JEOL GX-270-89 spectrometer. The EPR spectra were obtained from a Bruker 200 D-SRC instrument operating at 9.78 GHz (X-band) equipped with a Bruker variable-temperature ER 411 VT unit. The electrochemical apparatus and the purifications of solvents and supporting electrolytes have been described previously.[15-17] All potentials are referred to the saturated calomel electrode (SCE). Under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.38 V in MeCN and +0.49 V in CH_2Cl_2. Separation workup was brought about by SiO_2 column chromatography [eluent petroleum ether (40–70 °C) with increasing amount of CH_2Cl_2]. The identification of $Fe_2(CO)_6(PhC_2Ph)_2$ was achieved by IR and MS spectrometry and TLC comparison with autentical sample.

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Reactions of Disubstituted Alkynes with Bromotris(trimethylphosphine)cobalt(I). Synthesis and Molecular and Crystal Structures of $[Co(\eta^2\text{-}PhC{\equiv}CC_5H_{11})(PMe_3)_3]BPh_4$ and $[Co(\sigma^2\text{-}(CO_2Me)_4C_4)(MeCN)_2(PMe_3)_2]BPh_4$

Abdessalam Bouayad, Michèle Dartiguenave,* Marie-Joëlle Menu, and Yves Dartiguenave*

Laboratoire de Chimie de Coordination, 205 route de Narbonne, F31077-Toulouse, France

Francine Bélanger-Gariépy and André L. Beauchamp*

Département de Chimie, Université de Montréal, C.P.6128, Succ.A, Montréal, Québec, H3C 3J7 Canada

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Cationic cobalt(I)–alkyne complexes $[Co(RC{\equiv}CR')(PMe_3)_3]BPh_4$ (**1a**, R = Ph, R′ = C_5H_{11}; **1b**, R = R′ = Me; **1c**, R = Ph, R′ = Me) have been synthesized from $CoBr(PMe_3)_3$. Chemical and spectroscopic properties indicate that the alkyne ligand acts as a 4e donor but remains weakly bound. Under similar experimental conditions, the electron-poor ester-substituted alkynes dimethyl acetylenedicarboxylate and methyl propiolate form in acetonitrile cobaltacyclopentadiene complexes $[\overline{\mathrm{CoRC{=}CR'CR'{=}C}}\mathrm{R}(MeCN)_2(PMe_3)_2]BPh_4$ (**2a**, R = R′ = CO_2Me; **2b**, R = H, R′ = CO_2Me). Single-crystal X-ray diffraction work on **1a** ($P2_1/c$, a = 11.880 (1) Å, b = 14.629 (1) Å, c = 25.836 (3) Å, β = 90.33 (9)°, Z = 4, R = 0.055, R_w = 0.067 for 3897 reflections) confirmed the geometry deduced from spectroscopic data. The cation has a three-legged piano-stool geometry, with the alkyne unit lying in the Co–P1–C10–C11 plane and nearly parallel to the plane of the three P atoms. This structure is discussed in terms of a d^8 14e $[Co(PMe_3)_3]^+$ fragment interacting with the π-bonding alkyne. Complex stabilization by the phenyl substituents is discussed. The crystal structure of **2a** ($C2/c$, a = 41.344 (9) Å, b = 10.250 (4) Å, c = 25.377 (7) Å, β = 118.56 (2)°, Z = 8, R = 0.055, R_w = 0.061 for 3864 reflections) confirms the presence of an octahedral d^6 Co(III) monomer containing two trans phosphines, two cis acetonitriles, and a planar cobaltacyclopentadiene ring. From these results, it appears that in cationic d^8 metal complexes having two vacant $d\pi$ orbitals: (i) alkyl- and arylalkynes act as 4e donors, (ii) electron-withdrawing substituents as in dimethyl acetylenedicarboxylate or methyl propiolate are necessary to couple alkynes into cobaltacyclopentadiene complexes, and (iii) alkyne polymerization does not take place.

Introduction

Much of the current interest in the chemistry of alkynes originates in these unsaturated ligands having an important potential in organic synthesis. It is well established that their reactivity can be successfully modified by metal complexation, and this is generating increasing interest in mononuclear alkyne–metal complexes.

The binding of alkynes to metals depends on the metal configuration. Even though compounds have been reported with nearly all metals in the periodic table, there are relatively few monoalkyne complexes known.[1] Their chemistry is dominated by the presence of two filled orthogonal $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals and two empty $\pi_{\parallel}{}^*$ and $\pi_{\perp}{}^*$ counterparts. Metals with d^0 to d^5 configurations in low oxidation states allow the filled $\pi_{\perp}$ orbital in the alkyne to encounter a suitable vacant $d\pi$ orbital in the metal, thereby giving rise to stable metal–alkyne species. Metals in configurations d^6 and higher, when coordinatively saturated, generally exhibit only weak η^2-alkyne binding because of an unfavorable two-center, four-electron repulsion between the filled alkyne $\pi_{\perp}$ orbital and a filled metal $d\pi$ orbital. To overcome this situation, either the alkyne acts as a two-electron ligand like an alkene or the complex loses a ligand to become coordinatively unsaturated in order to provide a vacant orbital for the filled $\pi_{\perp}$ alkyne orbital.

Molybdenum and tungsten in d^2, d^4, and d^6 configurations have been thoroughly studied mainly by Templeton and his group.[2-10] As for d^8 systems, interest in metal–

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alkyne complexes never failed since the early work of Chatt and co-workers on platinum.[11,12] These d^8 complexes catalyze the dimerization, trimerization, or polymerization of alkynes, and this explains why few mononuclear alkyne compounds have been prepared.[1]

Extensive synthetic work based on the reaction of $CpCoL_2$ (L = CO, PR_3) with alkynes has shown that mononuclear $CpCo(RC_2R')L$ compounds can be isolated as first-step products.[13-17] The cationic $[Co(C_2Ph_2)(P(OMe)_3)_3]PF_6$ complex has also been prepared.[18] In a previous study on the reactions of $CoX(PMe_3)_3$ with diphenylacetylene,[19] we surprisingly obtained a pair of closely related monomeric species, $[Co(C_2Ph_2)(PMe_3)_3]^+$ and $[Co(C_2Ph_2)(MeCN)(PMe_3)_3]^+$, both corresponding to an effective atomic number of 18 electrons: in the former case, the alkyne acts as 4e donor and in the latter as a 2e donor. This study was extended to other disubstituted alkynes and to terminal alkynes, and the results were found to depend on alkyne substitution. Reactions with various terminal alkynes ($HC{\equiv}CC_4H_9$, $HC{\equiv}CC_3H_7$, $HC{\equiv}CPh$) lead to cobalt–alkynyl species to be discussed in a subsequent paper. We report here on the reactions of $CoBr(PMe_3)_3$ with the disubstituted alkynes $PhC{\equiv}CC_5H_{11}$, $MeC{\equiv}CMe$, $MeC{\equiv}CPh$, and $MeO_2CC{\equiv}CCO_2Me$ (dimethyl acetylenediacetate, DMAC) and with $HC{\equiv}CCO_2Me$ (methyl propiolate, MP).

Experimental Section

Materials and Methods. Solvent distillations and all other operations were carried out under argon by using standard Schlenk techniques. Tetrahydrofuran, pentane, and ether were distilled over Na/benzophenone just before use. Methylene chloride was distilled over Na_2CO_3 and stored on 4-Å molecular sieves. Methanol and acetonitrile were distilled over molecular sieves. All solvents were degassed by three freeze–thaw cycles. Trimethylphosphine[20] and $CoBr(PMe_3)_3$[21] were prepared by literature methods. Alkynes (Aldrich) were checked by NMR and purified by chromatography on alumina when needed.

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

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer as Nujol mulls prepared in the glovebox. The ^1H and $^1H\{^{31}P\}$ spectra were recorded at low temperature on a Bruker WM 250 or WH 90 spectrometer using CD_2Cl_2 as solvent. ^{13}C, $^{13}C\{^1H\}$ (62.89 MHz) and ^{31}P, $^{31}P\{^1H\}$ (101.27 MHz) spectra were also obtained with the Bruker WM 250 spectrometer. Chemical shifts were referenced to residual solvent signals for ^1H and ^{13}C NMR (CD_2Cl_2, δ_H 5.33 and δ_C 53.6 ppm; $(CD_3)_2CO$, δ_H 2.17 and δ_C 29.2 ppm) and to external H_3PO_4 (62.5% in D_2O) (δ 0 ppm) for ^{31}P NMR. The ^{13}C and ^1H spectra of all complexes contain the following BPh_4^- signals, which will not be further discussed: ^{13}C, 121, 125, 135, and 163 ppm; ^1H, 6.9, 7.0, and 7.4 ppm.

