22 ppm). Such a multiplicity is due to coupling of the vinylidene hydrogen to three equivalent phosphorus atoms, likely the terminal ones of PP$_3$, and to a fourth phosphorus, the bridgehead one. In agreement with the proton NMR data, the ^{31}P{^{1}H} NMR spectrum exhibits an AM$_3$ pattern. The spectrum is invariant down to 178 K, thus indicating that also at low temperature the vinylidene fragment is freely rotating in solution around the metal–carbon axis. Such a behavior is quite common for vinylidene complexes and is ascribed to a very low energy barrier for the interconversion between rotational isomers.[3,28] The ^{13}C{^{1}H} NMR spectrum of **8** (CD$_2$Cl$_2$, 298 K) confirms the vinylidene nature of the σ-organyl ligand as well as the TBP geometry of the complex. In fact, a doublet of quartets at δ +336.8 ppm with $J(C_\alpha P_{ap})$ = 48.2 Hz and $J(C_\alpha P_{eq})$ = 24.1 Hz is clearly consistent with the equivalence of the three equatorial P donors of the tripodal polyphosphine. The coupling constant values are in line with those reported for a variety of transition-metal vinylidene complexes containing tertiary phosphine ligands.[3,26] Due to the presence of the phenyl rings of the PP$_3$ ligand and of the BPh$_4$ counteranion, the C$_\beta$ resonance cannot be precisely assigned, as it most likely falls in the crowded region of aromatic carbon resonances.[26]

From a mechanistic viewpoint, it is most likely that the C$_\beta$ carbon atom of the acetylide ligand in **5** constitutes the primary target of the electrophilic attack by H$^+$. In other words, we are inclined to exclude the formation of a preliminary Co(III) cis hydride acetylide intermediate, followed by hydride shift. Actually, we find that the protonation of **5** in CD$_2$Cl$_2$ in an NMR tube at −78 °C does not show the formation of other products than **8**.

The formation of **8** has close precedents in the reactions of the related Rh(I) acetylides [(NP$_3$)Rh(C$\equiv$CR)] (NP$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$) with triflic acid, yielding vinylidene complexes of the formula [(NP$_3$)Rh{C=C(H)R}]BPh$_4$ (R = Ph, CO$_2$Et).[3]

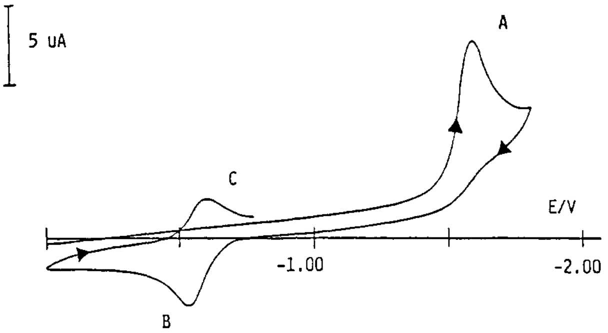

Figure 2. Cyclic voltammogram recorded at a platinum electrode on a deaerated CH$_2$Cl$_2$ solution containing **8** (9.7×10^{-4} mol dm^{-3}) and [NBu$_4$]ClO$_4$ (0.1 mol dm^{-3}) (scan rate 0.1 V s^{-1}).

To the best of our knowledge, no mononuclear vinylidene complex of cobalt has been reported so far. Only two examples of trinuclear cobalt carbonyl clusters containing bridging μ_3-vinylidene ligands have been described by Seyferth and Vahrenkamp.[29,30]

It has been recently reported by us[3,31] and other authors[26,32] that vinylidene metal complexes can be deprotonated by either one-electron oxidation or one-electron reduction to give σ-acetylide derivatives. In oxidation, the formal oxidation state of the metal increases by one unit, while in reduction, the metal retains its original oxidation state and dihydrogen is evolved. As an example, the NP$_3$Rh(I) vinylidenes [(NP$_3$)Rh{C=C(H)R}]$^+$ undergo one-electron oxidation, producing H$^+$ and converting into the Rh(II) acetylides [(NP$_3$)Rh(C$\equiv$CR)]$^+$, whereas as a result of the one-electron reduction, the Rh(I) acetylides [(NP$_3$)Rh(C$\equiv$CR)] and H$_2$ are formed.[3,31]

Due to the presence of the electrooxidizable counteranion BPh$_4^-$ it was not possible to examinate accurately the anodic behavior of the present vinylidene **8**. However, as shown in Figure 2, the cathodic behavior in CH$_2$Cl$_2$ solution is in agreement with the expected formation of the Co(I) acetylide **5**. In fact, **8** undergoes an irreversible cathodic reduction at peak A (E_p = −1.60 V), generating a species that can be oxidized and in turn reduced in correspondence to the peak system B/C. Such a peak system is just coincident with the peak system A/D in Figure 1.

