bach.[32] They observed that the CD spectrum of $[Co(sen)]^{3+}$ and its change with phosphate ions is similar to the Λ-$[Co(en)_3]^{3+}$ case. However, there was no interionic CT transition in the former system, unlike in the latter. Thus, it appears that the CT transition is not essential to the production of CD changes. We can find several other systems which show substantial CD changes due to additives but show no CT transition. These include Λ-$[Co(en)_3]^{3+}\cdots$*d*-tartrate^{2-} or sulfate.[3c,6e]

Conclusion

The finding that the association constants are different from one CD band to another has led us to postulate that detailed stereochemical information about ion pairs can be extracted from DCD studies. Though any detailed electronic mechanism leading to rotational strength changes could not be presented, we believe that the present finding should give an impetus to further works. Our own works aimed at the experimental demonstration of the validity of our postulate are in progress.

Acknowledgment is made to the Ministry of Education, Science and Culture (Japan) for the donation of Grants-in-Aid (No. B547043 and No. 434029).

Registry No. *cis*-$[Co(en)_2(N_3)_2]ClO_4$, 14877-87-3; *cis*-$[Co(en)_2(N_3)_2]I$, 79270-30-7; *cis*-$[Co(en)_2(N_3)_2]Br$, 15275-20-4; *cis*-$[Co(en)_2(N_3)_2]Cl$, 68265-39-4; *cis*-$[Co(en)_2(Cl)_2]ClO_4$, 23791-80-2; *cis*-$[Co(en)_2(Cl)_2]Br$, 79270-31-8; *cis*-$[Co(en)_2(CN)_2]ClO_4$, 21861-61-0; *cis*-$[Co(en)_2(NO_2)_2]ClO_4$, 14781-32-9; *cis*-$[Co(en)_2(NCS)_2]^+$, 21169-85-7; Λ-*cis*-$[Co(en)_2(CN)_2]^+$, 18660-79-2; Λ-*cis*-$[Co(en)_2(NO_2)_2]^+$, 18660-78-1; Λ-*cis*-$[Co(en)_2(NCS)_2]^+$, 50762-67-9; Λ-*cis*-$[Co(en)_2(N_3)_2]^+$, 56906-68-4; Λ-*cis*-$[Co(en)_2(Cl)_2]^+$, 18660-62-3; Cl^-, 16887-00-6.

(Trimethylphosphine)cobalt(I) Complexes. 1. Reactivity with Ethylene and Crystal Structure of $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4\cdot MeCN$

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Abstract: The reaction of $Co^IBr(PMe_3)_3$ with ethylene in various solvents was investigated at −80 and 35 °C by $^{31}P\{^1H\}$ NMR spectroscopy. In toluene, acetone, and methanol, ethylene adds reversibly to the paramagnetic tetrahedral d^8 Co^I complex to give the diamagnetic $CoBr(C_2H_4)(PMe_3)_3$ species with C_2H_4 and Br in equatorial positions. Adding acetonitrile (1:1) to acetone or methanol leads to a mixture of two pentacoordinate diamagnetic compounds: $[Co(L)(C_2H_4)(PMe_3)_3]Br$ (where L = C_2H_4 or MeCN) and $[Co(MeCN)(C_2H_4)(PMe_3)_3]Br$. In the former, L cannot be unambiguously identified, but both L and C_2H_4 have to be equatorial. In the latter species, the ligand distribution is the same as found in the crystals of the corresponding BPh_4^- salt, i.e., C_2H_4 equatorial and MeCN axial. The same spectrum was obtained with $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4\cdot MeCN$, which confirms that Br has been expelled from the coordination sphere of cobalt. The affinity of MeCN for Co^I in this system is evidenced by the formation of the trigonal-bipyramidal (TBP) adducts $[Co(MeCN)_2(PMe_3)_3]^+$ and $[Co(MeCN)(PMe_3)_4]^+$ in acetonitrile solutions of $CoBr(PMe_3)_3$ and $[Co(PMe_3)_4]BPh_4$, respectively, at −80 °C. The reaction of ethylene with $[Co(PMe_3)_4]BPh_4$ yields a TBP adduct $[Co(C_2H_4)(PMe_3)_4]BPh_4$ with equatorial C_2H_4. The crystals of $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4$, MeCN belong to space group $P2_1/c$ with a = 12.738 Å, b = 28.52 Å, c = 11.891 Å, and β = 106.85°. The structure contains a distorted TBP $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ cation in which MeCN and PMe_3 are axial, whereas C_2H_4 and two PMe_3 ligands are equatorial. The ethylene double bond lies on the equatorial plane, and it undergoes the usual structural changes upon coordination. The distortions in the TBP are related to the individual steric requirements of each type of ligand.

The d^8 $RhCl(PPh_3)_3$ complex is well-known for its ability to react with ethylene, giving rise to monomeric and dimeric molecular or cationic ethylene complexes. Its catalytic properties toward olefin isomerization and hydrogenation have been well investigated.[2]

The corresponding cobalt(I) compound $CoCl(PPh_3)_3$ is less reactive,[3] although recently, ethylene dimerization has been reported to be catalyzed by $CoBr(PPh_3)_3$ in presence of BF_3 as cocatalyst.[4] The type of phosphorus ligand has an influence, since $CoX(PR_3)_3$ complexes with $P(OEt)_3$, $P(OPh)_3$, and $P(OMe)_3$ have shown catalytic properties in the hydrogenation and isomerization of olefins.[5] However, up to now, few cobalt(I)–ethylene complexes with monodentate phosphorus ligands have been isolated. The synthesis of the first examples $CoR(C_2H_4)(PMe_3)_3$ (where R = Me, Ph, H), and $[Co(C_2H_4)(P(OMe_3)_3)_4]^+$ has been carried out recently by Klein et al.[6,7] and by Muetterties and Watson,[8] respectively. The alkyl and aryl complexes have been synthesized by adding methyl or phenyl lithium to a tetrahydrofuran solution of $CoCl(PMe_3)_3$ under 1 atm of ethylene at low temperature. The formation of an ethylene adduct of $CoCl(PMe_3)_3$ as an inter-

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mediate, according to eq 1, has been suggested to explain the color change of the solution from blue to red, but the species was not characterized.

$$CoCl(PMe_3)_3 + C_2H_4 \rightarrow [CoCl(C_2H_4)(PMe_3)_3] \xrightarrow[+LiCH_3]{} Co(CH_3)(C_2H_4)(PMe_3)_3 \quad (1)$$

We report here the reactions of ethylene on $CoBr(PMe_3)_3$ and $CoI(PMe_3)_3$ in different solvents. At room temperature, no detectable reaction occurs. However, lowering the temperature leads to the formation of new diamagnetic species which are characterized in solution by ^{31}P NMR. Solvent effect is important, since the use of a polar and coordinating solvent, such as acetonitrile, allows the isolation at low temperature of the ethylene cobalt(I) complex $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$. The crystal structure of this compound was examined for two reasons. First, it is, together with $[Co(C_6H_5)(C_2H_4)(PMe_3)_3]$, the only known X-ray structure of a cobalt(I)–ethylene complex and, although theoretical models have been proposed, there is a lack of experimental information on the mode of bonding of ethylene with first-row metal compounds in d^8 electronic state. The second reason is to determine the details of the stereochemistry, since such complexes may play an important role as intermediates in chemical processes such as olefin dimerization, isomerization, hydrogenation, and so on. Since cationic species may present a different reactivity toward ethylene,[2b] we also investigated the reactivity of $[Co(PMe_3)_4]^+$ with ethylene.

