Organometallics **1989**, *8*, 2564–2569

(Trimethylphosphine)cobalt(I) Complexes: Reactions of $CoBr(PMe_3)_3$ with the Terminal Alkynes HC≡C-*t*-Bu, HC≡CPr, and HC≡CPh. X-ray Structure of $[Co(C{\equiv}C\text{-}t\text{-}Bu)(HC{=}CH\text{-}t\text{-}Bu)(MeCN)(PMe_3)_3]BPh_4$

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Received November 7, 1988

$CoBr(PMe_3)_3$ reacted with the terminal alkynes HC≡C-*t*-Bu, HC≡CPr, and HC≡CPh under mild conditions in polar solvents. With HC≡C-*t*-Bu and HC≡CPr, (σ-alkynyl)(σ-alkenyl)cobalt(III) products $[Co(C{\equiv}CR)(CH{=}CHR)(MeCN)(PMe_3)_3]BPh_4$ (R = *t*-Bu, **1**; R = Pr, **2**) formed in two steps: oxidative addition of the alkyne to the cobalt center and then insertion of the second alkyne into the Co–H bond. The reaction is regioselective, giving only the *trans*-alkenyl isomer with the alkyne substituent in β-position of cobalt. The structure of **1** was determined by X-ray diffraction ($P2_1/c$, a = 22.139 Å, b = 10.315 Å, c = 24.265 Å, β = 121.57°, Z = 4, R = 0.035 for 4428 observed Mo K$\bar{\alpha}$ reflections). The unit cell contains BPh_4^- anions and distorted octahedral Co(III) complex cations. The metal is bonded to three roughly coplanar PMe_3 ligands in a *mer* arrangement, with the fourth corner in the same plane occupied by a *trans*-*tert*-butylvinyl ligand. The bonds perpendicular to this plane are formed with MeCN and a *tert*-butylacetylide ligand. The Co—(C≡C) and Co—(CH=CH) bonds occupy cis corners, and their lengths are 1.869 (4) and 1.985 (3) Å, respectively. HC≡CPh reacted differently, yielding four new species: a phosphonium salt, $[Me_3PCH_2CH(OMe)Ph]BPh_4$, a cobalt(I) complex, $[Co(HC{\equiv}CPh)(MeCN)(PMe_3)_3]BPh_4$, and two cobalt(III) species, $CoH(C{\equiv}CPh)_2(PMe_3)_3$ and $[Co(C{\equiv}CPh)_2(PMe_3)_4]BPh_4$. A reaction scheme is proposed whereby the second alkyne molecule, once bonded to cobalt, would undergo successive nucleophilic attacks by methanol and by trimethylphosphine. Alkyne polymerization was never observed in these systems under the present conditions.

Introduction

In their reactions with mononuclear transition-metal compounds, terminal alkynes often behave like their internal analogues, leading to π-alkynyl, π-cyclobutadienyl, or metallacyclopentadiene complexes, depending on the metal, the ancillary ligands, and the alkyne substituents.[1] However, the presence of a terminal hydrogen induces a specific reactivity, resulting in σ-alkynyl, σ-vinylidene, or carbene species.[1–3] In the case of d^8 systems, for instance, cationic platinum complexes were found to produce classic π-alkynyl compounds in benzene but σ-alkynyl, σ-alkenyl, and carbene products in methanol.[4,5] The d^9 rhodium complex $RhCl(PPh_3)_3$ catalyzes the dimerization of phenylacetylene into *trans*-1,4-diphenylbutenyne, whereas different oligomers are obtained by changing the ligands coordinated to rhodium.[6–9] In addition to being chemically versatile, terminal alkynes raise increasing interest because of their ability to generate polyacetylenes. Polymerization is catalyzed by metal complexes, and research effort is still needed in order to understand the mechanism of these reactions.[1,10,11]

We wish to report on the reactions between $CoBr(PMe_3)_3$ and the terminal alkynes HC≡CR with R = *tert*-butyl, *n*-propyl, and phenyl. These reactions differ from those of disubstituted alkynes, which were recently found to yield π-alkyne Co(I) adducts $[Co(RC{\equiv}CR)(PMe_3)_3]BPh_4$ when R = alkyl or aryl and the cobaltacyclopentadiene Co(III) compound $[\overline{CoC_4}R_4(MeCN)_2(PMe_3)_2]BPh_4$ when R = CO_2Me.[12,13] Whereas *tert*-butyl- and propylacetylene add oxidatively on the cobalt centre, phenylacetylene reacts in a most unexpected way. We describe here these various reactions and the characterization of the new alkynyl complexes obtained, including the single-crystal structure determination of $[Co(C{\equiv}C\text{-}t\text{-}Bu)(HC{=}CH\text{-}t\text{-}Bu)(MeCN)(PMe_3)_3]BPh_4$ (**1**). Alkyne polymerization was never observed to take place.

Experimental Section

Materials and Methods. Solvent distillations and all other operations were performed under an argon atmosphere by using standard Schlenk techniques. Methanol and acetonitrile were

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distilled over molecular sieves. All solvents were degassed by three freeze–thaw cycles before use. Trimethylphosphine[14] and CoBr(PMe$_3$)$_3$[15] were made by literature methods. Alkynes (Aldrich) were checked by NMR and purified by chromatography on alumina if needed.