Controlled-potential coulometry in correspondence to the cathodic process exhibited by **8** (E_w = −1.7 V, 0.2 mol dm^{-3} [NBu$_4$]ClO$_4$ as supporting electrolyte) consumes 1 faraday/mol and affords a yellow-orange solution from which crystals of **5** separate by addition of ethanol–*n*-hexane. We can therefore conclude that the redox pathway exhibited by **8** reflects the reaction sequence

$$[(PP_3)Co\{C{=}C(H)Ph\}]^+ + e^- \rightarrow [(PP_3)Co(C{\equiv}CPh)] + \tfrac{1}{2}H_2$$

Complex **8** is very stable in deareated CH$_2$Cl$_2$ or THF solutions even at reflux temperature. The vinylidene lig-

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and appears strongly bound to cobalt, since it is not displaced by monodentate ligands such as tertiary phosphines or halides even under forcible reaction conditions. Only carbon monoxide proves able to displace the vinylidene ligand from **8**, forming the known carbonyl derivative $[(PP_3)Co(CO)]BPh_4$[6] and phenylacetylene. The reaction occurs in refluxing THF, and the conversion to the carbonyl derivative is rather low (7% in 12 h).

The vinylidene complex **8** is readily deprotonated by nucleophiles such as NEt_3, $KOBu^t$, and H^- from $NaBH_4$ or $LiHBEt_3$ to re-form the σ-acetylide complex **5**. Interestingly, no trace of σ-alkenyl complexes was observed in the course of the reaction with H^-. This behavior markedly differs from that observed for the related rhodium vinylidenes $[(NP_3)Rh\{C{=}C(H)R\}]BPh_4$, for which the nucleophilic addition of H^- to the C_α atom to give σ-alkenyl complexes with an *E* structure competes with the deprotonation reaction.[3]

Synthesis and Chemistry of the Vinylphosphonium Complex $[\{(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)\}Co\{C{=}C(H)C(O)OEt\}]BPh_4$ (9). Like the rhodium derivative $[(PP_3)Rh(C{\equiv}CCO_2Et)]$, the acetylide **3** reacts in THF with triflic acid, yielding the vinylphosphonium complex $[\{(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)\}Co\{C{=}C(H)C(O)OEt\}]BPh_4$ (**9**). This can be precipitated as violet crystals by addition of $NaBPh_4$ in ethanol. The compound is slightly air sensitive also in the solid state and rapidly decomposes in solution unless air is excluded. The vinylphosphonium formulation can be safely assigned to **9** on the basis of its spectral properties, which are fully comparable with those of several rhodium congeners.[3,5] In particular, while the IR spectrum exhibits a medium-intensity band at 1565 cm^{-1} assignable to $\nu(C{=}C)$ of a vinyl moiety, no band is present in the 1600–1700-cm^{-1} region, where the C=O group of a free carbethoxy substituent is expected to vibrate. In contrast, a new strong band at 1410 cm^{-1} can be readily associated with a bonding interaction between the C=O group and the metal.