$[Co(PhC{\equiv}CC_5H_{11})(PMe_3)_3]BPh_4$ (1a). To $CoBr(PMe_3)_3$ (3.76 mmol, 1.38 g) in 15 mL of acetonitrile was added 7.52 mmol (1.25 g) of 1-phenyl-1-heptyne, and the solution was stirred at room temperature until it turned green. $NaBPh_4$ (3.75 mmol, 1.28 g) dissolved in 25 mL of methanol was then added, and the solution was stirred again for 0.5 h. Cooling at −25 °C overnight precipitated greenish blue crystals, which were filtered off, dried, and stored under argon (yield 92%). Anal. Calcd for $BC_{46}CoH_{63}P_3$: C, 70.96; H, 8.15; Co, 7.57; P, 11.93; B, 1.39. Found: C, 69.01; H, 8.08; Co, 7.14; P, 11.25; B, 1.31. IR: $\nu(C{\equiv}C)$ 1700 cm^{-1} (Nujol). NMR data, δ (CD_2Cl_2, 188 K): ^{31}P, 16 (s, br, PMe_3); ^{13}C, 19 ($P(CH_3)_3$, J_{CH} = 125 Hz, J_{CP} = 15 Hz), 13.5 (CH_3, J_{CH} = 124 Hz), 21.8, 27.9, 31.2, 32.3 (CH_2, J_{CH} = 130 Hz), 166, 174 ($C{\equiv}C$).

$[Co(MeC{\equiv}CMe)(PMe_3)_3]BPh_4$ (1b). This compound was prepared as for **1a**, but the reaction was done at −25 °C with excess $MeC{\equiv}CMe$ (10:1 $MeC{\equiv}CMe$:Co molar ratio). Greenish blue crystals were isolated from the solution kept at −25 °C overnight (yield 75%). Anal. Calcd for $BC_{37}CoH_{53}P_3$: C, 67.28; H, 8.09; Co, 8.92; P, 14.07; B, 1.64. Found: C, 66.18; H, 8.15; Co, 8.03; P, 13.69; B, 1.45. NMR data, δ (CD_2Cl_2, 188 K): ^{31}P, 20 (br, s, PMe_3); $^{13}C\{^1H\}$; 15.4 ($CH_3C{\equiv}CCH_3$), 19.5 ($P(CH_3)_3$), 169.3 ($CH_3C{\equiv}CCH_3$); ^1H, 1.64 (s, $P(CH_3)_3$, 27 H), 2.62 (alkyne CH_3, 6 H).

$[Co(PhC{\equiv}CMe)(PMe_3)_3]BPh_4$ (1c). Same preparation as for **1a**. Compound **1c** was obtained as a blue powder in 86% yield. Anal. Calcd for $BC_{42}CoH_{55}P_3$: C, 69.92; H, 7.67; Co, 8.16; P, 12.86; B, 1.50. Found: C, 69.80; H, 7.52; Co, 8.15; P, 12.37; B, 1.41. IR: $\nu(C{\equiv}C)$ 1700 cm^{-1}. NMR data, δ (CD_2Cl_2): ^{31}P (188 K), 20 (br, s, PMe_3); $^{13}C\{^1H\}$ (188 K), 15.8 ($CH_3C{\equiv}CC_6H_5$), 19.4 ($P(CH_3)_3$), 165.2, 173.1 ($CH_3C{\equiv}CC_6H_5$, respectively); $^1H\{^{31}P\}$ (223 K), 1.40 ($P(CH_3)_3$, 27 H), 2.63 ($CH_3C{\equiv}C$, 3 H).

$[Co(\sigma_{1,4}\text{-}1,2,3,4\text{-}(CO_2Me)_4C_4)(MeCN)_2(PMe_3)_2]BPh_4$ (2a). To 2.83 mmol (1.04 g) of $CoBr(PMe_3)_3$ dissolved in 10 mL of acetonitrile was added 5.7 mmol (0.69 mL) of dimethyl acetylenedicarboxylate. A brown yellow solution resulted, to which were added 2.83 mmol (0.97 g) of $NaBPh_4$ dissolved in methanol. The resulting solution was stirred at room temperature for 0.5 h. Cooling overnight at −25 °C precipitated a yellow powder, which was recrystallized in 1:1 acetonitrile/methanol. The yellow crystals were filtered off, dried, and kept under argon, yield 66%.

2a was also obtained in 86% yield by reacting dimethyl acetylenedicarboxylate (8.31 mmol, 1.18 g) with $[Co(PhC{\equiv}CPh)(MeCN)(PMe_3)_3]BPh_4$ (1.24 mmol, 1.02 g) in acetonitrile (20 mL). Anal. Calcd for $BC_{46}CoH_{56}O_8P_2N_2$: C, 61.62; H, 6.29; Co, 6.57; P, 6.91; B, 1.20. Found: C, 60.97; H, 6.29; Co, 6.15; P, 7.35; B, 1.06. NMR data, δ (CD_2Cl_2, 188 K): ^{31}P, 8 (s, PMe_3); $^{13}C\{^1H\}$ ($(CD_3)_2CO$, 188 K), 2.3 (CH_3CN), 11.2 ($P(CH_3)_3$), 51.3 (OCH_3), 128.6, 143.7 ($C{=}C{-}C{=}C$, respectively), 161.9, 172.9 (CO_2CH_3); $^1H\{^{31}P\}$ (CD_2Cl_2, 273 K), 1.28 (s, $P(CH_3)_3$, 18 H), 1.9 (s, CH_3CN, 6 H), 3.61 (s, OCH_3, 12 H).

$[Co\ (\sigma_{1,4}\text{-}2,3\text{-}(CO_2Me)_2C_4H_2)(MeCN)_2(PMe_3)_2]BPh_4$ (2b). To a solution of $CoBr(PMe_3)_3$ (3.5 mmol, 1.3 g) in 15 mL of acetonitrile cooled to −25 °C was added 10.5 mmol (0.95 mL) of methyl propiolate. The solution was stirred at this temperature for 2 h, and $NaBPh_4$ (3.5 mmol, 1.20 g) in methanol was added. Stirring was continued for 48 h. Yellow microcrystals of **2b** precipitated. They were filtered off, dried, and stored under argon; yields 61%. Anal. Calcd for $BC_{42}CoH_{52}O_4P_2N_2$: C, 64.62; H, 6.71; Co, 7.54;

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Table I. Crystal Data and Details of Data Collection and Structure Refinement

	1a	2a
formula	$C_{46}H_{63}BCoP_3$	$C_{46}H_{56}BCoN_2O_8P_2$
fw	778.67	896.66
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a, Å	11.880 (1)	41.344 (9)
b, Å	14.629 (1)	10.250 (4)
c, Å	25.836 (3)	25.377 (7)
β, deg	90.33 (9)	118.56 (2)
V, Å^3	4490	9446
Z	4	8
d_{calcd}, g/cm^3	1.151	1.261
radiatn	Mo K$\bar{\alpha}$	Cu K$\bar{\alpha}$
μ, cm^{-1}	5.1	40.4
λ, Å	0.71069	1.54178
T, °C	20	-100
2θ(max), deg	45	110
no. of reflctns measd	4376	5928
no. of unique data (m) with $I > 3\sigma(I)$	3897	3864
no. of parameters refined (n)	483	543
R^a	0.055	0.055
$R_w{}^b$	0.067	0.061
S^c	1.75	2.27

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. $^c S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

P, 7.93; B, 1.38. Found: C, 64.17; H, 6.83; Co, 6.97; P, 7.50; B, 1.33. NMR data, δ (CD_2Cl_2): ^{31}P (188 K), 12 (s, *P*Me$_3$); $^{13}C\{^1H\}$ (188 K), 3.0 (CH_3CN), 12.2 ($P(CH_3)_3$), 51.3 (OCH_3), 125.9 ($=CCO_2Me$), 146 ($=CH$, J_{CH} = 159 Hz), 172 (CO_2CH_3); $^1H\{^{31}P\}$ (273 K), 1.28 (s, $P(CH_3)_3$, 18 H), 1.5 (s, CH_3CN, 6 H), 3.64 (s, OCH_3, 6 H), 6.66 (t, $=CH$, J_{PH} = 5 Hz, 2 H).

Reaction of 2a with CO. Keeping a solution of **2a** (0.8 g, 0.85 mmol) in 1:1 acetonitrile/methanol (30 mL) under a CO atmosphere for 5 h resulted in the formation of a 1:1 mixture of $[Co(CO)_2(PMe_3)_3]BPh_4$ and $[Me_3PCH{=}C(CO_2Me)_2]BPh_4$. Workup of the residue after solvent evaporation yielded these two species in pure state. $[Co(CO)_2(PMe_3)_3]BPh_4$ was identified by comparison with a known sample.[22] $[Me_3PCH{=}C(CO_2Me)_2]BPh_4$ is a phosphonium salt: ^{31}P NMR ($(CD_3)_2CO$) 43 ppm (s); ^1H NMR ($(CD_3)_2CO$ 3.99, 4.05 ppm (s, CO_2CH_3), 5.94 (d, CH, J_{HP} = 21 Hz), 2.37 (d, $P(CH_3)_3$, J_{HP} = 14 Hz), 6.89, 7.05, 7.43 (m, $B(C_6H_5)_4$).