Elemental analyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer on Nujol mulls prepared in the glovebox. The ^{1}H and ^{1}H{^{31}P} NMR spectra were recorded at low temperature on Bruker WM 250 or WH 90 spectrometers using CD$_2$Cl$_2$ as solvent. ^{13}C, ^{13}C{^{1}H} (62.89 MHz) and ^{31}P, ^{31}P{^{1}H} (101.27 MHz) NMR spectra were also obtained with the Bruker WM 250 apparatus. Chemical shifts were referenced to the residual solvent signals for ^{1}H and ^{13}C NMR (CD$_2$Cl$_2$, δ_H 5.33 and δ_C 53.6 ppm; (CD$_3$)$_2$CO, δ_H 2.17 and δ_C 29.2 ppm) and to external H$_3$PO$_4$ (62.5% in D$_2$O) (δ 0 ppm) for ^{31}P NMR. The ^{13}C and ^{1}H NMR spectra of the complexes included the following BPh$_4^-$ signals, which will not be further discussed: ^{13}C, 121, 125, 135, and 163 ppm; ^{1}H, 6.9, 7.0, and 7.4 ppm.

[Co(C≡C-*t*-Bu)(HC═CH-*t*-Bu)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (1). Excess HC≡C-*t*-Bu (4.5 ml, 35 mmol) was added to CoBr(PMe$_3$)$_3$ (1.30 g, 3.5 mmol) in acetonitrile (10 mL). The blue solution immediately turned brown. Adding NaBPh$_4$ (3.5 mmol, 1.20 g) dissolved in methanol (10 mL) precipitated a yellow powder that was filtered off and dried in vacuo (yield: 2.55 g, 90%). Yellow crystals suitable for X-ray work were obtained by recrystallization in acetonitrile/methanol at −25 °C. Anal. Calcd for C$_{47}$H$_{70}$BCoNP$_3$: B, 1.33; C, 69.54; H, 8.69; N, 1.73; P, 11.45; Co, 7.26. Found: B, 1.25; C, 68.11; H, 8.39; N, 1.83; P, 11.52; Co, 7.22. ^{31}P{^{1}H} NMR (193 K, (CD$_3$)$_2$CO/(CH$_3$)$_2$CO): 6 (d, J_{PP} = 26 Hz), −3 (t, J_{PP} = 26 Hz). ^{1}H NMR (193 K, CD$_2$Cl$_2$): 1.14 (s, C(C*H*$_3$)$_3$), 1.22 (s, C(C*H*$_3$)$_3$), 1.58 (m, P(C*H*$_3$)$_3$, J_{HP} = 4 Hz), 1.64 (m, P(C*H*$_3$)$_3$, J_{HP} = 3 Hz), 2.00 (s, C*H*$_3$CN), 5.13 (d, *H*C═CHCo, J_{HH} = 18 Hz), 6.22 (m, HC═C*H*Co, J_{HH} = 18 Hz, J_{HP} = 6 Hz). ^{13}C NMR (193 K, (CD$_3$)$_2$CO): 2.5 (*C*H$_3$CN), 12.8 (P(*C*H$_3$)$_3$), 15 (P(*C*H$_3$)$_3$, J_{CH} = 128 Hz), 28.5, 31 (C(*C*H$_3$)$_3$, J_{CH} = 130 Hz), 102 (C≡*C*C(CH$_3$)$_3$), 116 (*C*(CH$_3$)$_3$), 139.5 (*C*H═CHCo, J_{CH} = 160 Hz).

[Co(C≡C-*n*-Pr)(CH═CH-*n*-Pr)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (2). Following the same procedure, 1-pentyne produced at −45 °C a yellow precipitate of 2 in 45% yield (1.25 g). Anal. Calcd for C$_{45}$H$_{66}$BCoNP$_3$: B, 1.38; C, 68.97; H, 8.49; N, 1.79; P, 11.86; Co, 7.52. Found: B, 1.40; C, 68.61; H, 8.79; N, 1.35; P, 12.02; Co, 7.63. ^{31}P{^{1}H} NMR (188 K, (CD$_3$)$_2$CO/(CH$_3$)$_2$CO): 8 (d, J_{PP} = 30 Hz), 3 (t, J_{PP} = 30 Hz). Atom labeling in carbon chains: Co(C^1≡C^{2}C^{3}H$_2$C^{4}H$_2$C^{5}H$_3$)(C$^{1'}$H═C$^{2'}$HC$^{3'}$H$_2$C$^{4'}$H$_2$C$^{5'}$H$_3$). ^{1}H NMR (188 K, (CD$_3$)$_2$CO): 0.97 (m, C^5*H*$_3$, C$^{5'}$*H*$_3$), 1.47 (m, C^4*H*$_2$, C$^{4'}$*H*$_2$), 1.55, 1.62 (P(C*H*$_3$)$_3$), 1.9 (C*H*$_3$CN), 2.27 (m, C^3*H*$_2$, C$^{3'}$*H*$_2$), 5.14 (d, C*H*═CHCo, J_{HH} = 16 Hz), 6.30 (CH═C*H*Co, J_{HH} = 16 Hz, J_{HP} = 6 Hz). ^{13}C NMR (188 K, (CD$_3$)$_2$CO): 2.6 (*C*H$_3$CN), 13, 15.2 (P(*C*H$_3$)$_3$), 13.8 (*C*^{5}H$_3$, *C*$^{5'}$H$_3$), 23.2 (*C*^{4}H$_2$, *C*$^{4'}$H$_2$, J_{CH} = 130 Hz), 24 (*C*$^{3'}$H$_2$, J_{CH} = 125 Hz), 39.8 (*C*^{3}H$_2$, J_{CH} = 130 Hz), 106.9 (*C*$^{2'}$H, J_{CH} = 196 Hz), 121.4 (C^2).

[Me$_3$PCH$_2$CH(OMe)Ph]BPh$_4$ (3), CoH(C≡CPh)$_2$(PMe$_3$)$_3$ (4), and [Co(C≡CPh)$_2$(PMe$_3$)$_4$]BPh$_4$ (5). Phenylacetylene (13.2 mmol, 1.50 mL) was mixed with CoBr(PMe$_3$)$_3$ (3.3 mmol, 1.22 g) dissolved in methanol (15 mL). An acetonitrile solution of 3.3 mmol (1.13 g) of NaBPh$_4$ was added. After the solution was stirred for 2 h, yellow crystals of 3 precipitated (2.1 g). Cooling the filtrate to −10 °C precipitated 4 as an orange air-sensitive crystalline compound in 15% yield (0.24 g). It was filtered off and dried under argon. Further cooling at −45 °C produced yellow crystals of 5 in 30% yield (0.87 g), also isolated under argon.