The $^{31}P\{^1H\}$ NMR spectrum consists of a first-order AM_2Q splitting pattern. The lowest field signal, a doublet of triplets at 97.37 ppm, is readily ascribed to the apical P_A atom of the PP_3 ligand. Its multiplicity arises from coupling to the P_Q phosphonium atom ($J(P_AP_Q)$ = 28.5 Hz) and to the equivalent P_M terminal atoms ($J(P_AP_M)$ = 22.3 Hz). The formation of the phosphonium P_Q–C_α bond is responsible for the high-field shift of this resonance. In fact, in canonical TBP cobalt complexes of PP_3, the bridgehead P_A atom resonates between 184 and 147 ppm.[9b,10b] This high-field shift of the resonance can be explained by taking into account that, following the formation of the P_Q–C_α phosphonium linkage, the P_A atom moves from a *high-deshielding* five-membered ring to a *high-shielding* six-membered ring.[33] A similar downfield ring contribution can be safely invoked to explain the relatively low-field resonance of the phosphonium P_Q atom (δ 15.05 ppm). This resonance appears as a doublet of triplets due to coupling of P_Q both to P_A ($J(P_AP_Q)$ = 28.5 Hz) and to the two terminal P_M phosphorus atoms ($J(P_MP_Q)$ = 6.3 Hz). Finally, the doublet of doublets at 72.44 ppm is assigned to the two equivalent P_M atoms, which resonate in the proper region for equatorial P atoms of five-coordinate PP_3 cobalt complexes.[9b,10b] Accordingly, the formation of the vinylphosphonium ligand does not significantly influence the magnetic properties of the two P_M atoms, which continue to be involved in a high-deshielding five-membered cobalta ring.

The $^{13}C\{^1H\}$ NMR spectrum of **9** (CD_2Cl_2, 294 K) is quite consistent with the formation of the vinylphosphonium P_Q–C_α bond. In fact, in addition to the resonances due to the carbons of PP_3, of BPh_4^-, and of the CO_2Et substituent ($\delta(COOEt)$ 174.7; $\delta(OCH_2CH_3)$ 61.7; $\delta(OCH_2CH_3)$ 14.7 ppm), the spectrum exhibits two broad doublets ($w_{1/2}$ = 7 Hz) at 21.4 ppm ($J(C_\alpha P)$ = 66.9 Hz) and 17.4 ppm ($J(C_\beta P)$ = 12.1 Hz), which can be assigned to the vinyl C_α and C_β carbons, respectively. In particular, the relatively high value of $J(C_\alpha P)$ is consistent with a spin–spin coupling interaction involving an sp^2 carbon atom directly bonded to a phosphorus nucleus.[34]

The proton NMR spectrum of **9** recorded in CD_2Cl_2 at 250 K is quite consistent with the vinylphosphonium formulation. In particular a doublet at 6.52 ppm (1 H) is assigned to the vinyl proton. The coupling constant between this proton and the phosphonium P_Q atom ($J(HP_Q)$ = 20.0 Hz) match well those found for other vinylphosphonium complexes in which the PC=CH unit is arranged in a cis stereochemistry.[28,35] Actually, the geometric requirements of the tripodal ligand are such that only a cis disposition of the vinyl hydrogen and of the phosphonium P_Q atom is allowed.

The formation of **9** reasonably proceeds as reported in Scheme III for the rhodium analogues. This involves the preliminary protonation of the σ-alkynyl complex **3** at the electrophilic C_β atom to form a transient carbethoxy vinylidene species that successively degrades to the final vinylphosphonium product. Likely, the presence of the strong electron-withdrawing carbethoxy substituent makes the C_α carbon very electron deficient so as to be able to promote the decoordination of a phosphine arm of the PP_3 ligand, which therefore can bring about a nucleophilic attack at the C_α atom. The electronic saturation of the metal center is provided by the coordination of the C=O ester group. However, externally added ligands can displace the C=O group, leading to five-coordinate species in which the vinylphosphonium moiety is η^1(C)-bonded to the metal. As an example, complex **9** slowly reacts at room temperature with CO (1 atm), affording deep violet crystals of the carbonyl vinylphosphonium derivative $[\{(Ph_2PCH_2CH_2)_2P(CH_2CH_2PPh_2)\}Co(CO)\{C{=}C(H)CO_2Et\}]BPh_4$ (**10**). As expected, the IR spectrum of **10** shows a strong absorption in the terminal carbonyl region ($\nu(C{\equiv}O)$ 1940 cm^{-1}), while $\nu(C{=}O)$ of the carbethoxy group appears shifted to high energy by ca. 280 cm^{-1} (1690 cm^{-1}). The ^1H and $^{31}P\{^1H\}$ NMR spectra of **10** are consistent with the structural formulation of the compound as given in Scheme II.

