

(Trimethylphosphine)cobalt(I) Complexes. 2. Reactivity with Diphenylacetylene: Chemical and Structural Evidence for Alkyne Ligand as Variable-Electron Donor in [Co(MeCN)(C₂Ph₂)(PMe₃)₃]BPh₄ and [Co(C₂Ph₂)(PMe₃)₃]BPh₄

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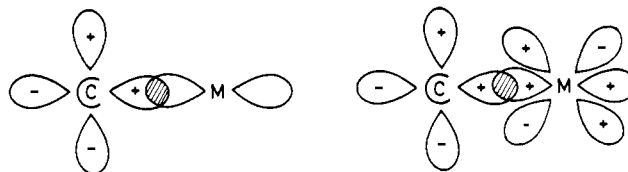
Abstract: The reaction of CoBr(PMe₃)₃ with diphenylacetylene, investigated at -80 °C by ³¹P{¹H} NMR, yields different mononuclear diamagnetic Co-alkyne species depending on the solvent. In toluene, only the molecular CoBr(C₂Ph₂)(PMe₃)₃ species (A) is identified. In acetone, the [Co(C₂Ph₂)(PMe₃)₃]Br compound (B) is also present, its concentration increasing when Br is abstracted by adjunction of NaBPh₄ to the solution. Adding acetonitrile to acetone gives rise, in addition to A and B, to [Co(MeCN)(C₂Ph₂)(PMe₃)₃]Br (C) and to [Co(MeCN)₂(PMe₃)₃]Br (D). Trigonal-bipyramidal structures with equatorial C₂Ph₂ are assigned to A and C on the basis of their ³¹P NMR A₂B spin systems. Confirmation is obtained for C by the crystal structure of the red BPh₄⁻ salt: *a* = 10.274 Å, *b* = 18.191 Å, *c* = 25.379 Å, β = 107.42°, *P*₂₁/*c*, *Z* = 4, *R* = 0.036 (2821 nonzero reflections). The cobalt center is in a distorted trigonal-bipyramidal environment, with C₂Ph₂ lying in the equatorial plane. The C≡C distance is 1.267 (7) Å, and the Co-C bond lengths average 1.979 (5) Å, a distance only slightly shorter than in the related ethylene complex (2.026 (8) Å). The green diamagnetic BPh₄⁻ salt of B was also examined by X-ray diffraction: *a* = 12.320 Å, *b* = 22.514 Å, *c* = 19.177 Å, β = 124.22°, *P*₂₁/*c*, *Z* = 4, *R* = 0.039 (2814 nonzero reflections). The cobalt atom is in a highly distorted tetrahedral environment, bonded to three PMe₃ and the middle of the C≡C bond. Strong Co-C₂Ph₂ binding is indicated by the Co-C distance of 1.852 (5) Å, the shortest reported metal-alkyne distance. The Co-P3 bond (2.127 (2) Å) is significantly shorter than the other two Co-P bonds (average 2.212 (2) Å). However, the C≡C distance (1.265 (7) Å) is the same as in C. From a comparison of the structures of B and C, it is proposed that, in complex C, C₂Ph₂ acts as a two-electron donor (as ethylene does), whereas in complex B, C₂Ph₂ is involved in a four-electron interaction.

Mononuclear metal complexes with alkyne ligands are not numerous. This is partly due to their reactivity which gives rise to dimeric or polymeric alkyne-bridged complexes or to alkyne insertion into a M-C or M-H bond. Consequently, there is still much to be learned about the mechanism of transition-metal-catalyzed alkyne chemistry. A review of the crystallographic results on some mononuclear alkyne complexes has been published.²

An interesting peculiarity of alkyne complexes is the dichotomy of the ligand in bonding to a metal center, i.e., its ability to act either as a two-electron or as a four-electron donor (with the participation of both π and π* sets of orbitals). Following King,³ these metal-alkyne binding modes are schematically represented in Chart I.

The classification of any particular species in one category or the other is usually not obvious. Provisional structures have been suggested on the basis of infrared stretching frequencies assigned to coordinated acetylenes,⁴ of ¹H and ¹³C NMR chemical shifts,^{5,6} and more recently, of the M-C bond lengths.⁷⁻⁹ Donation of three

Chart I



or four electrons has been proposed for the alkyne ligands in IrCl(PhC≡CPh)(PPh₃)₂,⁴ (pyH)[TaCl₄(py)(PhC≡CPh)],⁸ Fe-(PhC≡CPh)(P(OMe)₃)₃,¹⁵ and in a series of Mo and W d⁴ complexes extensively studied in McDonald,⁵ Templeton,⁶ and other workers (M = Mo and W, L = alkyne, dtc = dialkyl dithiocarbamate): M(CO)(dtc)₂L,⁵⁻⁷ MO(dtc)₂L,⁶ M(η⁵-C₅H₅)-(CO)(R)L,^{6,13} W(CO)L₃,^{3,6} [W(η⁵-C₅H₅)(CO)L₂]⁺,^{6,14} Mo(*t*-BuS)₂(*t*-BuNC)₂L,¹⁰ Mo(Porph)L,¹¹ Mo(CO)[S₂P(*i*-Pr)₂]₂L,⁵ Mo(dtc)₂LL',⁶ Mo(η⁵-C₅H₅)₂L,⁶ [Mo(Y)(CO)(PEt₃)₂]⁺, and [Mo(Y)(PMe₃)₂L₂]⁺¹² (Y = η⁵-C₅H₅ or η⁵-C₉H₇).

Description of this variable-electron-donor concept has been made by using extended Hückel molecular orbital calculations.^{6c,e} The resulting bonding picture indicates that ligand π donation plays a crucial role in destabilizing the LUMO in complexes with four-electron donor alkynes and thus stabilizes the complex.

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However, satisfactory comparisons between complexes with two- and four-electron donor alkyne ligands need to have at hand simple and closely related models, i.e., with the same metal center and the same ligands. Such complexes were not available, to our knowledge, before the two cobalt compounds which will be described hereafter.

As part of our research on the reactivity of $\text{CoX}(\text{PR}_3)_3$ with small molecules, we have observed that $\text{CoX}(\text{PMe}_3)_3$ ($\text{X} = \text{Br}, \text{I}$), which adds ethylene and ethylenic ligands,¹⁶ reacts still more easily with acetylenic species. Taking advantage of the capability of $\text{CoX}(\text{PMe}_3)_3$ to give rise, in acetonitrile, to the solvated five-coordinate $[\text{Co}(\text{MeCN})_2(\text{PMe}_3)_3]\text{X}$ species and, in acetone, to the unsolvated $\text{CoX}(\text{PMe}_3)_3$ species,¹⁷ we have been able to isolate, in presence of diphenylacetylene, two different Co-acetylenic complexes: in one, C_2Ph_2 can be considered as acting as a two-electron donor and, in the other, as a four-electron donor.

In this paper, we report the $^{31}\text{P}\{^1\text{H}\}$ NMR investigation of the reaction of diphenylacetylene on $\text{CoX}(\text{PMe}_3)_3$ ($\text{X} = \text{Br}, \text{I}$) and $[\text{Co}(\text{PMe}_3)_4]\text{BPh}_4$. The crystal structures of $[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ and $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ were also determined as an example of two related acetylenic complexes in which the alkyne may act as a two- and a four-electron donor, respectively.

Experimental Section

Procedure, Reagents, and Solvents. All operations were carried out under a purified argon atmosphere in a conventional vacuum system or in a Jaram vacuum glovebox.

All solvents were routinely purified and dried by refluxing and distilling over the following agents under argon: acetonitrile (molecular sieves 4 Å), tetrahydrofuran (Na/benzophenone), methanol (molecular sieves 4 Å), dimethyl ether (Na). The solvents were distilled just before use, transferred under argon, and degassed on the vacuum line. Diphenylacetylene (Fluka puriss) was used without purification. Trimethylphosphine was prepared following the method of Wolfsberger and Schmidbaur¹⁸ and stored under argon.

Physical Measurements. Solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured at 36.43 MHz with a Bruker HX-90 spectrometer in the Fourier transform mode, with ^2D as internal lock and complete ^1H decoupling. Chemical shifts δ are reported in parts per million with the upfield direction being negative. They were referenced to $\delta(\text{P}(\text{OMe})_3)$ 141 downfield from H_3PO_4 (62.5%), and no temperature correction was applied. All samples were prepared in the glovebox, using dry deoxygenated solvents ($\text{CD}_3\text{C}_6\text{D}_5$, $(\text{CD}_3)_2\text{CO}$, and CD_3CN were used in 1:1 ratio with $\text{CH}_3\text{C}_6\text{H}_5$, $(\text{CH}_3)_2\text{CO}$, and CH_3CN , respectively). Infrared spectra of Nujol mulls were recorded with a Perkin-Elmer 137 spectrometer. Magnetic susceptibility determinations in the solid state were done by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. The experimental values are averages over three determinations at variable field, at 295 K. They are corrected for the diamagnetism of the ligands. Elemental analyses were performed by the Centre National de la Recherche Scientifique, Centre de Microanalyse, Lyon, France.