Experimental Section

Reagents and Techniques. The air-sensitive complexes were handled in an inert atmosphere of purified argon. A Jaram vacuum glovebox was used for operations such as preparation of samples for IR, NMR, and chemical analysis. Schlenk techniques were used for manipulations at low temperature.

All solvents were routinely purified and dried by refluxing and distilling them over the following agents under argon: acetonitrile (molecular sieves 4 Å); THF (Na/benzophenone); methanol (molecular sieves 4 Å); dimethyl ether (Na). The solvents were distilled just before use and transferred under argon.

Solution ^{31}P NMR spectra were recorded at 36.43 MHz on a Brucker HX-90 spectrometer with ^2D as internal lock and complete ^1H decoupling. They were referenced to $P(OMe)_3$ contained in a sealed capillary within the NMR tube. The value $\delta(P(OMe)_3)$ +141 downfield from H_3PO_4 62.5% was used as reference, and no temperature correction was applied. All samples were prepared in the glovebox using dry deoxygenated solvents ($(CD_3)_2CO$ and/or CD_3CN) and saturated with ethylene at room temperature and 1 atm. Solution ^1H NMR spectra were measured with the same spectrometer, at variable temperature. They were referenced to tetramethylsilane.

IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer as Nujol mulls between KBr disks, using polystyrene as reference.

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 295 K. They are corrected for the diamagnetism of the ligands.[9]

Microanalyses were performed by the Centre National de la Recherche Scientifique, Centre de Microanalyse, Lyon, France.

Synthesis of the Complexes. PMe_3 was prepared following the method of Wolfsberger and Schmidbaur[10] and stored under argon. $CoBr(PMe_3)_3$ and $CoI(PMe_3)_3$ were synthesized following Klein and Karsch.[11] They are very air sensitive. We were unable to get $CoCl(PMe_3)_3$ free of $OPMe_3$, and reactions with ethylene were not studied.

$[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$. A solution of $CoBr(PMe_3)_3$ (1 g, 2.72 mmol) in acetonitrile (10 mL) is cooled to −10 °C and purged with ethylene. $NaBPh_4$ (0.93 g, 2.72 mmol), dissolved in a 1:1 methanol–dimethyl ether mixture, is added. The solution cooled at −80 °C turns brown. The precipitated orange-brown crystal are filtered and dried under ethylene at −80 °C.

Anal. Calcd for $C_{39}H_{57}BCoN_2P_3$: Co, 8.22; P, 12.97; N, 3.90; C, 65.37; H, 8.01. Found: Co, 8.12; P, 13.27; N, 3.26; C, 64.88; H, 7.83.

Crystal Data: Formula $C_{39}H_{57}BCoN_2P_3$; fw 716.57; monoclinic, space group $P2_1/c$, a = = 12.738 (4) Å, b = 28.52 (1) Å, c = 11.891 (4) Å, β = 106.85 (3)°, V = 4134.5 Å^3, d_{calcd} = 1.151 g cm^{-3}, Z = 4, μ(Mo Kα) = 5.5 cm^{-1}, T = 23 °C, λ(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite monochromator).

X-ray Data Collection. Crystals for structure determination were obtained from the reaction mixture. They are orange-brown plates, elongated along the c direction. They may be handled in air for the short time needed to seal them in a Lindemann capillary filled with nitrogen. The specimen used for data collection was cut from a longer plate, and the dimensions of the fragment were as follows: 0.11 mm between faces (100) and $(\bar{1}00)$, 0.26 mm between (010) and $(0\bar{1}0)$, and 0.58 mm along c. The fragment was not bounded by natural faces in the latter direction.

The space group $P2_1/c$ was unambiguously determined from a set of precession photographs. The final unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections centered in the counter aperture of an Enraf-Nonius CAD4 diffractometer.

The intensity data were collected by using the $\omega/2\theta$ scan technique. A fixed slit of 3.0 mm was used and the scan range was ω = (0.90 to 0.35 tan θ)° extended 25% on each side for backgrounds. Preliminary intensity I was obtained from a prescan at 6.7° min^{-1}. All reflections having $I/\sigma(I)$ < 1.0 were labeled "weak" and were not remeasured at lower speed. For the final scan, a rate S between 6.7 and 0.7° min^{-1} was automatically selected to make the $I/\sigma(I)$ ratio = 100, but a maximum scan time of 120 s was imposed. Three standard reflections were measured every hour. Their intensities decreased regularly by 20% as a result of crystal instability. The decay was taken into account to scale the data at the data reduction stage. Crystal orientation was checked every 100 measurements. The actual position of the scattering vectors and the directions derived from the orientation matrix always differed by <0.1°, and no crystal reorientation was needed during data collection.

A total of 5899 measurements (hkl, $hk\bar{l}$, $2\theta \leq 45°$) were collected by using option FLAT, a procedure to measure intensity at the ψ position that minimizes absorption. After the systematic absences were eliminated (144) and the equivalent measurements were averaged, the data file consisted of 5414 independent reflections.

The net intensity I was obtained from $I = (P - 2B)S$, where P is the total scan count and B is the total background count (measured during one half of the scan time). The standard deviation was calculated from $\sigma^2(I) = (P + 4B)S^2 + (0.02I)^2$. A total of 1965 reflections with $I/\sigma(I)$ > 2.5 was retained for structure determination. The low proportion of observed reflections was first ascribed to higher background counts due the capillary, but it is now clear that crystal decomposition in the X-ray beam made a contribution. In addition, thermal motion is important especially in the trimethylphosphine and acetonitrile molecules, which may explain the low number of observed data at 2θ > 40°. The data were finally corrected for the Lorentz and polarization effects. Absorption correction was deemed unnecessary because of the low absorption coefficient.