Unlike vinylidene **8**, the vinylphosphonium ligand in **9** is not deprotonated by bases. On the other hand, **9** reacts with $NaBH_4$ in refluxing THF to yield, upon addition of ethanol, the alkenyl complex $[(PP_3)Co\{(E)\text{-}CH{=}C(H)CO_2Et\}]$ (**11**). No spectroscopic evidence for the G isomer 4 was observed. Compound **11** is air stable in the solid state but slowly decomposes in solution unless air is excluded. Strong IR absorptions at 1650 and 1240 cm^{-1} are assigned to $\nu(C{=}O)$ and $\nu(COC)$ of a free carbethoxy substituent. This means that, following the reaction with $NaBH_4$, the C=O ester group is no longer involved in bonding to the cobalt atom. The presence of an alkenyl C=C double bond is evidenced by the appearance of a weak band at 1495 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum

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recorded in CH_2Cl_2 at 197 K shows an AM_3 pattern consistent with a TBP geometry in solution.

The stereochemistry of the σ-alkenyl ligand was established by the analysis of the proton NMR spectrum. Besides the signals of the PP_3 ligand and of the carbethoxy substituent, which fall in the expected range, the ^1H NMR spectrum of **11** shows resonances at 10.77 (1 H, m) and 6.10 ppm (1 H, br d, $J(HH)$ = 15.9 Hz) corresponding to the two alkenyl protons. The large value of $J(HH)$ suggests a trans stereochemistry of the alkenyl ligand and agrees well with several data reported in the literature.[4a,20]

The σ-alkenyl complex **11** reacts in THF with protic acids to form ethyl acrylate and the coordinatively and electronically unsaturated fragment $[(PP_3)Co]^+$. This can be trapped by N_2 to give the stable terminal dinitrogen complex $[(PP_3)Co(N_2)]BPh_4$ as red crystals (Scheme II).[9a] This result is quite interesting, since it suggests that, like $[(PP_3)RhH]$, **1** may function as a catalyst precursor for the catalytic synthesis of enol esters from 1-alkynes and carboxylic acids. In fact, a crucial step for such reactions was suggested to be the protonation of a TBP σ-alkenyl intermediate, followed by the reductive elimination of alkene.[5]

Experimental Section

General Data. Tetrahydrofuran (THF) and toluene were purified by distillation over $LiAlH_4$ and sodium under nitrogen just prior to use, respectively. All the other solvents and chemicals employed were reagent grade and were used as received by commercial suppliers. 1-Alkynes and ethyl acrylate were purchased from Aldrich and checked by ^1H NMR analysis. When necessary, they were distilled prior to use. The ligand PP_3 was purchased from Pressure Co. The compounds $[(PP_3)CoH]\cdot 0.5CH_3COCH_3$ (**1**),[6] $[(C_5H_5)_2Fe]PF_6$,[36] 1,3,5-tricarbethoxybenzene,[37] 1,2,4-tricarbethoxybenzene,[37] (*E*)-1,4-diphenylbutenyne,[38] (*Z*)-1,4-diphenylbutenyne,[39] 1,3,5-tri-*n*-pentylbenzene,[40] and 1,2,4-tri-*n*-pentylbenzene[40] 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 a 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 (294 K). Magnetic susceptibilities of solid samples were measured on a Faraday balance. GC analyses were performed both on a Perkin-Elmer Sigma 1 system equipped with a 2-m column packed either with OV1 (2.5%) on Chromosorb G AW-DMCS or with FFAP (5%) on Chromosorb G AW-DMCS 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 $^1/_8$-in. 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 by using a Hewlett-Packard Model 5970A chromatograph equipped with a mass detector: an OV-101 capillary column (25 m) was employed. The product composition of the reaction mixture was evaluated by using the total abundance of the mass peak. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[41] The potential values are relative to an aqueous calomel electrode (SCE) and refer to a controlled temperature of 20 ± 0.1 °C. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at +0.49 V in dichloromethane solution and at +0.56 V in THF solution.

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 50–70 °C) before being dried under a stream of nitrogen.

Preparation of $[(PP_3)Co(H)]PF_6$ (2). One equivalent of solid $[(C_5H_5)_2Fe]PF_6$ (0.33 g, 1.0 mmol) was added portionwise with stirring to a THF solution of **1** (0.76 g, 1.0 mmol). The light yellow solution turned red-brown. On addition of ethanol (30 mL) crystals of **2** separated; yield 90%. $\mu_{eff} = 2.01\ \mu_B$; $\Lambda_M = 83\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: ν(Co–H) 1815 cm^{-1} (br w). Anal. Calcd for $C_{42}H_{43}CoF_6P_5$: C, 57.61; H, 4.95; Co, 6.73. Found: C, 57.45; H, 5.03; Co, 6.61.