X-ray Diffraction Work. The crystallographic studies were carried out with an Enraf-Nonius CAD-4 diffractometer. The crystals were mounted in thin-walled glass capillaries and sealed under argon as a precaution against oxygen and moisture.

A set of 25 random reflections was collected by using the SEARCH procedure of the Enraf-Nonius CAD-4 software. After several recentering operations, the reduced cell was determined by the INDEX routine and its parameters were calculated by least-squares refinement on the setting angles of the 25 reflections. The Niggli parameters clearly indicated a primitive monoclinic cell for **1a**. The systematic absences ($h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$) subsequently determined by inspection of the complete data set unambiguously identified $P2_1/c$ as the space group. For **2a**, the Niggli parameters indicated a C-centered monoclinic lattice. The cell edges were transformed accordingly. Long-exposure oscillation photographs taken about the three new axes showed the expected line spacings, and a Laue mirror was observed for oscillation about b only, as expected. The systematic absences characteristic of space groups Cc and $C2/c$ (hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$) were subsequently identified from the full data set. The crystal data are summarized in Table I.

The intensity data (hkl and $hk\bar{l}$) were collected in the ω-2θ scan mode. A fixed slit of 4.0 mm was used, and the scan range (ω) was $(1.00 + 0.14 \tan\theta)°$ extended 25% on each side for background measurements. Scan speed was kept constant at 2° (ω) min^{-1}.

For **1a**, three standard reflections checked every hour fluctuated within ±1.2% during data collection. Crystal orientation was checked every 100 measurements, and no significant misorientation was detected. The data were corrected for polarization and the Lorentz effect. An empirical absorption correction based on Ψ scans for three top reflections was also applied.

The structure was solved by the heavy-atom method with SHELX86.[23] Refinement was carried out on $|F_o|$ with the SHELX76 package. The non-hydrogen atoms were refined isotropically, then anisotropically, and convergence (unit weights) was reached for $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.084$. The carbons in the pentyl chain had abnormally high thermal motion, and the ΔF map showed residuals of ~1.3 e/Å^3 in this region. Careful inspection of the map revealed that the four terminal carbons in the chain were disordered over two positions. These positions were arbitrarily assigned fixed occupancy factors of 0.5, and the eight half-carbons were isotropically refined. Constraints had to be applied during the refinement to maintain a reasonable geometry in these "half-chains". The hydrogens (except those attached to the disordered carbons) were fixed at idealized positions (U = 0.12 Å^2 for alkyl and 0.10 Å^2 for phenyl groups). At the end of the refinement, individual weights $1/\sigma^2(|F_o|)$ based on counting statistics were applied to each reflection. Anisotropic refinement of the non-hydrogen atoms (isotropic for the disordered pentyl carbons) converged to $R = 0.055$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.067$, and a goodness-of-fit ratio of 1.75. The final ΔF map showed a general background below ±0.25 e/Å^3, except for a few peaks in the range 0.30–0.45 e/Å^3 near the disordered carbon atoms.

A similar procedure was used to collect the data for **2a**, except that the reflections were scanned with option FLAT, a procedure to measure intensity at the Ψ position that minimizes adsorption. Seven standard reflections monitored every hour showed random fluctuations within ±2.7%. Only the reflections with $h + k = 2n$ were collected. The data were corrected for the Lorentz effect and polarization. An absorption correction based on crystal geometry was also applied (Gaussian integration, grid 10 × 10 × 10). The crystal had the following distances (mm) between the indicated pairs of faces: 100–$\bar{1}00$, 0.030; $\bar{1}01$–$10\bar{1}$, 0.107; 010–$0\bar{1}0$, 0.175. The transmission range was 0.41–0.79.

The structure was solved in the centric $C2/c$ space group by direct methods using the MULTAN80 package.[24] Isotropic refinement on $|F_o|$ (unit weights, full-matrix least squares) of all non-hydrogen atoms converged to $R = 0.090$. The phenyl hydrogens were fixed at idealized positions (C–H = 0.95 Å; U = 0.050 Å^2). The non-hydrogen atoms were refined anisotropically, and the block-diagonal approximation was used for the rest of the refinement. The subsequent ΔF map revealed the positions of the methyl hydrogens. These positions were used to calculate ideal coordinates (U = 0.063 Å^2). The parameters of the hydrogens were not refined, but their coordinates were recalculated after each least-squares cycle. In the latest stage of the refinement, individual weights $w = 1/\sigma^2(|F_o|)$ derived from counting statistics were applied. Convergence was reached for $R = 0.055$, $R_w = 0.061$, and a goodness-of-fit ratio of 2.27. The highest residuals on the final ΔF map were −0.74 and +0.40 e/Å^3.

The final atomic coordinates are given in Table II. The lists of structure factors, hydrogen coordinates, and anisotropic temperature factors are part of the supplementary material.

The scattering curves for the non-hydrogen atoms were taken from Cromer and Mann[25] and that of hydrogen was taken from Stewart, Davidson and Simpson.[26] The anomalous dispersion coefficients f' and f'' were included in the structure factor calculations for Co and P.[27]

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Table II. Refined Fractional Coordinates