Structure Determination and Refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares. The Co and one of the P atoms were located from a three-dimensional Patterson synthesis. A series of structure factor calculations and difference Fourier (ΔF) syntheses revealed the positions of all the remaining nonhydrogen atoms. Isotropic refinement converged to $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.079 (unit weights, observed reflections only). The 20 H atoms of the phenyl rings were then fixed at their calculated positions with temperature factors U = 7.0 Å^2. The nonhydrogen atoms were anisotropically refined, whereas the H atoms were fixed. This reduced the R factor to 0.048. In the subsequent ΔF map, most of the highest peaks (0.4–0.6 e/Å^3) corresponded to H atoms on the methyl group of acetonitrile or trimethylphosphine molecules. They were isotropically refined. They reached reasonable positions which were used to define the orientation of the methyl groups. Torsion angles τ(Co–P–C–H) were calculated from these positions, and the three methyl hydrogens were fixed at τ, τ + 120, and τ − 120° with C–H = 0.95 Å and ideal tetrahedral angles. An average orientation was used when two hydrogens on the same methyl group had been refined in the first place. These hydrogens were assigned temperature factors U = 7.6 Å^2. Subsequently, the parameters of the methyl and phenyl hydrogens were not refined, but their coordinates were recalculated after each least-squares cycle.

Block-diagonal least squares were used for the rest of the refinement. Anisotropic refinement at this stage converged to R = 0.040. In the new ΔF map, the four hydrogens of the ethylene molecule showed among the six highest peaks (0.4–0.5 e/Å^3). They were introduced into the structure and were isotropically refined, simultaneously with the nonhydrogen atoms. No hydrogens could be found for the lattice acetonitrile molecule.

In the latest stage of the refinement, individual weights are applied. The final R factor was 0.038 and the weighted residual $R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.042. The goodness-of-fit ratio was 1.08. In the

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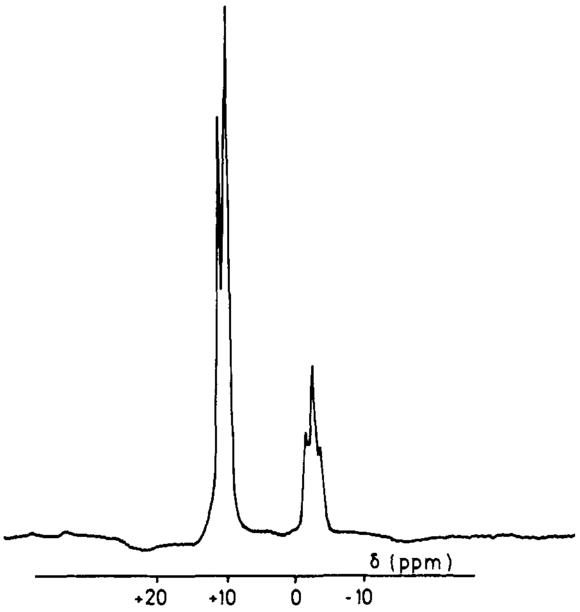


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of 0.1 M $CoBr(PMe_3)_3$ in $(CD_3)_2CO$ under an ethylene atomsphere (T = −80 °C).

final ΔF map, the six strongest peaks (0.30–0.18 e/Å^3) were within 1.0 Å of Co or P. The deepest valley was −0.22 e/Å^3.

The scattering curves were those of Cromer and Waber except for hydrogen. Anomalous scattering was taken into account for Co and P.[12] The refined coordinates are listed in Table I. The refined temperature factors and the coordinates of the fixed hydrogen atoms are part of the supplementary material.

Results

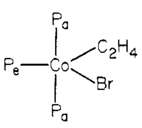
Solution Study. Figure 1 shows the −80 °C $^{31}P\{^1H\}$ NMR spectrum obtained when an ethylene atmosphere is introduced into an NMR tube containing a 0.1 M solution of $CoBr(PMe_3)_3$ in deuterated acetone. The spectrum indicates the presence of a diamagnetic stereorigid species, characterized by a near first-order AB_2 pattern, in good agreement with the expected pentacoordinate adduct $CoBr(C_2H_4)(PMe_3)_3$ (reaction 2). Increasing

$$CoBr(PMe_3)_3 + C_2H_4 \rightleftharpoons CoBr(C_2H_4)(PMe_3)_3 \qquad (2)$$

the temperature causes a broadening of the spectrum, mainly due to complex dissociation, as evidenced from the temperature reversible color change of the solution from brown to −80 °C to violet at room temperature. An analogous spectrum is observed in methanol and in toluene (Table II).

The ^1H NMR spectrum (−80 °C) in deuterated actone shows broad lines for free ethylene at δ 5.4, for coordinated ethylene at 2.1 ppm[8] and for the methyl protons of PMe_3 at 1.5 and 0.7 ppm, respectively. Raising the temperature produces minor modifications of the PMe_3 proton lines.

The ^{31}P chemical shifts (Table II) indicate that the geometry of the $CoBr(C_2H_4)(PMe_3)_3$ complex is most probably a distorted trigonal bipyramid with two axial and one equatorial PMe_3 ligands, corresponding to the low-field doublet (2 P_a) and the high-field triplet (1 P_e), respectively.



Deshielding is more important for the axial than for the equatorial PMe_3 ligands, in agreement with theoretical considerations.[13] Similar observations have been reported for the analogous $NiX_2(PMe_3)_3$ d^8 complexes.[14] This stereochemistry is also consistent with the expected ligand distribution in pentacoordinate d^8 complexes (ethylene, a π-acceptor ligand, and halogens prefer the equatorial positions of the TBP).

Table I. Refined Atomic Coordinates (×10^4; ×10^5 for Co; 10^3 for H)