Reactions of 1 with Ethyl Propiolate. (A) 1:1 at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic bar was charged with a solution of **1** (0.76 g, 1.0 mmol) in THF (30 mL) (or benzene or toluene) and ethyl propiolate (102 μL, 1.0 mmol) and closed by a Suba-Seal septum (Aldrich). The mixture was stirred for 12 h at room temperature. Addition of ethanol (40 mL) and slow evaporation of the solvent gave a crystalline orange solid, which was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, showing the presence of two PP_3 complexes in addition to the starting hydride. Accordingly the mixture was chromatographed under nitrogen on a silica gel column (eluent 4:1 benzene–*n*-hexane) to give the novel complexes $[(PP_3)Co(C{\equiv}CCO_2Et)]$ (**3**; yield 25%) and $[(PP_3)Co\{gem\text{-}C(CO_2Et){=}CH_2\}]$ (**4**; yield 20%). The yields reported are based on the starting cobalt complex. The mother liquor was analyzed by GC–MS, showing the presence of ethyl acrylate (0.25–0.30 mmol) but not that of ethyl propiolate.

3: IR $\nu(C{\equiv}C)$ 2020 cm^{-1} (s), $\nu(C{=}O)$ 1645 cm^{-1} (s), ν(COC) 1185 cm^{-1} (br m). Anal. Calcd for $C_{47}H_{47}CoO_2P_4$: C, 68.28; H, 5.73; Co, 7.13. Found: C, 68.02; H, 5.99; Co, 7.05.

4: IR $\nu(C{=}O)$ 1670 cm^{-1} (s), $\nu(C{=}C)$ 1535 cm^{-1} (vw), ν(COC) 1200 cm^{-1} (br s). Anal. Calcd for $C_{47}H_{49}CoO_2P_4$: C, 68.12; H, 5.96; Co, 7.11. Found: C, 68.14; H, 6.08; Co, 6.99.

(B) 1:10 at Room Temperature. A 100-mL Schlenk flask equipped with a magnetic stirrer was charged with a solution of **1** (0.76 g, 1.0 mmol) in THF (30 mL) and ethyl propiolate (1.02 mL, 10.0 mmol) and closed by a Suba-Seal septum. The mixture was stirred at room temperature for 12 h. GC analysis of the gas phase revealed no trace of H_2, whereas ethyl acrylate was found in solution. The ethyl propiolate–ethyl acrylate ratio was ca. 8:1, evidencing the consumption of 2 mmol of 1-alkyne/mmol of starting metal hydride. Addition of an ethanol–*n*-hexane mixture (40 mL, 1:1 v/v) gave **3** in ca. 95% yield.

(C) 1:10 at Reflux Temperature. A mixture of **1** (0.76 g, 1.0 mmol) and ethyl propiolate (1.02 mL, 10.0 mmol) in toluene (30 mL) was refluxed for 4 h (complete consumption of ethyl propiolate was observed by GC). After the mixture was cooled to room temperature, ethanol was added and pure **3** as yellow-orange needles was obtained in ca. 95% yield.

Reactions of 4 with Ethyl Propiolate. A stoichiometric amount of ethyl propiolate was added to a THF (15 mL) solution of **4** (0.25 g, 0.3 mmol). The resulting mixture was stirred at room temperature for 2 h. $^{31}P\{^1H\}$ NMR tests performed at various steps during the course of the reaction showed that **4** disappeared almost quantitatively after 10 min. GC analysis of the solution showed the disappearance of the ethyl propiolate and the formation of ethyl acrylate. On addition of ethanol (40 mL) the acetylide **3** precipitated in ca. 95% yield.

Reactions of 1 with Phenylacetylene. (A) At Room Temperature. No reaction is observed between $HC{\equiv}CPh$ and **1** in THF, toluene, or benzene even by using a 10-fold excess of 1-alkyne.

(B) 1:10 at Reflux Temperature. When a toluene (30 mL) solution of **1** (0.76 g, 1.0 mmol) containing a 10-fold excess of phenylacetylene (1.12 mL, 10.0 mmol) was refluxed for 3 h

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(complete consumption of phenylacetylene was observed by GC), the phenylacetylide complex [(PP$_3$)Co(C≡CPh)] (**5**) was obtained as yellow crystalline needles after working up as above; yield 95%. IR: ν(C≡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, 72.01; H, 5.86; Co, 6.93.