atom	x	y	z	atom	x	y	z
$C_{46}H_{63}BCoP_3$ (**1a**) (×10^4; Co × 10^5)							
Co	25220 (6)	16150 (4)	38346 (3)	C21	1636 (9)	−1166 (8)	5141 (3)
P1	3859 (2)	1843 (1)	44280 (6)	C22	1576 (7)	−349 (5)	4849 (3)
P2	3346 (1)	1930 (1)	31221 (6)	C31	2479 (4)	5114 (3)	5602 (2)
P3	1594 (2)	2860 (1)	38499 (8)	C32	1471 (4)	5361 (3)	5361 (2)
C1	4616 (7)	2908 (6)	4496 (4)	C33	1413 (5)	5672 (4)	4853 (2)
C2	5008 (8)	1020 (6)	4387 (4)	C34	2384 (5)	5748 (4)	4567 (2)
C3	3452 (11)	1625 (7)	5084 (3)	C35	3376 (5)	5513 (4)	4789 (2)
C4	4325 (7)	2854 (6)	3038 (3)	C36	3436 (4)	5203 (4)	5293 (2)
C5	2492 (7)	2053 (6)	2557 (3)	C41	3676 (4)	4262 (3)	6354 (2)
C6	4208 (8)	930 (7)	2974 (3)	C42	3778 (5)	3334 (4)	6289 (3)
C7	357 (9)	2877 (8)	3456 (7)	C43	4743 (6)	2856 (5)	6392 (3)
C8	1111 (14)	3053 (9)	4482 (5)	C44	5676 (6)	3298 (5)	6568 (2)
C9	2147 (8)	3960 (5)	3678 (4)	C45	5618 (5)	4220 (5)	6644 (2)
C10	1498 (5)	737 (4)	3640 (2)	C46	4637 (5)	4683 (4)	6533 (2)
C11	2033 (5)	453 (4)	4046 (2)	C51	2522 (4)	5805 (4)	6550 (2)
C12	600 (7)	434 (5)	3269 (3)	C52	2566 (5)	5807 (4)	7094 (2)
C13A[a]	94 (10)	−476 (10)	3394 (5)	C53	2580 (6)	6606 (5)	7390 (3)
C14A[a]	−851 (12)	−799 (11)	3065 (7)	C54	2578 (6)	7438 (5)	7150 (3)
C15A[a]	−1907 (11)	−195 (14)	3113 (8)	C55	2556 (5)	7484 (4)	6622 (3)
C16A[a]	−2581 (18)	−487 (23)	3593 (10)	C56	2525 (5)	6667 (4)	6333 (2)
C13B[a]	−297 (15)	−85 (14)	3538 (7)	C61	1371 (4)	4237 (4)	6343 (2)
C14B[a]	−1209 (16)	−453 (23)	3146 (10)	C62	1103 (5)	3482 (4)	6032 (2)
C15B[a]	−2264 (17)	−708 (28)	3458 (9)	C63	161 (6)	2943 (5)	6117 (3)
C16B[a]	−3323 (16)	−552 (19)	3122 (11)	C64	−568 (6)	3138 (5)	6513 (3)
C17	2109 (5)	−331 (4)	4390 (2)	C65	−344 (5)	3870 (6)	6816 (3)
C18	2743 (6)	−1095 (4)	4248 (3)	C66	595 (5)	4415 (4)	6740 (2)
C19	2812 (8)	−1863 (5)	4527 (4)	B	2514 (5)	4853 (4)	6217 (2)
C20	2248 (10)	−1908 (5)	4970 (4)				
$C_{46}H_{56}BCoN_2O_8P_2$ (**2a**) (×10^4; Co, P × 10^5)							
Co	38874 (3)	357 (10)	−233 (4)	C18	4280 (2)	1605 (7)	−768 (3)
P1	43258 (4)	13422 (17)	−315 (7)	C19	4800 (2)	875 (7)	418 (3)
P2	35077 (4)	−14102 (16)	703 (7)	C20	3644 (2)	−3107 (6)	201 (3)
O1	3982 (1)	−1276 (4)	−1350 (2)	C21	3421 (2)	−995 (6)	690 (3)
O2	3530 (1)	−2120 (4)	−1206 (2)	C22	3048 (2)	−1504 (6)	−557 (3)
O3	4859 (1)	−3203 (4)	157 (2)	C31	2959 (2)	4751 (6)	6365 (2)
O4	4309 (1)	−3705 (4)	−617 (2)	C32	2786 (2)	5924 (6)	6364 (3)
O5	5034 (1)	−1737 (5)	1547 (2)	C33	2538 (2)	6552 (6)	5825 (3)
O6	4725 (1)	−3590 (4)	1176 (2)	C34	2466 (2)	6023 (7)	5282 (3)
O7	4479 (1)	1093 (5)	1437 (2)	C35	2634 (2)	4896 (7)	5268 (3)
O8	4342 (1)	−860 (5)	1679 (2)	C36	2876 (2)	4284 (6)	5794 (3)
N1	3520 (1)	645 (4)	−808 (2)	C41	3251 (2)	2437 (6)	6921 (2)
N2	3725 (1)	1372 (5)	343 (2)	C42	2927 (2)	1755 (6)	6554 (2)
C1	4044 (1)	−1348 (6)	−360 (2)	C43	2909 (2)	394 (6)	6523 (3)
C2	4328 (1)	−2067 (6)	41 (2)	C44	3215 (2)	−319 (6)	6865 (3)
C3	4458 (2)	−1673 (6)	661 (2)	C45	3536 (2)	285 (6)	7240 (3)
C4	4274 (2)	−646 (6)	718 (2)	C46	3556 (2)	1661 (6)	7267 (3)
C5	3860 (2)	−1575 (6)	−1023 (3)	C51	3203 (2)	4311 (5)	7564 (3)
C6	3299 (2)	−2277 (6)	−1838 (3)	C52	2850 (2)	4416 (6)	7510 (2)
C7	4531 (1)	−3054 (6)	−115 (2)	C53	2791 (2)	4566 (6)	8003 (3)
C8	4498 (2)	−4458 (7)	−873 (3)	C54	3089 (2)	4602 (6)	8572 (3)
C9	4769 (2)	−2292 (7)	1173 (3)	C55	3440 (2)	4475 (6)	8643 (3)
C10	5026 (2)	−4294 (8)	1661 (3)	C56	3491 (2)	4326 (6)	8145 (3)
C11	4379 (2)	−23 (7)	1310 (2)	C61	3664 (1)	4651 (6)	7083 (2)
C12	4445 (2)	−334 (9)	2274 (3)	C62	3871 (2)	4074 (6)	6839 (3)
C13	3311 (2)	948 (5)	−1282 (3)	C63	4180 (2)	4671 (7)	6874 (3)
C14	3044 (2)	1274 (6)	−1892 (3)	C64	4298 (2)	5865 (7)	7142 (3)
C15	3622 (2)	2137 (6)	543 (3)	C65	4102 (2)	6452 (6)	7388 (3)
C16	3481 (2)	3108 (7)	814 (3)	C66	3794 (2)	5858 (6)	7356 (3)
C17	4327 (2)	2975 (7)	241 (3)	B	3266 (2)	4038 (7)	6981 (3)

[a] Half-occupancy.

Results and Discussion

[Co(RC≡CR′)(PMe$_3$)$_3$]BPh$_4$ (1a, R = Ph, R′ = C$_5$H$_{11}$; 1b, R = R′ = Me; 1c, R = Ph, R′ = Me). These complexes were prepared by the method previously described for the PhC≡CPh complex.[19] In a first step, reacting RC≡CR′ with CoBr(PMe$_3$)$_3$ gave the five-coordinate molecule CoBr(RC≡CR′)(PMe$_3$)$_3$ (reaction 1). This species was not stable enough to be isolated, but its formation, suggested by the darkening and color change from green to blue green in the solution, was confirmed by the characteristic A$_2$B spin system of the Co(PMe$_3$)$_3$ moiety in ^{31}P NMR.[19] Adding NaBPh$_4$, dissolved in methanol, gave good yields of 1a–c, which precipitated on cooling overnight at −25 °C.

$$\mathrm{CoBr(PMe_3)_3 + RC{\equiv}CR' \rightarrow CoBr(RC{\equiv}CR')(PMe_3)_3} \qquad (1)$$

$$\mathrm{CoBr(RC{\equiv}CR')(PMe_3)_3 + NaBPh_4 \rightarrow [Co(RC{\equiv}CR')(PMe_3)_3]BPh_4 + NaBr} \qquad (2)$$

1a: R = Ph, R′ = C$_5$H$_{11}$
1b: R = Me, R′ = Me
1c: R = Ph, R′ = Me

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Table III. Infrared C≡C Stretching Data for Some d^8 Metal-Alkyne Complexes

compound	ν(C≡C), cm^{-1}	ref
$Co(C_2Ph_2)Cp(CO)$	1818	15
$[Co(C_2Ph_2)(P(OMe)_3)_3]PF_6$	*a*	18
$[Rh(C_2(CO_2Me)_2)(P(OMe)_3)_4]$	1805	29
$Rh(C_2Ph_2)Cl(PCy_3)_2$	1860	30
$Rh(C_2Et_2)Cl(PCy_3)_2$	1943	30
$Rh(C_2PhCl)Cl(PPh_3)_2$	1883	31
$[Ir(C_2Ph_2)(CO)(PMe_2Ph)_2]BPh_4$	1818	32
$Ir(C_2(CO_2Me)_2)Cl(CO)(PPh_3)_2$	1770	33, 34
$[Ir(C_2(CO_2Me)_2)py(CO)(PPh_3)_2]BPh_4$	1785	33
$[Pt(C_2Ph_2)Cl_3]^-$	*a*	11, 12
$Pt(cycloheptyne)(PPh_3)_2$	1770	35
$Pt(cyclohexyne)(PPh_3)_2$	1721	35
$Pt(C_2Ph_2)(PPh_3)_2$	1740, 1768	36
$[Co(C_2Ph_2)(MeCN)(PMe_3)_3]BPh_4$	1785	19
$[Co(C_2Ph_2)(PMe_3)_3]BPh_4$	*a*	19
$[Co(C_2MePh)(PMe_3)_3]BPh_4$	1700	this work
$[Co(C_2PhC_5H_{11})(PMe_3)_3]BPh_4$	1700	this work
$[Co(C_2Me_2)(PMe_3)_3]BPh_4$	*a*	this work

[a] Not detected in the infrared spectrum.

With MeC≡CMe (bp 27 °C), excess alkyne (10:1 alkyne/Co molar ratio) was needed, and the reaction had to be carried out at −25 °C. Lower yields of **1** were observed when $NaBPh_4$ was added to $CoBr(PMe_3)_3$ before the alkyne because $[Co(PMe_3)_4]BPh_4$ and $Co(PMe_3)_2BPh_4$[28] side products resulting from reaction 3 precipitated immediately. Compounds **1a**, **1b**, and **1c** are blue or greenish blue. They can be handled in air for a short time. Although **1a** is dissociatively stable, solutions of **1b** and **1c** must be kept at 0 °C to avoid decomposition according to reaction 4. The kinetic stability of these alkyne adducts follows the steric bulk of the substituents and decreases in the order **1a** > **1c** > **1b**.

$$2CoBr(PMe_3)_3 + 2NaBPh_4 \rightarrow [Co(PMe_3)_4]BPh_4 + Co(PMe_3)_2BPh_4 + 2NaBr \quad (3)$$

$$2[Co(RC{\equiv}CR')(PMe_3)_3]BPh_4 \rightarrow Co(PMe_3)_2BPh_4 + [Co(PMe_3)_4]BPh_4 + 2RC{\equiv}CR' \quad (4)$$

Reaction with CO or phosphine resulted in complete substitution of the alkyne. Surprisingly, acetonitrile did not react with **1a**, **1b**, or **1c**, in spite of the remarkable stability of $[Co(PhC{\equiv}CPh)(MeCN)(PMe_3)_3]BPh_4$.[19]

The solid-state infrared spectra of **1a** and **1c** show a medium absorption band at 1700 cm^{-1}, assigned to the C≡C stretch of coordinated $PhC{\equiv}CC_5H_{11}$ and $PhC{\equiv}CMe$, respectively. Table III lists ν(C≡C) frequencies for various monomeric metal–alkyne complexes. The values for our cobalt compounds fall at the lower limit, a result that could be related to greater loss of triple-bond character of the C≡C bond as a result of the alkyne being a 4e donor.