Synthesis of the Complexes. $\text{CoBr}(\text{PMe}_3)_2$, $\text{CoI}(\text{PMe}_3)_3$, and $[\text{Co}(\text{PMe}_3)_4]\text{BPh}_4$ were synthesized following Klein and Karsch.¹⁹

$[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$. A 0.49-g (2.72-mmol) sample of diphenylacetylene was added to 1.00 g (2.72 mmol) of $\text{CoBr}(\text{PMe}_3)_3$ dissolved in 10 mL of acetonitrile. Into this solution was poured an equimolecular amount of NaBPh_4 (2.72 mmol, 0.93 g) dissolved in a methanol-dimethyl ether mixture. Within a few seconds, red microcrystals began to form. They were collected on a frit and dried. Single crystals suitable for X-ray work were obtained by recrystallization from an acetonitrile-methanol-dimethyl ether mixture. Anal. Calcd for $\text{C}_{49}\text{H}_{60}\text{BCoNP}_3$: C, 71.23; H, 7.27; P, 11.26; Co, 7.14. Found: C, 70.21; H, 7.20; P, 11.07; Co, 7.09.

$[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$. A 0.83-g (2.27-mmol) sample of $\text{CoBr}(\text{PMe}_3)_3$ was dissolved in 5 mL of acetone. A 0.78-g sample of NaBPh_4

(2.27 mmol) and 0.46 g (2.60 mmol) of diphenylacetylene were added, while the solution was stirred. After a few minutes, 25 mL of methanol were introduced into the Schlenk tube. The green solution was filtered to remove a small amount of impurities. The solution was cooled to -50°C , and green crystals were deposited, which were collected on a frit and dried. Anal. Calcd for $\text{C}_{47}\text{H}_{57}\text{BCoP}_3$: C, 71.95; H, 7.32; P, 11.84; Co, 7.51. Found: C, 72.15; H, 7.26; P, 11.65; Co, 7.50.

Crystallographic Results. $[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$: $\text{C}_{49}\text{H}_{60}\text{BCoNP}_3$; fw = 825.70; monoclinic; $P2_1/c$, $a = 10.274$ (3) Å, $b = 18.191$ (8) Å, $c = 25.739$ (7) Å, $\beta = 107.42$ (3) $^\circ$; $V = 4589.8$ Å³; $Z = 4$, $D_{\text{calcd}} = 1.195$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å (graphite monochromator); $\mu(\text{Cu K}\alpha) = 43.1$ cm⁻¹, $t = 22^\circ\text{C}$; crystal dimensions 0.56 mm (001-001) \times 0.14 mm (011-011) \times 0.15 mm (011-011).

The crystal was mounted in a Lindemann capillary filled with nitrogen. The c axis was approximately aligned along the capillary axis.

A set of 25 random reflections was collected by using the SEARCH procedure of the Enraf-Nonius CAD-4 diffractometer. After several recentering operations, the unit cell defined from the set of reflections 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. Oscillation photographs using Polaroid films (2-h exposures) were taken along each of the three axes. The films showed the expected layer-line separations, and a mirror symmetry was obtained only for the oscillation about the b axis, as expected for a $2/m$ symmetry. The systematic absences ($h0l$, $l \neq 2n$, and $0k0$ $k \neq 2n$) were determined by inspection of the complete data set subsequently collected, and they unambiguously identified $P2_1/c$ as the space group.

The data were collected as described elsewhere.²⁰ The intensities of the standard reflections showed random variations ($\sigma = \pm 2.5$ -3.1%) about their respective means during data collection. A set of 5754 unique reflections (hkl , hkl , $2\theta \leq 110^\circ$) was collected. A total of 2821 reflections with $I/\sigma(I) \geq 3.0$ were retained for structure determination. The data were corrected for absorption (Gaussian integration, grid $8 \times 8 \times 8$; transmission coefficients = 0.25-0.60).

The structure was solved by the heavy-atom method. Refinement of the positional and isotropic thermal parameters using full-matrix least squares converged to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.107$. The Co and P atoms were then refined anisotropically, and the R factor reduced to 0.091. A ΔF synthesis yielded positional parameters for 21 of the 29 methyl hydrogen atoms of the phosphines and all of those of the phenyl rings. The missing hydrogens were positioned at their calculated coordinates, and the parameters of the 59 hydrogen atoms were introduced into the least-squares program. Anisotropic temperature factors were then refined for all non-hydrogen atoms, whereas hydrogens were isotropically refined. At this stage, the structure was refined portion by portion (for instance the P, 3 C, and 9 H of each phosphine, or the B, 12 C, and 10 H of half of the tetraphenylborate ion) using full-matrix least squares. In the last cycles, individual weights $w = 1/\sigma^2(F)$ based on counting statistics were applied and all the parameters were simultaneously refined by block-diagonal least squares. At convergence, the R factor was 0.036. The weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.038, and the goodness-of-fit ratio was 1.23. The general background in the final ΔF map was lower than ± 0.2 e/Å³, except for two peaks of 0.27 and 0.21 e/Å³, respectively, near Co.

$[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$. $\text{C}_{47}\text{H}_{57}\text{BCoP}_3$; fw = 784.6; monoclinic; $P2_1/c$; $a = 12.320$ (6) Å, $b = 22.514$ (11) Å, $c = 19.177$ (9) Å, $\beta = 124.22$ (7) $^\circ$; $V = 4398.3$ Å³, $D_{\text{calcd}} = 1.185$ g cm⁻³; $\lambda(\text{Cu K}\alpha) = 1.54178$ Å; $\mu(\text{Cu K}\alpha) = 44.6$ cm⁻¹; $t = 22^\circ\text{C}$; crystal dimensions 0.37 mm (011-011) \times 0.34 mm (011-011) \times 0.64 mm (100-100).

A dark green crystal was mounted in a Lindemann capillary filled with nitrogen. The techniques of data collection and structure resolution were essentially the same as above. A total of 5530 independent hkl and hkl reflections ($2\theta \leq 110^\circ$) were measured (average σ on standard fluctuations = $\pm 1.6\%$). A set of 2814 reflections with $I/\sigma(I) \geq 3.0$ was retained for structure determination. An absorption correction was applied (transmission coefficient = 0.15-0.35).

Full-matrix isotropic refinement of all non-hydrogen atoms converged to $R = 0.126$. The rest of the refinement was carried out by block-diagonal least squares. The hydrogen atoms on the phenyl rings were positioned at the ideal coordinates ($B = 6.0$ Å²). Their parameters were not refined, but the coordinates were recalculated after each cycle. After the anisotropic refinement of the nonhydrogen atoms, a ΔF map was calculated, from which at least one H atom on each methyl group of the phosphines was located. The parameters of these hydrogens were isotropically refined and converged to reasonable positions. These positions were used to calculate a reference torsion angle (Co-P-C-H) from which

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(17) In fact, as can be deduced from the chemical reaction, a small amount of the solvated species $[\text{CoS}(\text{PMe}_3)_3]\text{X}$ is formed. Its concentration may be increased by adding NaBPh_4 , which helps extracting X from the cobalt coordination sphere. The solvent S is easily replaced by C_2H_4 .

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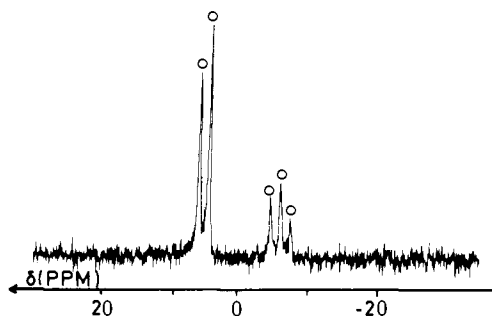


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a toluene solution of $\text{CoBr}(\text{PMe}_3)_3$ (0.10 M) and C_2Ph_2 (excess) at 193 K. An A_2B pattern is observed.