Reaction of 1 with 1-Heptyne. No reaction of **1** occurs between HC≡CC$_5$H$_{11}$ and **1** under all of the above-reported reaction conditions.

Preparation of [(PP$_3$)Co(C≡CCO$_2$Et)]BPh$_4$ (6). Method A. One equivalent of [(C$_5$H$_5$)$_2$Fe]PF$_6$ (0.07 g, 0.21 mmol) was added to an acetone solution of **3** (0.17 g, 0.21 mmol), and the resulting mixture was stirred for 30 min. The color gradually turned deep orange. Addition of NaBPh$_4$ (0.20 g, 0.59 mmol) and ethanol (30 mL) gave brick red crystals of **6**; yield 80%. μ_{eff} = 2.06 μ_B; Λ_M = 39 Ω^{-1} cm^2 mol^{-1}. IR: ν(C≡C) 2060 cm^{-1} (m), ν(C=O) 1670 cm^{-1} (s), ν(COC) 1210 cm^{-1} (br m). Anal. Calcd for $C_{71}H_{67}BCoO_2P_4$: C, 74.42; H, 5.89; Co, 5.14. Found: C, 74.21; H, 5.97; Co, 5.02.

Method B. Complex **3** (0.17 g, 0.21 mmol) dissolved in a 0.2 M CH$_2$Cl$_2$ solution of [NBu$_4$]ClO$_4$ as supporting electrolyte (20 mL) was exhaustively electrolyzed at 0.0 V. The resulting red-brown solution gave red microcrystals of [(PP$_3$)Co(C≡CCO$_2$Et)]ClO$_4$ after addition of ethanol–heptane (40 mL, 1:2 v:v). The pure tetraphenylborate salt **6** was obtained after recrystallization from a CH$_2$Cl$_2$–ethanol mixture in the presence of excess NaBPh$_4$; yield 90%.

Preparation of [(PP$_3$)Co(C≡CCPh)]BPh$_4$ (7). The Co(II) phenylacetylide complex **7** was synthesized as described above for **6** by substituting **5** for **3**; yield 75% (method A), 80% (method B, E_w = 0.0 V). μ_{eff} = 2.11 μ_B; Λ_M = 41 Ω^{-1} cm^2 mol^{-1}. IR: ν(C≡C) 2070 cm^{-1} (m). Anal. Calcd for $C_{74}H_{67}BCoP_4$: C, 77.29; H, 5.87; Co, 5.12. Found: C, 77.07; H, 5.88; Co, 4.96.

Preparation of [(PP$_3$)Co{C=C(H)Ph}]BPh$_4$ (8). To a stirred suspension of **5** (0.40 g, 0.48 mmol) in THF (25 mL) was added via syringe HOSO$_2$CF$_3$ (45 μL, 0.51 mmol). The starting yellow acetylide dissolved to produce a deep purple solution, from which red-purple crystals of **8** were obtained after addition of NaBPh$_4$ (0.40 g, 1.17 mmol) in ethanol (30 mL); yield 85%. Λ_M = 48 Ω^{-1} cm^2 mol^{-1}. IR: ν(C=C) 1640, 1615 cm^{-1} (m), 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, 76.80; H, 6.01; Co, 5.00.

Preparation of [{(Ph$_2$PCH$_2$CH$_2$)$_2$P(CH$_2$CH$_2$PPh$_2$)}Co{C=C(H)C(O)OEt}]BPh$_4$ (9). To a solution of **3** (0.41 g, 0.50 mmol) in THF (30 mL) was added 45 μL (0.51 mmol) of neat HOSO$_2$CF$_3$. The initial yellow color immediately turned deep violet. Well-formed deep violet crystals of **9** were obtained in 80% yield after addition of NaBPh$_4$ (0.40 g, 1.17 mmol) in ethanol (50 mL). Λ_M = 46 Ω^{-1} cm^2 mol^{-1}. IR: ν(C=O) 1410 cm^{-1} (s), ν(COC) 1170 cm^{-1} (m). Anal. Calcd for $C_{71}H_{68}BCoO_2P_4$: C, 74.35; H, 5.98; Co, 5.14. Found: C, 74.17; H, 6.06; Co, 4.98.