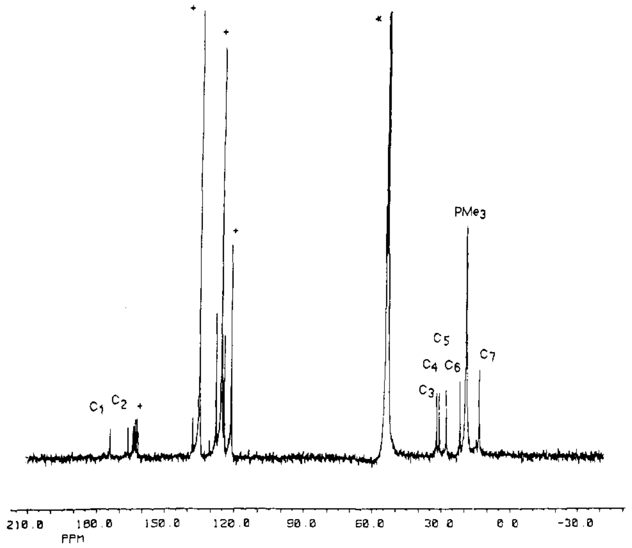

Figure 1. ^{13}C NMR spectrum of **1a** in CD_2Cl_2 at 183 K (+, BPh_4^-; *, PMe_3; S, solvent).

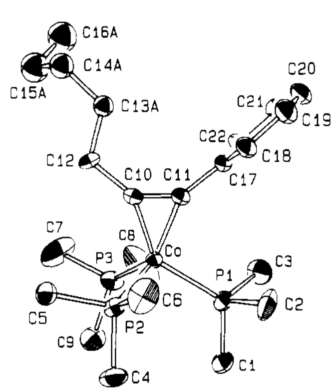

Figure 2. Perspective view and numbering scheme for the complex cation in $[Co(PhC{\equiv}CC_5H_{11})(PMe_3)_3]BPh_4$ (**1a**). Ellipsoids correspond to 50% probability. Atoms C13A to C16A have 50% occupancy. The alternate positions C13B to C16B for the disordered pentyl chain and the hydrogens are omitted for simplicity.

Table IV. ^{13}C NMR Resonances of the C≡C Groups (δ, ppm; 188 K; CD_2Cl_2)

compound	δ	no. of electrons donated
C_2Ph_2	90.7	
$[Co(C_2Ph_2)(PMe_3)_3]BPh_4$	168	4e
$[Co(C_2Ph_2)(MeCN)(PMe_3)_3]BPh_4$	132, 133	2e
C_2MePh	79, 86	
$[Co(C_2MePh)(PMe_3)_3]BPh_4$	165, 173	4e
$C_2PhC_5H_{11}$	81, 90	
$[Co(C_2PhC_5H_{11})(PMe_3)_3]BPh_4$	166, 174	4e
C_2Me_2	74	
$[Co(C_2Me_2)(PMe_3)_3]BPh_4$	169	4e

The ^{13}C NMR spectra exhibit the chemical shifts expected for the BPh_4^- anion, PMe_3 ligand, and alkyne substituents (Figure 1). The two alkyne carbons appear as weak signals, shifted downfield compared to the free ligand (Table IV). As already pointed out for Mo and W complexes,[4,7] the downfield displacement can be roughly correlated with the extent of π donation from the alkyne. Consequently, ^{13}C values of ca. 170 are indicative of the alkynes acting as 4e donor ligands in **1a**, **1b**, and **1c**. The presence of broad singlets in the $^{31}P\{^1H\}$ NMR spectra at 183 K indicates that the complexes are still stereochemically nonrigid at this temperature.

Crystal Structure of 1a. The unit cell contains the BPh_4^- anion and the complex cation shown in Figure 2 with the atom numbering scheme. Selected interatomic

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Table V. Interatomic Distances and Angles in $[Co(PhC{\equiv}CC_5H_{11})(PMe_3)_3]^{+}$[a]

	Distances (Å)		
Co–P1	2.168 (2)	Co–C10	1.820 (6)
Co–P2	2.183 (2)	Co–C11	1.887 (5)
Co–P3	2.131 (2)	Co–C_x[b]	1.742
P1–C1	1.802 (9)	P2–C4	1.804 (9)
P1–C2	1.827 (9)	P2–C5	1.737 (7)
P1–C3	1.818 (9)	P2–C6	1.839 (10)
P3–C7	1.739 (13)	P3–C8	1.794 (13)
P3–C9	1.803 (8)	C10–C11	1.264 (8)
C10–C12	1.461 (10)	C11–C17	1.450 (8)
C17–C18	1.407 (9)	C20–C21	1.398 (15)
C17–C22	1.377 (10)	C21–C22	1.414 (13)
C18–C19	1.335 (10)	C19–C20	1.355 (15)
C12–C13A[c]	1.50 (2)	C12–C13B	1.51 (2)
C13A–C14A	1.45 (2)	C13B–C14B	1.54 (3)
C14A–C15A	1.55 (2)	C14B–C15B	1.57 (3)
C15A–C16A	1.57 (3)	C15B–C16B	1.50 (3)
	Angles (deg)		
P1–Co–P2	102.6 (1)	Co–P1–C1	122.8 (3)
P1–Co–P3	102.4 (1)	Co–P1–C2	112.1 (3)
P1–Co–C10	138.9 (2)	Co–P1–C3	114.1 (4)
P1–Co–C11	99.1 (2)	C1–P1–C2	101.8 (4)
P1–Co–C_x[b]	118.7	C1–P1–C3	102.7 (5)
P2–Co–C10	104.0 (2)	C2–P1–C3	100.3 (5)
P2–Co–P3	95.3 (1)	Co–P2–C4	125.7 (3)
P2–Co–C11	126.5 (2)	Co–P2–C5	117.5 (3)
P2–Co–C_x	116.6	Co–P2–C6	106.9 (3)
P3–Co–C10	105.7 (2)	C4–P2–C5	99.8 (4)
P3–Co–C11	126.6 (2)	C4–P2–C6	101.5 (4)
P3–Co–C_x	117.7	C5–P2–C6	102.3 (4)
C10–Co–C11	39.8 (3)	Co–P3–C7	114.9 (4)
Co–C10–C12	147.8 (5)	Co–P3–C8	110.5 (4)
Co–C11–C10	67.2 (4)	Co–P3–C9	124.2 (3)
Co–C10–C11	73.0 (4)	C7–P3–C8	102.3 (7)
Co–C11–C17	151.7 (4)	C7–P3–C9	98.7 (5)
C11–C10–C12	139.2 (6)	C8–P3–C9	103.3 (6)
C10–C11–C17	141.1 (6)	C17–C18–C19	123.0 (7)
C11–C17–C18	119.0 (5)	C18–C19–C20	118.6 (8)
C11–C17–C22	121.8 (6)	C19–C20–C21	121.4 (8)
C18–C17–C22	119.2 (6)	C20–C21–C22	119.9 (9)
C13A–C12–C10[c]	114.5 (7)	C17–C22–C21	117.7 (7)
C14A–C13A–C12	118.0 (11)	C13B–C12–C10[c]	111.0 (9)
C15A–C14A–C13A	111.8 (13)	C14B–C13B–C12	111.2 (15)
C16A–C15A–C14A	111.2 (17)	C15B–C14B–C13B	107.2 (19)
		C14B–C15B–C16B	109.4 (20)

[a] Distances and angles in the BPh_4^- ion given in supplementary material. [b] C_x = middle of the C10–C11 bond. [c] Labels A and B for atoms C13 to C16 correspond to the two disordered alkyl chains.

distances and angles are listed in Table V.

As expected, the alkyne is side-on coordinated, with Co–C distances (1.820, 1.887 Å) similar to those found in the corresponding Ph_2C_2 complex.[19] The differences between the Co–P distances (2.168 Å, P1; 2.183 Å, P2; 2.131 Å, P3; σ = 0.002 Å) are significant, but small. There is no unique way of describing the environment of Co that could account for the observed angles. A square pyramid could be defined from the three Co–P and two Co–C vectors, with either P2 or P3 occupying the apical site, but the distortion would be very large. On the other hand, considering the middle of the "triple" bond as being the point of attachment to cobalt, the coordination could be envisioned as an approximate tetrahedron, with angles varying from 95.3 to 118.7°. The weakness of this description arises form the tetrahedral Co(I) complexes with standard ligands being normally paramagnetic, which is not the case here. Since the C10≡C11 bond is parallel to the plane of the three P atoms,[37] our preference goes to the three-legged "piano stool", which is particularly well suited to support our subsequent discussion of the complex in terms of alkyne coupling with a ML_3 fragment.