3. Anal. Calcd for C$_{36}$H$_{40}$BOP: B, 2.03; C, 81.51; H, 7.60; P, 5.84. Found: B, 1.94; C, 81.71; H, 7.40; P, 5.73. ^{31}P{^{1}H} NMR (294 K, (CD$_3$)$_2$CO): 31 (br, s). ^{1}H NMR (294 K, (CD$_3$)$_2$CO): 2.22 (d, P(C*H*$_3$)$_3$, J_{HP} = 15 Hz), 3.13 (m, C*H*$_2$, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 11 Hz, J_{HP} = 12 Hz), 3.02 (m, C*H*$_2$, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 4 Hz, J_{HP} = 12 Hz), 3.37 (s, OC*H*$_3$), 6.3 (m, C*H*, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 4 Hz, J_{HP} = 4 Hz), 7.5 (m, C$_6$*H*$_5$).

4. Anal. Calcd for C$_{25}$H$_{38}$CoP$_3$: C, 61.23; H, 7.81; P, 18.95; Co, 12.02. Found: C, 58.95; H, 7.38; P, 17.90; Co, 10.17. ^{31}P{^{1}H} NMR (193 K, CD$_2$Cl$_2$): 9 (s). ^{1}H NMR (193 K, CD$_2$Cl$_2$): −12.5 (dt, Co–*H*, J_{HP} = 120 Hz, J_{HP} = 60 Hz), 1.37, 1.50 (br, s, P(C*H*$_3$)$_3$), 7.11 (m, C$_6$*H*$_5$).

5. Anal. Calcd for C$_{52}$H$_{66}$BCoP$_4$: B, 1.22; C, 70.59; H, 7.52; P, 14.00; Co, 6.66. Found: B, 1.15; C, 71.71; H, 7.38; P, 13.49; Co, 6.03. ^{31}P NMR (183 K, (CD$_3$)$_3$CO/(CH$_3$)$_2$CO): 10 (br, s); ^{1}H NMR (183 K, CD$_2$Cl$_2$): 1.66, 1.71 (1:3 ratio, P(C*H*$_3$)$_3$), 7.22 (C$_6$*H*$_5$). ^{13}C NMR (183 K, (CD$_3$)$_2$CO): 18 (stronger), 14 (P(*C*H$_3$)$_3$), 102 (Co*C*≡C); 112 (CoC≡*C*).

Co(C≡CPh)$_2$(PMe$_3$)$_4$]BF$_4$ (6). Same as for the previous case, except that NaBF$_4$ in 1/1 MeOH/MeCN was added. Anal. Calcd for C$_{28}$H$_{46}$BCoF$_4$P$_4$: B, 1.66; C, 51.56; H, 7.11; P, 18.99; Co, 9.03; Found: B, 1.77; C, 51.90; H, 7.29; P, 19.15; Co, 9.53.

[Co(HC≡CPh)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (7). Phenylacetylene (13 mmol, 0.6 mL) was mixed with CoBr(PMe$_3$)$_3$ (3.3 mmol, 1.22 g) dissolved in acetonitrile. NaBPh$_4$ (3.3 mmol, 1.13 g) dissolved in methanol was added to this red solution. By cooling to −45 °C, red crystals precipitated in 70% yield (1.73 g) and were isolated under argon. Anal. Calcd for C$_{43}$H$_{56}$BCoNP$_3$: C, 68.90; H, 7.53; N, 1.87. Found: C, 68.86; H, 7.52; N, 2.09. ^{31}P{^{1}H} NMR (183 K, (CD$_3$)$_2$CO/(CH$_3$)$_2$CO): 18 (br, s). ^{31}P{^{1}H} NMR (183 K, (CD$_3$)$_2$CO/CH$_3$CN): 17, 11, -0.5 (br, m). ^{1}H NMR (183 K, (CD$_3$)$_2$CO): 14.1 (br, P(C*H*$_3$)$_3$), 1.99 (s, C*H*$_3$CN), 7 (m, C$_6$*H*$_5$).

Crystallographic Measurements and Structure Determination. Crystal data: C$_{47}$H$_{70}$BCoNP$_3$, fw = 811.75, monoclinic, $P2_1/c$, a = 22.139 (11) Å, b = 10.315 (3) Å, c = 24.265 (9) Å, β = 121.57 (3)°, V = 4721 Å^3, D_{calcd} = 1.142 g cm^{-3}, Z = 4, λ(Mo K$\bar{\alpha}$) = 0.710 69 Å, μ(Mo Kα) = 5.0 cm^{-1}, T = 160 K.

The sample was handled in air only a few minutes for crystal mounting. A parallelepiped of dimensions (mm) 0.43 × 0.37 × 0.27 was cut from a large block and glued to a glass fiber that was immediately transferred to the Enraf-Nonius CAD-4 diffractometer, where its temperature quickly decreased to 160 K in the nitrogen stream of the cooling system.

Monoclinic Laue symmetry and cell dimensions were determined from 25 reflections centered in the diffractometer counter. Indexing yielded the above monoclinic cell whose Niggli matrix clearly indicated the absence of higher symmetry. This cell was checked with axial photographs, showing the proper layer line spacings and a mirror plane for oscillation about the b axis.

Intensity data were collected at 160 K under conditions explained elsewhere.[16] A total of 6144 independent hkl and $hk\bar{l}$ reflections (Mo K$\bar{\alpha}$, 2θ < 45°) were collected. The seven standard reflections fluctuated within ±1.7% during data collection. A set of 4428 reflections with $I > 3\sigma(I)$ were retained for structure determination. These data were corrected for the Lorentz effect and polarization. An absorption correction was not considered necessary. Inspection of the full data set revealed conditions of systematic absences ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with space group $P2_1/c$ only.