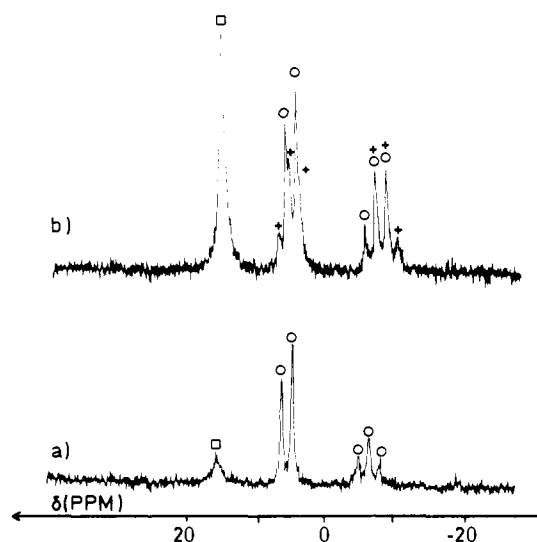


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an acetone solution of $\text{CoBr}(\text{PMe}_3)_3$ (0.10 M) and C_2Ph_2 (excess) at 193 K: (a) without NaBPh_4 ; (b) with NaBPh_4 (~ 0.10 M) (\circ , A; \square , B; $+$, E).

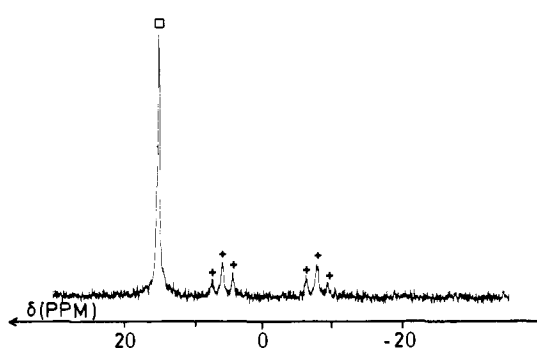


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an acetone solution of $[\text{Co}(\text{PMe}_3)_4]\text{BPh}_4$ (0.10 M) and C_2Ph_2 (excess) at 193 K (\square , B; $+$, E).

the orientation of each methyl group about the P-C bond could be defined. The hydrogens already found, as well as those missing, were fixed at ideal positions ($\text{C}-\text{H} = 0.95 \text{ \AA}$, tetrahedral angles around C, $B = 7.5 \text{ \AA}^2$). These coordinates were recalculated after each cycle. Anisotropic refinement of the nonhydrogen atoms with fixed hydrogen parameters converged to $R = 0.039$ and $R_w = 0.045$. The goodness-of-fit ratio was 1.51. The final ΔF map showed maximum residual electron densities of $\pm 0.17\text{--}0.22 \text{ e/\AA}^3$ within 1.1 \AA from Co or P atoms and a general background $< \pm 0.14 \text{ e/\AA}^3$.

The scattering curves were taken from Cromer and Waber,²¹ except for hydrogen.²² Anomalous dispersion corrections were applied to the scattering curves of P and Co.²³ The refined coordinates for both structures are collected in Table I. Tables of thermal parameters and of structure factor amplitudes have been deposited.

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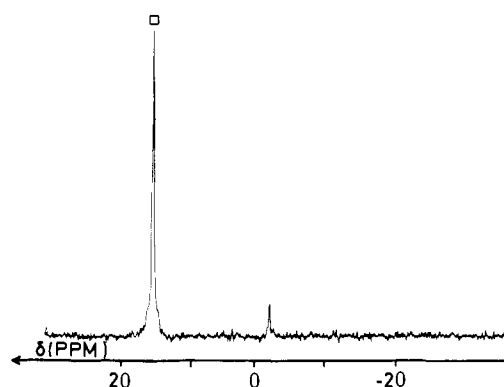


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an acetone solution of $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ (~ 0.10 M) at 193 K. (\square , E).

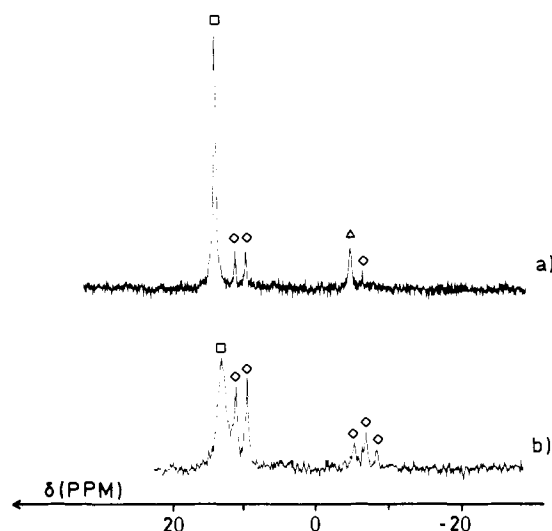
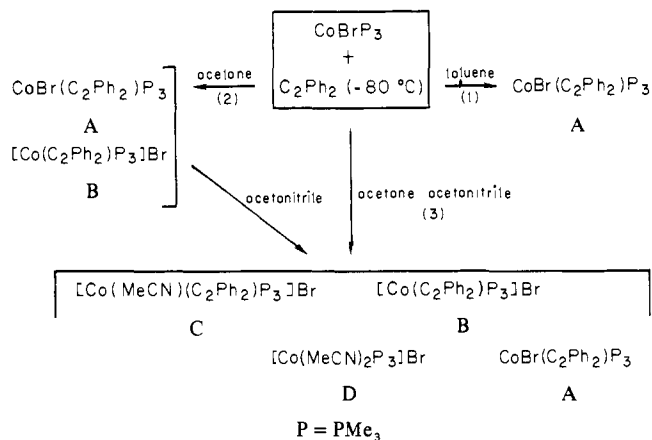


Figure 5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of an acetone-acetonitrile solution of $[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ (~ 0.10 M): (a) at 193 K, three complexes can be identified, B, C, and D; (b) at 183 K in presence of excess C_2Ph_2 , two species B and C are apparent (\square , B; Δ , D; ϕ , C).

Scheme I



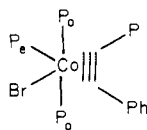
Results

$^{31}\text{P}\{^1\text{H}\}$ Low-Temperature Nuclear Magnetic Resonance Studies.

The reaction of $\text{CoX}(\text{PMe}_3)_3$ ($\text{X} = \text{Br}, \text{I}$) with diphenylacetylene has been investigated in toluene, acetone, and a 1:1 acetone-acetonitrile mixture. The chemistry of these 16-electron paramagnetic complexes with small molecules (two-electron donors: CO , PR_3 , C_2H_4 , ...) is dominated by the formation of diamagnetic pentacoordinate 18-electron adducts which can be stabilized at low temperature. The study of these species has been made possible by using low-temperature FT $^{31}\text{P}\{^1\text{H}\}$ NMR. The results are summarized in Scheme I, and the spectra are shown in Figures

1–5. In these spectra, a singlet corresponding to phosphine oxide, OPMe_3 , often appears (at $\sim +41$ ppm in acetone), owing to the air sensitivity of the solutions.

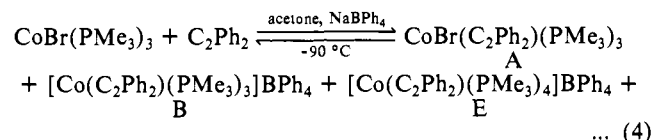
Figure 1 shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum corresponding to reaction 1 (Scheme I), which is that of $\text{CoBr}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3$ (A). This complex has a stereorigid structure, presumably trigonal-bipyramidal (A_2B spin system).



A similar structure has been proposed for the ethylene complex $\text{CoBr}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3$.¹⁶ It agrees with the preference of halogens and unsaturated ligands for the equatorial positions of the trigonal bipyramid and with the NMR chemical shifts observed for axial and equatorial phosphines in this series of complexes. A greater downfield shift is observed for axial, than for equatorial, PMe_3 ligands (Table II and ref 16), in agreement with the electronic effects in trigonal-bipyramidal d^8 species. When $\text{X} = \text{I}$, the corresponding $\text{CoI}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3$ molecule is obtained.²⁴

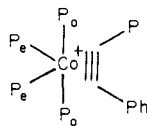
Increasing the temperature broadens the spectrum, as expected, as a result of the displacement of equilibrium 1 toward the starting $\text{CoX}(\text{PMe}_3)_3$ paramagnetic complex. Attempts to isolate complex A failed, and only impure material was obtained.

In acetone at -80°C , the same A_2B spin system corresponding to A is observed as the major component (Figure 2a). However, an additional single line appears at ~ 15 ppm (for $\text{X} = \text{Br}$ and I), corresponding to the new species B, $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{X}$. This line is broad, indicating that exchange is still presumably occurring with either the paramagnetic starting complex or another diamagnetic complex in very low concentration. The concentration of B in acetone could be increased by adding an equimolecular quantity of NaBPh_4 to the solution. Figure 2b shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum corresponding to reaction 4.