atom	x	y	z
Co	13929 (9)	11572 (4)	3723 (9)
P(1)	2859 (2)	1183 (1)	−1951 (2)
P(2)	330 (2)	1780 (1)	398 (2)
P(3)	2164 (2)	1479 (1)	−847 (2)
N(1)	551 (5)	861 (2)	1268 (5)
N(2)	3608 (8)	3019 (3)	1377 (8)
C(1)	1608 (7)	498 (2)	−167 (7)
C(2)	646 (7)	702 (3)	−916 (7)
C(3)	−502 (7)	413 (3)	2490 (7)
C(4)	74 (6)	668 (3)	1795 (6)
C(5)	4565 (9)	3157 (3)	1710 (9)
C(6)	5630 (8)	3321 (4)	2121 (10)
C(11)	2768 (7)	791 (4)	3120 (7)
C(12)	4161 (7)	968 (4)	1771 (7)
C(13)	3256 (8)	1715 (4)	2754 (8)
C(21)	−1048 (8)	1722 (4)	−555 (8)
C(22)	617 (9)	2383 (3)	106 (9)
C(23)	62 (8)	1877 (3)	1810 (7)
C(31)	3002 (8)	1097 (2)	−1455 (7)
C(32)	3094 (9)	1962 (3)	−363 (8)
C(33)	1248 (8)	1720 (3)	−2188 (7)
C(41)	7294 (6)	1654 (2)	4886 (6)
C(42)	6372 (6)	1865 (3)	4183 (7)
C(43)	5994 (7)	2310 (3)	4404 (8)
C(44)	6580 (8)	2546 (3)	5403 (9)
C(45)	7503 (7)	2360 (3)	6088 (8)
C(46)	7866 (7)	1924 (3)	5847 (7)
C(51)	7116 (6)	827 (3)	5667 (6)
C(52)	7706 (6)	791 (3)	6869 (6)
C(53)	7231 (7)	585 (3)	7675 (7)
C(54)	6183 (7)	426 (3)	7326 (7)
C(55)	5566 (7)	462 (3)	6163 (7)
C(56)	6062 (6)	660 (3)	5371 (6)
C(61)	8971 (6)	1053 (2)	5052 (6)
C(62)	9613 (6)	1389 (3)	4726 (6)
C(63)	10703 (6)	1327 (3)	4863 (6)
C(64)	11249 (6)	927 (3)	5371 (7)
C(65)	10650 (6)	575 (3)	5680 (6)
C(66)	9539 (6)	644 (3)	5533 (6)
C(71)	7188 (6)	909 (3)	3399 (6)
C(72)	6907 (6)	450 (3)	3158 (7)
C(73)	6588 (7)	266 (3)	2036 (8)
C(74)	6548 (7)	551 (3)	1095 (7)
C(75)	6844 (7)	1003 (3)	1297 (7)
C(76)	7163 (6)	1194 (3)	2425 (6)
B	7657 (7)	1108 (3)	4766 (7)
H(11)	141 (6)	24 (2)	42 (6)
H(12)	216 (6)	48 (2)	−54 (6)
H(21)	51 (5)	82 (2)	−157 (5)
H(22)	−3 (6)	57 (2)	−79 (6)

In Figure 2 is represented the $^{31}P\{^1H\}$ NMR spectrum obtained when an ethylene atmosphere is maintained in an NMR tube containing a 0.01 M solution of $CoBr(PMe_3)_3$ or $CoI(PMe_3)_3$ in a mixture of deuterated acetone and acetonitrile (1:1 ratio). The presence of acetonitrile drastically changes the spectrum. Two species are formed, both stereorigid. No modification in the resonances occurs between −80 and −35 °C. Above −35 °C, the signals are broadened because the diamagnetic species undergo dissociation into paramagnetic molecules (reaction 3 backward and C_2H_4 dissociation leading to the $[Co(MeCN)(PMe_3)_3]Br$ species), while the solution changes from brown to green.

$$CoBr(PMe_3)_3 + C_2H_4 \underset{+35\ ^\circ C,\ MeCN/Me_2CO}{\overset{-80\ ^\circ C}{\rightleftharpoons}} [Co(MeCN)(C_2H_4)(PMe_3)_3]Br + [Co(L)(C_2H_4)(PMe_3)_3]Br \qquad (3)$$

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Table II. $^{31}P\{^1H\}$ NMR Results (-80 ± 5 °C)[a]

compd	solvent	$\delta(P_a)$	$\delta(P_e)$	$J_{P_aP_e}$, Hz
$CoBr(C_2H_4)(PMe_3)_3$	methanol[b]	9.3 d	−4.3 t	39
	acetone[b]	10.3 d	−3.6 t	39
	toluene[b]	9.8 d	−3.6 t	39
$CoI(C_2H_4)(PMe_3)_3$	methanol[b]	6.8 d	−9.1 t	39
$[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4$	acetonitrile/methanol[b]	23.0 t	−3.8 d	59
$[Co(L)(C_2H_4)(PMe_3)_3]BPh_4$	acetonitrile/methanol[b]	19.0 d		38
$[Co(MeCN)(C_2H_4)(PMe_3)_3]I$	acetonitrile/methanol[b]	23.4 t	−4.3 d	59
$[Co(L)(C_2H_4)(PMe_3)_3]I$	acetonitrile/methanol[b]	19.0 d	−2.2 t	39
$[Co(MeCN)(C_2H_4)(PMe_3)_3]Br$	acetonitrile/methanol[b]	23.4 t	−4.5 d	59
$[Co(L)(C_2H_4)(PMe_3)_3]Br$	acetonitrile/methanol[b]	19.1 d		39
$[Co(C_2H_4)(PMe_3)_4]BPh_4$	acetone[b]	8.5 t	3.7 t	54
$Co(CH_3)(PMe_3)_4$[d]	toluene[c]	24.0 q	−5.4 d	48
$Co(CH_3)(C_2H_4)(PMe_3)_3$[e]	toluene[c]	32 t (br)	−9.9 d (br)	
$Co(C_6H_5)(C_2H_4)(PMe_3)_3$[e]	toluene[c]	17.2 d	−3.6 t	32
$[Co(MeCN)_2(PMe_3)_3]Br$	acetonitrile/acetone[b]	−5.4 s		
$[Co(MeCN)_2(PMe_3)_3]I$	acetonitrile/acetone[b]	−5.5 s		
$[Co(MeCN)(PMe_3)_4]BPh_4$	acetone	no signal		

[a] All chemical shifts expressed in ppm from H_3PO_4, 62.5%; br = broad, d = doublet, t = triplet, q = quartet. [b] Measured with $P(OMe)_3$ as reference (δ 141 upfield H_3PO_4, 62.5%), not corrected for temperature. [c] Measured with PMe_3 as reference (δ −61 from H_3PO_4). [d] Reference 26. [e] References 6 and 7.

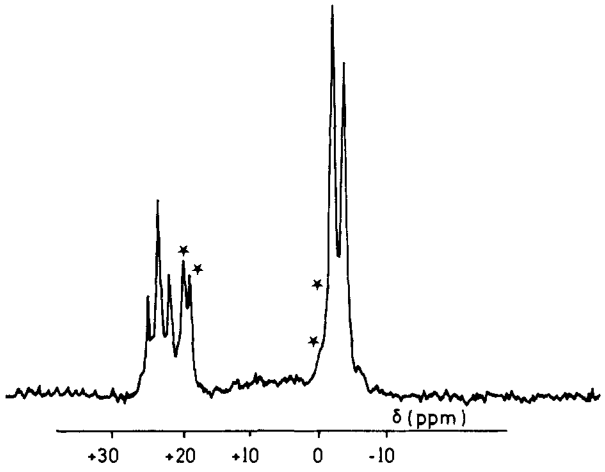
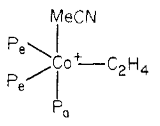


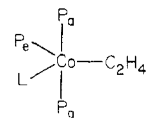
Figure 2. $^{31}P\{^1H\}$ NMR spectrum of 0.01 M $CoBr(PMe_3)_3$ in a 1:1 $(CD_3)_2CO$–CD_3CN mixture under an ethylene atmosphere ($T = -80$ °C), indicating the presence of the two species: $[Co(MeCN)(C_2H_4)(PMe_3)_3]Br$ and $[CoL(C_2H_4)(PMe_3)_3]Br$ (asterisk).