The structure was solved by using the SHELX package.[17] The position of the Co atom was found by using automated direct methods. The non-hydrogen atoms were located by using Fourier difference syntheses and were allowed to refine anisotropically. The full set of hydrogen atom peaks then appeared on the difference map. They were included in the model at idealized positions (B = 4.0 Å^2), and their coordinates were recalculated after each least-squares cycle. The final cycles of refinement were carried out by using our local least-squares program[18] to allow a block-diagonalized treatment of the complete model. The final agreement factors were $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.035$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.034$, with $w = 1/\sigma^2(|F_o|)$. The goodness-of-fit ratio was 1.98. The background in the final difference Fourier map was below ±0.4 e Å^{-3}. The atomic positional parameters and equivalent temperature factors are listed in Table I. The scattering curves were from standard sources.[19]

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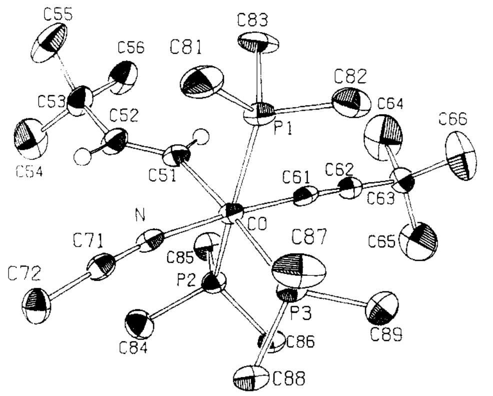

Figure 1. ORTEP drawing of the complex cation in [Co(C≡C-*t*-Bu)(HC=CH-*t*-Bu)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (1). Ellipsoids correspond to 50% probability.

The f' and f'' contributions to anomalous dispersion for Co and P were from Cromer.[20]

Results and Discussion

Reactions with HC≡C-*t*-Bu and HC≡C-*n*-Pr. CoBr(PMe$_3$)$_3$ reacted instantaneously with the terminal alkynes HC≡C-*t*-Bu or HC≡CPr in methanol. The very air-sensitive red crystals precipitating at −40 °C were undoubtedly [CoH(C≡CR)(HC≡CR)(PMe$_3$)$_3$]Br.[21] The infrared spectra included vibrations originating from the PMe$_3$ ligands and the characteristic σ-alkynyl ν(C≡C) and π-alkynyl ν(HC≡CR) bands at 2100 and 1720 cm^{-1}, respectively, together with a weak signal ca. 1920 cm^{-1} that can be assigned to ν(Co—H).[2] By adding NaBPh$_4$ in acetonitrile, complexes 1 and 2 were isolated as yellow crystalline solids, stable in air for a short time. The yellow

$$\mathrm{CoBr(PMe_3)_3} + 2\mathrm{HC{\equiv}CR} \xrightarrow{+\mathrm{NaBPh_4}} \underset{\substack{1:\ R\,=\,t\text{-Bu} \\ 2:\ R\,=\,Pr}}{[\mathrm{Co(C{\equiv}CR)(CH{=}CHR)(MeCN)(PMe_3)_3}]\mathrm{BPh_4}} + \mathrm{NaBr}$$

compounds display the expected ν(C≡CR) infrared absorption at 2100 cm^{-1} for 1 and 2120 cm^{-1} for 2, corresponding to σ-alkynyl ligands.[2] Coordinated acetonitrile is detected in both compounds from the ν(CN) bands at 2200 cm^{-1}. The ^{31}P{^{1}H} NMR spectra at −80 °C show an A$_2$B pattern with a doublet at 6 ppm (2 P, J_{PP} = 26 Hz) and a triplet at −3 ppm (1 P, J_{PP} = 26 Hz) for 1 and a doublet at 8 ppm (2 P, J_{PP} = 30 Hz) and a triplet at 3 ppm (1 P, J_{PP} = 30 Hz) for 2, consistent with the presence of two types of PMe$_3$ ligands in a 1:2 ratio. Beside the signals for PMe$_3$, MeCN, BPh$_4^-$, and the alkyne substituents, the ^{1}H{^{31}P} NMR spectra show signals at 5.13 (1 H, J_{HH} = 18 Hz) and 6.22 ppm (1 H, J_{HH} = 18 Hz, J_{HP} = 6 Hz) for 1 and 5.14 (1 H, J_{HH} = 16 Hz) and 6.30 ppm (1 H, J_{HH} = 16 Hz, J_{HP} = 6 Hz) for 2, corresponding to the two alkenyl protons. These data establish the most probable geometry around cobalt as octahedral, with two trans phosphines and the alkenyl group trans to the third phosphine. Only the ^{1}H NMR signals at 6.2–6.3 ppm due to the protons of the alkenyl carbon σ-bonded to cobalt show coupling to ^{31}P.