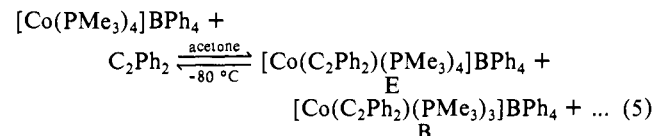


Species A is identified by its A_2B spectrum ($\delta(\text{P}_a)$ 5.3 and $\delta(\text{P}_e)$ -6.5 , $J_{\text{PP}} = 56$ Hz) and B by the singlet at 15.4 ppm. Species E presents an A_2B_2 spin system ($\delta(\text{P}_a)$ 5.5 and $\delta(\text{P}_e)$ -8.4 , $J_{\text{PP}} = 59$ Hz). With time, the concentration of A decreases and the amount of B + E simultaneously increases. Thus, adding NaBPh_4 in acetone generates a third species E which has not been detected before.

Confirmation of reaction 4, together with the characterization of species E as the trigonal-bipyramidal cation



has been done by following the reaction of $\text{PhC}\equiv\text{CPh}$ on $[\text{Co}(\text{PMe}_3)_4]\text{BPh}_4$ in acetone at -80°C (reaction 5).



(24) A distorted square-pyramidal structure cannot be totally ruled out. The trigonal-bipyramidal structure is preferred because all the complexes structurally characterized so far in this series are trigonal bipyramidal. Moreover, DuBois and Meek (*Inorg. Chem.* **1976**, *15*, 3076–3083) have suggested that J_{PP} for a square-pyramidal geometry should be smaller than for a trigonal-bipyramidal structure. This is not the case in this work.

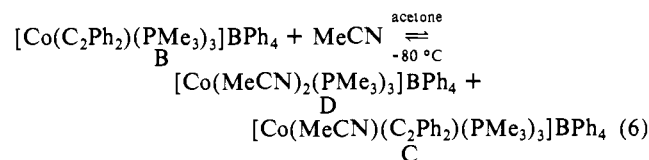
It appears from the spectrum (Figure 3) that B is the major species in solution. Attempts to isolate E in the solid state failed, but with use of $\text{P}(\text{OMe})_3$ instead of PMe_3 , Muettterties and Watson²⁵ could isolate $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{P}(\text{OMe})_3)_4]\text{BPh}_4$ as an impure material and confirmed in solution the trigonal-bipyramidal structure with equatorial diphenylacetylene.

Adding methanol to the products of reaction 4 does not modify the nature of the species but allows the precipitation of methanol-insoluble, not very air-sensitive, green crystals which analyze as B, $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$. They are diamagnetic in the solid, indicating presumably a $\text{Co}(\text{I})$ 18-electron species, as expected for a complex in which $\text{PhC}\equiv\text{CPh}$ acts a four-electron donor ligand. No $\text{C}\equiv\text{C}$ stretching frequency is detected in the IR spectrum. A related iron complex $\text{Fe}(\text{C}_2\text{Ph}_2)(\text{P}(\text{OMe})_3)_3$ has been isolated.¹⁵

When the green crystals are dissolved in acetone, the -80°C $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows, as expected, the singlet at 15 ppm, indicating that B is the major species in solution (Figure 4). However, a new singlet appears at +3 ppm. It is rather weak and has not been attributed yet. Thus, complex B either remains stereochemically nonrigid at -80°C , or the three phosphorus atoms are magnetically equivalent. Since $\text{Fe}(\text{C}_2\text{Ph}_2)(\text{P}(\text{OMe})_3)_3$ presents a pseudotetrahedral structure in the solid state, the X-ray structure determination of B was undertaken (vide infra).

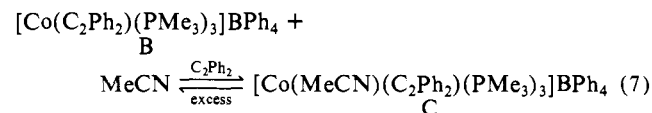
When acetonitrile is added to the acetone solution (1:1 ratio, in order to reach a lower temperature without freezing the solution) (reaction 3, Scheme I), the low-temperature NMR spectrum reveals the presence of A as the major component. There are also three minor components: $[\text{Co}(\text{MeCN})_2(\text{PMe}_3)_3]^+$ (D) identified by its singlet around -5 ppm, complex B, and a new species C. Their overall concentration increases, at the expense of A, when the NMR tube is allowed to stand for an hour at room temperature and is frozen again.

B, C, and D are also present when $[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ is dissolved in acetone–acetonitrile (Figure 5a) (reaction 6). The



new species C is characterized by an A_2B spin system ($\delta(\text{P}_a)$ 11 ppm (d) and $\delta(\text{P}_e)$ -7 ppm (t), $J_{\text{PP}} = 59$ Hz). Thus, a trigonal-bipyramidal structure, with two axial PMe_3 ligands and diphenylacetylene, acetonitrile, and PMe_3 molecules occupying the three equatorial sites, is the most likely. Support for this conclusion is obtained by the X-ray structure determination of C (vide infra). Lowering the temperature to -35°C and adding methanol to the products of reaction 6 allows the precipitation of red crystals of C, which analyze as $[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$. They are diamagnetic. The IR spectrum shows the $\text{C}\equiv\text{C}$ stretching vibration at 1785 cm^{-1} , indicating coordination of the diphenylacetylene. No $\nu(\text{CN})$ band is apparent, as was the case for the corresponding ethylene– $\text{Co}(\text{I})$ complex.¹⁶ When dissolved in acetone–acetonitrile, C gives rise to an NMR spectrum identical with that on Figure 5a, which corresponds to reaction 4. However, when acetone is used as the solvent, B is the only component in the solution.

Thus, compounds B and C are both related by equilibrium 7, which is a solvation reaction (acetonitrile being the solvent).



Excess C_2Ph_2 is required (Figure 5) to prevent alkyne lability and formation of $[\text{Co}(\text{MeCN})_2(\text{PMe}_3)_3]^+$ (D).

(25) Muettterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978–6989.

(26) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944–955, 956–966.