To the first compound A, characterized by a near first-order A_2B spectrum ($J_{PP} = 59$ Hz) with a low-field triplet (axial PMe_3) and high-field doublet (equatorial PMe_3) in the ratio of 1:2, is attributed the trigonal-bipyramidal structure $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ (A).



A

In the second species B, displaying a near first-order A_2B pattern with a low-field doublet and a high-field triplet ($J_{PP} = 39$ Hz), a trigonal-bipyramidal geometry with two axial and one equatorial PMe_3 ligands is likely. The two equatorial positions of B may be filled either by one ethylene and one acetonitrile ligand or by two ethylene ligands. Indeed, a diolefin complex was isolated for the isoelectronic Fe(0) compound $Fe(CO)_3(olef)_2$ (olef = methyl acrylate),[15] whereas recent X-ray work on $[Co(MeCN)(diphenylacetylene)(PMe_3)_3]BPh_4$ showed that acetonitrile, PMe_3 and the unsaturated ligand are distributed as in B.[16] An NMR spectrum run with a higher concentration of ethylene showed a very slight increase of the [B]/[A] ratio. Although this favors the formulation of B as a diolefin adduct, we do not consider this result as fully conclusive, and both of the above possibilities for B are retained as equally reasonable.



B

An identical $^{31}P\{^1H\}$ spectrum, showing the presence of both species A and B, is obtained when $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$ (isolated as described below) is dissolved in a 1:1 acetone–acetonitrile mixture under ethylene at −80 °C. This confirms that the halogen was not present in the coordination sphere when the halide compound was used as the starting material. On the other hand, when the BPh_4^- salt is dissolved in acetone at −90 °C under ethylene, no signal appears in the ^{31}P NMR spectrum. Thus, in acetone, $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ dissociates to give, as major products, paramagnetic species which have not yet been characterized. Consequently, the formulation of complex B as a diethylene adduct or as an isomer of A with ethylene and acetonitrile in equatorial positions is still uncertain. Species B presents a coupling constant ($J_{PP} = 39$ Hz) sensibly lower than A ($J_{PP} = 59$ Hz). Thus, one could expect for B a distorted trigonal-bipyramidal structure as observed for $Co(C_2H_4)(Ph)(PMe_3)_3$, for which a similar J_{PP} value of 32 Hz was found.[7] On the other hand, according to Meek et al.,[27] in d^8 five-coordinate Co(I) compounds, square-pyramidal species exhibit J_{PP} values lower than trigonal-bipyramidal complexes. Consequently, it cannot be totally excluded that our low value of J_{PP} can be related to a square-pyramidal geometry, but we have not retained this possibility in view of the marked preference of pentacoordinate Co(I) compounds with monodentate PR_3 ligands for the trigonal-bipyramidal structure.

The only information provided by the ^1H NMR spectrum between −35 and −80 °C is that there seems to be no intermolecular exchange process between free and coordinated ethylene, the singlet due to free ethylene remaining unmoved at 5.1 ppm. Three broad lines for the PMe_3 protons and those of coordinated ethylene are observed at 1.1, 1.5, and 2.1 ppm and undergo no appreciable shape modification between −80 and −35 °C.

Figure 3 shows the −80 °C $^{31}P\{^1H\}$ NMR spectrum of $[Co(PMe_3)_4]BPh_4$ (0.01 M) in deuterated acetone under ethylene. A diamagnetic stereorigid species is present, displaying a near

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(15) Grevels, F. W.; Schulz, D.; Koerner von Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 534–536.

(16) Capelle, B.; Beauchamp, A. L.; Dartiguenave, M.; Dartiguenave, Y., to be submitted for publication.

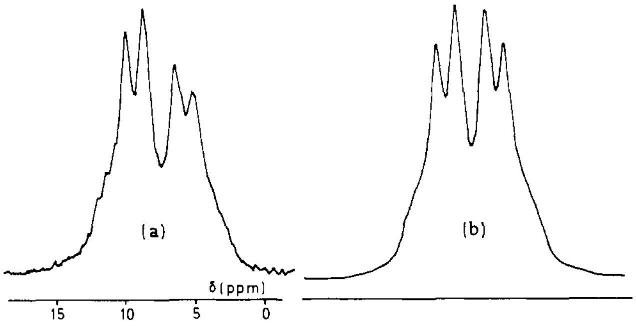

Figure 3. $^{31}P\{^1H\}$ NMR spectra of 0.01 M $[Co(PMe_3)_4]BPh_4$ in $(CD_3)_2CO$ under an ethylene atmosphere: (a) experimental; (b) calculated for $\Delta(\delta(P_a) - \delta(P_e)) = 145$ Hz, $J_{P_aP_e} = 54$ Hz, and band width = 34 Hz.

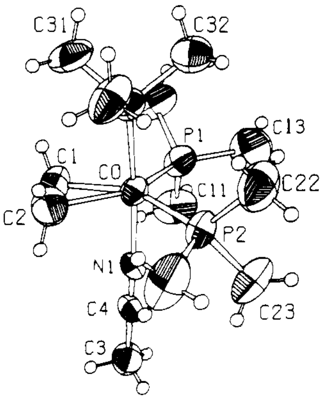

Figure 4. View of the $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ ion. Unidentified nonhydrogen atoms can be recognized by reference to Figure 5. The elliposoids correspond to 50% probability, except for hydrogens, which are shown as spheres of arbitrary size.

first-order A_2B_2 pattern, in good agreement with the formation of the pentacoordinate $[Co(C_2H_4)(PMe_3)_4]BPh_4$ compound (reaction 4). The analogous TBP complex $[Co(C_2H_4)[P(OMe)_3]_4]PF_6$ was recently isolated by Muetterties and Watson,[8] who observed that the $[Co(P(OMe)_3)_4]^+$ cation is very reactive toward ethylene, since the reaction took place even in the solid state. Such a reactivity is not observed for $[Co(PMe_3)_4]BPh_4$.

$$[Co(PMe_3)_4]BPh_4 + C_2H_4 \rightleftharpoons [Co(C_2H_4)(PMe_3)_4]BPh_4 \qquad (4)$$

Solid-State Study. The only ethylene cobalt(I) complex that we were able to isolate in a crystalline form is $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4{\cdot}MeCN$. It was obtained at −80 °C under ethylene by adding $NaBPh_4$ dissolved in a methanol-ether mixture to $CoBr(PMe_3)_3$ dissolved in acetonitrile. Orange-brown plates, reasonably stable in the solid state under argon and in acetonitrile solution under an atmosphere of ethylene, precipitated. The IR spectrum indicates the presence of acetonitrile (ν(CN) at 2280 and 2240 cm^{-1}). The ν(C=C) vibration observed at 1150 cm^{-1} in $CoH(C_2H_4)(PMe_3)_3$ is hidden by bands of the BPh_4^- ion. The complex is diamagnetic in the solid state, a result consistent with a five-coordinate low-spin d^8 complex.