Of particular interest is the stereochemistry of the coordinated alkenyl group. Examples of both cis and trans isomers have been reported.[6] They can be distinguished from their chemical shifts and J_{HH} couplings, high-field shifts and low J_{HH} values being characteristic of the cis arrangement. The trans isomer is the only one present here. Its J_{HH} value of 18 Hz agrees with the coupling constants observed between protons trans to an alkenyl double bond.[22-24]

Table I. Refined Fractional Coordinates (×10^4; Co, P × 10^5) and Equivalent Temperature Factors (×10^3)

atom	x	y	z	U_{eq}, Å^2
Co	23015 (2)	31313 (4)	573 (2)	23
P1	18718 (5)	13755 (9)	−5604 (4)	31
P2	23369 (5)	49738 (9)	5537 (4)	26
P3	32447 (4)	21448 (9)	9307 (4)	28
N	2997 (1)	3655 (3)	−149 (1)	24
C11	6189 (2)	2358 (3)	1113 (1)	23
C12	5464 (2)	2112 (3)	698 (1)	29
C13	5171 (2)	1747 (3)	59 (2)	36
C14	5593 (2)	1610 (3)	−201 (2)	38
C15	6313 (2)	1872 (3)	189 (2)	34
C16	6598 (2)	2240 (3)	826 (2)	28
C21	6488 (2)	4427 (3)	1833 (1)	23
C22	7046 (2)	5218 (3)	1928 (2)	33
C23	6997 (2)	6556 (3)	1866 (2)	40
C24	6373 (2)	7171 (3)	1697 (2)	44
C25	5802 (2)	6432 (3)	1582 (2)	40
C26	5860 (2)	5098 (3)	1650 (2)	28
C31	7343 (2)	2306 (3)	2345 (1)	23
C32	7593 (2)	1148 (3)	2241 (2)	30
C33	8267 (2)	665 (3)	2657 (2)	37
C34	8728 (2)	1345 (4)	3216 (2)	37
C35	8500 (2)	2472 (3)	3350 (2)	36
C36	7824 (2)	2940 (3)	2923 (2)	29
C41	6085 (1)	2231 (3)	2177 (1)	21
C42	5801 (2)	972 (3)	2023 (2)	28
C43	5456 (2)	419 (3)	2305 (2)	36
C44	5391 (2)	1088 (4)	2757 (2)	40
C45	5679 (2)	2312 (3)	2940 (2)	34
C46	6023 (2)	2861 (3)	2649 (2)	28
C51	1546 (2)	4043 (3)	−721 (1)	27
C52	1574 (2)	4654 (4)	−1180 (2)	33
C53	974 (2)	5347 (4)	−1770 (2)	40
C54	1183 (2)	6739 (4)	−1760 (2)	72
C55	880 (2)	4664 (5)	−2376 (2)	65
C56	272 (2)	5264 (4)	−1803 (2)	47
C61	1682 (2)	2658 (3)	328 (1)	26
C62	1296 (2)	2384 (3)	524 (1)	26
C63	840 (2)	2039 (3)	778 (2)	31
C64	85 (2)	2485 (5)	300 (2)	86
C65	1136 (3)	2676 (5)	1444 (2)	80
C66	857 (3)	583 (4)	877 (2)	75
C71	3448 (2)	4045 (3)	−192 (1)	25
C72	4044 (2)	4578 (3)	−212 (2)	34
C81	2260 (2)	983 (4)	−1035 (2)	54
C82	1904 (2)	−152 (4)	−177 (2)	46
C83	927 (2)	1394 (4)	−1167 (2)	50
C84	2869 (2)	6233 (3)	492 (2)	41
C85	1495 (2)	5802 (3)	238 (2)	39
C86	2635 (2)	4933 (3)	1405 (2)	31
C87	3681 (2)	852 (4)	758 (2)	53
C88	4016 (2)	3181 (3)	1382 (2)	36
C89	3124 (2)	1437 (4)	1545 (2)	48
B	6530 (2)	2832 (4)	1866 (2)	24

Few complexes of this type have been reported. Since such an important species likely plays a role in the polymerization of alkynes (vide infra), X-ray diffraction work was carried out on 1.

X-ray Structure of [Co(C≡C-*t*-Bu)(CH=CH-*t*-Bu)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (1). The geometry anticipated from the spectral data for the cation in 1 was confirmed by the solid state structure shown on Figure 1,

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Table II. Interatomic Distances (Å) and Bond Angles (deg) in the Complex Cation

Distances			
Co-P1	2.222 (1)	P3-C89	1.801 (4)
Co-P2	2.229 (1)	C51-C52	1.309 (5)
Co-P3	2.292 (1)	C52-C53	1.527 (5)
Co-C51	1.985 (3)	C53-C54	1.506 (6)
Co-C61	1.869 (4)	C53-C55	1.543 (6)
Co-N	1.929 (3)	C53-C56	1.516 (6)
P1-C81	1.807 (5)	C61-C62	1.209 (6)
P1-C82	1.812 (4)	C62-C63	1.476 (6)
P1-C83	1.822 (5)	C63-C64	1.523 (7)
P2-C84	1.812 (4)	C63-C65	1.538 (6)
P2-C85	1.815 (4)	C63-C66	1.518 (6)
P2-C86	1.810 (3)	N-C71	1.131 (5)
P3-C87	1.820 (5)	C71-C72	1.454 (6)
P3-C88	1.816 (4)		
Angles			
P1-Co-P2	160.17 (4)	Co-P3-C87	116.7 (1)
P1-Co-P3	97.06 (4)	Co-P3-C88	114.2 (1)
P1-Co-C51	83.9 (1)	Co-P3-C89	119.1 (1)
P1-Co-C61	83.7 (1)	C87-P3-C88	97.2 (2)
P1-Co-N	99.9 (1)	C87-P3-C89	102.7 (2)
P2-Co-P3	96.98 (4)	C88-P3-C89	103.9 (2)
P2-Co-C51	83.3 (1)	Co-C51-C52	130.2 (3)
P2-Co-C61	81.8 (1)	C51-C52-C53	128.1 (3)
P2-Co-N	95.4 (1)	C52-C53-C54	108.8 (3)
P3-Co-C51	174.8 (1)	C52-C53-C55	107.3 (3)
P3-Co-C61	92.3 (1)	C52-C53-C56	112.8 (3)
P3-Co-N	84.2 (1)	C54-C53-C55	109.7 (3)
C51-Co-C61	92.9 (2)	C54-C53-C56	110.6 (3)
C51-Co-N	90.6 (1)	C55-C53-C56	107.5 (3)
C61-Co-N	175.3 (1)	Co-C61-C62	177.4 (3)
Co-P1-C81	115.7 (2)	C61-C62-C63	178.6 (4)
Co-P1-C82	118.3 (1)	C62-C63-C64	109.1 (3)
Co-P1-C83	116.2 (1)	C62-C63-C65	109.1 (3)
C81-P1-C82	103.2 (2)	C62-C63-C66	109.8 (3)
C81-P1-C83	102.4 (2)	C64-C63-C65	111.4 (4)
C82-P1-C83	98.3 (2)	C64-C63-C66	110.2 (4)
Co-P2-C84	114.0 (1)	C65-C63-C66	107.2 (4)
Co-P2-C85	115.8 (1)	Co-N-C71	170.7 (3)
Co-P2-C86	119.0 (1)	N-C71-C72	176.8 (4)
C84-P2-C85	101.3 (2)		
C84-P2-C86	104.3 (3)		
C85-P2-C86	100.0 (2)		