Table I. Refined Positional Parameters

atom	x	y	z	atom	x	y	z
$[\text{Co}(\text{MeCN})(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ ($\times 10^4$; Co and P, $\times 10^5$; H, $\times 10^3$)							
Co	46698 (8)	21021 (4)	11353 (3)	HP21	205 (5)	316 (3)	26 (2)
P1	29777 (15)	19893 (8)	3443 (6)	HP22	98 (5)	260 (3)	36 (2)
P2	32188 (16)	23391 (8)	16247 (6)	HP23	108 (5)	256 (3)	-24 (2)
P3	65489 (14)	22426 (8)	18421 (5)	HP31	153 (6)	102 (3)	49 (2)
N1	4917 (4)	3094 (2)	901 (1)	HP32	267 (5)	85 (3)	16 (2)
C1	3570 (7)	2065 (4)	-259 (2)	HP33	146 (5)	112 (3)	-15 (2)
C2	1622 (6)	2667 (3)	168 (2)	HP41	172 (5)	139 (3)	141 (2)
C3	2075 (6)	1112 (3)	216 (3)	HP42	92 (5)	204 (3)	108 (2)
C4	1578 (6)	1866 (4)	1452 (3)	HP43	112 (5)	203 (3)	167 (2)
C5	3708 (7)	2175 (4)	2364 (2)	HP51	386 (5)	166 (3)	238 (2)
C6	2718 (7)	3304 (3)	1606 (3)	HP52	461 (5)	240 (2)	255 (2)
C7	8124 (6)	2265 (3)	1668 (2)	HP53	300	238	250
C8	6676 (6)	3114 (3)	2199 (2)	HP61	212 (5)	339 (3)	125 (2)
C9	6931 (6)	1552 (3)	2364 (2)	HP62	198 (5)	333 (3)	180 (2)
C10	5732 (5)	1408 (2)	831 (2)	HP63	361 (6)	365 (3)	180 (2)
C11	6692 (5)	1416 (3)	515 (2)	HP71	815 (5)	271 (3)	147 (2)
C12	7395 (5)	790 (3)	441 (2)	HP72	835 (5)	181 (2)	157 (2)
C13	8289 (6)	814 (3)	128 (2)	HP73	885 (4)	236 (2)	200 (2)
C14	8464 (6)	1450 (3)	-124 (2)	HP81	683	349	197
C15	7830 (6)	2074 (3)	-42 (2)	HP82	734 (4)	313 (2)	247 (2)
C16	6948 (5)	2058 (3)	270 (2)	HP83	577 (5)	322 (2)	230 (2)
C20	5095 (5)	1045 (2)	1098 (2)	HP91	766 (4)	161 (2)	260 (2)
C21	4738 (5)	321 (2)	1259 (2)	HP92	632 (5)	157 (2)	256 (2)
C22	5005 (5)	-307 (3)	1007 (2)	HP93	684 (5)	111 (3)	220 (2)
C23	4652 (6)	-993 (3)	1151 (2)	H12	728 (4)	35 (2)	63 (2)
C24	4005 (6)	-1068 (3)	1542 (2)	H13	883 (4)	37 (2)	12 (2)
C25	3740 (7)	-463 (3)	1792 (2)	H14	917 (5)	147 (3)	-34 (2)
C26	4087 (6)	235 (3)	1656 (2)	H15	797 (5)	254 (2)	-19 (2)
C31	2905 (5)	696 (3)	3474 (2)	H16	650 (4)	252 (2)	32 (1)
C32	3782 (5)	1195 (3)	3808 (2)	H22	546 (4)	-20 (2)	73 (2)
C33	5166 (6)	1227 (3)	3876 (3)	H23	488 (4)	-138 (2)	98 (1)
C34	5734 (6)	759 (4)	3596 (2)	H24	380 (4)	-155 (2)	165 (2)
C35	4936 (6)	240 (3)	3263 (2)	H25	334 (5)	-52 (2)	207 (2)
C36	3566 (5)	217 (3)	3212 (2)	H26	395 (4)	69 (2)	188 (2)
C41	661 (5)	1439 (3)	3497 (2)	H32	337 (4)	152 (2)	397 (1)
C42	-411 (5)	1556 (3)	3718 (2)	H33	562 (5)	162 (3)	405 (2)
C43	-988 (6)	2237 (3)	3741 (2)	H34	661 (4)	76 (2)	364 (2)
C44	-538 (6)	2840 (3)	3529 (2)	H35	532 (4)	-8 (2)	309 (2)
C45	477 (6)	2760 (3)	3293 (2)	H36	306 (3)	-13 (2)	300 (1)
C46	1045 (5)	2072 (3)	3277 (2)	H42	-72 (4)	117 (2)	389 (2)
C51	1299 (5)	92 (3)	3959 (2)	H43	-168 (4)	227 (2)	389 (2)
C52	1544 (5)	362 (3)	4481 (2)	H44	-91 (4)	332 (2)	353 (2)
C53	1595 (6)	-98 (3)	4920 (2)	H45	85 (4)	315 (2)	314 (2)
C54	1425 (6)	-835 (3)	4849 (2)	H46	170 (3)	200 (2)	313 (1)
C55	1199 (6)	-1130 (3)	4346 (2)	H52	166 (4)	86 (2)	454 (2)
C56	1153 (6)	-667 (3)	3906 (2)	H53	176 (4)	12 (2)	525 (2)
C61	342 (5)	307 (2)	2861 (2)	H54	146 (4)	-115 (2)	512 (2)
C62	-868 (5)	-73 (3)	2802 (2)	H55	105 (4)	-166 (2)	427 (1)
C63	-1741 (6)	-328 (3)	2314 (2)	H56	99 (3)	-89 (2)	358 (1)
C64	-1382 (6)	-213 (3)	1849 (2)	H62	-112 (4)	-13 (2)	310 (1)
C65	-228 (6)	166 (3)	1873 (2)	H63	-254 (4)	-55 (2)	229 (2)
C66	626 (6)	419 (3)	2370 (2)	H64	-203 (4)	-40 (2)	150 (2)
C71	5044 (5)	3649 (3)	721 (2)	H65	1 (4)	27 (2)	157 (2)
C72	5201 (6)	4342 (3)	468 (2)	H66	145 (4)	68 (2)	242 (2)
B	1300 (6)	633 (3)	3443 (2)	H711	572 (7)	421 (4)	32 (3)
HP11	375 (6)	261 (3)	-29 (2)	H712	568	467	76
HP12	422 (4)	171 (2)	-25 (2)	H713	455 (5)	455 (3)	31 (2)
HP13	255 (6)	203 (3)	-60 (2)				
$[\text{Co}(\text{C}_2\text{Ph}_2)(\text{PMe}_3)_3]\text{BPh}_4$ ($\times 10^4$; Co, $\times 10^5$)							
Co	8825 (8)	3702 (3)	35577 (5)	C12	3554 (5)	57 (2)	6112 (3)
P1	543 (2)	1213 (1)	4004 (1)	C13	4524 (6)	225 (3)	6930 (4)
P2	-1107 (1)	33 (1)	2610 (1)	C14	5427 (6)	645 (3)	7068 (3)
P3	1187 (2)	730 (1)	2655 (1)	C15	5409 (6)	854 (3)	6397 (4)
C1	-465 (6)	1816 (2)	3299 (4)	C16	4449 (5)	680 (3)	5593 (3)
C2	1959 (6)	1632 (3)	4816 (4)	C20	1850 (4)	-319 (2)	4042 (3)
C3	-263 (7)	1055 (3)	4525 (4)	C21	2118 (5)	-959 (2)	4025 (3)
C4	-1537 (6)	-351 (3)	1650 (4)	C22	3110 (5)	-1238 (2)	4746 (3)
C5	-1487 (6)	-523 (3)	3126 (4)	C23	3414 (6)	-1829 (2)	4733 (4)
C6	-2502 (6)	537 (3)	2187 (4)	C24	2713 (6)	-2139 (2)	3982 (4)
C7	-13 (7)	1145 (3)	1750 (4)	C25	1729 (6)	-1879 (2)	3266 (4)
C8	1599 (9)	166 (3)	2176 (5)	C26	1397 (5)	-1281 (2)	3272 (4)
C9	2578 (8)	1227 (4)	3126 (5)	C31	3072 (5)	1689 (2)	-320 (3)
C10	2374 (5)	111 (2)	4552 (3)	C32	2070 (5)	1894 (2)	-1108 (3)
C11	3467 (5)	275 (2)	5425 (3)	C33	2234 (6)	2051 (2)	-1736 (4)

Table I (Continued)

atom	x	y	z	atom	x	y	z
[Co(C ₂ Ph ₂)(PMe ₃) ₃]BPh ₄ (×10 ⁴ ; Co, ×10 ⁵)							
C34	3427 (7)	2016 (2)	-1622 (4)	C53	398 (6)	2353 (2)	704 (4)
C35	4483 (6)	1823 (2)	-841 (4)	C54	-792 (6)	2183 (3)	8 (4)
C36	4295 (5)	1670 (2)	-217 (3)	C55	-884 (5)	1790 (3)	-568 (4)
C41	4145 (5)	1681 (2)	1353 (3)	C56	291 (5)	1563 (2)	-429 (3)
C42	4610 (5)	1361 (2)	2094 (3)	C61	2876 (4)	725 (2)	427 (3)
C43	5574 (6)	1549 (3)	2889 (3)	C62	3886 (5)	393 (2)	490 (3)
C44	6147 (6)	2101 (3)	2991 (4)	C63	3946 (5)	-225 (2)	522 (3)
C45	5720 (6)	2431 (3)	2288 (4)	C64	2962 (5)	-542 (2)	483 (3)
C46	4756 (5)	2234 (2)	1495 (3)	C65	1958 (5)	-238 (2)	434 (4)
C51	1525 (5)	1722 (2)	255 (3)	C66	1926 (5)	378 (2)	409 (3)
C52	1540 (5)	2122 (2)	836 (3)	B	2906 (6)	1462 (2)	420 (4)

Table II. ³¹P {¹H} NMR Data^a

compound		solvent	temp, K	δ(P _{ax}) ^b	δ(P) ^c	δ(P _{eq}) ^b	J _{P_{ax}P_{eq}} , Hz
CoBr(C ₂ Ph ₂)(PMe ₃) ₃	A ₁	toluene	193	4.8 d		-6.7 t	54
		acetone	193	5.3 d		-6.5 t	56
CoI(C ₂ Ph ₂)(PMe ₃) ₃	A ₂	acetone	193	3.4 d		-11.8 t	54
CoI(C ₂ H ₂)(PMe ₃) ₃	A ₃	toluene	188	1.1 d		-8 t	50
[Co(C ₂ Ph ₂)(PMe ₃) ₃]Br	B	acetone	193		15.4 s		
[Co(C ₂ Ph ₂)(PMe ₃) ₃]I	B	acetone	193		14.9 s		
[Co(C ₂ Ph ₂)(PMe ₃) ₃]BPh ₄	B	acetone	193		15 s		
					2.8 s		
		acetone-acetonitrile	193	10.4 d	14.1 s	-7.1 t	53
[Co(MeCN)(C ₂ Ph ₂)(PMe ₃) ₃]BPh ₄	C	acetone-acetonitrile	193	11 d	15.1 s	-7 t	59
					5.4 s		
[Co(C ₂ Ph ₂)(PMe ₃) ₄]BPh ₄	E	acetone	193	5.5 t		-8.4 t	59
[Co(MeCN) ₂ (PMe ₃) ₃]BPh ₄	D	acetone-acetonitrile	193		-5.4 s		

^a PMe₃ as reference (δ -62 upfield from H₃PO₄, 62.5%), not corrected for temperature. δ's are given in ppm (±0.5). ^b δ(P_{ax}) and δ(P_{eq}): chemical shifts of axial (P_{ax}) and equatorial (P_{eq}) PMe₃ ligands in the TBP Co(C₂Ph₂)(S)(PMe₃)₃⁺ species. ^c δ(P): chemical shifts of the other species, characterized by a singlet.