Description of the Crystal Structure. The cationic part of the structure has an idealized trigonal-bipyramidal geometry (Figure 4). The numbering scheme and bond lengths are given in Figure 5. Selected bond angles are listed in Table III. The ligand distribution around Co is not unexpected. The best π acceptor, ethylene, is found on an equatorial site. The double bond lies in the equatorial plane to maximize π interactions, and it is symmetrically coordinated as usual. Acetonitrile, which is a poor π acceptor, occupies an axial position. The two Co–P distances to the equatorial PMe_3 are equal (2.237 (3) Å) but are significantly greater than the Co–P(3) axial distance (2.175 (3) Å). These features are in good agreement with Hoffmann's predictions.[13]

Olfein double bonds are lengthened by coordination, and the substituents are displaced away from the metal. These structural changes have been discussed by Ittel and Ibers.[17] The present C(1)–C(2) bond (1.41 (1) Å) is longer than in the free olefin (1.337 (2) Å). It lies in the middle of the reported range for ethylene (1.35–1.46 Å). This distance, as well as the Co–ligand bond lengths, compare well with the corresponding values reported for $Co(C_6H_5)(C_2H_4)(PMe_3)_3$.[7]

The hydrogens are positioned with low accuracy, but the overall ligand geometry is consistent with previous studies.[17] Nonplanarity

Table III. Bond Angles (Deg) in the Complex Cation

P(1)–Co–P(2)	108.9 (1)	Co–P(1)–C(11)	113.6 (3)
P(1)–Co–P(3)	96.7 (1)	Co–P(1)–C(12)	117.0 (3)
P(1)–Co–N(1)	90.8 (2)	Co–P(1)–C(13)	121.0 (4)
P(1)–Co–C(1)	98.1 (3)	C(11)–P(1)–C(12)	98.3 (4)
P(1)–Co–C(2)	138.9 (3)	C(11)–P(1)–C(13)	100.7 (5)
P(2)–Co–P(3)	93.8 (1)	C(12)–P(1)–C(13)	102.8 (5)
P(2)–Co–N(1)	84.5 (2)	Co–P(2)–C(21)	113.6 (4)
P(2)–Co–C(1)	151.2 (3)	Co–P(2)–C(22)	126.4 (4)
P(2)–Co–C(2)	111.5 (3)	Co–P(2)–C(23)	114.0 (3)
P(3)–Co–N(1)	172.4 (2)	C(21)–P(2)–C(22)	100.5 (5)
P(3)–Co–C(1)	93.0 (3)	C(21)–P(2)–C(23)	100.7 (5)
P(3)–Co–C(2)	88.3 (3)	C(22)–P(2)–C(23)	97.8 (5)
N(1)–Co–C(1)	85.1 (3)	Co–P(3)–C(31)	116.4 (3)
N(1)–Co–C(2)	85.5 (3)	Co–P(3)–C(32)	119.5 (3)
C(1)–Co–C(2)	40.8 (3)	Co–P(3)–C(33)	116.4 (3)
Co–N(1)–C(4)	177.2 (6)	C(31)–P(3)–C(32)	100.2 (5)
N(1)–C(4)–C(3)	178.0 (8)	C(31)–P(3)–C(33)	100.4 (4)
N(2)–C(5)–C(6)	177.7 (11)	C(32)–P(3)–C(33)	100.8 (5)
Co–C(1)–C(2)	69.3 (5)	Co–C(2)–C(1)	69.9 (5)
C(2)–C(1)–H(11)	111 (4)	C(1)–C(2)–H(21)	132 (5)
C(2)–C(1)–H(12)	111 (4)	C(1)–C(2)–H(22)	112 (4)
H(11)–C(1)–H(12)	127 (6)	H(21)–C(2)–H(22)	111 (6)

Table IV. Angles (Deg) in the Coordinated Ethylene Ligand

Angle, deg			
between the normals to C(1)–H(11)–H(12) and C(2)–H(21)–H(22) (α)	56 (8)		
between C(1)–C(2) bond and C(2)–H(21)–H(22) plane (β)	70 (8)		
between C(1)–C(2) bond and C(1)–H(11)–H(12) plane (β)	54 (8)		
between Co–C(1)–C(2) and Co–P(1)–P(2) (θ)	10 (1)		
Torsion (δ)			
Co–C(1)–C(2)–H(21)	102 (6)	Co–C(2)–C(1)–H(11)	104 (5)
Co–C(1)–C(2)–H(22)	−106 (5)	Co–C(2)–C(1)–H(12)	−108 (5)
Torsion (γ)			
H(11)–C(1)–C(2)–H(21)	−154 (8)		
H(11)–C(1)–C(2)–H(22)	−2 (8)		
H(12)–C(1)–C(2)–H(21)	−6 (8)		
H(12)–C(1)–C(2)–H(22)	146 (8)		

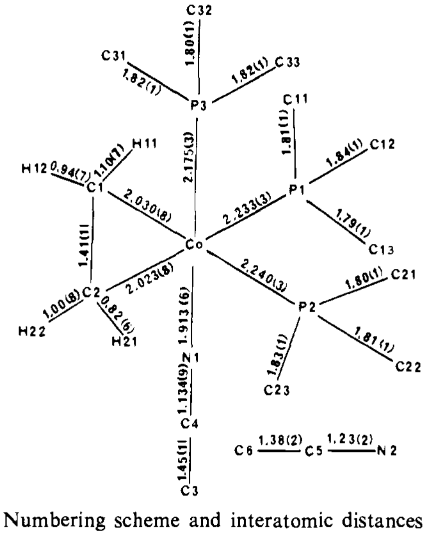

Figure 5. Numbering scheme and interatomic distances in the $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ ion.

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[17] Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61.