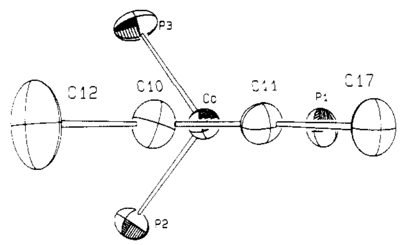

Figure 3. Simplified view of the coordination sphere of **1a**, showing the coplanarity of the Co–P1 bond with the C12–C10–C11–C17 fragment of the alkyne.

The C10–C11 distance (1.264 (8) Å), almost equal to that found in the Ph_2C_2 complex, is only 0.06 Å greater than for a free triple bond and lies at the lower limit of the C–C distances (1.26–1.35 Å) reported for unidentate alkyne complexes.[19] The coordinated alkyne is bent into a cis geometry as usual. This deformation occurs in the plane of the cobalt–alkyne metallacycle, the Co–C10–C11–C12–C17 atoms being coplanar.[37] The PhC≡C and $H_{11}C_5C{\equiv}C$ angles of 141.1 (6)° and 139.2 (6)°, respectively, are among the smallest reported.

A peculiar feature of the present structure is the coplanarity of P1, Co, C10, and C11 (Figure 3).[37] P2 and P3 are symmetrically displaced on opposite sides of this plane. Interestingly, the alkyne in the $[Co(C_2Ph_2)(PMe_3)_3]^+$ cation was not oriented parallel to any of the Co–P bonds but was perpendicular to one of these bonds. These orientations can be rationalized by considering an interaction of the alkyne frontier orbitals with a $Co(PMe_3)_3$ fragment behaving like the $M(CO)_3$ fragment described by Elian and Hoffmann.[38] This approach has been used by Tatsumi, Hoffmann, and Templeton[39] to discuss alkyne complexes with d^6 Mo units.

The three frontier energy levels and orbital shapes proposed by Elian and Hoffmann[38] for $M(CO)_3$ are shown in Figure 4 together with those of a "bent" alkyne. Three low-lying metal orbitals (not drawn in Figure 4) contain six of the eight Co(I) electrons. Two metal electrons remain in the higher levels. Interactions can take place between three alkyne orbitals and the three higher metal orbitals of Figure 4. Orbital a_1 has cylindrical symmetry about the z axis, and the overlap with the alkyne $\pi_{\parallel}$ orbital is independent of alkyne or CoP_3 rotation about z. However, for the $\pi_{\perp}$ and $\pi_{\parallel}{}^*$ orbitals to overlap with the e metal orbitals, the CoP_3 fragment should adopt one of the two orientations depicted in Figure 4. In structure I, donation of the "second" alkyne electron pair takes place with the $e_{\perp}$ orbital perpendicular to the Co–P1 bond. Simultaneously, the two remaining metal electrons are paired in the $e_{\parallel}$ orbital and participate in back-bonding into the alkyne $\pi_{\parallel}{}^*$ orbital. In structure II, the $e_{\perp}$ orbital, perpendicular to Co–P1, is used for back-bonding to $\pi_{\parallel}{}^*$, whereas the donation of the "second" alkyne electron pair takes place from $\pi_{\perp}$ to the $e_{\parallel}$ orbital.

This model accounts for the fact that structure I is observed in the present $PhC{\equiv}CC_5H_{11}$ and structure II was found for the PhC≡CPh complex[19] and that both complexes are diamagnetic. Obviously, the orbital overlap between the CoP_3 fragments and the alkyne does not differ much in the two geometries, which is also consistent with the low rotation barrier observed by NMR.[40]

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[37] Distances to the P1–P2–P3 plane: C10, −2.698; C11, −2.794 Å. Distances to the P1–Co–C10–C11 plane: P1, 0.001; Co, 0.000; C10, 0.022; C11, −0.013; C12, 0.071; C17, −0.010; P2, 1.622; P3, −1.567 Å.

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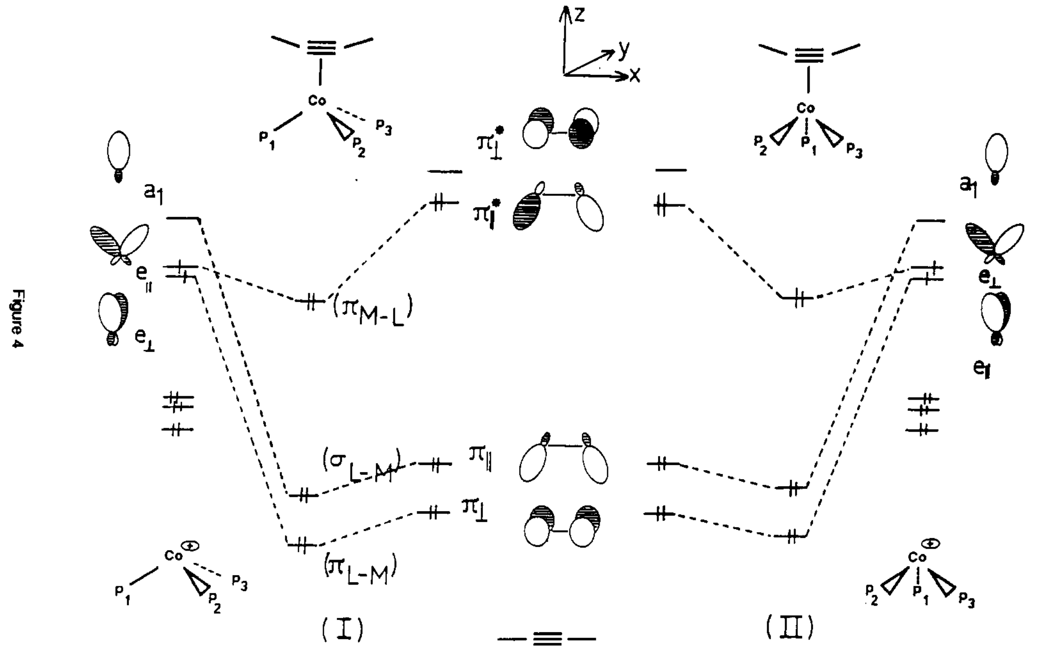

Figure 4. Qualitative diagram of the interaction of the alkyne π and π* orbitals with the highest orbitals of the CoP_3^+ fragment.

Another interesting feature of these structures is the orientation of the phenyl substituent, which may give some indication about contributions to π* acidity and/or π basicity of the alkyne. The phenyl ring makes an angle of 97° with the C17–C11–C10 plane, that is, the two planes are nearly orthogonal. One of the phenyl rings in the diphenylacetylene compound[19] was similarly oriented. In this orientation, the phenyl π system is symmetry suited to overlap with the $\pi_\parallel$* orbital of the alkyne. The electron-acceptor phenyl ring probably improves Co-to-$\pi_\parallel$* back-donation. In contrast, near coplanarity of the phenyl ring with the metallacycle, more frequently observed,[19,36,41] favors overlapping of the phenyl π system with the $\pi_\perp$ alkyne orbital. This effect may indirectly improve alkyne basicity by accepting electron density from the filled $\pi_\perp$ alkyne orbital, thereby decreasing the destabilization due to four-electron, two-orbital repulsions when the alkyne acts as a two-electron donor to a coordinatively saturated metal center.

[$\overline{\text{CoRC=CR'CR'=C}}$R(MeCN)$_2$(PMe$_3$)$_2$]BPh$_4$. The reaction of DMAC and MP with $CoBr(PMe_3)_3$ in presence of $NaBPh_4$ has been examined in acetone, acetonitrile, methanol, and tetrahydrofuran (reaction 5). Color changes have been observed in all cases, but crystalline compounds (**2a** and **2b**) could be isolated only from acetonitrile. An alternate preparation method was alkyne substitution of diphenylacetylene in [Co(PhC≡CPh)(MeCN)(PMe$_3$)$_3$]BPh$_4$ (reaction 6). The mixtures were stirred at room temperature for 0.5 h and cooled to isolate the products.

$$\begin{aligned}&\mathrm{CoBr(PMe_3)_3 + 2RC{\equiv}CR' + NaBPh_4} \rightarrow\\ &\quad [\overline{\mathrm{CoRC{=}CR'CR'{=}C}}\mathrm{R(MeCN)_2(PMe_3)_2]BPh_4} +\\ &\quad \mathbf{2a}\text{: } \mathrm{R = R' = CO_2Me}\\ &\quad \mathbf{2b}\text{: } \mathrm{R' = CO_2Me;\ R = H}\\ &\qquad\qquad \mathrm{PMe_3 + NaBr} \quad (5)\end{aligned}$$

$$\begin{aligned}&\mathrm{[Co(PhC{\equiv}CPh)(MeCN)(PMe_3)_3]BPh_4 + 2RC{\equiv}CR'} +\\ &\quad \mathrm{MeCN} \rightarrow\\ &\quad [\overline{\mathrm{CoCR{=}CR'CR'{=}C}}\mathrm{R(MeCN)_2(PMe_3)_2]BPh_4} +\\ &\qquad\qquad \mathrm{PhC{\equiv}CPh + PMe_3} \quad (6)\end{aligned}$$

2a and **2b** crystallize as yellow, air-stable crystals, soluble in polar solvents without appreciable decomposition. No crystalline complexes could be isolated when BF_4^- or PF_6^- were used as counterions.