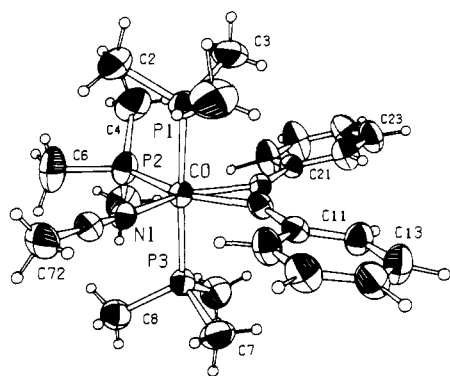


Figure 6. ORTEP drawing of the [Co(MeCN)(C₂Ph₂)(PMe₃)₃]⁺ cation. The ellipsoids correspond to 50% probability, except for hydrogen atoms, which are shown as spheres of arbitrary size.

Since both diamagnetic C₂Ph₂ complexes can be obtained as single crystals, their crystal structures were determined.

Description of the Structures

[Co(MeCN)(C₂Ph₂)(PMe₃)₃]BPh₄. The structure of the [Co(MeCN)(C₂Ph₂)(PMe₃)₃]⁺ ion is shown in Figure 6. The numbering scheme and the interatomic distances are given in Figure 7, whereas the bond angles are listed in Table III. Co(I) exhibits a distorted trigonal-bipyramid structure with the unsaturated ligand lying in the equatorial plane. This cation is structurally close to [Co(MeCN)(ethylene)(PMe₃)₃]⁺, with the major difference that MeCN is found in axial position in the latter case,¹⁶ but in equatorial position in the present compound. Some of the structural features of these two complexes are compared in Table IV.

The Co-C distances in the C₂Ph₂ compound (1.979 (5) Å) are 0.05 Å shorter than in the case of ethylene, which is not highly significant. Such an effect was noted by Ibers and Ittel,² who

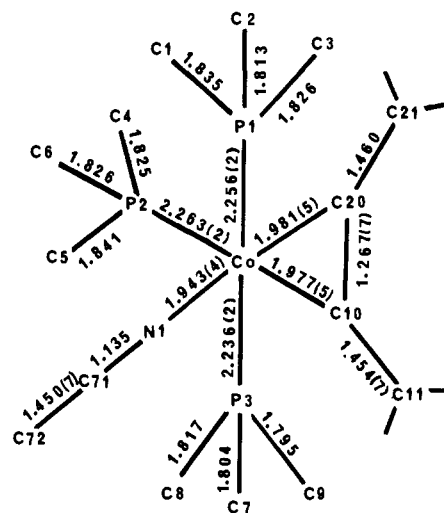


Figure 7. Numbering scheme and interatomic distances in [Co(MeCN)(C₂Ph₂)(PMe₃)₃]⁺. Unless otherwise stated, σ = 0.006 Å.

related it to the reduction in the radius of carbon when hybridization is changed from sp² to sp. On the other hand, the Co-P and Co-N bonds are all longer in the C₂Ph₂ complex. The largest difference is found in the Co-P_{ax} distances, which are ~0.07 Å greater than that of the ethylene complex.¹⁶ This can be ascribed to the mutual trans influence of the two axial phosphines, which is expected to be greater than the trans influence of the axial MeCN ligand on the opposite phosphine in the case of ethylene.

The triple bond lies in the equatorial plane as expected, and the alkyne molecule undergoes structural changes which will be discussed below. It is noteworthy that the phenyl rings lie close to the equatorial plane.

The MeCN ligand, which shows no unusual features, was found to occupy an axial site in the ethylene complex. Its presence in

Table III. Selected Bond Angles (deg) in the Complex Cations

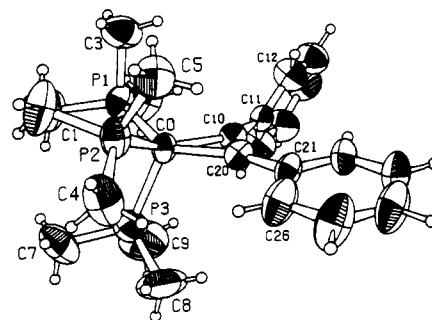
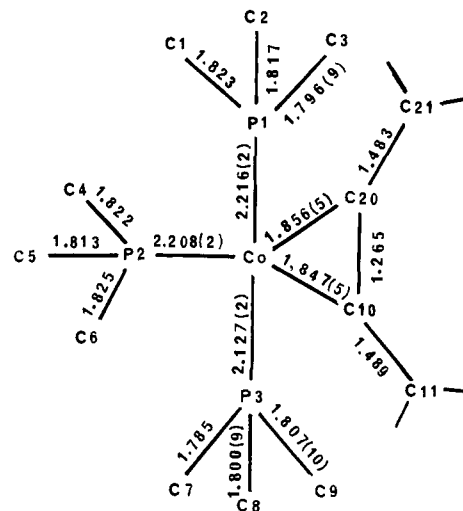
[Co(MeCN)(C ₂ Ph ₂)(PMe ₃) ₃] ⁺ *			
P1-Co-P2	93.53 (6)	Co-P1-C1	113.3 (2)
P1-Co-P3	171.50 (7)	Co-P1-C2	119.4 (2)
P1-Co-N1	86.6 (1)	Co-P1-C3	117.1 (2)
P1-Co-C10	87.2 (1)	C1-P1-C2	99.3 (3)
P1-Co-C20	89.4 (1)	C1-P1-C3	101.1 (3)
P2-Co-P3	94.45 (6)	C2-P1-C3	103.8 (3)
P2-Co-N1	99.5 (1)	Co-P2-C4	119.3 (2)
P2-Co-C10	151.1 (1)	Co-P2-C5	121.5 (2)
P2-Co-C20	113.8 (1)	Co-P2-C6	113.3 (2)
P3-Co-N1	89.1 (1)	C4-P2-C5	97.0 (3)
P3-Co-C10	87.2 (1)	C4-P2-C6	102.4 (3)
P3-Co-C11	90.1 (1)	C5-P2-C6	99.8 (3)
N1-Co-C10	109.3 (2)	Co-P3-C7	114.9 (2)
N1-Co-C20	146.6 (2)	Co-P3-C8	115.1 (2)
C10-Co-C20	37.3 (2)	Co-P3-C9	118.1 (2)
Co-C10-C11	139.7 (4)	C7-P3-C8	99.9 (3)
Co-C20-C21	141.6 (4)	C7-P3-C9	101.0 (3)
Co-C10-C20	71.5 (3)	C8-P3-C9	105.4 (3)
Co-C20-C10	71.2 (3)	Co-N1-C71	174.1 (4)
C10-C20-C21	147.0 (5)	N1-C71-C72	177.4 (5)
C20-C10-C11	148.8 (5)		
[Co(C ₂ Ph ₂)(PMe ₃) ₃] ⁺ *			
P1-Co-P2	104.42 (7)	Co-P3-C7	124.2 (3)
P1-Co-P3	98.41 (8)	Co-P3-C8	112.1 (3)
P1-Co-C10	99.6 (2)	Co-P3-C9	112.4 (3)
P1-Co-C20	136.9 (1)	Co-C10-C20	70.4 (3)
P1-Co-C _X ^a	118.5 (2)	Co-C10-C11	145.9 (4)
P2-Co-P3	94.78 (8)	C11-C10-C20	143.6 (5)
P2-Co-C10	137.8 (2)	Co-C20-C10	69.6 (3)
P2-Co-C20	103.2 (2)	Co-C20-C21	152.8 (4)
P2-Co-C _X ^a	120.9 (2)	C21-C20-C10	137.5 (5)
P3-Co-C10	115.6 (2)	C1-P1-C2	100.0 (3)
P3-Co-C20	111.6 (2)	C1-P1-C3	101.6 (3)
P3-Co-C _X ^a	115.2 (2)	C2-P1-C3	101.0 (3)
C10-Co-C20	40.0 (2)	C4-P2-C5	101.9 (3)
Co-P1-C1	123.3 (2)	C4-P2-C6	100.4 (3)
Co-P1-C2	118.5 (3)	C5-P2-C6	101.8 (3)
Co-P1-C3	109.2 (3)	C7-P3-C8	101.0 (4)
Co-P2-C4	123.5 (2)	C7-P3-C9	101.3 (4)
Co-P2-C5	107.2 (2)	C8-P3-C9	103.4 (4)
Co-P2-C6	118.9 (2)		

^a Middle of the C10-C20 bond.Table IV. Comparison of Selected Distances (Å) and Angles (deg) in Co(I) Complexes with C₂H₄ and C₂Ph₂