where the atom numbering scheme is defined. Bond distances and angles are collected in Table II.

The cobalt atom is hexacoordinated, surrounded by two trans PMe_3, an alkenyl ligand trans to the third PMe_3, and an alkynyl ligand trans to acetonitrile. The three roughly coplanar phosphines have the *mer* configuration previously observed in $Co(NCS)_3(PMe_3)_3$[25] and in $Co(CH_3)_3(PMe_2Ph)_3$.[26]

The most interesting feature is the presence of one alkenyl and one alkynyl ligand on the same metal atom and in a cis arrangement. Both are σ-bonded to Co, and the alkenyl group is bonded via the less substituted carbon. The alkynyl group, which is the strongest σ-donor ligand, lies trans to acetonitrile as expected. η^1-*tert*-Butylacetylide and η^1-*tert*-butylvinyl entities have each been found so far in only one crystal structure.[22,27] The geometry observed here is in good agreement with these precedent results. The Co—(CH═C) and Co—(C$\equiv$C) distances of 1.985 (3) and 1.869 (4) Å, respectively, are normal for σ-alkenyl and σ-alkynyl complexes. However, the C═C distance in the cobalt complex (1.309 (5) Å) is shorter than that of $CpMo(P(OMe)_3)_3$(*tert*-butylalkenyl) (1.336 (3) Å).[22] The C$\equiv$C distance in the η^1-*tert*-butylalkynyl unit (1.209 (6) Å) is similar to that of Cp_2V(*tert*-butylacetylide) (1.191 (7) Å).[27]

The Co–P distances are on the high side of the range reported for the Co(III) complexes $Co(NCS)_3(PMe_3)_3$[25] and $Co(CH_3)_3(PMe_2Ph)_3$[26] and more in the range usually observed in Co(I) compounds. Hence, any bond contraction resulting from increased Co oxidation state is balanced by a lengthening due to greater coordination number. Moreover, the Co–P3 bond, trans to the alkenyl group, is significantly lengthened by the trans effect of the alkenyl ligand. The generally greater distances for these Co–P bonds may be ascribed in part to the mutual steric effect of the phosphines and of the alkyne *tert*-butyl substituent, since the trans phosphines P1 and P2 are displaced away from P3 (P1–Co–P2 = 160.17 (4)°, P1–Co–P3 = 97.06 (4)°, P2–Co–P3 = 96.98 (4)°), introducing a large distorsion in the octahedron. The linear acetonitrile is end-on coordinated (Co–N–C = 170.7 (3)°).

The P–C bond lengths in PMe_3 average the normal value of 1.813 Å. Departure from tetrahedral geometry around P is significant as commonly observed: Co–P–C = 116.6° (average) and C–P–C = 101.5° (average). The BPh_4^- ion has its usual structure, whose details are provided in the supplementary material.

To our knowledge, there are only four crystal structures of complexes containing nonbridging η^1-alkynyl and η^1-alkenyl groups coordinated to the same metal atom. In one of these compounds,[29] the two groups do not have a common origin. Of the two compounds where they are derived from the same parent alkyne, one is the reaction product of ethynyldicarbadodecaborane with trans-$IrCl(CO)(PPh_3)_2$,[23] which resembles the present Co complex in being a six-coordinate species with η^1-alkynyl and η^1-*trans*-alkenyl moieties bonded to cis corners of an octahedron. The alkenyl group is also bonded via the unsubstituted carbon. Two $Pt(PPh_3)_2$(alkynyl)(alkenyl) compounds were obtained from phenylacetylene and isopropenylacetylene, respectively.[29,30] These compounds have a trans square-planar structure, and contain one alkenyl group σ-bonded to the metal via a substituted carbon atom.

Reaction with HC$\equiv$CPh. Phenylacetylene was found to react in a very different manner. Whereas the reactions of HC$\equiv$C-*t*-Bu and HC$\equiv$CPr were selective, three main products were observed with phenylacetylene. Compounds 3, 4, and 5 were successively isolated by fractional crystallization from the methanol/acetonitrile solution obtained when excess HC$\equiv$CPh was reacted with $CoBr(PMe_3)_3$ dissolved in methanol, and $NaBPh_4$ dissolved in acetonitrile was subsequently added.