The solid-state infrared spectra show two medium absorptions at 1708 and 1216 cm^{-1} due to the alkyne ester substituents. Presence of two cis MeCN ligands is deduced from the two ν(CN) vibrations at 2316 and 2286 cm^{-1}, slightly shifted upward from free acetonitrile (2250 cm^{-1}). Singlets at 3.61, 1.90, and 1.28 ppm in the ^{1}H NMR of **2a** were assigned to the CO_2Me groups, acetonitrile, and trimethylphosphine, respectively. The corresponding values are 3.64, 1.50, and 1.28 ppm, respectively, in **2b**. The triplet at 6.66 ppm ($^3J_{HP}$ = 5 Hz) in **2b**, although in the range for terminal acetylenic protons in alkyne π complexes, is also consistent with two equivalent vinyl protons, coupled with the two cis P nuclei, in a cobaltacyclopentadiene ring resulting from oxidative coupling of two alkynes. This signal becomes a singlet by ^{31}P decoupling. Such a low-field shift is expected for protons of vinyl groups σ-bonded to a metal: lower field values of 6.9 and 8.38 ppm were obtained for [CpMo(CH=CH^{t}Bu)(P(OMe)$_3$)$_3$]BF$_4$[42] and [CpCl$_3$W=C(CMe$_3$)(HC=CH^{t}Bu)],[43] respectively, where more electrophilic metal centers are present. Equivalence of the two vinyl hydrogens in **2b** indicates the presence of only one isomer in which the two secondary carbons are σ-bonded to cobalt. These two carbon atoms appear as a singlet at 143.7 ppm for **2a** and a doublet at 146 ppm for **2b** (J_{CH} = 159 Hz) in the ^{13}C NMR spectra. No coupling with phosphorus is observed. The two other ring carbons are found at 128.6 ppm (**2a**) and 125.9 ppm (**2b**). ^{13}C{^{1}H} singlets were assigned to the alkyne methoxy carbons, the trimethylphosphine, and the acetonitrile methyl carbons at 51.3, 11.2, and 2.3 ppm in **2a** and 51.3, 12.2, and 3.0 ppm in **2b**, respectively. The ^{31}P nuclei appear as broad singlets at 8 and 12 ppm in the 188 K spectrum of **2a** and **2b**, respectively.

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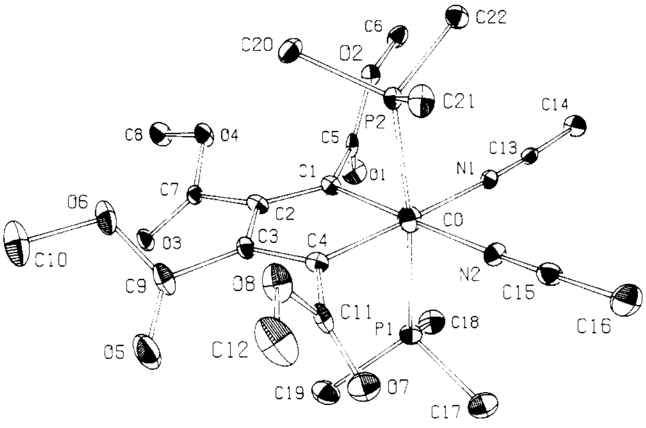

Figure 5. Perspective view and numbering scheme for the complex cation in $[Co(C_{12}H_{12}O_8)(MeCN)_2(PMe_3)_2]BPh_4$ (**2a**). Ellipsoids correspond to 50% probability. Hydrogens are omitted for simplicity.

Crystal Structure of 2a. The presence of a cobaltacyclopentadiene ring deduced from the spectral data was confirmed by the solid-state structure. Beside the BPh_4^- anion, the unit cell contains the complex cation shown in Figure 5, where the atomic numbering scheme is defined. Selected distances and angles are listed in Table VI.

The octahedral environment of the Co(III) atom is completed by two cis acetonitrile molecules coplanar with the $\overline{\text{Co–C1–C2–C3–C4}}$ ring and by two PMe_3 ligands above and below this plane. Except for the small C1–Co–C4 angle of 82.4 (3)° imposed by the ring, deviations from the ideal 90° or 180° values are relatively small. The only other distortion worth being mentioned is a slight displacement of the trans phosphines in the direction of the ring (P1–Co–P2 = 173.0 (1)°). The Co–P bond lengths (P1, 2.262 (2); P2, 2.253 (2) Å) are similar to those reported for *mer*-$CoMe_2(N_3)(PMe_3)_3$ (average 2.240 Å)[44] and $Co(NCS)_3(PMe_3)_3$ (average 2.275 Å).[45]

The two acetonitriles are end-on coordinated as usual (Co–N1–C13 = 176.1(5)°; Co–N2–C15 = 178.2 (5)°), with normal Co–N distances (average 1.944 Å). The C–C and C–N distances are similar to those observed in free[46] and coordinated[47] acetonitrile.

Table VI. Bond Distances and Angles in $[Co(\sigma\text{-}1,4\text{-}C_4(CO_2Me)_4)(MeCN)_2(PMe_3)_2]^{+\,a}$

	Distances (Å)		
Co–P1	2.262 (2)	C3–C4	1.346 (9)
Co–P2	2.253 (2)	C1–C5	1.497 (8)
Co–N1	1.942 (5)	C5–O1	1.199 (8)
Co–N2	1.946 (5)	C5–O2	1.335 (8)
Co–C1	1.921 (6)	O2–C6	1.430 (7)
Co–C4	1.925 (6)	C2–C7	1.484 (9)
P1–C17	1.810 (7)	C7–O3	1.202 (8)
P1–C18	1.806 (7)	C7–O4	1.339 (7)
P1–C19	1.799 (8)	O4–C8	1.454 (9)
P2–C20	1.809 (7)	C3–C9	1.465 (9)
P2–C21	1.823 (7)	C9–O5	1.196 (9)
P2–C22	1.806 (7)	C9–O6	1.343 (8)
N1–C13	1.139 (7)	O6–C10	1.456 (9)
C13–C14	1.447 (8)	C4–C11	1.493 (8)
N2–C15	1.123 (8)	C11–O7	1.207 (8)
C15–C16	1.479 (11)	C11–O8	1.332 (8)
C1–C2	1.347 (8)	O8–C12	1.462 (8)
C2–C3	1.456 (8)		
	Angles (deg)		
P1–Co–P2	173.0 (1)	Co–N2–C15	178.2 (5)
P1–Co–N1	92.2 (2)	N2–C15–C16	178.0 (7)
P1–Co–N2	92.8 (2)	Co–C1–C2	115.2 (5)
P1–Co–C1	89.5 (2)	C1–C2–C3	113.8 (5)
P1–Co–C4	85.9 (2)	C2–C3–C4	113.4 (6)
P2–Co–N1	94.4 (2)	Co–C4–C3	115.3 (5)
P2–Co–N2	89.8 (2)	Co–C1–C5	121.1 (4)
P2–Co–C1	87.8 (2)	C2–C1–C5	123.7 (6)
P2–Co–C4	87.3 (2)	Cl–C2–C7	124.8 (6)
N1–Co–N2	89.1 (2)	C3–C2–C7	120.9 (5)
N1–Co–C1	92.6 (2)	C2–C3–C9	123.5 (6)
N1–Co–C4	174.7 (2)	C4–C3–C9	123.0 (6)
N2–Co–C1	177.1 (2)	C3–C4–C11	122.3 (6)
N2–Co–C4	95.9 (2)	Co–C4–C11	122.3 (4)
C1–Co–C4	82.4 (3)	C1–C5–O1	125.6 (6)
Co–P1–C17	113.6 (3)	O1–C5–O2	124.4 (6)
Co–P1–C18	114.2 (3)	C1–C5–O2	110.0 (5)
Co–P1–C19	118.2 (3)	C5–O2–C6	117.4 (5)
C17–P1–C18	103.7 (4)	C2–C7–O3	124.1 (6)
C17–P1–C19	101.6 (4)	O4–C7–O3	123.7 (6)
C18–P1–C19	103.8 (4)	C2–C7–O4	112.1 (5)
Co–P2–C20	118.7 (2)	C7–O4–C8	114.8 (5)
Co–P2–C21	111.8 (2)	C3–C9–O5	125.5 (6)
Co–P2–C22	115.8 (2)	O5–C9–O6	122.8 (6)
C20–P2–C21	103.8 (3)	C3–C9–O6	111.7 (6)
C20–P2–C22	102.4 (3)	C9–O6–C10	115.6 (6)
C21–P2–C22	102.4 (3)	C4–C11–O7	124.9 (6)
Co–N1–C13	176.1 (5)	O8–C11–O7	124.3 (6)
N1–C13–C14	177.5 (7)	C4–C11–O8	110.9 (5)
		C11–O8–C12	114.5 (5)

[a] Distances and angles in the BPh_4^- ion given in the supplementary material.