	[Co(MeCN)-(C ₂ H ₄)-(PMe ₃) ₃] ⁺ 16	[Co(MeCN)-(C ₂ Ph ₂)-(PMe ₃) ₃] ⁺ a	[Co(C ₂ Ph ₂)-(PMe ₃) ₃] ⁺ a
Co-P	2.175 (3) ^{ax}	2.256 (2) ^{ax}	2.127 (2)
	2.233 (3) ^{eq}	2.236 (2) ^{ax}	2.208 (2)
	2.240 (3) ^{eq}	2.263 (2) ^{eq}	2.216 (2)
Co-N	1.913 (6) ^{ax}	1.943 (4) ^{eq}	
Co-C	2.030 (8)	1.981 (5)	1.856 (5)
	2.023 (8)	1.977 (5)	1.847 (5)
C-Co-C	40.8 (3)	37.3 (2)	40.0 (2)
C-Co-P(eq)	98.1 (3)	113.8 (1)	
C-Co-P(N)(eq)	111.5 (3)	109.3 (2)	
P-Co-P(N)(eq)	108.9 (1)	99.5 (1)	

^a This work.

equatorial position here can be ascribed to the greater steric demand of the C₂Ph₂ ligand. To cast some light on this point, a scale drawing was made by using the atomic positions for the Co(PMe₃)₂(C₂H₄) equatorial plane of the ethylene complex and replacing ethylene by C₂Ph₂. Exceedingly short contacts are found to result between the ortho hydrogens of the phenyl rings and the methyl groups of PMe₃. Replacing one PMe₃ by MeCN relieves steric hindrance in two ways: (i) even when the C-Co-N angle (109.3 (2)°) is kept close to the corresponding C-Co-P angle (111.5 (3)°) of the model, the steric effect with the nearby ortho hydrogen is considerably reduced because of the tube-like shape of the MeCN molecule; (ii) the remaining PMe₃ molecule can move away from the adjacent ring (C-Co-P = 113.8 (1)° vs. 98.1

Figure 8. ORTEP drawing of the [Co(C₂Ph₂)(PMe₃)₃]⁺ cation.Figure 9. Numbering scheme and interatomic distances in [Co(C₂Ph₂)(PMe₃)₃]⁺. Unless otherwise stated, $\sigma = 0.006-0.007$ Å.

(3)°) and fill the available space on the side of MeCN (P-Co-N = 99.5 (1)° vs. P-Co-P = 108.9 (1)°). With the assumption that the more stable arrangement in terms of Co-P and Co-N bond strength would favor coordination of MeCN in axial position, it can reasonably be assumed that the interchange of MeCN and PMe₃ should not lead to a dramatic loss in bond energy and that the small difference can be balanced by reduced steric hindrance.

The above discussion is based on a model in which the phenyl rings lie exactly in the equatorial plane. An obvious way to relieve steric strain would be rotation of the rings out of the equatorial plane, about the C-Ph bond. This does take place, but only to a very limited extent (dihedral angles of 7.6° and 15.4°, respectively). It is tempting to relate this tendency to an electronic effect involving the pair of electrons in the bonding π orbital not used to coordinate to cobalt. This pair of electrons can link the aromatic rings into an extended π system, but this is best achieved if the rings are coplanar with the C-Co-C unit.

[Co(C₂Ph₂)(PMe₃)₃]BPh₄. The geometry of [Co(C₂Ph₂)(PMe₃)₃]⁺ is shown in Figure 8. This cation can be described as a four-coordinate species with the three P atoms and the middle of the unsaturated bond (designated C_X hereafter) defining a very distorted tetrahedron. The distances and angles are given in Figure 9 and Table III, respectively.

The Co-P and Co-C distances are all shorter than in the previous five-coordinate compound (Table IV), an effect consistent with the reduced coordination number. However, the Co-C distances (average 1.852 Å) undergo an unexpectedly large decrease compared with the previous case (1.979 Å). This suggests different binding modes for C₂Ph₂ in these two compounds. Another interesting peculiarity, which will be discussed hereafter, is the difference between the bond lengths of Co-P3 (2.127 Å) and those of Co-P1 and Co-P2 (average 2.212 Å).

One of the phenyl rings of C₂Ph₂ is roughly coplanar with the C-Co-C plane (dihedral angle 9.3°), but the other one is not (114.9°). The lesser tendency of the aromatic rings to be coplanar

Table V. Geometry of Coordinated Diphenylacetylene in Various Complexes

	C≡C, Å	C≡C-C, deg	M-C, Å	ref
C ₂ Ph ₂	1.198 (3)	178.2 (2)		28
Ni(C ₂ Ph ₂)(CN- <i>t</i> -Bu) ₂	1.283 (14)	148.6 (12)	1.899 (19)	29
Pt(C ₂ Ph ₂)(PPh ₃) ₃	1.32 (9) ^a	140 (5)	2.03 (6) ^a	30
Pt(C ₂ Ph ₂) ₂	1.280 (6)	153 (1) ^a	2.025 (5)	31
Pt ₂ (C ₂ Ph ₂) ₂ (PMe ₃) ₃	1.26 (5)	153 ^a	2.01 (3)	31
(C ₅ H ₅) ₂ Ti(CO)(C ₂ Ph ₂)	1.285 (10)	142.3 (7)	2.107 (7)	32
			2.230 (7)	
(C ₅ H ₅) ₂ Mo(C ₂ Ph ₂)	1.269 (7)		2.144 (6)	11
(C ₅ H ₅) ₃ Nb(O ₂ C ₂ Me ₃)(C ₂ Ph ₂)	1.29 (3) ^a	143 (4) ^a	2.18 (2) ^a	33
Mo(CNBu) ₂ (SBU) ₂ (C ₂ Ph ₂)	1.28 (2)	139 (1)	2.055 (10)	10
(C ₅ H ₅)(C ₄ Ph ₄)Nb(CO)(C ₂ Ph ₂)	1.26 (3) ^a	142 (4) ^a	2.22 (2) ^a	33
[Co(MeCN)(C ₂ Ph ₂)(PMe ₃) ₃]BPh ₄	1.267 (7)	147.9 (5)	1.979 (5)	this work
Fe(C ₂ Ph ₂)(P(OMe) ₃) ₃ ^c	1.332 (10)			15
(C ₅ H ₅)WO(Ph)(C ₂ Ph ₂) ^c	1.29 (3)	143 (4)	2.11 (4)	34
Mo(Porph)(C ₂ Ph ₂) ^c	1.324 (5)	136.4 (4)	1.974 (4)	11
		145.4 (4)		
W(CO)(C ₂ Ph ₂) ₃ ^c	1.30 (1) ^a	139.6 (10) ^a	2.06 (1) ^a	35
(C ₅ H ₅)Nb(CO)(C ₂ Ph ₂) ₂ ^c	1.35 (2)	138 ^a	2.19 ^a	36
(pyH)[TaCl ₄ (py)(C ₂ Ph ₂)] ^c	1.325 (12)	139.7 (8)	2.068 (8)	8
[Co(C ₂ Ph ₂)(PMe ₃) ₃]BPh ₄ ^c	1.265 (7)	143.6 (5)	1.851 (5)	this work
		137.5 (5)		
Mo(S ₂ CNET ₂) ₂ (CO)(C ₂ Ph ₂) ^c	1.313 (4)	140.3 (3)	1.974 (6)	10
μ (10 structures)	1.364 (12)	139.7 (8)		this work ^b
μ ₃ (4 structures)	1.385 (18)	124.4 (9)		this work ^b
μ ₄ (1 structure)	1.46 (2)	126.9 (10)		this work ^b

^a Esd's not given in the original paper. ^b μ, μ₃, and μ₄ are average values from crystal structures in which C₂Ph₂ is bridging two, three, and four metal atoms, respectively (see Table XVI, supplementary material). ^c C₂Ph₂ believed to act as a four-electron donor.

with the C-Co-C portion would be consistent with a different role for the second pair of π electrons in the "triple" bond.

Other Remarks. The PMe₃ ligands in both structures have the normal geometry. The mean P-CH₃ distance is 1.81 Å; the Co-P-C and C-P-C angles are, on the average, 116.6° and 101.2°, respectively.

The BPh₄⁻ ions shows an average B-C bond length of 1.642 Å. The pattern of internal angles in the phenyl rings mentioned previously¹⁶ is observed in both structures: the average values are 113.8° (at the B-bonded carbon), 123.6° (ortho), and 119.7° (others). Details are provided in the supplementary material.

Packing diagrams of both structures are provided in the supplementary material. In both cases, individual complex cations and BPh₄⁻ ions are packed in the unit cell with normal van der Waals contacts.