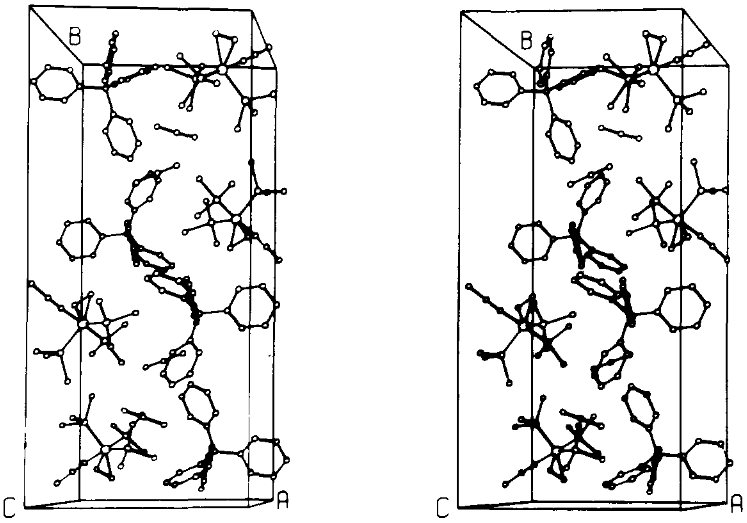

Figure 6. Packing diagram of the structure. Atoms are represented by spheres of arbitrary size. Hydrogens are omitted for simplicity.

can be defined in terms of the various angles listed in Table IV, which agree within experimental errors with the standard values[17] for ethylene. The twist angle (10°) between the planes through Co–C(1)–C(2) and Co–P(1)–P(2), respectively, probably reflects steric hindrance between the phosphines rather than tensions involving ethylene itself (vide infra).

The P–C bond lengths in PMe_3 average the normal value of 1.81 (1) Å. The departure from tetrahedral symmetry around P is significant as usual:[14,18] Co–P–C = 117.3° (average) and C–P–C = 100.2° (average).

The linear acetonitrile molecule is end-on coordinated: Co–N(1)–C(4) = 177.2 (6)°. The C–C and C–N distances are similar with those observed in free[19] and coordinated[20] acetonitrile.

The angular distortions of the Co bipyramid can be rationalized in terms of the particular steric requirements of each type of ligands. For instance, ethylene fills more space in the equatorial plane than a one-atom donor. This decreases the opposite P(1)–Co–P(2) angle 11.1° below its ideal value, an effect previously noted by other workers for similar situations.[21] The C–Co–P angles in the plane differ considerably (98.1 (3), 111.5 (3)°). This appears to result from differences in nonbonded ethylene–phosphine contacts. Indeed, even though both equatorial phosphines have one methyl group each in the equatorial plane, C(21) is facing ethylene directly, leading to a large P(2)–Co–C(2) angle. The corresponding C(13) methyl group on phosphine 1 is oriented toward phosphine 2. The P(1)–Co–C(1) angle can be reduced to 98.1 (3)° without introducing much repulsion between ethylene and the methyl groups C(11) and C(12). Steric effects of the axial phosphine are not noticeable with ethylene (P(3)–Co–C = 93.0 (3) and 88.3 (3)°), but more significant with the equatorial phosphines, which C(32) displaces below the plane by 0.045 (P(1)) and 0.360 Å (P(2)). As a result, the phosphines are not coordinated exactly along the lone-pair direction and a measure of this effect is provided by the 13° range observed for the Co–P–methyl angles which should otherwise be equal as found for phosphine P(3). Acetonitrile is also tipped in the direction of ethylene with a N(1)–Co–P(3) angle of 172.4 (2)°. Although this could be ascribed to intramolecular steric effects, the distortion may result from crystal packing, which would especially affect the tube-shaped acetonitrile ligand extending far out into the structure.

The detailed geometry of the BPh_4^- ion is given in the supplementary material. The B–C and C–C bond lengths average 1.64 (1) and 1.38 (1) Å, respectively. The angles centered at the B-bonded carbons (average 115.0 (7)°) are systematically smaller and those at the ortho carbons (average 122.8 (7)°) are greater than 120°, as commonly found.[22]

A packing pattern is shown in Figure 6. The structure consists of discrete units, i.e., individual anions, cations, and lattice acetonitrile molecules. There are a few short contacts of 2.8–2.9 Å between hydrogens on C(3) of the coordinated acetonitrile and carbon atoms of phenyl rings 6 and 7 $(-1 + x, y, z)$. The lattice acetonitrile molecule fills space between ions interacting only through normal van der Waals contacts.

Discussion

The present work emphasizes the effect of acetonitrile on the reactivity of the $CoX(PMe_3)_3$ d^8 complexes with ethylene. Among the different solvents used in this study (acetone, methanol, dichloromethane, acetonitrile, toluene, i.e., solvents with various polarities and coordinative capabilities), only acetonitrile is able to act, in the presence of ethylene, as a ligand which (i) opens and occupies a coordination site at the cobalt centre by displacing the anionic ligand and (ii) stabilizes the cobalt(I)–ethylene complexes to such an extent that one of them could be isolated. However, at the moment, we have no evidence that this is related only to enhanced thermodynamic stability of the MeCN complex, since the stabilization due to crystal packing is difficult to assess.

The particular role of acetonitrile in the chemistry of $CoX(PR_3)_3$ (where R = OEt, OPh, O-*i*-Pr) has already been pointed out by other authors. Gosser[5b] noticed in this solvent a disproportionation reaction into Co(O) and Co(II) compounds, which was accelerated in presence of water, and Rakowski and Muetterties[5c] suggested the formation of the $[Co(MeCN)_2(P(O\text{-}i\text{-}Pr)_3]Cl$ and $[Co(MeCN)(P(O\text{-}i\text{-}Pr)_3Cl]$ species. For the PMe_3 complexes, disproportionation is noticeable only for $CoCl(PMe_3)_3$. In contrast, the green solutions of $CoBr(PMe_3)_3$ or $CoI(PMe_3)_3$ cooled to −80 °C in 1:1 mixtures of acetonitrile with methanol or acetone (the second solvent is used to lower the freezing point) turn red and a singlet appears at δ −5.5 in the $^{31}P\{^1H\}$ NMR spectrum. This suggests $[Co(MeCN)_2(PMe_3)_3]X$ as the most likely formula for the resulting diamagnetic species. This δ value lies in the range of chemical shifts observed for equatorial phosphine ligands in trigonal-bipyramidal d^8 Co(I) complexes (Table II), and, con-

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sequently, a trigonal-bipyramidal structure with axial MeCN ligands is probable. No temperature-dependent color change of the solutions is observed when $CoBr(PMe_3)_3$ and $CoI(PMe_3)_3$ are dissolved in acetone, methanol, or toluene. Similarly, the green acetonitrile solution $[Co(PMe_3)_4]BPh_4$ at room temperature turns red at 80°C, but no resolved $^{31}P\{^1H\}$ signal is apparent on the NMR spectrum. The $[Co(MeCN)(PMe_3)_4]^+$ cation, the analogue of which with $P(OMe)_3$ has been fully characterized,[8] has not been identified with PMe_3. In neither case, with PMe_3, was it possible to isolate the acetonitrile adduct as a solid.