The cobaltacycle can be viewed as a metallacyclopentadiene with double bonds between C1–C2 and C3–C4, and the cobalt σ-bonded to the ring C1 and C4 atoms. The C1–C2 and C3–C4 distances (1.347 (8) and 1.346 (9) Å) are indicative of double bonds, whereas C2–C3 (1.456 (8) Å) corresponds to a single C–C bond. A similar alternance of bond lengths has been found in compounds containing a similar ring with Pd[48] and Ru.[49] These distances are comparable to the values of 1.32 Å (average) and 1.44 (4) Å obtained for cyclopentadiene.[50] The C1–C4 ring is planar,[51] and the deviation of Co from this plane (0.016 (1) Å) is significant, but small. There are large deviations from the plane for the bonds to the methoxycarbonyl substituents, especially C7 (0.192 (6) Å). These deviations as well as the orientation of the CO_2 units with respect to the ring are probably controlled to a large extent by packing. The dihedral angles between the CO_2 plane and the five-membered ring are as follows: C5, 75°; C7, 38°; C9, 54°; C11, 62°. Corresponding bond lengths and angles in the CO_2Me groups also exhibit significant deviations. These are similar to those reported for ruthenium complexes[49] and for many ionic complexes of $C_5(CO_2Me)_5$.[52] The $C(sp^2){=}O$ and $C(sp^2){-}O$ distances are equal to their

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(51) Distances (Å) to the C1–C2–C3–C4 plane: C1, –0.003 (7); C2, 0.005 (6); C3, –0.005 (7); C4, 0.003 (7); Co, 0.016 (1); C5, –0.011 (7); C7, 0.192 (6), C9, 0.032 (7); C11, 0.091 (7).

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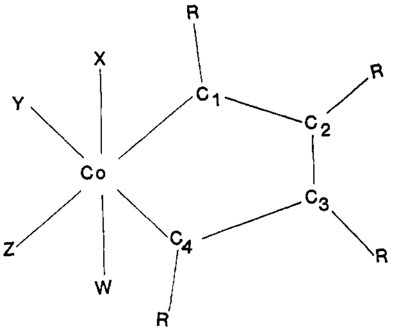
Table VII. Comparison of the Geometry of Cobaltacylcopentadiene Complexes[a]

	A	B	C	D	this work
R[b]	H	H	CF_3	C_6F_5	CO_2Me
W	PPh_3	PPh_3	[c]	PPh_3	PMe_3
X					PMe_3
Y	C_5H_5	$C_5H_4CO_2Me$	C_5H_5	C_5H_5	NCMe
Z					NCMe
Co–C1	1.943 (6)	1.928 (6)	1.933 (8)	1.995 (11)	1.921 (6)
Co–C4	1.947 (6)	1.933 (7)	1.929 (6)	1.993 (11)	1.925 (6)
C1–C2	1.338 (9)	1.333 (10)	1.374 (8)	1.326 (15)	1.347 (8)
C3–C4	1.351 (10)	1.341 (9)	1.374 (12)	1.335 (15)	1.346 (9)
C2–C3	1.447 (10)	1.442 (10)	1.472 (12)	1.467 (16)	1.456 (8)
C1–Co–C4	83.2 (3)	82.6 (3)	83.3 (3)	82.4 (4)	82.4 (3)
Co–C1–C2	113.7 (5)	114.0 (5)	114.5 (6)	112.1 (8)	115.2 (5)
Co–C4–C3	112.8 (5)	114.1 (5)	113.6 (7)	113.1 (7)	115.3 (5)
C1–C2–C3	114.8 (6)	114.9 (6)	112.8 (7)	116.8 (9)	113.8 (5)
C2–C3–C4	115.2 (6)	114.0 (6)	114.2 (6)	114.8 (9)	113.4 (6)

[a] Complexes: A, $Cp(PPh_3)CoCH{=}CHCH{=}CH$;[53] B, $(\eta^5\text{-}C_5H_4CO_2Me)(PPh_3)CoCH{=}CHCH{=}CH$;[53] C, $SMe[CpCo]_2SMeCpCoC(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)$;[54] D, $Cp(PPh_3)CoC(C_6F_5){=}C(C_6F_5)C(C_6F_5){=}C(C_6F_5)$;[55] this work, $(PMe_3)_2(MeCN)_2CoC(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}C(CO_2Me)$. [b] W, X, Y, and Z defined in I; R = cobaltacyclopentadiene substituent. [c] $SMe[Cp_2Co]_2SMe$.

mean values of 1.201 and 1.337 Å, respectively. The O–Me bonds average 1.450 Å and lie close to the carboxylate plane.

Comparison is made in Table VII between the structural parameters of a series of cobaltacyclopentadienes bearing different ligands on the cobalt and different substituents on the ring (I). Compound **2a** is the first crystallographic example of a cobaltacyclopentadiene which is cationic or does not bear a Cp ligand. The distances of 1.921 (6) and 1.925 (6) from Co to the sp^2 carbons C1 and C4, respectively, are in fair agreement with the value fo 1.934 Å calculated by an ab initio molecular orbital method.[56] They are definitely smaller than the $Co\text{–}C(sp^3)$ distance of 2.024 Å (average) in $CpPhCo\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2$.[54] The highest values of 1.995 (11) and 1.993 (11) Å in Table VII correspond to a $CoC_4(C_6F_5)_4$ ring in which there is steric constraint from the C_6F_5 groups.[55] The nature of the substituents on the cobaltacyclopentadiene ring is important, since electron-withdrawing groups such as CO_2Me should lower electron density on the α-carbon and thus reinforce the Co–C bond and weaken the Co–P bond. This is indeed what is observed, the $Co\text{–}C(sp^2)$ bond being shorter and the Co–P bond being longer than those already reported.[53-55,57]



I

Conclusion

The 14e $[Co(PMe_3)_3]^+$ fragment, liberated when $CoBr(PMe_3)_3$ is dissolved in polar solvents, is coordinatively unsaturated and provides two vacant metal d orbitals to interact with the two filled π alkyne orbitals. Thus, the disubstituted alkynes take part in a four-electron donation in the d^8 $[Co(\eta^2\text{-alkyne})(PMe_3)_3]^+$ complexes.[58] Such compounds have been isolated with alkyl- and arylalkynes, but neither with acetylene nor with terminal alkynes. Stability increases in the order $MeC{\equiv}CMe < MeC{\equiv}CPh < C_5H_{11}C{\equiv}CPh < PhC{\equiv}CPh$, i.e. with the π acidity of the alkyne substituents. In solution, excess alkyne or lower temperature are needed to prevent complex dissociation. Reaction with CO leads to total alkyne substitution and formation of $[Co(CO)_2(PMe_3)_3]^+$. Reaction with acetonitrile occurs only with $[Co(PhC{\equiv}CPh)(PMe_3)_3]^+$, allowing the synthesis of the five-coordinate species $[Co(PhC{\equiv}CPh)(MeCN)(PMe_3)_3]^+$, where the alkyne acts as a 2e ligand.

Dimerization or polymerization of these alkynes, reported to occur for $CpCo(CO)_2$ or $CpCo(PPh_3)_2$, is not observed here because of the less nucleophilic character of the cobalt center in these cationic complexes. A more electrophilic alkyne, like DMAC, is required to promote oxidative coupling of two alkynes and yield a cobaltacyclopentadiene, a reaction which already occurred with dimethyl- and diphenylacetylene in presence of the more nucleophilic $CpCo(CO)_2$ complex. Oligomerization of dimethyl acetylenediacetate is not observed, and nucleophilic attack of the coordinated alkyne by phosphine or carbon monoxide does not take place. Only a phosphonium salt is detactable when the reaction is run with excess alkyne.

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Supplementary Material Available: Tables of temperature factors, coordinates of the hydrogen atoms, distances to least-squares planes, and complementary distances and angles for both structures (14 pages); listings of observed and calculated structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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