Discussion

The bonding of alkyne ligands in mononuclear metal complexes is generally considered to follow the Dewar-Chatto-Duncanson model.²⁷ This way [Co(MeCN)(C₂Ph₂)(PMe₃)₃]⁺ is clearly an 18-electron species, in which the alkyne donates one electron pair. If C₂Ph₂ behaved similarly in [Co(C₂Ph₂)(PMe₃)₃]⁺, this complex would be a 16-electron Co(I) species, which should be tetrahedral and paramagnetic. Its diamagnetism and the short Co-C distances suggest that it may be described as an 18-electron species, with C₂Ph₂ assuming the role of a 4-electron donor (i.e., donation to the Co d orbitals not only from the acetylene π_{||} orbital but also from the second filled π_⊥ orbital). This suggestion is supported by the fact that even if the analogous 18-electron [Co(MeCN)(C₂H₄)(PMe₃)₃]⁺ complex has been isolated, no diamagnetic [Co(C₂H₄)(PMe₃)₃]⁺ has ever been detected.

Moreover, whereas the reduction of the coordination number affects only to a small extent the Co-P distances, the Co-C lengths are considerably reduced (from 1.98 to 1.85 Å), in agreement with stronger metal-C₂Ph₂ binding. They are in fact the shortest metal-alkyne distances reported so far (Table V). Thus, comparison of these two closely related structures supports the interpretation proposed by other workers,^{7-9,12} that a 4-electron donor role for C₂Ph₂ produces a significant reduction in the metal-carbon distances. However, as also observed by others, no significant

differences on the remaining distance and angle values are noted.

In these two cobalt(I) complexes, the C≡C distances are equal (1.266 Å). They are on the short side of the range observed for several mononuclear C₂Ph₂ complexes (Table V). Bond order reduction below 3 is evidenced from the C≡C distance being greater than in free C₂Ph₂ (1.198 (3) Å).³⁸ However, the bond order remains above 2, the normal C=C double bond distance being 1.339 Å in free ethylene,³⁷ 1.327 Å in the σ-bonded vinyl species Ni(PPh₃)(acac)(PhC=CPhMe),³⁸ and 1.300 Å in cyclopropene.³⁹ The lack of sensitivity of the C≡C distance to the number of electrons involved is surprising, since this distance is affected when C₂Ph₂ acts as a bridging ligand. As shown in Table V, it increases to 1.364 (12) and 1.385 (18) Å when the alkyne is bridging two and three metal atoms, respectively. When bridging four metal atoms, the C≡C distance (1.46 Å) suggests a bond order between 1 and 2, lower than observed for ethylene (1.41 Å) in [Co(MeCN)(ethylene)(PMe₃)₃]BPh₄.¹⁶

Coordination of C₂Ph₂ displaces the phenyl rings backwards as usually observed.² The C≡C-Ph angles in [Co(MeCN)(C₂Ph₂)(PMe₃)₃]⁺ are 6° above, and one of those in [Co(C₂Ph₂)(PMe₃)₃]⁺ is 5° below the value of 142° predicted for C₂Ph₂ in its cis bent excited state.⁴⁰ The differences in this and

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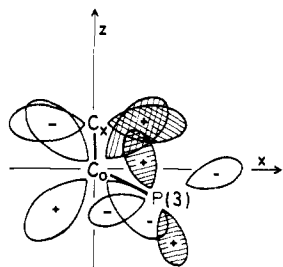


Figure 10. Diphenylacetylene binding as a four-electron donor. Electron delocalization scheme in the C_x -Co-P3 (xz) plane.

other structures (Table V) are not obviously related to the number of electrons provided by C_2Ph_2 .

In the context of a cobalt atom in the +1 oxidation state, and a two- or four-electron donor capability for the C_2Ph_2 ligand, C is a pentacoordinate species, in which C_2Ph_2 lies in the equatorial plane of the TBP. This configuration is predicted by theoretical calculations (in d^8 pentacoordinate complexes, a π -donor or π -acceptor ligand prefers the in-plane equatorial position of the bipyramid).⁴¹ In the TBP coordination sphere around the cobalt atom, the dsp^3 Co orbitals are involved in σ bonding with MeCN, C_2Ph_2 , and three PMe_3 . The remaining d orbitals are filled (d^8), allowing only π back-bonding to the two empty π^* orbitals on the acetylene. Thus, the description of the Co- C_2Ph_2 bonding in C is a direct extension of the Co-olefin bonding. Comparison with the structure of the ethylene analogue $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ shows similar Co-C bond distances: 1.979 (5) Å in C and 2.026 (8) Å in the ethylene complex. Thus, C is a complex in which C_2Ph_2 acts as a two-electron donor ligand.

The structure of B indicates that C_2Ph_2 lies in a plane nearly perpendicular to the C_x -Co-P3 plane (Figure 10, xz plane, Co- C_x along z, dihedral angle = 92.3°). In this pseudotetrahedral coordination, the $C\equiv C$ orientation favors the overlap of the two diphenylacetylene π orbitals with the Co orbitals, forming a σ bond along the Co- C_x direction (overlap with the empty sp^3 Co orbital) and a π bond in the C_x -Co-P3 plane (overlap with the empty Co hybrid orbital of high d_{xz} content) (Figure 10). It is also apparent from this figure that P3, located in the same plane, may be participating in the bonding, allowing electron delocalization over the three centers C_2Ph_2 , Co, and P3. Support for this may be found in the significant shortening of the Co-C and Co-P distances in B compared with C and in the short C_x -P3 distance (3.272 Å) compared with C_x -P2 (3.444 Å) and C_x -P1 (3.409 Å).

The participation of P3 in the bonding scheme, by sharing with the empty C_2Ph_2 π^* orbitals the electron density accumulated on the cobalt center through the C_2Ph_2 four-electron donation, is also a possible explanation for the same $C\equiv C$ distance being observed in complexes B and C, a distance which would be expected to be

greater in B than in C. Thus in B, the structure and the diamagnetism of the molecule may be explained by the donation of electrons from both filled acetylene π orbitals, i.e., with acetylene acting as a four-electron donor.

On the other hand, these two compounds can also be viewed as dicarbene ($C_2Ph_2^{2-}$) complexes of cobalt(III). Thus, C can be considered as a distorted octahedron (18-electron species) with C_2Ph_2 occupying two equatorial sites and B as a distorted square pyramidal (16-electron species) with $C_2Ph_2^{2-}$ occupying two basal sites. Moreover, the apical Co-P3 distance is shorter than the other two, as was observed in the d^6 $RuCl_2(PPh_3)_3$ square-pyramidal complex.⁴² Reduction of the Co-C distances in B would be related to the change of coordination number from six to five. However, few d^6 five-coordinate complexes are known and, to our knowledge, no Co(III) complex with nonsterically hindered ligands have been reported.

In conclusion, this work shows that diphenylacetylene reacts with $CoBr(PMe_3)_3$ and gives rise to many species, two of which have been isolated and characterized both structurally and by their physicochemical data. Discussion of the bonding in such molecular species can be done in terms of a cobalt(I) atom and a variable-electron-donor property for C_2Ph_2 . However, a description involving the other extreme forms (Co(III) and $C_2Ph_2^{2-}$) has to be considered as well. In order to extend this study on the reactivity of the acetylenic ligands in connection with a two- or four-electron donor capability, we are now exploring the steric effect of the acetylenic ligand, together with the reactions of these complexes with small molecules.

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Registry No. $CoBr(C_2Ph_2)P_3$, 85650-41-5; $[Co(C_2Ph_2)P_3]Br$, 85650-42-6; $[Co(MeCN)(C_2Ph_2)P_3]Br$, 83691-43-4; $[Co(MeCN)_2P_3]Br$, 81554-62-3; $[Co(MeCN)(C_2Ph_2)(PMe_3)_3]BPh_4$, 83691-44-5; $[Co(C_2Ph_2)(PMe_3)_3]BPh_4$, 83691-46-7; $CoBr(PMe_3)_3$, 53432-07-8; $CoI(PMe_3)_3$, 53432-08-9; $CoI(C_2Ph_2)(PMe_3)_3$, 85650-43-7; diphenylacetylene, 501-65-5.

Supplementary Material Available: Anisotropic temperature factors (Tables VI and XI), distances and angles in the phenyl rings (Tables VII and XIII), least-squares planes through the phenyl rings (Tables IX and XIV), observed and calculated structure factor amplitudes (Tables X and XV) for both structures, coordinates of the hydrogen atoms of structure B (Table XII), distances and angles involving the hydrogen atoms of structure $[Co(MeCN)(C_2Ph_2)(PMe_3)_3]BPh_4$ (Table VIII), geometry of the C_2Ph_2 ligand in various complexes (Table XVI), and ORTEP drawings of the unit cell for both compounds (Figures 11 and 12) (76 pages). Ordering information is given on any current masthead page.

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