Preparation of [{(Ph$_2$PCH$_2$CH$_2$)$_2$P(CH$_2$CH$_2$PPh$_2$)}Co(CO){C=C(H)CO$_2$Et}]BPh$_4$ (10). Carbon monoxide was bubbled for 30 min throughout a THF solution (20 mL) of **9** (0.30 g, 0.26 mmol). Addition of ethanol (30 mL) and concentration under a fast stream of nitrogen gave lustruous deep violet microcrystals of **10**, yield 90%. Λ_M = 45 Ω^{-1} cm^2 mol^{-1}. IR: ν(C≡O) 1940 cm^{-1} (s), ν(C=O) 1690 cm^{-1} (m), ν(COC) 1160 cm^{-1} (m). Anal. Calcd for $C_{72}H_{68}BCoO_3P_4$: C, 73.60; H, 5.83; Co, 5.02. Found: C, 73.44; H, 5.95; Co, 4.86.

Preparation of [(PP$_3$)Co{(*E*)-CH=C(H)CO$_2$Et}] (11). A solution of NaBH$_4$ (0.15 g, 3.97 mmol) in boiling ethanol (25 mL) was added portionwise to a well-stirred hot solution of **9** in THF (30 mL); then the mixture was refluxed for 30 min. The starting violet color disappeared to produce an orange solution, which was cooled down to room temperature. Addition of ethanol (20 mL) yielded orange crystals of **11**, yield 75%. IR: ν(C=O) 1650 cm^{-1} (s), ν(C=C) 1495 cm^{-1} (w), ν(COC) 1240 cm^{-1} (m). Anal. Calcd for $C_{47}H_{49}CoO_2P_4$: C, 68.12; H, 5.96; Co, 7.11. Found: C, 68.16; H, 6.01; Co, 6.97.

Reaction of 8 with LiHBEt$_3$ (or NaBH$_4$). LiHBEt$_3$ (0.25 mL of a 1.0 M THF solution, 0.25 mmol) (or NaBH$_4$ (0.04 g, 1.06 mmol) in ethanol (10 mL)) was added to a THF solution (25 mL) of **8** (0.26 g, 0.25 mmol) to produce a clear yellow solution that gave yellow microcrystals of **5** by addition of ethanol (30 mL); yield 90%.

Reaction of 8 with NEt$_3$ (or KOBu^t). Addition of neat NEt$_3$ (0.10 mL, 0.72 mmol) (or solid KOBu^t (0.11 g, 1.0 mmol)) to a THF solution (20 mL) of **8** gave **5** after the usual workup; yield 90%.

Reaction of 11 with HOSO$_2$CF$_3$. Neat triflic acid (0.05 mL, 0.50 mmol) was syringed into a THF solution (25 mL) of **11** (0.37 g, 0.45 mmol) under nitrogen. The resultant deep red solution gave red crystals of [(PP$_3$)Co(N$_2$)]BPh$_4$ after addition of NaBPh$_4$ (0.40 g, 1.17 mmol) and ethanol (30 mL); yield 85%. The compound was identified by comparison of its IR and ^{31}P{^{1}H} NMR spectra with those of an authentic specimen.[9a] GC analysis of the solution revealed the quantitative formation of ethyl acrylate.

Reaction of 8 with Carbon Monoxide. Carbon monoxide was bubbled through a refluxing THF solution (30 mL) of **8** (0.26 g, 0.25 mmol) for 12 h. The solution was then cooled to room temperature, and *n*-heptane (50 mL) was added. ^{31}P{^{1}H} NMR analysis of the crude dark violet powder showed, besides the starting vinylidene complex, the presence of the known carbonyl complex [(PP$_3$)Co(CO)]BPh$_4$ (ca. 7%).

Oligomerization Runs. In a typical experiment, to a stirred solution of **1**, **3**, or **5** (0.25 mmol) in toluene (12 mL) under nitrogen in a 25-mL Schlenk flask, fitted with a reflux condenser and a thermometer, was added by means of a syringe the appropriate acetylene (25 mmol). The mixture was refluxed for 4 h. After the mixture was cooled to room temperature, its composition was determined by GC–MS techniques through comparison with retention times and mass spectral data of authentic specimens.

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