Elemental analysis, infrared, and NMR results for **3** were consistent with its being formulated as $[Me_3PCH_2CH(OMe)Ph]BPh_4$. This trimethyl(2-phenyl-2-methoxyethyl)phosphonium salt was isolated as yellow crystals, and its structure was ascertained by X-ray diffraction.[31]

Compound **4** was precipitated as air-sensitive orange crystals at −10 °C. Its structure cannot be established with certainty. As a solid, it could be formulated as the *fac* isomer **4a** of $CoH(C\equiv CPh)_2(PMe_3)_3$ on the basis of elemental analysis and the presence of one ν(Co—H) band

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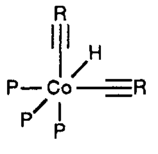
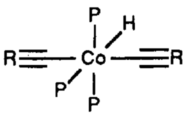
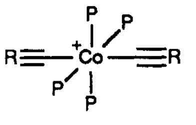
at 1920 cm^{-1} and two $\nu(C\equiv C)$ bands at 2077 and 2055 cm^{-1} in the IR spectrum. Also consistent with this structure is the triplet of doublets observed at −12.5 ppm ($^1J_{HP}$ = 120 Hz, $^1J_{HP}$ = 60 Hz) in the ^{1}H NMR spectrum, which becomes a singlet upon ^{31}P decoupling, indicating that the hydrido ligand lies trans to a phosphine. However, these NMR data are also in agreement with the mer isomer **4b**, whose presence in toluene solution is suggested by the IR spectrum showing a single $\nu(C\equiv C)$ band at 2080 cm^{-1}. Hence, a crystal structure is required to settle this point.


4a


4b

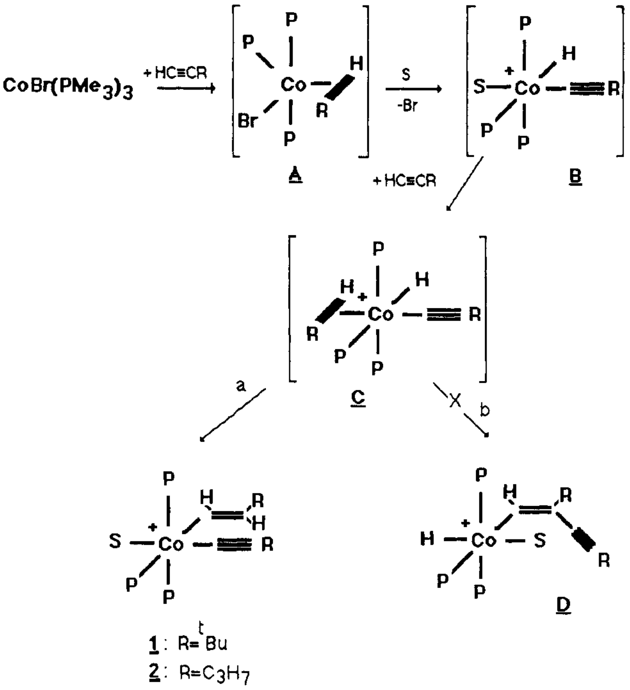

5

Further cooling of the solution to −45 °C produced orange microcrystals of compound **5** in 30% yield. Microanalysis, infrared, and NMR data confirmed **5** as [Co(C≡CPh)$_2$(PMe$_3$)$_4$]BPh$_4$. The tetrafluoroborate analogue **6** was also prepared. Only one $\nu(C\equiv C)$ band was observed for the solids at 2060 (**5**) and 2055 cm^{-1} (**6**), which identified structure **5**. Two inequivalent PMe$_3$ signals in a 3:1 ratio were apparent in the ^{1}H NMR spectrum, showing that alteration, probably isomerization, occurred in solution. However, only a broad band was observed at 10 ppm in the ^{31}P NMR spectrum at −90 °C. The original compound was recovered when the solvent was removed. This process could not be fully clarified.

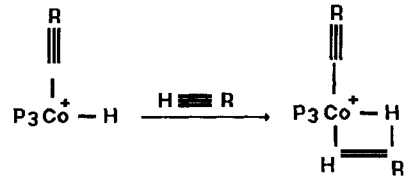
The solvent used and the order of addition of the reactants are important variables. When the alkyne was first mixed with CoBr(PMe$_3$)$_3$ dissolved in acetonitrile and NaBPh$_4$ was then added as a methanol solution, red crystals of a new species, **7**, precipitated at −45 °C in 70% yield. From microanalysis, infrared, and NMR data, **7** was formulated as the cationic Co(I) compound [Co(HC≡CPh)(MeCN)(PMe$_3$)$_3$]BPh$_4$, with HC≡CPh π-bonded to cobalt as previously observed with disubstituted alkynes.[12,13] The $\nu(C\equiv C)$ frequency of 1743 cm^{-1} was consistent with an alkyne acting as a two-electron donor. The ^{31}P{^{1}H} spectrum of **7** in acetone/acetonitrile at −90 °C showed ill-resolved multiplets (probably doublets of doublets with nearly coincident central lines) at 17, 11, and −0.5 ppm, corresponding to the ABC spin system of a [Co(PMe$_3$)$_3$]$^+$ fragment containing three inequivalent phosphines. This species could have the same structure as [Co(ethylene)(MeCN)(PMe$_3$)$_3$]$^+$,[32] with MeCN and one phosphine in axial positions. The dissymmetry of the alkyne renders the equatorial phosphines inequivalent, as found in other systems.[33] The spectrum also shows a broad singlet at 18 ppm. This signal is the only one detected when **7** is dissolved in acetone and it probably corresponds to species **8**. A similar dissociative equilibrium is known to occur for the diphenylacetylene analogue,[12] leading to a species similar to **8** and containing an alkyne acting as a four-electron donor. This emphasizes the coordinative ability of acetonitrile which allows stabilization of the cobalt(I)–π-alkyne complex [Co(HC≡CPh)(MeCN)(PMe$_3$)$_3$]BPh$_4$ at the expense of the cobalt(III) hydrido alkynyl complex.

$$\underset{\mathbf{7}}{[\mathrm{Co(HC{\equiv}CPh)(MeCN)(PMe_3)_3}]\mathrm{BPh_4}} \rightleftharpoons \underset{\mathbf{8}}{[\mathrm{Co(HC{\equiv}CPh)(PMe_3)_3}]\mathrm{BPh_4}} + \mathrm{MeCN}$$