Besides the crystal structure studied here, an example of acetonitrile coordination to Co(I) is provided by $CoH(MeCN)(P(OR)_3)_3$ compounds,[23] which are efficient catalysts for selective hydrogenation of terminal olefins, a property undoubtedly related to the easy dissociation of the nitrile ligand.

The reaction of ethylene with the Co–PMe_3 compounds gives rise in solution to four different types of species depending on the experimental conditions (X = Br, I): $CoX(C_2H_4)(PMe_3)_3$, $[Co(MeCN)(C_2H_4)(PMe_3)_3]X$, $[Co(L)(C_2H_4)(PMe_3)_3]X$ (with L = MeCN or C_2H_4), and $[Co(C_2H_4)(PMe_3)_4]BPh_4$. Only $[Co(MeCN)(C_2H_4)(PMe_3)_3]^+$ was isolated in the solid state as the BPh_4^- salt. According to the $^{31}P\{^1H\}$ NMR spectra, all these species could have TBP structure. They possess a common $Co(PMe_3)_3$ entity, leaving two coordination sites to accept different ligands: ethylene, halide, acetonitrile, or another phosphine molecule. Depending on their own steric and electronic requirements, these ligands may prefer either an axial or an equatorial position. Because of its π-acceptor character, ethylene usually lies in the equatorial plane of a TBP, as well as it lies in the plane of a trigonal-planar molecule or stands perpendicular to the plane in a square-planar species. These orientations result from electronic, rather than steric, effects, since more d orbitals are available for π coordination in equatorial than in axial sites.[13] In all the examples studied so far, the halogens have also been found to occupy equatorial sites,[14,24] although in this case the reasons are not clear. Acetonitrile and PMe_3, which may act as σ-donor and π-acceptor ligands, are thus found to occupy the remaining positions. From these considerations and the phosphine positions deduced from the $^{31}P\{^1H\}$ NMR spectra, structures were proposed for all, but one, of the species identified in solution. We were unable to determine unambiguously whether L is C_2H_4 or MeCN in $[Co(L)(C_2H_4)(PMe_3)_3]X$. This unassigned site has to be equatorial, and C_2H_4 would be electronically favored over MeCN to occupy it, although some steric hindrance is to be anticipated. This might lead either to important distortions in the TBP or even to a preference for MeCN over C_2H_4 if the steric effects are severe.

It is interesting to note that the equatorial/axial distribution of the PMe_3 ligands is 2 P_e/1 P_a in the crystal structure reported here but 1 P_e/2 P_a in $Co(C_6H_5)(C_2H_4)(PMe_3)_3$.[7] Our axial Co–P distance (2.175 (3) Å) seems to be shorter than those of the phenyl compound (2.192 (3) Å) and of most PMe_3 complexes.[24] This may be related to the presumably very weak trans influence of the MeCN ligand, compared with PMe_3. Ethylene coordination is essentially identical in both Co(I) molecules: the Co–C distances are comparable, as well as the C–C bond lengthening. For the phenyl compound, the ethylene double bond perfectly coincides with the equatorial plane, which is a crystallographic mirror plane. In the present compound, the distortion is significant (see Table IV), but it apparently results from steric hindrance between the phosphines.

The presence of the phenyl substituent lying flat in the equatorial plane creates severe distortions in the TBP. As seen from the following angles, the ring occupies a somewhat larger space than a PMe_3 molecule in the equatorial plane (Et = center of the double bond): P–Co–Ph = 111.7° and Ph–Co–Et = 137.9°, for $Co(C_6H_5)(C_2H_4)(PMe_3)_3$,[7] and P(1)–Co–P(2) = 108.9° and P(2)–Co–Et = 131.3°, in the present structure. The two structures also differ by the amount of space available for the axial groups to move away from the bulkier equatorial phosphines. As a result, the distortion of the axial bonds in this case are rather small, only acetonitrile being slightly tipped toward ethylene. In the phenyl compound, the axial PMe_3 ligands more roughly above the Co-Ph bond, away from the equatorial phosphine. As pointed out by Klein et al.,[7] this creates a large distortion of the TBP in the direction of a square pyramid. It is difficult to sort out the respective effects of crystal packing and intramolecular nonbonded interactions on these distortions or to determine whether the departure of the P_{ax}–Co–P_{eq} angle from 90° is electronically helped by the large Ph–Co–Et angle imposed by the flat ring. At any rate, the orientation of the ring in the equatorial plane is not the most favorable in terms of intramolecular steric effects. It is tempting to relate this particular orientation to some participation of the π system of the σ-bonded aromatic ring, as proposed for $RePh_3(PEt_2Ph)_2$, in which the phenyl rings are equatorial and tend to lie close to the equatorial plane.[25] The axial position of the alkyl group in $Co(CH_3)(C_2H_4)(PMe_3)_3$ molecule[6] would support the assumption of some π bonding in the corresponding phenyl compound.

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Registry No. $[Co(MeCN)(C_2H_4)(PMe_3)_3]BPh_4$, 81554-57-6; $CoBr(C_2H_4)(PMe_3)_3$, 81554-58-7; $CoI(C_2H_4)(PMe_3)_3$, 81554-59-8; $[Co(MeCN)(C_2H_4)(PMe_3)_3]I$, 81600-78-4; $[Co(MeCN)(C_2H_4)(PMe_3)_3]Br$, 81600-79-5; $[Co(C_2H_4)(PMe_3)_4]BPh_4$, 81554-61-2; $[Co(MeCN)_2(PMe_3)_3]Br$, 81554-62-3; $[Co(MeCN)_2(PMe_3)_3]I$, 81554-41-8; $[Co(MeCN)(PMe_3)_4]BPh_4$, 81554-43-0; $CoBr(PMe_3)_3$, 53432-07-8; $CoI(PMe_3)_3$, 53432-08-9; ethylene, 74-85-1; acetonitrile, 75-05-8.

Supplementary Material Available: Refined anisotropic temperature factors (Table V), fixed coordinates of hydrogen atoms (Table VI), bond lengths and angles in the BPh_4^- ion (Table VII), details of least-squares plane calculations (Table VIII), and observed and calculated structure amplitudes (Table IX) (27 pages). Ordering information is given on any current masthead page.

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