Scheme I



Scheme II



Discussion

tert-Butyl- and *n*-propylacetylene reacted cleanly with the CoBr(PMe$_3$)$_3$ to form compounds including one alkynyl ligand and one alkenyl ligand. The regioselectivity of alkyne addition (cis addition) is the same as for alkyne addition to coordinatively unsaturated hydridometal complexes,[6] suggesting that such a Co–H species probably forms as an intermediate. A possible pathway for the formation of compounds **1** and **2** is outlined in Scheme I. Although CoBr(π-alkyne)(PMe$_3$)$_3$ (A) and [CoH(C≡CR)(MeCN)(PMe$_3$)$_3$]$^+$ (B) were not detected, even at low temperature, the precipitation of **1** and **2** as the cis isomers supports the oxidative addition of the first alkyne molecule to the cobalt centre to give the cis hydrido alkynyl intermediate. Subsequently, the second alkyne can add on the cobalt center (species C, observed at −40 °C) and give rise to the *cis*-alkenyl complex via a concerted process involving a four-center cyclic transition state followed by migratory insertion of the alkyne into the Co–H bond (Scheme II). The steric effect of the alkyne substituents and the presence of a coordinatively saturated metal center can explain the absence of the *trans*-alkenyl isomer.[5] Thus, CoBr(PMe$_3$)$_3$ behaves as a hydrogenation reagent, not as a polymerization catalyst. The latter reaction would require a pathway favoring isomerization of intermediate C, so as to allow the second alkyne molecule to be cis to the alkynyl group, in a suitable position to react with the Co–C bond. Reductive elimination of the alkynes to yield *trans*-1,4-diphenylbutenyne, as was reported for RhCl(PPh$_3$)$_3$,[8] is not observed here.

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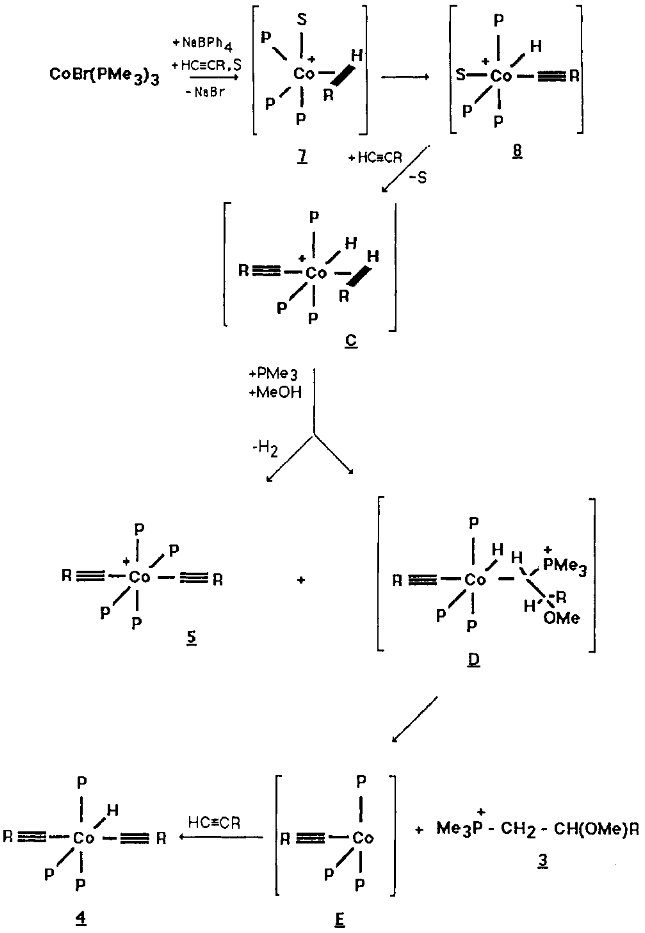
Scheme III



In the case of phenylacetylene, reactivity is apparently increased by the alkyne acidity. No alkynylalkenylcobalt complex was observed. A mechanism that reasonably accounts for our results is presented in Scheme III. Formation of products 3 and 4 could occur sequentially via initial formation of C, a species directly observed for HC≡C-*t*-Bu and HC≡CPr, but not with phenylacetylene. Species C would further react with methanol and PMe_3, generating D by a transmethoxymetalation reaction of the substituted β-carbon atom and by nucleophilic attack of PMe_3 on the α-carbon atom. There are precedents for both reactions. Transmethoxymetalation occurred with Pd and Pt complexes, but the reaction involved the less substituted alkyne carbon.[34,35] On the other hand, a few metal complexes bearing a phosphine-substituted vinyl ligand resulting from nucleophilic attack of coordinated alkyne by phosphine are known.[36,37] The cobalt species D has not been observed even at low temperature. Its decomposition occurred readily via reductive elimination of the hydrido ligand and phosphorus entity, leading to the phosphonium salt 3 and a coordinatively unsaturated Co(I) species, E, which would react with excess alkyne to give 4. Synthesis of a phosphonium salt by reaction of a phosphine on a coordinated alkyne is to our knowledge unprecedented.[38] Formation of the minor product 5 also involves the reaction of intermediate C with PMe_3 in excess.

Acknowledgment. Support from the Centre National de la Recherche Scientifique, the Université P. Sabatier, the Natural Sciences and Engineering Research Council of Canada, and the Ministère de l'Education du Québec is gratefully acknowledged. This work was made possible by travel grant (No. 85/0245) in the framework of the NATO Research Program for International Cooperation.

Registry No. **1**, 122519-58-8; **2**, 122519-60-2; **3**, 122519-56-6; **4**, 122539-40-6; **5**, 122519-62-4; **6**, 122519-63-5; **7**, 122519-65-7; HC≡C-*t*-Bu, 917-92-0; $CoBr(PMe_3)_3$, 53432-07-8; 1-pentyne, 627-19-0; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables anisotropic temperature factors, coordinates of hydrogen atoms, distances and angles in the BPh_4^- ion, and distances to least-squares planes (10 pages); listing of structures factors (22 pages). Ordering information is given on any current masthead page.

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